CHAPTER I

INTRODUCTION
1.1 Introduction

Solid state ionics is a relatively new field of materials science and technology dealing with solids that exhibit high ionic conductivities (10 to $10^4$ Sm$^{-1}$) comparable to that of liquid electrolytes. Hence these solids are termed as superionic conductors (SIC) or fast ion conductors (FIC). They possess low value of activation energy for ion migration at temperatures much below their melting point. The technological importance of this class of materials can be explained on the basis of their use in solid state batteries, fuel cells, sensors etc. Search for solid electrolytes has originated as most of the liquid electrolytes have many inherent disadvantages like short life time, non-functioning of the devices below the freezing point and above the boiling point of the electrolyte, leakage of the electrolyte from the device etc. To overcome these deficiencies, the search for an alternative was initiated and as a result we have today materials with reasonably high ionic conductivity. High conducting solid electrolytes have been known since Faraday's discovery of electrical conduction in non-metallic PbF$_2$ and Ag$_2$S solids at temperatures well below their melting point during the period 1833-1838 [1]. These two materials are still of great interest as examples of fast ion conductors. During 20$^{th}$ century, Frenkel [2] proposed the classic mechanism that explains how electricity can be conducted through ionic solids by the flow of ions. This has established a clear structural basis for the occurrence of ionic conductivity in a crystalline solid like Ag$_2$Hgl$_4$ [3]. Modern work in this area essentially began by the report from Yao and Kumar [4] on sodium beta alumina, which has sodium ion conductivity at room temperature comparable to that of an aqueous sodium chloride solution. The simultaneous fabrication of the sodium/beta alumina/sulfur battery by Yao and Kumar [4] at the Ford Motor Company has intensified interest in the commercial applications of solid electrolytes. Subsequently many other super ionic conductors were synthesized.

1.2 Classification of ionic solids

The ionic conduction in these solids is possible due to the presence of defects or imperfections. Based on the defect idea, these ionic solids can be classified into two types-point defect and molten sub-lattices. In the point defect type of solids, ion
transport is through Frenkel or Schottky defects and hence, the conductivity increases with temperature [5, 6]. In molten sub-lattice type of solids, ions can move freely from one position to another, since all ions are available for transport [5]. In this type of solids, the activation energy is comparatively less and hence, conductivity is high.

Based on the amount of available mobile ions and defect concentration (n), these ionic solids can be classified into two categories.

1. Normal ionic conductors (NICs)
2. Super ionic conductors (SICs).

**Normal ionic conductors (NICs)**

Solids like KCl, NaCl etc, are known to have very low ionic conductivity at ambient temperatures (conductivity $10^{-14} - 10^{-12}$ Scm$^{-1}$) and hence, these are called normal ionic conductors (NICs). These materials will have dilute point defects of the order of $10^{-8}$ cm$^{-3}$. In these solids, thermally generated imperfections are responsible for migration of ions [6, 7]. Since the conduction is due to thermally generated defects, the activation process involves both energy due to defect formation ($h_d$) as well as energy due to ion migration ($h_m$). The conductivity is expressed as

$$\sigma = (\sigma_0 / T) \exp (-h_d / 2kT) \exp (-h_m / 2kT) \tag{1.1}$$

where $\sigma_0$ is pre exponential factor, k is Boltzmann constant and T is the absolute temperature.

**Super ionic conductors (SICs)**

The temperature dependence of conductivity ($10^5$-$10^4$ Scm$^{-1}$) of these solids shows an unusual behaviour with the conductivity increasing abruptly by several orders of magnitude, leading to a high ionic conduction phase at higher temperatures. A number of compounds exhibiting very high ionic conductivity at room temperature as well as at higher temperatures have also been synthesized [8-12]. These materials are called superionic conductors. In SICs, the carrier concentration is very high and the
enthalpy of formation of defects is almost zero. The conductivity expression is written as

\[ \sigma = (\sigma_0 / T) \exp (-E_a / kT) \]  \hspace{1cm} (1.2)

where the activation energy, \( E_a \), is only due to ion migration and \( \sigma_0 \) is the pre-exponential factor, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.

1.3 Characteristic features of super ionic conductors (SICs)

In these solids, the observed high ionic conductivity is achieved through phase transitions at a particular temperature i.e. insulator- SIC phase transition and order-disorder phase transition. [13-14]. Insulator- SIC phase transition is characterized by

- a discontinuity in conductivity vs. \( 1/T \) curve.
- A latent heat, typical of a first order transition
- A change in lattice symmetry

Order- disorder phase transition is characterized by

- absence of abrupt change in conductivity
- continuity in conductivity vs \( 1/T \) curve with change of state at a transition point
- no change in lattice symmetry

The characteristic features of such conductors are

- The bonding is essentially ionic in nature
- Their electronic conductivity is low (\( \sim 10^{-4} \) S/cm) and activation energy is low (\( < 0.5 \) eV).
- The conduction is predominantly due to ions and their ionic transference number is close to unity.
Transport of ions occurs through the favourable conduction pathways across intergranular as well as inter particle boundaries.

The chemical and electrochemical compatibility and good adhesion for mechanical contact with solid electrode materials are observed.

The electronic conductivity contribution towards total conductivity is almost negligible.

The number of energetically equivalent sites available for the migration of ions is greater than the number of mobile ions.

1.4 Classification of super ionic conductors

The superionic solids are primarily classified based on

1) Bonding type
2) State of solid
3) Mobile ion due to which the conduction occurs
4) Polarity of the sample

The flowchart (Figure 1.1) shows clearly the classification. The super ionic solids may be either covalent or ionic bonded solids. In the covalent solids, particularly in crystals, the constituent particles do not take part in the conduction process since covalent bond forms a stable structure. However, the crystals may have a structure such that foreign ions can diffuse within the crystal. The covalent bonded fast ionic conductors are less in number. Among the ionic solids, they may be purely ionic or partially semiconductor, depending on the temperature range. These fast ionic conductors can also be classified as crystalline and amorphous based on the state of the solid.
Fig 1.1: Classification of super ionic conducting materials

The crystalline ionic solids can be divided into two categories according to the number of defects as

1) Point defect type
   (i) Dilute (less than $10^{18}$ cm$^{-3}$)
   (ii) Concentrated ($10^{18}$-$10^{20}$ cm$^{-3}$)

2) Molten sublattice type ($\sim 10^{22}$ cm$^{-3}$)

Broadly, superionic solids belong to the category of 1(ii) or 2. The materials may also be polycrystalline in nature and the main advantage of the polycrystalline samples is that they could be used in technological applications especially in batteries simply because of the ease and cost of preparation. Some of the polycrystalline super ionic compounds and their conductivity values reported by various workers are given in table 1.1 [15-31].
Under the amorphous solids, glasses, ion exchange resins and polymers are the entities to be noted with special reference. Amorphous materials as solid electrolytes in electrochemical devices have attracted a great deal of attention because of their advantageous characteristic features like

(a) The absence of grain boundary
(b) Ease of glass formation
(c) Isotropic properties and use of glass forming cations as spectroscopic probes
(d) Ease of shaping them into thin film form of any size and shape

**Glasses**

Arresting the disorder phase of normal ionic conductors in the presence of glass modifiers at ambient temperatures is known as glassy ionics. High ionic conductivity in the glassy electrolytes has been attributed to the disordered distribution of mobile ions in the random structure of the glass. Table 1.2 [32-39] gives some examples of the glassy super ionic conducting materials.

**Solid polymer electrolyte materials**

Solid polymer electrolytes are materials of current interest due to their special mechanical properties, ease of fabrication in thin films of desirable sizes and proper electrode-electrolyte contacts in different electrochemical devices. The dominant class of polymer electrolytes comprises the neutral polar polymers complexed with alkali metals / divalent / transition metal / ammonium salts and acids. Fenton et al. [40] and Wright [41] were the first to show that polyethylene oxide (PEO)-alkali metal salt complexes are ionic conductors. Later, Armand et al. [42] demonstrated the technological importance of these polymer electrolytes. Since then, the subject of polymer electrolytes has been pursued vigorously [43, 44]. In order to increase the conductivity of these polymer electrolyte films, recently method of heterogeneous doping is employed. In this method ultra fine insoluble and insulating particles are dispersed in to the matrix of ionically conducting electrolytes.
Table 1.1: Some examples of polycrystalline superionic conductors

