Chapter 1

Introduction

1.0 INTRODUCTION

1.1 Solid State Ionics

Solid state ionics is a new branch of Science and Technology which deals with materials and devices based on the flow of 'ions' in solids instead of electron flow which forms the basis of the well known Solid State Electronics Technology. The well known ionic solids like KCl and NaCl have room temperature ionic conductivity around 10^{-12}Scm $^{-1}$. These solids could not be used in most electrochemical devices due to their low ionic conductivity [1].

Development of solid state ionic devices had to wait until the discovery of good solid electrolytes. One of the first applications of solid electrolytes in devices is the oxygen ion electrolytes in determining the thermodynamic properties of high temperature materials [2-3]. Then, in 1967, with the discovery of fast sodium ion conduction in alumina and silver ion conduction in Ag_4I_5 [4-5], a large number of solids with high ionic conductivity have been discovered and numerous applications have been found. Their applications range from small batteries for pacemaker implants [6], to high power batteries in energy storage systems [7], electrochromic windows for energy conservation [8], sensors for chemical pollutant detection [9] etc.

A solid state ionics electrochemical device is designed to have an electronic current in the load of the external circuit and a predominantly ionic current in some parts of the internal circuit. The most important criteria in developing useful solid state ionics devices, has been, to identify and synthesize solid state ionically conducting materials, with adequate conductivity properties and chemical properties, to serve as electrolytes and/or electrodes. Figure 1.1 shows the influencing parameters of the electrochemical response of a solid state ionics material.

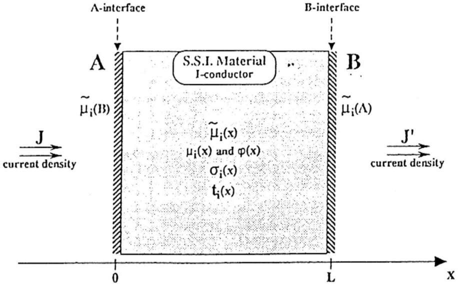


Figure 1.1 : Illustration of the influencing parameters of the electrochemical response of a solid state ionics material [10]

μ_i , σ_i , t_i and φ are respectively the chemical potential, ionic conductivity, transport number and the electrostatic potential of i - ions.

Solids with high ionic conductivity are known as "superionic solids"' or "fast ion conductors" or "solid electrolytes". A superionic solid has the following characteristics :

i) electrical conductivity is high (10^{-1} to 10^{-4} S/cm)

ii) principal charge carriers are ions.

iii) electronic conductivity is small.

The solid electrolytes can be classified into four groups according to their microstructure and physical properties, namely :

i) Framework crystalline materials
ii) Ion conducting glasses
iii) Composite electrolytes
iv) Polymer electrolytes

1.1.1 Framework crystalline materials

Most of the earlier discovered superionic solids belong to this group of materials. They generally consist of mobile ions in a more or less rigid crystalline framework [11]. These materials are further divided into two subgroups :

i) Soft framework crystals
ii) Hard framework crystals

The soft framework crystals are characterized by ionic bonding, polarizable and heavy ions. AgI, CuI and Ag_2HgI_2 are the examples of the soft framework crystals[12]. The hard framework crystals have predominantly covalent bonding and low polarizability of mobile ions. NASICONS and β - alumina are two important examples of hard framework crystals. NASICON is a series of solid solutions with the general formula $Na_{1+x}Zr_2(SiO_2)_x(PO_4)_{3-x}$ ($0 \leq x \leq 3$). These are good sodium ion conductors [13-14].

1.1.2 Ion conducting glasses

Glasses with high Ag^+ ion conduction (~10^{-2} S/cm) at room temperature were discovered by Kunze in the system AgI - Ag_2SeO_4 [15]. Since then, a number of glasses with high Li^+, Na^+, Cu^+ and F^- ion conduction have been reported. Amongst the various superionic glasses, Ag^+ ion conducting systems exhibited relatively high room temperature conductivity and are easy to prepare and handle.

Ion conducting glasses are generally obtained by quenching a mixture of glass former oxides (such as B_2O_3 , SiO_2 and P_2O_5) and a network modifier (Ag_2O, Cu_2O and alkali oxides). The addition of metallic salts like AgI and CuI into the glass matrix enhances the ionic conductivity. The glass formation is also possible by replacing oxygen in the glass forming oxides with sulphur.

1.1.3 Composite electrolytes

Composite solid electrolytes typically consist of a solid electrolyte matrix containing well dispersed submicron sized second phase particles such as γ - Al_2O_3 [16]. Although activated alumina powder has been the most commonly used dispersoid, several other second phased materials ranging from semiconducting to insulating particles like NiO, CeO_2 , Bi_2O_3 and ZrO_2 [17] to electronically conducting particles like Cu, Ni and Ni_3S_2 have been added as dispersoids [18]. The addition of the finely dispersed powder greatly improves the morphological and the electrochemical properties of the composite electrolytes. The high electronic conductivity in such composite electrolytes is believed to occur essentially at the electrolyte dispersoid interfaces [19].

Table 1.1 illustrates a variety of composite electrolytes with corresponding enhancements in their conductivities that range between 10 - 2500 times, in relation to their hosts.