<table>
<thead>
<tr>
<th>Type of superionic conductor</th>
<th>Conductivity Scm⁻¹</th>
<th>Temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lithium ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiClO₄</td>
<td>1.0 x 10⁻⁶</td>
<td>27</td>
<td>[15]</td>
</tr>
<tr>
<td>Li₂SO₄</td>
<td>1.0 x 10⁻⁴</td>
<td>800</td>
<td>[16]</td>
</tr>
<tr>
<td><strong>Sodium ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>1.2 x 10⁻³</td>
<td>100</td>
<td>[17]</td>
</tr>
<tr>
<td>Sodium-β Alumina</td>
<td>1.4 x 10⁻²</td>
<td>25</td>
<td>[18]</td>
</tr>
<tr>
<td><strong>Potassium ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O-Ga₂O₃</td>
<td>1.00 x 10⁻¹</td>
<td>300</td>
<td>[19]</td>
</tr>
<tr>
<td>Potassium-β Alumina</td>
<td>6.5 x 10⁻⁵</td>
<td>300</td>
<td>[20]</td>
</tr>
<tr>
<td><strong>Silver ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbAgI₅</td>
<td>0.27</td>
<td>25</td>
<td>[21]</td>
</tr>
<tr>
<td>α-Ag₃Sl</td>
<td>2.00</td>
<td>240</td>
<td>[22]</td>
</tr>
<tr>
<td><strong>Copper ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Cul</td>
<td>9 x 10⁻²</td>
<td>450</td>
<td>[23]</td>
</tr>
<tr>
<td>α-Cu₂Se</td>
<td>0.11</td>
<td>150</td>
<td>[24]</td>
</tr>
<tr>
<td><strong>Oxygen ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO₂·Y₂O₃</td>
<td>1.2 x 10⁻¹</td>
<td>1000</td>
<td>[25]</td>
</tr>
<tr>
<td>Bi₂O₃·WO₃</td>
<td>1.0 x 10⁻¹</td>
<td>750</td>
<td>[26]</td>
</tr>
<tr>
<td><strong>Fluoride ion conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-PbF₂</td>
<td>1.00</td>
<td>500</td>
<td>[27]</td>
</tr>
<tr>
<td>CaF₂</td>
<td>4 x 10⁻²</td>
<td>700</td>
<td>[28]</td>
</tr>
<tr>
<td><strong>Proton conductors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄ClO₄</td>
<td>1.05 x 10⁻⁵</td>
<td>27</td>
<td>[29]</td>
</tr>
<tr>
<td>Sb₂O₃·4H₂O</td>
<td>3 x 10⁻⁴</td>
<td>25</td>
<td>[30]</td>
</tr>
<tr>
<td>H₃PO₄·H₂O</td>
<td>10⁻⁶</td>
<td>30</td>
<td>[31]</td>
</tr>
</tbody>
</table>
Table 1.2: Some examples of glassy Superionic conducting materials

<table>
<thead>
<tr>
<th>Types of glass</th>
<th>Conductivity (Scm$^{-1}$)</th>
<th>Temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45%LiI-18%P$_2$S$_5$-37%Li$_2$S</td>
<td>1.0x10$^{-3}$</td>
<td>25</td>
<td>[32]</td>
</tr>
<tr>
<td>Li$_2$W$_2$O$_7$</td>
<td>1.17x10$^{-5}$</td>
<td>60</td>
<td>[33]</td>
</tr>
<tr>
<td>Sodium glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39%Na$_2$O-8%Y$_2$O$_3$-53%SiO$_2$</td>
<td>3.39x10$^{-3}$</td>
<td>300</td>
<td>[34]</td>
</tr>
<tr>
<td>60%Na$_2$S-40%GeS$_2$</td>
<td>1.5x10$^{-4}$</td>
<td>100</td>
<td>[35]</td>
</tr>
<tr>
<td>Silver glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%AgI-30%Ag$_2$O-10%B$_2$O$_3$</td>
<td>8.5x10$^{-3}$</td>
<td>25</td>
<td>[36]</td>
</tr>
<tr>
<td>55%Ag$_2$S-45%GeS$_2$</td>
<td>1.4x10$^{-3}$</td>
<td>25</td>
<td>[37]</td>
</tr>
<tr>
<td>Copper glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cul-Cu$_2$O-P$_2$O$_5$</td>
<td>1.0x10$^{-2}$</td>
<td>25</td>
<td>[38]</td>
</tr>
<tr>
<td>Cul-Cu$_2$O-MoO$_3$</td>
<td>10$^{-2}$</td>
<td>25</td>
<td>[39]</td>
</tr>
</tbody>
</table>

These multi phase materials known as "composite electrolytes" or "dispersed phase solid electrolytes" or "heterogeneous electrolytes" have been reported to exhibit ionic conductivity of 2 - 3 orders of magnitude higher than that of the pure host solid electrolytes. Table 1.3 [45-50] illustrates a variety of available composite solid electrolytes.
### Table 1.3 Some examples of composite electrolytes

<table>
<thead>
<tr>
<th>Type of electrolyte</th>
<th>Conductivity S cm⁻¹</th>
<th>Temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN0₁₋₃₋₃₋₃</td>
<td>9.9 x 10⁴</td>
<td>25</td>
<td>[45]</td>
</tr>
<tr>
<td>CuCl₂₋₃₋₃₋₃</td>
<td>5.0 x 10⁶</td>
<td>400</td>
<td>[46]</td>
</tr>
<tr>
<td>Li₂SO₄₋₃₋₃₋₃</td>
<td>3.6 x 10⁻¹</td>
<td>500</td>
<td>[47]</td>
</tr>
<tr>
<td>Li₂SO₄₋₃₋₃₋₃</td>
<td>1.02 x 10⁻¹</td>
<td>30</td>
<td>[48]</td>
</tr>
<tr>
<td>LiAsF₆₋₃₋₃₋₃</td>
<td>6.6 x 10⁻¹</td>
<td>30</td>
<td>[49]</td>
</tr>
<tr>
<td>LiC₁₋₃₋₃₋₃</td>
<td>1.01 x 10⁻¹</td>
<td></td>
<td>[50]</td>
</tr>
</tbody>
</table>

Apart from these classifications, the superionic solids could be separated with respect to the type of mobile ion responsible for conduction namely

- oxide ion conductors
- fluoride ion conductors
- proton conductors
- lithium ion conductors
- β-alumina
- silver and copper ion conductors.

### Oxide ion conductors

Generally, these oxides take the fluorite structure, for example CeO₂ and ThO₂, between the room temperature and melting points. These oxides are distinctive in that they form solid solutions in an unusually wide composition range with alkaline earth or rare earth oxides such as CaO and Y₂O₃. Later, other compounds like yittria stabilized thoria and calcia stabilized zirconia with distorted fluorite structure have been found to have good oxygen ion conduction. In general, under this classification, a homogeneous solid solution phase is easily formed when the cation sizes of a host (such as CeO₂) and a guest (such as Gd₂O₃) are almost equal. These oxygen ion conductors are found to have a good scope in solid state ionic devices like sensors, partial pressure gauges and fuel cells.
Fluoride ion conductors

Fluoride ions can conduct through its vacancies and hence these ions are more conductive in solids than oxide ions, because the former is univalent while the ionic radii of these two ions are almost the same. For example, CaF$_2$ incorporated with 1mol% NaF exhibits a conductivity of $10^{-3}$ ohm$^{-1}$ cm$^{-1}$ through its vacancies generated by partial replacement of Ca$^{2+}$ ion sites with a monovalent cation such as Na$^+$. A conductivity upto $10^{-4}$ ohm$^{-1}$ cm$^{-1}$ at room temperature is available in sintered material (eg. TISn$_2$F$_5$) and a maximum conductivity around $10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at 327°C in La$_{0.95}$Ba$_{0.05}$F$_2$ single crystals is observed. β-PbF$_2$ exhibits conductivity as large as $10^{-1}$ ohm$^{-1}$ cm$^{-1}$ at 400°C and $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ even at room temperature without aliovalent impurities. Meanwhile, other halides (such as SrCl$_2$) exhibit notable anionic conduction at higher temperatures such as 1000°C. But their conductivity at room temperature is much lower than that of fluorides. Rare earth fluoride, by themselves and added as dopant with fluorides like CaF$_2$ prove themselves to be good F$^-$ ion conductors. Many other fluoride ion conductors of the type KBiF$_4$ and LaF$_3$ also have high ionic conductivity of the order of $10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at 100°C. Fluoride ion conducting amorphous electrolytes have also been reported to possess relatively high conductivity for practical applications in solid state ionic devices.

Proton conductors

The proton, the atomic nucleus of hydrogen, is extremely small compared with the ionic radii of ordinary ions, hence enabling the H$^+$ ions to conduct through a channel composed of non-structural or zeolitic water as if it is in a solution phase. The H$^+$ ions will never move as it is but it would bind itself to a molecular unit in a crystal and transfer from one site to another by molecular rotation. The “vehicular mechanism” theory explains that the proton conducts as an ion with ordinary radius such as H$_3$O$^+$ or NH$_4^+$. In this case, counter diffusion of a vehicle molecule such H$_2$O or NH$_3$ is required for conduction. Apart from this, ion exchange membranes (polymers) exhibit proton conduction of the order of $10^2$ ohm$^{-1}$ cm$^{-1}$ if they are swollen with 10% to a few multiples of 10% weight of water. The motional behaviour of H$^+$ ions in the swollen polymer is similar to that in acid solution. As membranes are dried, the conductivity
decreases and hence these are intermediates between solid electrolytes and acidic solution. But PEO-CF3SO3Li shows a high ionic conductivity even after it dries completely.

**Lithium ion conductors**

All LiX (X = F, Cl, Br and I) crystals exhibit NaCl type structure. Except Lil, they are all almost ionic crystals and insulators at room temperature. Even though the bonding nature of Lil is covalent to some extent, it yields conductivity of the order of \(10^{-1}\) ohm\(^{-1}\)cm\(^{-1}\) because of the large polarisability of I\(^-\) ions (six orders smaller than that of RbAg\(_4\)I\(_5\)).