No	Composite	Order of enhancement in ionic conductivity at RT	Ref.
1	AgCl (Al_2O_3)	10	20
2	CaF_2 (Al_2O_3)	100	21
3	HgI_2 (Al_2O_3)	100	22
4	CaF_2 (CeO_2)	1000	21
5	AgI (Al_2O_3)	2500	23

Table 1: Composite electrolytes with corresponding enhancements in their conductivities

1.1.4 Polymer Electrolytes

Since the first ionic conductivity measurements of PEO based polymer electrolytes by Wright and co-workers [24-25], followed by the proposal of use of these materials in batteries by Armand's group [26], intensive research has been directed towards ambient temperature ion conducting polymer electrolytes. Polymer electrolytes are described in detail in section 1.2.

1.2. Polymer Electrolytes

Polymer electrolytes have occupied an important position in solid state ionics because of their unique properties. They have thin film forming property, good processibility, flexibility, light weight, elasticity (plasticity), relatively high ionic conductivity and wide potential window in the solid states. Some of these characteristics cannot be attained by hard inorganic solid electrolytes, including glasses, particularly in the formation of favourable interfaces between electrode materials and solid electrolytes in actual solid ionic devices. This is because of the change in volume of electrode materials in the devices during operation. The use of polymer electrolytes solves these problems due to their elastic property [27].

1.2.1 Classification of Polymer Electrolytes

Polymer electrolyte materials can broadly be classified into the following groups:

i) Solvent swollen polymers

Some solvents swell the basic polymer host like polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP) and the dopant ionic solute like H_3PO_4 are accommodated in swollen lattice which allow the ionic motion in solvent rich swollen region of the polymer host. These materials are in general, unstable, as their conductivity depends on the ambient and concentration of the solvent in the swollen region [1].

ii) Polyelectrolytes

Polyelectrolytes are a class of polymers that have self ion generating groups, responsible for the ionic conductivity, attached to the main chain of the polymers. Some important examples are polysulphonic acid based polyelectrolytes, such as Nafion and sodium polysterene sulphate. The main attraction of such polymers are the single ion transport in the bulk [28].

iii) Solvent free polymer salt complex

These are most common materials and have been very extensively studied. These materials are prepared in the form of films by solution cast technique, in which the solution of polymers and salts of monovalent alkali metal/divalent/transition metals and ammonium salts are mixed, stirred thoroughly and coated on teflon or polypropylene dishes. The solution is slowly evaporated followed by vacuum drying. The final film is 'solvent free' and is essentially an ion complexed polymer [29].

1.2.2 Criteria for Polymer/ Salt Complexation

The dominant class of polymer electrolytes is formed using a neutral polar polymer complexed with a uni-univalent metal salt, MX, where M is normally an alkali metal and X is a fairly 'soft' anion (I^- , SCN^- ,$CF_3SO_3^-$,BF_4^- etc.). These can be schematically written as,

$$\text{---}(\text{--AB--})_n\text{---} + MX \rightarrow \text{---}(\text{--AB--})_n\text{---}\bullet MX$$

where ---AB--- denotes the polymeric subunit.

For effective complexation or solvation of salts in polymers, the following criteria have to be satisfied [30].

i) The salt should have a relatively small lattice energy. This will be aided by choosing anion X^- to be 'soft' and large.

ii) The polymers should be of low glass transition temperature (T_g) for their flexible backbone which will ensure the complexation. The low T_g can be attained either by choosing the polymers at low cohesive energy (such as PEO, PPO and PEI) or by plasticizing the polymers of higher T_g.

iii) The concentration of polar groups or solvating heteroatoms responsible for complexation of cations should be as large as possible.

1.3 Conductivity Mechanism in Polymer Electrolytes

Important information on the transport mechanisms have been gleaned from dynamic (frequency-dependent) conductivity as obtained using complex impedance spectroscopy [31-32]. It has been observed that the temperature dependence of conductivity for most polymer electrolytes exhibit one of the following behaviour [30]:

i) Vogel-Tamman-Fulcher (VTF) behaviour throughout the available thermal range.

ii) Arrhenius behaviour for low temperature and VTF behaviour at higher temperatures.

iii) Arrhenius behaviour throughout, but with two different activation energies, high E_A closer to T_g and a small E_A at higher temperatures.

iv) VTF behaviour for temperatures slightly greater than T_g but Arrhenius behaviour at higher temperatures.

v) Behaviour which is very unlike either Arrhenius or VTF at all temperatures.

The first three forms of behaviour are most common in polymer electrolytes. Behaviour (iv) is explained on the basis of the free-volume theory whereas behaviour (v) is the most complicated and difficult to understand. The Arrhenius behaviour follows an activated law :

$$\sigma T = A_1 \exp(-B_1/RT) \qquad (1.1)$$

The VTF behaviour obeys an empirical relationship that was first derived by Vogel, Tamman and Fulcher :

$$\sigma T = A_2 \exp[-B_2/R(T - T_0)] \qquad (1.2)$$

suggesting an asymptotic decrease of the ionic transport towards a temperature, T_0.

For salt polymer complexes, the conductivity data are generally obtained only for temperatures higher than their glass transition temperature, T_g. Above T_g, the conductivity data obeys an empirical VTF relationship and below T_g, it follows a classical Arrhenius relationship [33-34].

A hybrid form of relationship which associates equations (1.1) and (1.2) has been found by Miyamoto and Shibayama [35] and by Cheradame [36] to give a better fit to conductivity data .

$$\sigma T = A_3 \exp\left[-\frac{B_3}{R(T - T_0)} - \frac{B_3'}{RT}\right] \qquad (1.3)$$

Point defect theory and free volume approach are proposed to provide physical meanings to the parameters A_i and B_i [33-34].

Below T_g, the Arrhenius behaviour is explained by the dissociation of ionic pairs, leading to the formation of interstitial defects migrating by an indirect interstitial mechanism. Under such conditions, the term B_l is related to the energy of defect formation, H_f and the energy of defect migration, H_m ;

$$B_l = \left(\frac{\Delta H_f}{2} \right) + \Delta H_m \qquad (1.4)$$

Above T_g, the ionic transport involves a co-operative mechanism of the macromolecular chains or of the neighbouring atoms. This is the free volume approach which is mainly applied in polymer complexes. The term B_2 is then related to the local redistribution of the mean free volume, evenly distributed throughout the supercooled liquid. The temperature T_0 , then corresponds to the temperature at which the entropic redistribution of the free volume disappears.

Although these two processes differ fundamentally, the continuous behaviour observed around the glass transition temperature seems to suggest that these approaches can be unified. In order to unify the ionic transport below and above T_g, the defect concentration, C_+ follows that :

$$C_+ = C \exp\left(- \Delta G_f / 2RT \right) \qquad (1.5)$$

where,

$$\Delta G_f = \Delta H_f - T\Delta S_f \qquad (1.6)$$

is the Gibb's free energy associated with the formation of a defect.

Then the defect migration under the electric field E is derived from the Brownian movement equation :

$$U_+ = \frac{F}{RT} \; \frac{I^2}{6} \; \nu_0 P \qquad (1.7)$$

where U_+ is the electrical mobility, I is the mean distance between two cationic sites, ν_0 the attempt frequency, P is the probability of a successful displacement, F is the Faraday's constant and T is the absolute temperature.

For $T < T_g$, P is the probability for the interstitial cation to receive an energy greater than ΔH_m, which is the energy necessary for the cation to jump into a neighbouring position as illustrated in Figure 1.2.

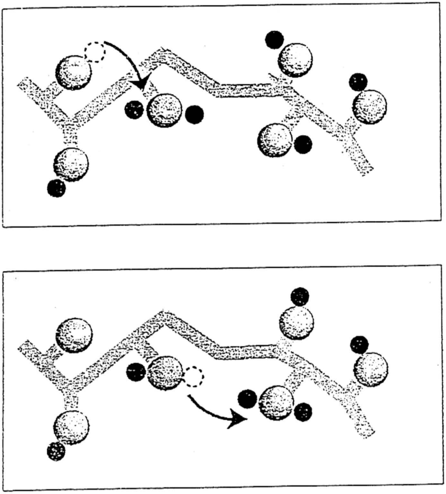


Figure 1.2 : Cation jump into a neighbouring position.

P is given by,

$$P = P_1 = \exp\left(- \Delta H_m / RT \right) \qquad (1.8)$$

At $T > T_g$, another displacement mechanism arises, which is schematised in Figure 1.3. A local deformation at the macromolecular chain enables the defect to be transferred to a neighbouring position. The probability, P_2, is given by :

$$P_2 = \exp\left(- V_f^* / < V_f > \right) \qquad (1.9)$$

where $< V_f >$ is the mean free volume and V_f^* is the minimum free volume for the defect displacement. $< V_f >$ is temperature dependent and can be expressed as :

$$< V_f > = V_0 \; \alpha_f (T - T_0) \qquad (1.10)$$

where α_f is the thermal expansion coefficient of the free volume. Then P_2 can be rewritten as :

$$P_2 = \exp \; [V_f^* / V_0 \; \alpha_f (T - T_0)] \qquad (1.11)$$

This equation confirms that this second mechanism appears only above the ideal vitreous transition temperature, T_0 . Above this temperature, the cationic displacement may occur either by an activated jump (P_1) or by an entropic free volume mechanism (P_2) .

$$P = P_1 + P_2 \; (1 - P_1) \qquad (1.12)$$

Under such conditions, the cationic conductivity is expressed as :

$$\sigma_+ = FC_+ U_+ \qquad (1.13)$$

By combining equation (1.5) , (1.7) and (1.13), the following is obtained ;

$$\sigma_+ = \frac{F^2C}{RT} \frac{l^2}{6} \nu_0 \exp\left(-\frac{\Delta G_f}{2RT}\right)[P_1 + P_2(1 - P_1)] \qquad (1.14)$$

If $P_1 >> P_2$, the conductivity expression is equivalent to the Arrhenius form (eq.1.1) with,

$$A_1 = (\frac{F^2C}{R} \frac{l^2}{6} \nu_0 \exp\left(-\frac{\Delta S_f}{2R}\right)$$

and $$B_1 = \left(\frac{\Delta H_f}{2}\right) + \Delta H_m$$

On the other hand, if $P_1 << P_2$, the conductivity expression simplifies to equation (1.3) with,

$$A_3 = A_1, \quad B_3 = \frac{RV_f^*}{\nu_0 \alpha_f} \quad \text{and} \quad B_3' = \left(\frac{\Delta H_f}{2}\right)$$

Due to the exponential dependence of P_1 and P_2 on T, the Arrhenius form prevails below T_g and the equation (1.3) prevails above T_g.

Although the microscope model presented above involves only one charge carrier, for salt polymer complexes, the anionic conductivities are found to be of the same order of magnitude as cationic conductivities. This is illustrated in Figure 1.4.