Complex metal halides with the inverse spinal structure, Li\(_3\)MX\(_4\), are the examples of the halide type Li\(^+\) conductors. Lithium nitrides, Li\(_3\)N, as such do not have higher conductivity but Li\(_3\)N intentionally doped with hydrogen exhibits higher conductivity. Some lithium salts with simple oxyacids such as Li\(_3\)PO\(_4\) and Li\(_4\)SiO\(_4\) exhibit considerable Li\(^+\) conduction at high temperatures. These compounds possess an 'open structure' for ion transport.

**1.5 Classification of solid polymer electrolyte materials**

The polymer electrolyte materials are broadly classified into the following groups:

- a) Solvent swollen polymers
- b) Polyelectrolytes
- c) Solvent free polymer-salt complexes

**Solvent swollen polymers**

Some solvents (aqueous/ non-aqueous) swell the host lattice of some basic polymers like polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP). The dopant ionic solutes like H\(_3\)PO\(_4\) are accommodated in these swollen lattices and assist the ionic motion in solvent rich swollen regions of the polymer host [51]. These materials are, in general, unstable as their conductivity depends on the ambient temperature and the concentration of the solvent in the swollen region.
Polyelectrolytes

Polyelectrolytes are the polymers that have self-ion generating groups responsible for ionic conductivity attached with the main chain of the polymer. Some important examples are polysulphonic acid based polyelectrolytes such as Nafion, sodium polystyrene sulphate etc. The main attraction of such polymers is the single ion transport in the bulk [52,53].

Solvent free polymers-salt complexes

These are most common materials and have been extensively studied. These materials are prepared, in general, in the form of films, by solution-cast technique (common solvents: acetonitrile, methanol, ethanol, propanol water, etc.) in which the solution of polymers and salt of monovalent alkali metal/ divalent/transition metals and ammonium salts are mixed, stirred thoroughly and cast on teflon/polypropylene dishes. The solutions are slowly evaporated by vacuum drying and heating to make the final film, solvent free and is essentially an ion-complexed polymer only.

Polymer electrolytes are thin solid films consisting of ionic salts dissolved in an appropriate polymer. Mechanically they behave like solids but the internal structure, and consequently the conductivity behaviour, closely resembles those expected of the liquid state.

1.6 Criteria for polymer - salt complexation

For effective complexation/solvation of salts in polymers, the following criteria can be taken as “thumb rules”.

i) The polymers should have low glass transition temperature ($T_g$) and flexible backbone which will ensure complexation. Low $T_g$ can be attained either by choosing the polymers of low cohesive energy (such as PEO, PPO, PEI, etc.) or by plasticizing the polymer.

ii) The concentration of polar groups (or solvating hetero-atoms) responsible for complexation of cations should be as large as possible.
1.7 Applications of Solid polymer electrolytes:

Polymer electrolytes have several applications in solid state electrochemical devices such as solid state batteries, fuel cells, sensors and electrochromic display devices, super capacitors. The application of super ionic conductors can be broadly classified into two categories namely battery and non-battery applications. This following section briefly discusses about such applications.

1.7.1 Battery applications

An electrochemical emf will be developed when a solid electrolyte is stacked between two electrodes of different chemical potentials. Over the liquid electrolytic cells, solid electrolyte galvanic cells have the advantage of long operating temperature range, long operating life and feasibility of miniaturization as the electrolyte could be coated as thin films. Good reviews are available on solid state batteries based on different superionic conductors [54-59]. A typical design of the lithium polymer electrolyte battery as shown in fig. 1.2.

Generally solid state electrochemical cells can be classified into two categories.

1) Primary batteries

2) Secondary/ rechargeable batteries

If the product of the cell reaction can be decomposed into the original reactants simply by applying a sufficient voltage to the battery for a long enough period of time, then the battery is called a secondary battery and is rechargeable. If the cell reaction is not reversible in this way, the battery is called primary battery. A battery during the discharge is called a galvanic cell and a secondary battery under recharge is called an electrolytic cell. For secondary batteries the polarity of the electrodes, + or -, stays the same whether the battery is under charge or discharge conditions but, since reversing of the cell reaction involves changing oxidation process into a reduction process and vice versa, the position of the anode and cathode are interchanged as shown in fig 1.3. The direction of electron flow through the external circuit and flow of the ionic current through the electrolyte is shown in fig 1.4. General classification of the solid state batteries along with other details is given in table 1.4.
Table 1.4
Classification of solid state batteries

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass</th>
<th>Ceramic</th>
<th>Compacted powder</th>
<th>Sulphate</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>A:S</td>
<td>A:P/S</td>
<td>A:S</td>
<td>C:P</td>
<td>B/C:P</td>
</tr>
<tr>
<td>25-125°C</td>
<td>40-160°C</td>
<td>TiS₂</td>
<td>350-400°C</td>
<td>25°C</td>
<td>745°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PbI₂</td>
<td>MnO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37°C</td>
</tr>
<tr>
<td>Na⁺</td>
<td>B/C:S</td>
<td>B/C:S</td>
<td>A:S</td>
<td>C:P</td>
<td>-</td>
</tr>
<tr>
<td>25-98°C</td>
<td>25-98°C</td>
<td>TiS₂</td>
<td>350-400°C</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ag⁺</td>
<td>C:S</td>
<td>C:P</td>
<td>C:S</td>
<td>B:P</td>
<td>C:P</td>
</tr>
<tr>
<td>25-125°C</td>
<td>25°C</td>
<td>TiS₂</td>
<td>350-400°C</td>
<td>25°C</td>
<td>25 or 745°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I₂</td>
<td>MnO₂</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cu⁺</td>
<td>C:S</td>
<td>C:P</td>
<td>-</td>
<td>B:P/S</td>
<td>-</td>
</tr>
<tr>
<td>25°C</td>
<td>25°C</td>
<td>TiS₂</td>
<td>350-400°C</td>
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<td>I₂, TiS₂</td>
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<tr>
<td>H⁺</td>
<td>Used as fuel cells</td>
<td>-</td>
<td>Used as fuel cells</td>
<td>A/C:P</td>
<td>-</td>
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<tr>
<td></td>
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<td>25°C</td>
<td>MnO₂PbO₂</td>
</tr>
<tr>
<td>M⁺</td>
<td>C:P/S</td>
<td>A/B:S</td>
<td>B/C:S/P</td>
<td>C:P</td>
<td>-</td>
</tr>
<tr>
<td>25°C</td>
<td>350-400°C</td>
<td>TiS₂, MnO₂</td>
<td>25°C</td>
<td>745°C</td>
<td>MnO₂</td>
</tr>
</tbody>
</table>

Legend: Line 1: Category A (ready for commercialization); B (developed to some extent); C (tried but undeveloped) P (primary), S (secondary)
Line 2: Temperature range of operation
Line 3: Typical cathode materials

Abbreviation: P2VP B (poly(2-vinylpyridine)), PA - polyacetylene
Fig 1.2: Typical design of solid state battery.

Fig 1.3: Three layer rechargeable batteries consisting of left hand electrode/electrolyte/right hand electrode
Conventional cells

The nickel-cobalt cells are the commercial batteries available for long since after the dry cells. These batteries have the mechanism almost similar to the zinc anode and manganese-dioxide cathode with KOH or NH₄Cl + ZnCl₂ dry cells with the proton and electron diffusion. The proton diffusion enables a reversible reaction at the nickel electrode and hence the cells could be recharged. Similarly, lithium cells have been commercialized from mid 1970, as a power source for calculators, watches and semiconductor devices. These batteries couldn’t be recharged. They are divided into two major types of cathode materials, graphite fluoride and MnO₂ type LiClO₄ and LiBF₄/Propylene carbonate are often used.
Among various solid electrolytes, stabilized zirconia and β-alumina are widely used in sodium-sulphur batteries. The principle of sodium – sulphur batteries was established in 1967 by Kummer and his co-workers. These batteries generate an emf of about 2.17 V. Sodium – sulphur batteries are high energy density batteries compared with the conventional batteries. They possess high operating temperature range and the actual energy density is 200 to 300 Wh/kg. These features are favorable to use them as power sources for electric vehicles and power storage systems.

Solid state batteries with copper and silver as active material have also been brought into scientific picture but they exhibit an emf of 0.67-0.69 V only which is less than half the value of the manganese dry cells.