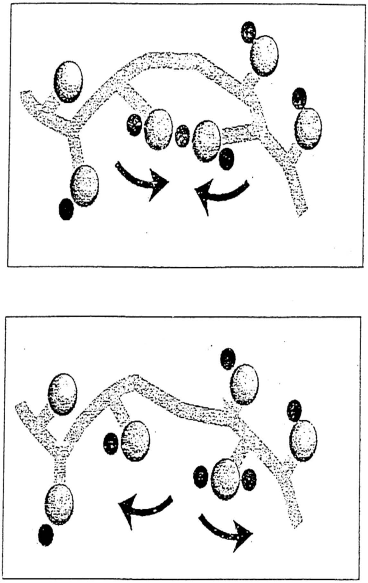


Figure 1.3 : Segmental motion of the polymer chain which leads to the transfer of charge[33].

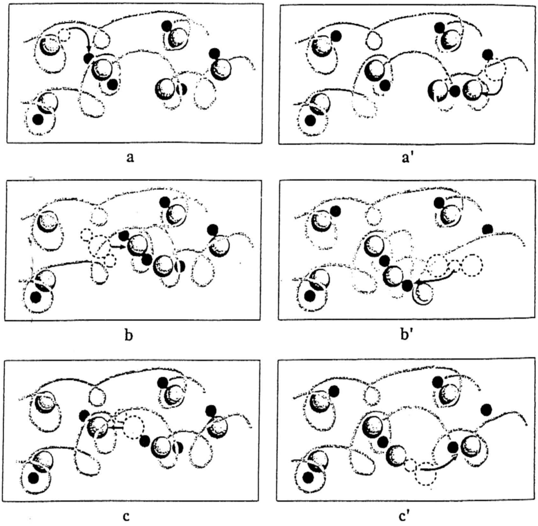


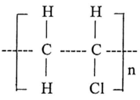
Figure 1.4 : A representation of the cationic (a,b,c) and anionic (a',b',c',) migration in a salt polymer complex [33].

1.4 Poly (vinyl chloride)

Poly (vinyl chloride) (PVC) is a widely used synthetic plastic. The widespread use of PVC is attributed mainly to its high chemical resistance and its unique ability to be mixed with additives to produce a large number of compounds with a wide range of physical and chemical properties [37]. PVC is one of the 'big three' of plastics, along with polyethylene (PE) and polystyrene [38].

PVC was first produced in Germany in the early 1930's but its extensive use did not start until the second world war, when mixtures with certain organic liquids producing a flexible material found wide application [39].

A generally accepted structure of the PVC molecule is as follows :



$$-\left[\mathrm{CH_2} - \mathrm{CHCl} \right]_n-$$

where n ranges from approximately 700 to 2000 in commercial resins. These polymer chains are considered to be linear and to contain a minimum amount of branching [40].

Vinyl alcohol monomer, $CH_2 = CHCl$, is a non-toxic colourless gas at room conditions and is soluble in ethyl alcohol, but is essentially soluble in water. Selected properties of this monomer is given in Table 1.2 [38].

Property	Value
Molecular Weight	62.50
Normal boiling point	-13.7°C
Freezing point	- 153.8°C
Density at 20°C	0.910 g/ml
Flash point	- 78°C
Explosive limits in air	4 – 22 % by volume
Viscosity at - 10°C	0.25 cps
Index of refraction, 15°C	1.38

Table 1.2 : Selected properties of Vinyl Chloride monomer

1.4.1 Characterization of PVC

a) Solubility

PVC is soluble in many common ketones and esters. It swells in aromatic hydrocarbons, but it is unaffected by alcohols or aliphatic hydrocarbons. The polymer is insoluble in some organic chlorides, including its own monomer. Low molecular weight PVC is soluble in aromatic hydrocarbons whereas the high molecular weight polymer merely swells in such solvents. The preferred or most widely used solvents are tetrahydrofuran (THF), cyclohexanone and ethyl methyl ketone [41].

b) Molecular Weight

Commercial PVC has an average molecular weight of 50,000 to 150,000. Usually the molecular weight of this polymer is characterized by measurements of the viscosity of dilute solutions rather than by the direct measurement of molecular weight. For dilute solutions, the viscosity and molecular weight are related by the Mark-Houwink equation :

$$[\eta] = kM^a \tag{1.15}$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, k and a are constants. Some of the relationships are shown below [41]:

$$[\eta] = 1.38 \times 10^{-4}\ M^{0.78}\ \text{, cyclohexane , 25°C} \tag{1.16}$$

$$[\eta] = 1.50 \times 10^{-4}\ M^{0.77}\ \text{, THF , 25°C} \tag{1.17}$$

c) Tacticity

In vinyl polymers - CH_2 CHR - , there are different arrangements for the R group and the hydrogen bond in the CHR grouping. These different positions are relative to the plane containing the backbone carbon-carbon bonds.

The PVC chain may be represented as in Figure 1.5, where the carbon atoms lie in the plane and there is no order to the configuration. This configuration is termed as atactic. In such a chain configuration, the regularity necessary for the chains to pack and crystallize does not occur.

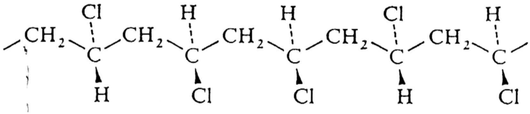


Figure 1.5 : Atactic Configuration [41]

If all the chlorine atoms are found in the same relative position, an isotactic chain results as shown in Figure 1.6.