**Fuel cells**

A fuel cell is not a storage battery but a apparatus which converts power, from chemical energy to electrical energy with the help of an ion conducting material [60]. Fuel cells are being used as power sources in space crafts. Recently, many efforts have been undertaken to develop fuel cells as terrestrial power generators. The efficiency of fuel cells is high in principle because they are not heat engines and therefore cannot be subjected to Carnot’s engine. Fuel cells provide many advantages over traditional energy conversion systems such as high energy conversion efficiency, fuel flexibility because of internal reforming, very low levels of NOx and SOx emissions, versatile size plants and long life time. Fuel cells consist of two porous electrodes separated by a dense oxygen-ion electrolyte in either tube or disc form [55]. Fuel cells are of three types namely

1) Sodium electrolyte type (For eg. with phosphoric acid)

2) Molten salt type using mixed fused alkaline carbonate

3) Solid electrolyte type based on clacia stabilized (CSZ). Recently CSZ has been replaced by yettria stabilized zirconia.
1.7.2 Non battery applications

Sensors

Mostly all the sensing devices measure chemical or physical quantities. But for making the device to be handy, speedy and easy, the quantity measured is made to be electrical signal. Determination of the concentration of the ions (chemical sensing) is more probable for making this a successful one. Sensors have been widely used throughout the world as hazard alarms for home use to control units for automated production lines. Automated oxygen sensors based on zirconia are used in the combustion control and for preventing air-pollution. Chemical sensors are of four types namely

- EMF type: Transducing the difference of chemical potential into emf (YSZ and CSZ are widely used for this type of sensors)
- Limiting current type: Transducing the concentration of the species concerned into the limited current of an electrolytic cell
- Semiconductor type: Utilizing the conductivity change of the semiconductor on adsorption or partial reduction
- FET type: Utilizing changes of the source drain current of a FET on absorption of chemical species on to its gate electrode.

Typical diagram of potentiometric hydrogen sensor using PVA-H$_3$PO$_4$ as an electrolyte is shown in fig 1.5.

![Diagram of hydrogen sensor](image)

**Fig 1.5: Schematic diagram of hydrogen sensor**
Electrochromic display devices

Electrochromic display devices are based on the colour changes of certain kind of materials due to electrochemical reduction or oxidation. Organic compounds like dipathalocyanine complexes containing lanthanide elements or polythiophens exhibits electrochromisim, inorganic compounds like WO₃, IrO₂, H₂O and Prussian blue possess electrochromism. Organic solvent electrolytes containing LiClO₄ could also be used for the same purpose. Mostly the hydrogen content or water content of the compound is more important for these applications.

![Schematic diagram of an electrochromic display device](image)

**Fig 1.6: Schematic diagram of an electrochromic display device**

Apart from the above mentioned applications, solid electrolytes also find useful applications in other devices. Solid state double layer capacitors or super capacitors have the advantage of capacity than ordinary capacitors and they can be reversibly oxidized or reduced over a wide potential range [61]. Potential memory cells with silver ion conducting solid electrolyte of the configuration Ag/solid electrolyte/Ag with Ag₆₄WO₄ have also been developed by Ikeda and Tada [62] of the Sanyo Electric Company, Japan, and are commercially available.

1.8 Earlier work on polymer electrolytes

Many polymers have excellent electrical properties, as well as a variety of physical, chemical and mechanical properties that make them suitable for solid state electrolytes. Since knowledge of the nature of electrical conduction in insulating...
materials is incomplete, it is sometimes not clear whether the charge transfer process involves the transportation of ions or electrons for certain polymers. However, it would appear that the electrical conduction of polar polymers in a relatively low electric field is ionic. Support for the ionic mechanism can be supplied from Faraday's law observed in a gas evolution experiment with an applied voltage and from the dependence of electrical conductivity on pressure, free volume, and degree of crystallinity [63-66]. The free volume is a central concept in considering both equilibrium thermodynamic properties and transport phenomena in liquids or polymers.

Despite the wide-spread interest of polymer electrolytes which arises from their suitability for technological applications, it is interesting to note that divalent polymer electrolytes were first studied approximately three decades earlier [67]. The next benchmark date was 1973 when PEO: LiX system was developed [40]. Later complexes were formed between polyethylene oxide and a few sodium and potassium salts and studied [41].

(a) Electrical conductivity and transference numbers

Research on polymer electrolytes consisting of polyvinyl alcohol (PVA) and alkali metal salts was reported in literature for its application to several kinds of electrochemical devices, e.g. batteries/fuel cells, electrochromic display devices/smart windows, photo electrochemical solar cells etc. [68-70]. PVA is polar polymer with carbon chain as flexible backbone. The ionic transport in PVA-MX complexes may be interpreted on the basis of hopping mechanism between the polymer chains [71]. It is understandable how the conductivity dramatically increases above the crystalline-amorphous transition temperature. In fact above this temperature, the polymer behaves as a highly viscous liquid (elastomer) and the mobility of ions greatly increases because of the disordered movements of the chains [72].

The studies in the field of polymeric electrolytes are devoted to PEO-based electrolytes using alkali salts LiBF₄, LiPF₆ and LiB(C₆H₅)₄ [73], LiSCN [74], etc... Abrantes et al. [75] reported electrolytes containing PEO with ZnX₂ salts, in which X is Cl, Br, I and ClO₄ over a wide range of compositions. The best ionic conductors of each
anion type are \( \text{ZnCl}_2(\text{PEO})_{2n}, \text{ZnBr}_2(\text{PEO})_{2n}, \text{ZnI}_2(\text{PEO})_{16} \) and \( \text{Zn(ClO}_4)_2(\text{PEO})_{2n} \). Of these, \( \text{ZnI}_2(\text{PEO})_{16} \) has the highest conductivity of \( 3.6 \times 10^{-4} \text{ Scm}^{-1} \) at 140°C. Transport number measurements on \( \text{ZnX}_2 \) electrolytes indicated values as high as 0.9.

Chandra et al. [76] studied the optical microscopy, X-ray diffraction, differential thermal analysis (DTA), infrared absorption, transference number measurements and electrical conductivity of proton conducting polymer electrolytes based on polyethylene oxide (PEO) complexed with ammonium perchlorate (\( \text{NH}_4\text{ClO}_4 \)) salt. The highest conductivity at 30°C was of the order of \( 1.05 \times 10^{-5} \text{ Scm}^{-1} \), and \( \text{H}^+ \) ion transference number was 0.85.

Abraham et al. [77, 78] have reported mixed polymer electrolytes composed of Li salt complexes of poly [bis - (methoxy - ethoxy ethoxide) phosphazene] (MEEP) with excellent dimensional stability and high conductivity. MEEP/(PEO)-(LiX)\textsubscript{m} mixed polymer electrolytes exhibited conductivities at 60°C which are comparable to the conductivity of PEO-(LiX)\textsubscript{n} at 100°C. The higher conductivity of the mixed electrolytes compared to PEO complexes has been attributed to the higher degree of amorphous character introduced by the presence of MEEP.

Complexes of certain Li salts and inorganic polymer poly [bis - methoxy ethoxy ethoxide phosphazene], known as MEEP have been reported by Blonsky et al. [79]. These complexes belong to the class of highly conducting polymer electrolytes. For example, conductivity of the order of \( 2 \times 10^{-5} \text{ Scm}^{-1} \) has been reported for MEEP (\( \text{LiBF}_4 \))\textsubscript{0.25} complexes at room temperature. The MEEP - (LiX)\textsubscript{n} polymer electrolytes, however, have shown poor mechanical properties and could not be cast as free standing thin films for use as electrolytes in solid state batteries.

Moryoussef et al. [80] reported that the conductivity of \( \text{PEO}_{15}: [\text{CaBr}_2]_{0.5} / [\text{CaI}_2]_{0.5} \) at temperatures up to 80°C was found to be higher than that of either the pure bromide and iodide electrolytes and the conductivity-temperature behaviour was observed to follow the VTF equation. The authors ascribed this to a plasticizing effect with which they could explain the conductivity enhancement relative to pure systems that they found for the \( \text{PEO}_{15}: [\text{Ca (CF}_3\text{SO}_3]_{2}]_{0.5} / [\text{MgCF}_3\text{SO}_3]_{0.5}, \text{PEO}_{15} \):
[Ca(CF$_3$SO$_3$)$_2$]$_{0.5}$ / [NaCF$_3$SO$_3$]$_{0.5}$ systems. These studies indicated that the resulting enhancement of conductivity can be attributed to topologic disorder induced by the presence of foreign species. This favours the formation of an amorphous phase at the expense of crystalline phase.

Lee et al. [81] studied the effect of silica on the electrochemical characteristics of the plasticized polymer electrolytes based on the (PAN-CO-PMMA) copolymer. The maximum ion conductivity for the plasticized electrolyte was found be of the order of $10^{-4}$ Scm$^{-1}$ at ambient temperature. The decrease in the ion conductivity with silica at higher content is expected to be attributed to the increase of viscosity of the plasticizer-rich phase and the decrease in the charge carrier numbers. Similar studies using plasticizer effect on polymer electrolytes have been reported by the other researchers [82-83].

Rajendran et al. [84] prepared polymer electrolytes comprising a blend of poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) with different concentrations of LiBF$_4$ using a solvent-casting technique. The structure and complexation of the electrolytes are studied by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The ionic conductivities of the electrolytes were measured in the temperature range 302-373 K. The maximum conductivity ($1.2886 \times 10^{-3}$ S cm$^{-1}$) was obtained for a polymer complex with 8 wt.% LiBF$_4$. The thermal stability of this electrolyte was examined by thermo gravimetric/differential thermal analysis (TG/DTA).