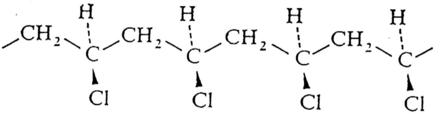


Figure 1.6 : Isotactic configuration [41]

When the chlorine atoms are in an alternating configuration, a syndiotactic chain results, as in *Figure 1.7*.

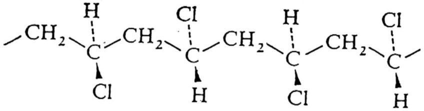


Figure 1.7 : Syndiotactic Configuration [41]

The isotactic and syndiotactic chains are regular and allow chain crystallization to occur.

d) Crystallinity

PVC is not generally classified as a crystalline polymer. Its crystallinity varies from 7% to 20% [42]. The crystallinity is apparently associated with syndiotatic sequences. While PVC prepared in the usual fashion does not contain a high degree of crystallinity, when the polymer is polymerized below room temperature, there is a marked increase in crystallinity. For example, polymer prepared at -15°C has about 57% crystallinity and at -75°C about 85% crystallinity [41].

The generally accepted model of the crystalline lattice for PVC is that as presented by Natta and Corradini based on the stacking of syndiotactic sequences along neighbouring lengths of the polymer chain [43] (Figure 1.8).

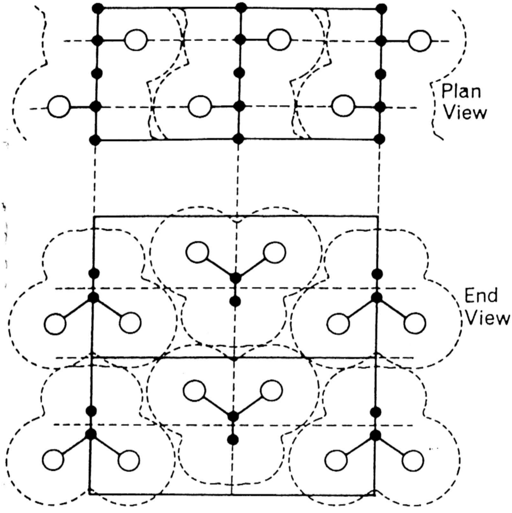


Figure 1.8: PVC lattice based on syndiotactic structure [43]

○ Carbon chain atom ● Chlorine atom

1.4.2 Physical Properties

PVC is a hard, brittle polymer at room temperature.

a) Glass transition temperature

The temperature at which an amorphous polymer changes from its hard or glassy state to a soft or rubbery material is known as the glass transition temperature, T_g. The T_g of PVC varies from 75°C to 105°C [44].

Plasticization or copolymerization of PVC generally reduces the T_g, increasing softness and flexibility [38]. The temperature employed during polymerization also affects the T_g value. Figure 1.9 shows that there is essentially a linear dependence of T_g on polymerization temperature. It appears that the variation in stereoregularity that occurs when the polymer is polymerized at low temperatures could account for the increase in T_g [45].

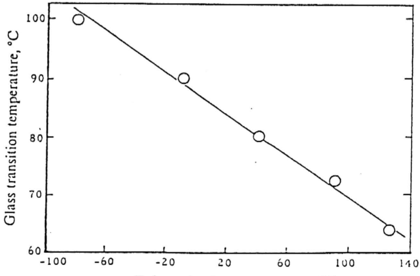


Figure 1.9 : Glass transition temperature as a function of polymerization temperature [45].

b) Melting point

The melting point of PVC is markedly affected by polymerization temperature or more specifically, by stereoregularity and crystallinity. The melting decreases with increasing polymerization temperature. PVC has a melting point of approximately 204°C [37].

1.4.3 Chemical Properties

Poly (vinyl chloride) is intrinsically unstable and decomposes by itself at only moderately elevated temperatures. Labile structures in the polymer are responsible for decomposition reactions in which HCl is split off.

a) Crosslinking

Many studies have been conducted for crosslinking of PVC through thermal degradation, UV or radioactive ray irradiation and chemical treatments. The great many cases using these methods are industrially undesirable, because considerable dehydrochlorination and discoloration occur with crosslinking reaction. Recently, the method of radioactive ray irradiation has been developed, on which the industrial interest is being focused [46-47].

b) Chlorination

PVC reacts readily with chlorine yielding a resinout product of higher chlorine content than the original, along with hydrogen chloride as a by product. Chlorination proceeds readily to a total chlorine content of about 73%, corresponding to one chlorine per carbon atom [46].

1.4.4 Mechanical Properties

Numerous studies have been devoted to understanding the mechanical behaviour of PVC [48-53]. Table 1.3 illustrates some of the typical properties of unmodified commercial PVC.

Property	Value	Reference
Young Modulus	1612 MPa	48
Stress at yield	37 MPa	48
Stress at break	25MPa	48
Strain at yield	3.2%	48
Strain at break	6%	48
Impact strength	19 MPa	49
Tensile strength	62 MPa	49

Table 1.3 : Properties of Unmodified Commercial PVC

1.4.5 PVC Compounding

PVC can only be used for a few applications without the addition of a number of compounds to the basic material so that it can be processed and converted into a finished product. Compounds added to PVC include plasticizers, heat stabilizers, lubricants, fillers and pigments.