Hiran Kumar et al. [85] prepared proton conducting polymer electrolytes of pure polyvinyl alcohol and polyvinyl alcohol complexed with ammonium acetate having different compositions by solution cast technique. FTIR spectrum confirmed the complexation process. The conductivity of the pure polyvinyl alcohol was in the order $10^{-1}$ S/cm at ambient temperature and its value increased $10^4$ times when complexed with 20% ammonium acetate. The Arrhenius plots for all electrolytes showed two different regions above and below the glass transition temperature. A high dielectric loss value was observed for the case of complexed PVA in comparison to pure PVA.
Based on the study of relaxation spectra, it was found that the relaxation time decreased with increase in temperature and dopant concentration.

Sen and Das [86] studied the conductivities of poly 2 vinyl pyridine (P 2VP) and (P 2VP HCl) in the temperature range 30-110°C. The addition of Cl⁻ ion increases the conductivity. Wagner's polarization technique was employed to determine the transference numbers.

Rajendran et al. [87] studied the ionic conductivity of a solid polymer electrolyte based on PVA complexed with LiClO₄, LiCF₃SO₃ and LiBF₄ and also dimethylphthalate (DMP) as plasticizer. Electrolytes were characterized by XRD, FTIR and impedance spectroscopic studies. Conductivity was significantly improved by the addition of plasticizer. Temperature dependent conductivity of the polymer electrolyte films seemed to obey the VTF mechanism.

Maurya et al. [88] studied optical microscopy, x-ray diffraction, differential thermal analysis, infrared spectroscopy, transport number and conductivity of a proton conducting polymer electrolyte (PEO + NH₄I) system. Maximum conductivity of (PEO+NH₄I) film was found to be 10⁻⁵ S cm⁻¹ at room temperature. The x-ray diffraction results revealed that the degree of amorphosity of the polymer increased with increase of NH₄I salt.

Uma et al. [89] studied the influence of lithium ions on structural and conductivity of composite electrolyte consisting of PVC and PMMA. The addition of ZrO₂ to the polymer improved both electrical and mechanical properties of the electrolyte.

Lewandowski and Stepniak [90] studied the ionic conductivity of a solid polymer electrolyte based on copper (II) trifluoromethanesulfonate dissolved in poly (ethylene oxide) (PEO). The ionic conductivity was significantly improved by the addition of a non-volatile solvent sulfolane (tetramethylene sulfone, TMS). The bulk conductivity of (PEO)₁₅ Cu(CF₃SO₃)₂ thin-film electrolyte increased from 10⁻⁹ S cm⁻¹ to 5x10⁻⁴ S cm⁻¹ at ambient temperature for (PEO)₁₅ Cu(CF₃SO₃)₂ TMS₂₀ wt% composite electrolyte.
Polymer electrolytes based on PEO complexed with NH$_4$SCN by Srivastava et al. [91] and with silver thiocynate by Sekhon et al. [92] were reported in literature. Conducting solid polymer electrolytes comprising random polyethylene oxide-co-propylene oxide with lithium, sodium, potassium, cesium and rubidium salts was studied by Florjanczyk et al. [93]. Polymer electrolytes containing lithium or sodium salts achieved conductivity levels as high as 10$^{-5}$-10$^{-4}$ Scm$^{-1}$ at room temperature and a still higher (10$^{-3}$ Scm$^{-1}$) conductivity at 100°C.

Liu et al. [94] studied electrochemical transport properties such as ionic conductivity and Li$^+$ transference number of PEO-SiO$_2$ composite mixed with LiBF$_4$. A significant increase in the Li$^+$ transference number was found together with a slight decrease in the ionic conductivity.

Kalita et al. [95] reported that the addition of calix pyrrole to poly ether based electrolytes doped with LiBF$_4$ results in a considerable increase in the cation transport number t$_{Li^+}$ as confirmed by dc-ac current techniques as well as by PFG NMR studies. The increase in Li$^+$ transport number was associated with a decrease in ionic conductivity of composite polymeric electrolytes compared to the pure PEO-LiBF$_4$.

Jingyu Xi et al. [96] studied the effect of molecular sieves ZSM-5 on the crystallization behaviour of PEO-based composite polymer electrolyte. An adequate amount of ZSM-5 could enhance the room temperature ionic conductivity of PEO-LiClO$_4$ based polymer electrolyte by more than two orders of magnitude. The interaction between ZSM-5 and PEO matrix were studied using DSC and SEM techniques.

Amrtha Bhide and Hariharan [97] studied a new ion conducting polymer electrolyte system based on PEO and sodium meta phosphate (NaPO$_3$). Polymer host was confirmed by XRD, DSC, SEM and FTIR. The complexation (PEO)$_n$: NaPO$_3$ was found to exhibit the least crystallinity but the highest conductivity of 2.8x10$^{-8}$ Scm$^{-1}$ at 351 K.

Jaipal Reddy et al. [98] reported the result on a mesoporous silica (SBA-15) composite poly (ethylene oxide) PEO solid lithium polymer electrolyte. The ion
conductivity of the mesoporous composite PEO: LiClO₄ increased with SBA-15 content and an optimum value was found at 10 wt% of SBA-15 with one order improvement compared to the PEO: LiClO₄ electrolyte.

Jingyu Xi [99] et.al investigated PVDF-PEO blends based microporous polymer electrolyte. The addition of PEO improved the pore configuration of PVDF-based micro porous membrane, such as pore size, porosity, and pore connectivity. As a result, room temperature ionic conductivity was greatly enhanced.

An efficient, solventless process for synthesing solid polymer electrolytes in the PEO: LiN (SO₂CF₂CF₃)₂·Al₂O₃ system was developed by Joykumar et.al [100]. A three-step process involving energy milling, hot pressing and annealing provided specimens with high ionic conductivity. The conductivity of the polymer was found to be dependent upon the O:Li ratio.

Dissanayake et.al [101] studied ionic conductivity of PEOₓ:Cu(CF₃SO₃)ₓ·Al₂O₃ nano-composite solid polymer electrolyte. The presence of micro-size and nano-size alumina filler grains enhanced the ionic conductivity substantially with grains having 5.8 nm pore size and maximum surface area showing the maximum conductivity enhancement.

Devendrappa et.al [102] studied DC conductivity of polyethylene oxide/poly aniline and its composites for battery applications. The electrical conductivity and electrochemical cell parameters are obtained for PEO: PANI and PEO: PANI: X (X=AgNO₃, NaNO₃) composites with different wt% ratios. The temperature dependence of the conductivity increased with increase in the PANI content in PEO due to a strong hopping mechanism between conducting PANI and PEO.

(b) Dielectric and impedance properties

The dielectric properties are important factors in design and fabrication of devices. The study of these properties as a function of temperature and frequency reveals much information on the physical and chemical state of the electrolyte. A brief review of the work reported on polymer electrolytes in literature is presented below.
Khare and Jain [103] studied the dielectric properties of acrylic acid (AA) doped ethyl cellulose (EC) films in the temperature range 50-170°C and frequency range 0.1 - 100 KHz. Doping with AA was found to affect the magnitude and position of the loss peak observed in the dielectric loss spectra.

R.L Mohamed and Gadou [104] et al. studied the stability as well as the electrical properties of both unirradiated and γ-irradiated poly (vinyl alcohol)-PVA films doped with MnSO₄·H₂O at a definite concentration of 15%. The dielectric loss tangent tan δ, electrical conductivity σ and dielectric constant ε' in the frequency range 100 Hz-20 KHz were measured at different temperatures. It was demonstrated that the suitable mechanism of conduction is the correlated barrier hopping model. The exponent S according to the relation σ(ω)=A(ω)S was estimated and was found to be less than unity and decreased with increasing temperature.

Basak and Manorama [105] reported studies on solid polymer electrolyte systems based on semi-interpenetrating polymer networks of poly(ethylene oxide)-polyurethane and poly(acrylonitrile) (PEO-PU/PAN) doped with lithium trifluoromethanesulfonate (LiCF₃SO₃). Room temperature FT-IR analysis indicates a salt solvation process that occurs predominantly in the polyether segments of the semi-IPNs and incorporation of salt was also seen to favor a morphological change in the matrix with a transition from semi-crystalline to amorphous phase. From the relative band areas a critical concentration (C_c) of salt was identified where concentration of ionic species, morphology and amount of transient crosslinks was optimal to impart maximum conductivity, which was in agreement with the room temperature conductivity results. Thermal analysis of the semi-IPN lent further support to this observation. The temperature dependence of conductivity was found to follow the Arrhenius behavior at low temperatures (∼ upto 328 K) and VTF dependence at higher temperatures. This crossover in temperature dependent conductivity was attributed to the change in the phase morphology of the semi-IPNs beyond the crystalline melting temperature (T_m) of the polyether segments.

EL-Shahawy and Elkholy [106] prepared samples of poly(vinyl alcohol) doped with hydrous cobalt chloride (5-30%) by casting technique. Dielectric measurements
were performed at various temperatures and frequencies in order to investigate the
effect of CoCl₂ doping on the relative permittivity ($\varepsilon'$) and dielectric loss factor (tan$\delta$)
of the polymer. The absorption peaks in the tan$\delta$ Vs Temperature spectra were analysed
and interpreted. The low temperature loss peak was attributed to the cooperative
rotational motions of dipole groups within the main chain and the high temperature loss
peak to segmental diffusional motion in the amorphous parts of the polymer. Calculated
relaxation times and activation energies were discussed in terms of the increase in the inter- and intramolecular interactions due to COCl₂ addition.