Plasticizers impart flexibility to polymeric materials. They are usually high molecular weight compounds which are selected to be completely miscible and compatible with the basic material. For PVC, phthalate esters are commonly used as plasticizers.

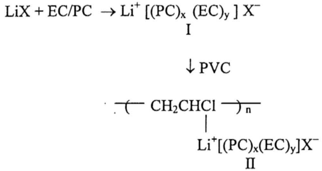
Heat stabilizers are added to PVC to prevent thermal degradation during processing. Typical stabilizers used are usually organometallic compound based on tin, lead and zinc.

Lubricants aid the melt flow of PVC compound during processing and prevent adhesion to metal surfaces. Fillers such as calcium carbonate are added mainly to lower the cost of PVC compounds. Pigments are used to give color, opacity and weatherability to PVC compounds [37].

1.5 PVC as an Ion Conducting Polymer

As mentioned earlier, since the first ionic conductivity measurements of PEO based polymer electrolytes, intensive research has been directed towards ambient temperature in ion conducting polymer electrolytes. Although the structural aspects of these polymers differ, the basic principle remains the same. A salt is dissolved in a solvating polymer matrix through direct interaction between the lone pair electrons by a heteroatom such as oxygen, nitrogen, chlorine etc. This interaction yields a conductive ion solution.

PVC with Cl bearing the lone pair electrons can be made into an ion conducting polymer. Earlier attempts were carried out by Watanabe and co-workers [54]. Later, Armand and co-workers overcame this difficulty by using the single solvent method. Scheme A illustrates the formation of a new solid electrolyte. The Li-solvate, I, formed when the Li salt is dissolved in the ethylene carbonate (EC) / propylene carbonate (PC) solvent mixture is immobilized in the PVC polymer host by electrostatic forces between the solvate and the polymer as shown in II [55].



$$\mathrm{LiX + EC/PC \rightarrow \underset{I}{Li^{+}\,[(PC)_x\,(EC)_y\,]\,X^{-}}}$$

$$\downarrow \mathrm{PVC}$$

$$\mathrm{-\!\!\left(\!-\; CH_2\underset{\underset{\underset{II}{Li^{+}[(PC)_x(EC)_y]X^{-}}}{|}}{CHCl} \;-\!\right)_{n}}$$

Scheme A

Since then, attention has been directed towards polymer electrolytes with PVC as a host polymer [48,56-57].

The major obstacle in developing a successful polymer electrolyte (SPE) is the low ionic conductivity at ambient temperature which is due to the low segmental mobility of polymer chains [58]. The realization that Li^+ has low mobility in SPE matrices has led numerous research groups to develop different approaches which gave improved conductivity. Some of the approaches include :

i) Cross linking two polymers [59-60]
ii) New polymer synthesis [61-62]
iii) Adding plasticizers to polymer electrolytes [63-64]
iv) Cross linking high molecular weight polymers through γ-irradiation [65]
v) Fillers to make composite polymer electrolytes [66]
vi) Blending of two polymers [67-68]

Some of the approaches like addition of salts, plasticizers and γ-irradiation, which are used in this work are described below :

1.5.1 Addition of Salts

Alkali ion conducting polymer electrolytes are mainly for Li^+ possibly because of small ionic radii of Li^+ . The specific capacity of lithium metal is 3.86 Ahr/g. The small ionic radius of the lithium ion can provide high volumetric capacity. The electrochemical potential for a lithium system is 3.01V for Li/Li^+ [69]. Thus, lithium ion conducting polymer electrolytes have been more widely studied due to their potential use in rechargeable high energy density batteries [70-73].

The lattice energy of the salts should be lower (below 720 J/mol $^{-1}$) for which salts with larger anions are most suitable [74-75]. The lattice energies are determined principally by the reciprocal of the sum of the ionic radii, 1/ (r_+ + r_-). The radius of the negative ion is much greater than that of the positive ions, and thus r_+ + r_- is insensitive to variations in r_+ [69].

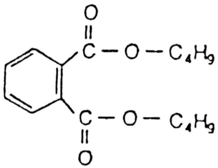
Salts having low lattice energies are generally expected to promote greater dissociation of the salt, thereby providing higher concentrations of ions. The lithium salts used for Li^+ conductive PVC electrolytes, such as $LiClO_4$, $LiBF_4$ and $LiCF_3SO_3$, have large anions and low lattice energies to promote high conductivity, compared with halides such as LiCl, LiI and LiBr, which have relatively high lattice energies [30]. About a decade ago, Armand and co-workers [76] discovered lithium bis (trifluoromethylsulfonyl) imide [$LiN(CF_3SO_2)_2$], a lithium salt of much lower lattice energy. According to the authors, the large flexible anion of this salt acts as a plasticizer in its complexes with PEO.

1.5.2 Addition of Plasticizers

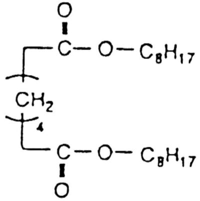
A plasticizer is a substance incorporated in a material to increase the flexibility, workability or distensibility [40]. The plasticizers used for the polymer electrolytes are generally a low molecular weight aprotic solvent having a high dielectric constant to ensure strong charge dissociation [77-80]. In plasticized polymer electrolytes, the role of the host polymer is secondary in the conducting matrix. The salt solvating power and the sufficient mobility of ion necessary for ionic conduction are imparted by the incorporated plasticizers.