Jayathilaka et al. [107] studied the dielectric relaxation, ionic conductivity and
thermal studies of the gel polymer electrolyte system PAN/EC/PC/LiTFSI in the
frequency range 1 MHz - 1.8 GHz and temperature range -20-50°C. The €" spectra of
gel electrolytes with various compositions showed the presence of a high frequency
peak in the 0.5 GHz region, attributed to the $\alpha$-relaxation process and a peak in the
10 MHz region, attributed to the ion-pair relaxation.

Bhaskaran et al. [108] studied the dielectric properties of polyvinyl acetate
(PVAc) based electrolyte with different concentrations of LiClO₄. The ionic
conductivity was found to vary between $2.5 \times 10^{-5}$ Scm⁻¹ and $1.7 \times 10^{-3}$ Scm⁻¹ with
the increase of LiClO₄. The modulus spectrum showed the non-Debye behaviour of
the electrolyte films. The low frequency dispersion of the dielectric constant implied
the space charge effects arising from the electrodes.

Nada et al. [109] studied the dielectric properties of polyethylene glycol (PEG)
based electrolyte in the frequency range 100 Hz - 5 MHz and temperature range
20-100°C. The decrease in the dielectric constant ($\varepsilon'$) was observed with the increase in
the frequency due to dielectric dispersion. The dielectric loss behaviour exhibited two
$\beta$-relaxation peaks, due to orientation of polar side groups present in the polymer
electrolyte.

Raja et al. [110] measured capacitance and dissipation factor of polymethyl
methacrylate-co-poly 4vinyl pyridine N-oxide (PMMA-CO-P4VPNO) in the frequency
range 0.01-100 kHz and temperature range 300-410 K. Dielectric permittivity $\varepsilon'$ was
obtained by capacitance data. The decrease in dielectric permittivity was observed with increasing frequency as well as temperature. The loss peak was observed in the dielectric loss spectra and was identified as the $\beta$-relaxation. Real part of impedance ($Z'$) and imaginary part of impedance ($Z''$) were evaluated from the dielectric data. Frequency dependent conductivity ($\sigma_\omega$) was obtained from complex impedance plots (Cole–Cole plots).

Marzantowicz et al. [111] observed that the decrease of conductivity in impedance spectra during crystallization is related to the closing at amorphous conductivity pathways by growing spherulites. In the dilute system, composition 50:1 EO: Li, amorphous areas were still visible in the film after the growth of spherulites ceased. In the film of composition 6:1, corresponding to the polymer–salt complex, densification of the structure and interfacial phenomena caused a large drop of conductivity at the late stage of crystallization. In the dense structure of crystallized P(EO)$_{50}$:LiN(CF$_3$SO$_2$)$_2$ film no amorphous areas were visible. Differences in the structure have a reflection in the relative change of conductivity caused by crystallization, which decreased six times for the 50:1 composition and 500 times for the 6:1 composition.

Marzantowicz et al. [112] investigated impedance spectra of PEO: LiTFSI polymer electrolytes. The results indicate that the decrease of conductivity observed in impedance spectra during crystallization is related to the closing of amorphous conductivity pathways by growing spherulites.

Subba Reddy et al. [113] studied the thermal behavior of (PVP + PVA) polyblend film using differential scanning calorimetry and scanning electron microscopy. Capacitance and loss tangent values of polyvinyl pyrrolidone (PVP) + polyvinyl alcohol (PVA) polyblend film were measured in the frequency range 1–100 kHz and temperature range 298–423 K. Dielectric permittivity of real part ($\varepsilon'$) was obtained from capacitance data and dielectric permittivity of imaginary part ($\varepsilon''$) was obtained from loss tangent values. The decrease in dielectric permittivity was observed with increasing frequency. They observed increase in dielectric permittivity with increasing temperature.
Oliveira et al [114] studied the spectroscopic and dielectric properties of polypyrrole (PPY) particles dispersed within a polyvinyl alcohol (PVA) matrix. These systems, prepared by using a surfactant to encapsulate PPY chains into micelles that were subsequently dispersed in a PVA gel or film, presented hybrid electrical characteristics. Their electrical properties were determined by the number, size and state of the aggregation of the micelles, since macroscopic charge transfer must involve charge percolation through the PPY chains followed by hopping between neighboring micelles.

Basak and Manorama [115] reported synthesis and characterization of a new class of solid polymer electrolytes based on semi-interpenetrating polymer networks (semi-IPN) of poly(ethylene oxide)-polyurethane and poly(acrylonitrile) (PEO-PU/PAN) doped with lithium perchlorate. With varying amount of PAN and LiClO₄, room temperature conductivity increased over four orders of magnitude from 10⁻¹⁰ to 10⁻⁶ S cm⁻¹. The change in physical properties of the bulk was seen to govern the conductivity behavior. The temperature dependence of conductivity showed a transition from Arrhenius to VTF behavior above ~328 K, which becomes more prominent with increasing salt content. By correlating the trends in DSC and XRD with the temperature dependence of conductivity, the change over to VTF behavior was attributed to the transition from semicrystalline to amorphous phase. The glass transition temperature for all the compositions was well below room temperature, in the range of ~20 to ~50 °C and the semi-IPN structure improved the tensile strength and modulus while retaining the flexibility of the host polymer. These studies have shown the feasibility of the synthesized PEO-PU/PAN semi-IPNs to be used as an ideal host for solid polymer electrolytes.

Feng et al [116] prepared and studied the dielectric properties of Ag-/PVA nanocomposite. The property of nano-powder was reviewed with emphasis on its coulomb blockade effects. Ag-colloid of different concentration with different particle size was prepared. Ag-/PVA composite colloid was obtained by mixing Ag-colloid with PVA solution. TEM showed that Ag particles (~100 nm) were uniformly dispersed in PVA. The resistivity at room and low temperatures and breakdown field strength of samples
were investigated. The results showed that dielectric properties of the composite changed Ag content. The composite with 20 -/30 nm Ag particles had a higher resistivity and breakdown field than its matrix. They concluded that Coulomb blockade effects of metal powders could improve resistivity and breakdown field of its matrix.

Ahmed and Abo-Ellil [117] studied the "effect of dopant concentration on the electrical properties of polyvinyl alcohol (PVA). The real part of the dielectric constant of pure and doped polyvinyl alcohol (PVA) with 1, 2 and 3wt% vanadate was measured as a function of temperature and frequency. It decreased with increasing frequency due to a rapid variation of the field accompanied with the applied frequency as well as the disordering of the segmental parts of the polymer chain.

Singh and Gupta [118] made an attempt to study the relaxation characteristics of PVA:H$_3$PO$_4$ and PVA:H$_2$SO$_4$ complex electrolytes in the form of thin films. Various dielectric parameters such as dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon_\delta$) and loss tangent (tan$\delta$) were determined in the temperature range 20-160$^\circ$C at different frequencies and molar ratios. Using Cole-Cole plots ($\varepsilon$ ' vs $\varepsilon$ ''), the values of $\varepsilon_0$ (static dielectric constant), $\varepsilon_\infty$ (infinitely large frequency dielectric constant) and relaxation times have been calculated at room temperature. Relaxation time was determined from the variation of loss tangent with temperature at different frequencies. It was observed that relaxation characteristics show Arrhenius type behaviour and there was a decrease in activation energy with an increase in acid concentration for various complexes. The study of dielectric relaxation as a function of temperature at constant frequency showed two types of relaxation processes which are interpreted in terms of dipole segmental motion ($\alpha$- relaxation) and side chain dipole group motion ($\beta$-relaxation).

Arvind Awadhia et al. [119] investigated the dielectric properties of the gel electrolytes based on PVA and PVA-PEG prepared in NH$_4$SCN (ammonium thiocyanate) solution in the temperature range 273-373 K and frequency range 40 Hz-100 KHz. Conductivity, segmental and dipolar relaxations were observed in temperature and frequency dependent studies of dielectric loss. The relaxation time for these processes seemed to follow Arrhenius nature with energy of activation being quite low in comparison to solvent free PVA-NH$_4$SCN complexes.
Saikia and Kumar [120] studied ionic transport in (PVDF-HFP)-PMMA-LiCf$_2$SO-(PC+DEC)-SiO$_2$ composite gel polymer electrolyte. Addition of filler to the polymer electrolyte was found to result in an enhancement of the ionic conductivity. XRD patterns exhibited increased amorphicity in polymer electrolytes. SEM showed the dispersion of SiO$_2$ particles in the polymer electrolyte.

Subba Reddy et al [121] studied SBA-15 doped PEO-LiClO$_4$ polymer electrolytes for electrochemical cell applications. They found that SBA-15 doped PEO-LiClO$_4$ polymer electrolytes showed improved conductivity over the pure PEO and PEO-LiClO$_4$ electrolytes.

Wu et al [122] prepared PVA/PAA based solid polymer electrolyte membranes with varying composition ratio. They found that the highest room temperature conductivity for PVA/PAA/KOH electrolyte system was 0.301 S/cm. These electrolyte systems were found to be suitable candidates for alkaline batteries and other electrochemical systems.