The most important advantage of the plasticized polymer electrolytes over the other polymer electrolytes is the relatively higher ionic conductivity, but the major drawbacks of the plasticized electrolytes are the solvent volatility, the poor mechanical properties due to high degree of plasticization and the reactivity of a polar solvent with lithium electrode [57].

PVC is compatible with large amount of plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), dibutyl phthalate (DBP) and dioctyl adipate (DOA) [55-56].Figure 1.10 gives the structure of these plasticizers.



DBP



DOA

EC PC

Figure 1.10 Structure of plasticizers

1.5.3 γ - irradiation technique

γ - irradiation technique was selected to make the polymer structure crosslinked. Ionic conduction preferentially occurs in the amorphous phase. According to Y. Song *et al* [65], by lightly crosslinking the high molecular weight polymer through γ - irradiation and further suppressing the crystallinity by plasticizing, the room temperature ionic conductivity of polymer electrolytes can be raised.

Although numerous investigations on γ - irradiation crosslinking of PEO in the dissolved state have been performed since 1960s [81], reports concerning crosslinking in the bulk state appeared only in recent years [65, 82].

1.6 Comparison with other Polymer Electrolytes

Most of the early research activities on polymer electrolytes have been concentrated on systems related to poly (ethylene oxide) (PEO) with oxygen as a heteroatom. Pure polymers have low ionic conductivity (~ 10^{-9} Scm $^{-1}$), but the ionic conductivity can be enhanced by adding salts, plasticizers etc.

Today, many other examples of polymer with different atoms having lone pair electrons have been found. These include PVC with Cl as the heteroatom, Polyacrylonitrile (PAN) with N as the heteroatom, Poly (vinylidine fluoride) (PVDF) with lone pair electrons at the F atom etc.

Table 1.4 compares the ionic conductivity of PVC based polymer electrolytes with other polymer electrolytes.

No	Electrolyte Composition	Temp. (°C)	Hetero atom	Conductivity (S/cm)	Ref
1	PVC : PC : $LiClO_4$ (15 : 80 : 5)	20	Cl	0.9×10^{-3}	55
2	PVC : PC : EC : $LiClO_4$ (15 : 40 : 40 : 5)	20	Cl	1.2×10^{-3}	55
3	PVC : DBP : LiTFSI (33 : 55 : 12)	25	Cl	1.0×10^{-4}	56
4	PVC:PMMA:EC:PC: $LiCF_3SO_3$ (7.5 : 17.5 : 42 : 28 : 5)	20	Cl	1.0×10^{-3}	57
5	PEO – $LiCF_3SO_3$	25	O	2.5×10^{-4}	83
6	PEO – LiTFSI	25	O	1.2×10^{-4}	84
7	PEO – $LiClO_4$	25	O	6.1×10^{-5}	85
8	PAN : EC : BL : $LiClO_4$ (20 : 35 : 40 : 5)	22	N	2.2×10^{-3}	86
9	PAN : DMSO : $AgClO_4$	20	N	7.0×10^{-4}	79
10	PVDF : PC : $LiClO_4$ (70 : 10 : 20)	20	F	2.0×10^{-4}	87
11	PVDF : $LiClO_4$: PEO (80 : 20)	30	F	2.6×10^{-5}	88
12	AC – $AgNO_3$	25	N,O	2.6×10^{-5}	77
13	AC – $LiNO_3$	25	N,O	2.7×10^{-4}	89
14	AC - NaI	25	N,O	4.9×10^{-5}	90

Table 1.4 : Polymer Electrolytes and their Conductivity Values

Abbreviations :

LiTFSI	- Lithium bis (trifluoromethylsulfonyl) imide
PMMA	- Poly (methyl methacrylate)
BL	- 1,4 - butyrolactone
DMSO	- dimethyl sulfoxide
AC	- Ajax Chemicals

1.7 Polymer Batteries

Batteries are energy devices which store their chemical reactants. Many batteries are capable of a simple discharge but are incapable of having the original chemistry restored by electrical means internal to a cell. These correspond to primary batteries. Batteries which can be recharged and restored to their chemical composition through reversal of current flow are called "secondary batteries" or "storage batteries" [10].

Solid state ionic materials, which are solids which possess unusually high diffusion coefficients and conductance for specific ions, have assumed considerable importance in recent years for battery research [91]. Table 1.5 shows the development of secondary batteries.

Year	Type	Chemistry
1860	Lead – acid	PbO_2 / H_2SO_4 / Pb
1900	Ni - Cd cell	Ni / 2NiOOH / Cd
1965	Beta cell	Na / β-Al_2O_3 / S
1970	Zinc – chlorine	Zn / $ZnCl_2$ / Cl_2
1980 - 1990	Li / solid solution electrode	Li / PC–Li_2ClO_4 / MX_2
	Polymeric cells	Li / PEO–$LiClO_4$ / TiS_2
	Glassy cells	Li / Li^+- glass / TiS_2
1991	Li – microbatteries	Li / Li^+- glass / TiS_2
1992	Rocking - chair cells	$LiMn_2O_4$ / elect. / carbon $LiCoO_2$ / elect./carbon

Table 1.5 : Secondary Battery developments [92].

Polymer batteries were originally conceived to overcome the volume change requirements inherent in the use of intercalation cathode materials for solid state secondary batteries. The main development thrust has been towards lithium systems, initial work concentrating on medium temperature (~ 100°C) cells, but the present emphasis being towards room temperature batteries. In general, they are of the form Li / polymer electrolyte / intercalation electrode [93].