(c) **Optical absorption studies**

Optical studies in thin films deal primarily with optical reflection, transmission, absorption and their relation to the optical constants of the material. As a result of these studies complex multilayer optical device systems with remarkable reflection, antireflection, interference and polarization properties have emerged for both laboratory and industrial applications. The absorption studies have led to a variety of interesting thin film optical phenomena which have thrown considerable light on the band structure of solids and phonic states. A brief review of the recent work reported in literature on optical absorption studies of some polymer films is given below.

Tabata et al. [123] measured electrical and optical properties of poly (p-phenylene) films and the effect of AsF$_6$ doping on them. For the undoped specimen a strong absorption peak at 3.4 eV was observed and was associated with the transition from ground to excited state. The remarkable changes observed in the absorption spectra below 3.0 eV were related to the polaron and on bipolar states of the polymer.
Madi et al. [124] studied the influence of gamma radiation on the properties of modified polyvinyl chloride. The optical absorption spectra of polyvinyl chloride doped with Cd and Pb were presented. The calculated absorption coefficient, the absorption index and the optical energy gap were found to be radiation and dopant dependent.

Yoshino et al. [125] studied the optical absorption properties of poly (3,4-dialkylthiophene) prepared by both electrochemical and chemical methods utilizing FeCl₃ as catalyst. These films exhibited much larger band gap compared to non-substituted and 3-substituted poly thiophene films. Poly (3,4-dimethylthiophene) with large band gap also demonstrated drastic spectral ESR and conductivity changes upon doping due to an insulator-metal transition.

Ramadin et al. [126] studied the optical properties of poly (ethylene oxide) based thin films containing 0, 10, 20, 40 and 50% by weight of dead sea salts and found that the optical band width and band gap varied with the concentration of dead sea salts dispersed in the polymer matrix.

Saq'an et al. [127] studied the optical and thermal properties of poly (ethylene as a function of salt concentration. The values of the optical energy gap (Eₜₐₚ) were found to decrease with the increasing salt concentration, while the energy gap tails (ΔE) were found to decrease to about half its value by the addition of 5 wt% of MnCl₂. The absorption coefficient decreased to about half its value by the addition of 5 wt% of MnCl₂.

Raja et al. [128] studied the optical properties of pure and doped PMMA-CO-P4VPN0 polymer films, such as direct and indirect optical energy gap, optical absorption edge. It was found that the energy gaps and band edge values shifted to lower energies on doping with KIO₃, KBrO₃, KClO₃ salts up to a dopant concentration of 10% wt.

Subba Reddy et al. [129] studied the optical properties like direct and indirect band gaps and optical absorption edge in pure and doped (PVP + PVA) and (PVP + PVA + PEO) Balaji polyblend electrolytes. The band edge and band gap (both direct and indirect) values showed decreasing trend with increased concentration of PEO.
Siva Kumar et al. [130] prepared ion conducting thin film polymer electrolytes based on polyethylene oxide (PEO) complexed with NaHCO₃ salt using solution-cast technique. The complexation of NaHCO₃ salt with PEO is confirmed by XRD and IR studies. DC conductivity in the temperature range 303–368 K has been evaluated. The conductivity is found to increase in the PEO complex with the NaHCO₃ salt and also with an increase in temperature. Using this polymer electrolytes, an electrochemical cell with the configuration Na/(PEO + NaHCO₃)/(I₂ + C + electrolyte) has been fabricated and its discharge characteristics studied. Open Circuit Voltage (OCV) and Short Circuit Current (SCC) are found to be 2.69 V and 1.28 mA, respectively.

Mohan et al. [131] prepared sodium ion conducting polymer electrolyte based on polyethylene oxide (PEO) complexed with sodium lanthanum tetrafluoride (NaLaF₄) using solution cast technique. The complexation of the salt with PEO was confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FTIR) studies. Differential scanning calorimetry (DSC) was carried out to determine the melting temperature of these electrolyte films. Electrical conductivity was measured in the temperature range 300–370 K as a function of dopant concentration as well as temperature. Optical absorption studies were made in the wavelength range 200–600 nm. It was found that the energy gaps and band edge values shifted to lower energies on doping with NaLaF₄ salt.

Hiran Kumar et al. [132] prepared solid polymer proton conductors comprising of poly(vinyl alcohol), ammonium acetate and water by solution cast method for different NH₄⁺/OH⁻ ratios. The XRD spectra for the electrolyte indicated that the amorphous nature of PVA increased with the concentration of ammonium acetate. The DSC curves showed the a low glass transition temperature for the ratio (NH₄⁺/OH⁻) = 0.25 which relates to higher conductivity of the sample. The ionic conductivity at room temperature depended strongly on NH₄⁺/OH⁻ ratio. The variation of electrical conductivity with temperature showed two regions of activation above and below glass transition temperature. The optical absorption studies show the similar trend for pure PVA and salt-doped PVA with different absorption intensity. The direct and indirect band gap energy was observed to be constant for pure PVA and salt-doped PVA.
samples and was found to be 5.4 eV and 4.8 eV, respectively. The dc polarization measurement showed that the conductivity was mainly due to ions.

Subba Reddy et al [133] prepared sodium ion conducting polymer electrolyte based on poly (vinyl chloride) (PVC) complexed with NaI\(_4\) using a solution-cast technique. Optical properties such as direct and indirect optical energy gap, and optical absorption edge were investigated in pure and doped PVC films from their optical absorption spectra in the 200–600 nm wavelength region. The direct optical energy gap for pure PVC was observed at 3.14 eV while it ranged from 2.60 to 3.45 eV for different compositions of the doped films. Similar behavior was observed for the indirect optical energy gap and absorption edge. It was found that the energy gaps and band edge values shifted to higher energies on doping with NaI\(_4\) up to a dopant concentration of 10 wt%. Measurements of ionic conductivity and transference number were made to investigate the order of conductivity and charge transport in this polymer electrolyte. Transference number values showed that the charge transport in this polymer electrolyte was predominantly due to ions (\(t_{\text{ion}} = 0.93\)). The conductivity increased with increase in concentration of the salt and with temperature. Using this electrolyte, cells were fabricated and their discharge profiles were studied under constant load.

Uma Devi et al [134] studied the optical absorption spectra of silver nitrate doped polyvinyl alcohol (PVA) polymer electrolyte films in the wavelength range 200–600 nm. The values of absorption edge, direct band gap and indirect band gap were evaluated.

(d) Review of polymer batteries

One promising application of solid state polymer electrolytes is in the area of solid state electrochemical cells. Polyvinyl alcohol (PVA) is a polar polymer with carbon chain as backbone, which dissolves high concentrations of a wide variety of ionic salts to form electrolytes that resemble both solids and liquids.

Patrick et al. [135] reported solid polymer electrolyte cells based on poly (ethylene oxide) complexed with divalent salts like Mg, Ca, Zn. The open circuit
voltages (OCV) of the cells using Mg as anode and TiS₂, V₆O₁₃, MnO₂, NiO₂, CoO₂, MoO₂, MoO₃, V₂O₅, WO₃ as cathodes were in the range of 1.5 to 2.0 volts.

Syuichi Izuchi et al. [136] reported on ionic conductivity, mechanical characteristics, thermal stability and electro chemical stability of solid polymer electrolytes that use a cross-linked PEO and cross linked PEO copolymer both containing a plasticizer. Batteries are using these electrolytes showed stable and better discharge characteristics.

Solid polymer electrolyte comprising of LiI, PEO and Al₂O₃ was used as an electrolyte for Li battery applications with TiS₂ as cathode [137] and its capacity was found to be 100 mAh. Carbon derived from (p-phenylene) was used as one of the electrodes in solid state lithium cells containing poly acrylonitrile based electrolyte by Alamgir et al.[138]. The amount of reversible capacity was influenced by the current density and the plasticizer solvent and Li salt in the electrolyte.

Sreepathi Rao et al. [139] reported electrochemical cells based on poly (ethyleneoxide) (PEO) and poly (acrylamide) (PA) complexed with AgNO₃ salt with Ag as anode and the (I₂+C+electrolyte) as the composite cathode material. The open circuit voltage (OCV), power density, energy density, plateau region time for these cells were evaluated.

A solid polymer electrolyte battery system which consists of PEO-PEG based composite polymer blend with LiCF₃SO₃ salt and Li/V₆O₁₃ as its anode/cathode electrode materials was reported by Prasad et al. [140]. The open circuit voltage (OCV) of the cells was in the range of 3.3 - 3.6 V.

Yang et al. [141] reported a cell with the PEO- LiClO₄ as electrolyte material with the sequence Li/(PEO-LiClO₄)/polyaniline (PAN), whose charge potentials were in the range 2.5 to 4.0 volts. Thin film prototype of rechargeable lithium batteries were fabricated using a poly (ethylene oxide) based composite polymer electrolyte and composite cathodic mixture by Capuano et al. [142]. A lithium solid polymer electrolyte (LiClO₄ - PEO) which exhibited a high ionic conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$ at room
temperature was used as a separator between two electrodes Li/V\textsubscript{6}O\textsubscript{13} in lithium polymer battery at room temperature and its charge and discharge cycles were examined by Yu et al. [143].