Lithium is a very attractive material for high energy density batteries because of its equivalent weight and high standard potential [94]. The first commercially available polymer electrolyte lithium rechargeable battery was introduced by Valence Technology of San Jose, Ca. The battery has a laminar structure as shown in Figure 1.11 [95].

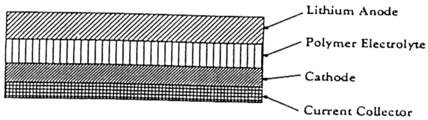


Figure 1.11 : Basic structure of the battery laminate

The polymer electrolyte plays three important roles in the solid polymer electrolyte (SPE) battery [96].

i) It is a lithium ion carrier and can be formed into thin films to improve the energy density

ii) It acts as an electrode spacer, which eliminates the need to incorporate an innate porous separator.

iii) It is a binder, which ensures good electrical contacts with the electrodes.

The differences between SPE lithium batteries and existing aqueous systems are shown in table 1.6 [96].

	Lead - acid battery	Nickel-cadmium battery	SPE battery
Theoretical Energy density (Whkg^{-1})	250	245	480
Practical Energy density (Whkg^{-1})	25 - 35	35	120
Secondary Reaction	$H_2O \rightarrow H_2 + ½ O_2$	$H_2O \rightarrow H_2 + ½ O_2$	No
% Efficiency	70 - 75 %	60 - 65 %	85 - 95 %
Cycling Characteristic	Short cycle life (300 cycles)	Good cycle life (500-1000 cycles)	Full discharge capacity (60 cycles)
Operative Temperature Range	- 20 to 40°C	- 40 to 50°C	-10 to 130°C

Table 1.6 : Main differences between SPE lithium batteries and existing aqueous system.

1.8 Intercalation Materials

1.8.1 Anode Materials

The cycleability of the lithium electrode can be improved by the use of lithium inserting substrates. The most common materials are lithium - carbon and lithium aluminium. Other suitable substrates are Sn, Pb, Bi and As.

The anodes based on LiAI alloys can be cycled up to 1000 times. Using substrate forming intercalation compounds with lithium, the reactivity against the electrode can be decreased. Therefore, the lithium in the host material will be "shielded" and the formation of dendrites will be reduced or avoided if the diffusion velocity inside the host material is high enough [97].

The main problems of lithium in the alloys matrix are connected with the significant differences in the between the pure basic material and the formed lithium alloy. In the case of carbon, the volume difference during the formation of LiC_6 is only 9.4% [98]. Carbon has therefore been the most favoured host material in recent years.

Many different kinds of carbonaceous materials have been developed, such as graphite, coke or carbon fibre materials [99]. Due to its layered structure, it can insert lithium according to the following scheme :

$$x\,Li + 6C \rightarrow Li_xC_6 \quad \text{with } 0 \leq x \leq 1$$

1.8.2 Cathode Materials

Manganese dioxide is an interesting material for battery applications. Besides being suitable for the intercalation of small ions (H^+, Li^+), it is also inexpensive, non - polluting and readily available.

The spinel $LiMn_2O_4$ has been extensively studied for the most promising cathode materials for lithium secondary batteries with high energy density. The transport of Li^+ is achieved at interstitial positions in the $[Mn_2]O_4$ sublattice. The spinel itself is stable over a wide range of stoichiometry $Li_x[Mn_2O_4]$ with $0 \le x \le 2$ [97, 100].

Lithiated nickel and cobalt oxides of the general formula $LiMeO_2$ (where Me=Ni , Co) are insertion compounds for high voltage lithium batteries. The compounds $Li_{1-x}NiO_2$ ($0 \le x \le 0.5$) and $Li_{1-x}CoO_2$ ($0 \le x \le 0.5$) are suitable cathode materials for 4V rechargeable lithium cells using a carbon anode. The cell reaction in the $C/LiMeO_2$ systems can be summarised by the following electrochemical process :

$$LiMeO_2 + 6C \leftrightarrow Li_{1-x}MeO_2 + Li_xC_6$$

1.9 Objectives of the Present Work

The main aim of this work is to study some characteristics of PVC based electrolytes in rechargeable solid state electrochemical cells. In this study, PVC based electrolytes complexed with double salt system, lithium triflate ($LiCF_3SO_3$) and lithium tetrafluoroborate ($LiBF_4$). The concentration that gives the highest electrical conductivity film is to be obtained.

Having determined the appropriate concentration to use, it would be useful to study the possibility of enhancing the electrical conductivity. In this work, attempts to enhance the electrical conductivity include the use of plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) and irradiating the PVC powder with γ - rays from a ^{60}Co source under vacuum at room temperature. All samples will be prepared by the solution cast technique to form a thin film.

The electrical conductivity of all the samples will be measured by impedance spectroscopy. Measurements of electrical conductivity at various temperature will be carried out to determine the mechanism of ionic conduction in the films.

Before the film with the highest electrical conductivity is used to fabricate electrochemical cells, all samples prepared will be characterized. X - ray diffraction (XRD) will be used to study the effect of dissolution of the salt on the nature of the polymer and to determine the occurrence of complexation. Complexation is an important criteria for a polymer to be considered as an electrolyte. The transference number will be measured to determine which species of ions acts as the major conductor. Thermal characterization will be carried out by using Differential Scanning Colorimetry (DSC) and Thermogravimetric Analysis (TGA).