Noda et al. [144] developed a lithium solid polymer electrolyte having a conductivity of $2\times10^{-3} \text{S cm}^{-1}$ at 25°C. They fabricated a polymer cell with Li and MnO\textsubscript{2} electrodes using this electrolyte and obtained an energy density of 400 Wh/kg. A galvanostatic charge and discharge cell was constructed using (PEO)\textsubscript{8}-LiCF\textsubscript{3}SO\textsubscript{3} polymer electrolyte with the configuration Li/(PEO)\textsubscript{8}-LiCF\textsubscript{3}SO\textsubscript{3}/TiS\textsubscript{2} by Doyle et al. [145].

Cahandrasekhar and Selladurai. [146] reported electrochemical cells based on PEO and PEG complexed with NaClO\textsubscript{3} and (NaClO\textsubscript{3} + DMF). The open circuit voltage, short circuit current, power density, energy density of the cells were evaluated.

Li et al. [147] studied the rechargeable electro-chemical cells based on PEO with hyperbranched polymer poly[bis (triethylene glycol) benzoate] capped with an acetyl group (HBP) and a ceramic filler, BaTiO\textsubscript{3}, observed excellent charge discharge cycling performance.

Osaka et al. [148] and Kakuda et al.[149] reported solid state lithium/polypyrrole (PPY) battery using poly (ethylene oxide) PEO-LiClO\textsubscript{4} and poly (acrylonitrile) based solid polymer electrolytes and investigated effects of the morphology of the PPY film cathode on the battery performance. The electrode morphology did not considerably influence the charge discharge cycling response and the solid state Li/PPY battery exhibited high efficiency approaching 90%. The copolymer poly (ethylene glycol) ethyl ether methacrylate (PEGEEM) blended with PEO and LiClO\textsubscript{4} to form PEO-copolymer-LiClO\textsubscript{4} complexed film electrolyte was used to fabricate a lithium solid state battery with V\textsubscript{2}O\textsubscript{5} as cathode material by Gnanaraj et al. [150] for which the open circuit voltage (OCV) and short circuit current (SSC) were found to be 3.3 V and 1.3 mA respectively.
Mohamed and Arof[151] fabricated a battery based on PVDF based polymer electrolytes. The discharge characteristics of cells stored / heated at different temperatures were in the 4.2-2.5 V voltage range.

Raja et al [152] developed a new polymer electrolyte films based on a co-polymer polymethyl methacrylate-co-poly 4 vinyl pyridine N-oxide (PMMA-Co-P4VPNO) complexed with KClO₃ by solution cast technique. Measurements of d.c conductivity, and transference numbers were carried out to investigate the charge transport in the electrolyte system. Solid state electrochemical cells were fabricated with the configuration (K)-(PMMA-CO-P4VPNO+KClO₃) - (I₂+C+electrolyte) and various parameters of cells were evaluated.

Subba Reddy et al.[153] fabricated an electrochemical cell with configuration Na/(PVP+NaClO₃)/(V₂O₅) and studied its discharge characteristics. The open circuit voltage and short circuit current were observed as 2.11 V and 0.120 mA respectively.

Cheng et al.[154] fabricated an electrochemical cell based on (PVDF - HFP) copolymer as polymer matrix, PEG as plasticizer and polyethylene glycol dimethacrylate (PEGDMA) as a chemical cross linking oligomer and studied its charge and discharge characteristics.

Ruoyuan Tao and Fujinami [155] studied the rechargeable electrochemical cells based on PEO with mixed (lithium borate and lithium aluminate) salts. These electrolytes exhibited better electrochemical stability and good cycle performance.

Janakirami Reddy et al [156] studied the properties of a potassium ion conducting electrolyte based on polyvinyl chloride (PVC) complexed with potassium bromate (KBrO₃) prepared using solution-cast technique was investigated. Various experimental techniques, such as electrical conductivity (composition and temperature dependence) and transport number measurements were used to characterize these polymer electrolyte films. Electrochemical cells of configuration K/PVC+KBrO₃/ (I₂+C+electrolyte) and K/PVC+KBrO₃+plasticizer/(I₂+C+electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load of 100 kΩ.
The open-circuit voltage, short-circuit current, and discharge time for the plateau region were measured.

Subba Reddy et al [157] prepared sodium ion conducting polymer electrolyte based on polyvinyl chloride (PVC) complexed with NaClO₄ using a solution-cast technique. The transference number measurement was performed to characterize the polymer electrolyte for battery applications. Transference number values showed that the charge transport in this electrolyte was predominantly due to the ions ($t_{\text{ion}} = 0.98$). Using the electrolyte, cells with a configuration Na/(PVC + NaClO₄)/(I₂ + C + electrolyte) were fabricated and their discharge profiles studied.

Subba Reddy et al. [158] prepared composite polymer electrolyte films consisting of polyethylene oxide (PEO), LiAsF₆ and mesoporous silica (MCM-41) with fixed PEO/LiAsF₆ = 90/10 but different weight percent ratios of MCM-41 using the solution casting method. The electrochemical performance of fabricated electrochemical cells of configuration Li/(PEO + LiAsF₆ + MCM-41)/(MoO₃ + C + PTFE) were investigated.

Jaipal reddy et al [159] reported new polymer electrolyte films based on PEO complexed with KIO₃ prepared using solution cast technique. Several experimental techniques such as DSC, composition and temperature dependence conductivity and transport number measurements were performed to characterize these polymer electrolyte films. The conductivity – temperature plots show two different regions above and below the melting point. The transport number data suggests that the charge transport in these electrolyte system is predominantly due to ions. Electrochemical cells were fabricated and their discharge characteristics were studied. The open circuit voltage and short circuit current were found to be 2.69 V and 346 μA.

M. Jaipal Reddy et al [160] prepared polymer electrolyte films based on poly (vinyl pyrrolidone) (PVP) complexed with NaNOS salt. The conductivity of the (PVP:NaN0₃) electrolyte was about 10⁴ times larger than that of pure PVP at room temperature. The transference number measurements showed that the charge transport in this polymer electrolyte system was predominantly due to ions. Using this polymer
electrolyte, an electrochemical cell with the configuration Na/(PVP:NaNO₃) (I₂ + C + electrolyte) was fabricated and its discharge characteristics studied. The open circuit voltage (OCV) and short circuit current (SCC) observed for the cell were 2.65 V and 1.1 mA respectively.

1.9 Aim and scope of the present investigations

The above review on polymer electrolytes and electrochemical cells clearly indicate the extensive amount of research work carried on lithium based polymer electrolytes. The review also indicates that less effort has been made on solid polymer electrolytes based on sodium complexed films. Apart from the scientific interest, the use of sodium has several advantages over its lithium counterpart. Sodium is available in abundance at a lower cost than lithium. It may be possible to obtain solid electrolytes of sufficiently high conductivity. Furthermore, the softness of sodium complexed films makes them easier to achieve and maintain contact with other components in the battery. The basic requirement for the solid-state electrochemical cells is higher conductivity with the value of transference number close to unity. In the present investigations solid polymer electrolytes based on polyvinyl alcohol complexed with various sodium halide salts have been prepared to investigate their potential in the fabrication of solid state electrochemical cells.

The present thesis entitled "Studies in Thin Films – Physical Investigations on PVA Based Polymer Electrolytes Films for Electrochemical Cell Applications" consists of five chapters containing the following aspects.

✓ Films of pure PVA, (PVA: NaF), (PVA:NaCl) (PVA:NaBr) and (PVA: NaI) in various compositions were prepared by solution cast technique

✓ X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra were recorded for these films and analysed to confirm the structure and complexation of salt with the polymer. The differential scanning calorimetry data was used to determine the glass transition temperature of these polymer electrolyte systems.

✓ DC - conductivity as a function of composition and temperature was studied and the results are explained in terms of existing theories.
Transference number measurements were made using Wagner's polarization method to study the ionic contribution to conductivity in these electrolyte films. The cationic and anionic contribution to the total ionic transference number was measured using a combination of DC and AC techniques as suggested by Watanbe et al.

Dielectric constant and dielectric loss of polymers were measured in the frequency range 100 Hz – 1 MHz and in the temperature range 303-373 K. Real and imaginary part of impedance ($Z'$, $Z''$) were measured in the frequency range and analysed in the complexed plane. Frequency dependant conductivity ($\sigma_{ac}$) was obtained from the complex impedance plots (Cole-Cole plots).

Optical absorption spectra of these polymer electrolytes were recorded in the wavelength range 200-600 nm and the parameters like optical band gap (both direct and indirect) and band edge were determined.

Electrochemical cells were fabricated in the configuration anode/electrolyte/cathode, using (PVA: NaF), (PVA:NaCl), (PVA: NaBr) and (PVA: NaI) polymer electrolytes. Various cell parameters like open circuit voltage (OCV), short circuit current (SCC) etc, were measured.

1.10 Details of the materials used in the present investigations.

- **Polymer Material**: Polyvinyl Alcohol (PVA) obtained from Aldrich Chemicals
- **Molecular weight (M.W)**: 1,00,000
- **Glass transition temperature**: $\sim 77^\circ$ C
- **Structure**

![Polyvinyl Alcohol Structure](image)

- **Dopants used**: NaF, NaCl, NaBr and NaI
- **Solvent**: Triple distilled water
- **Method of film preparation**: Solution cast technique
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