Chapter 3- Experimental details

In this chapter, description of materials used, preparation of samples and different characterization techniques employed to the prepared samples are discussed in detail.
3.1 Introduction

This chapter describes the sample preparation method and theories of characterization (experimental techniques). The experimental techniques includes X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC), Fourier transform infra red spectroscopy (FT-IR), Scanning electron microscope (SEM) and Wagner’s polarization technique.

3.2 Materials and methods

3.2.1 Details of the materials used in the present investigation

I. Poly (ethylene oxide) (PEO) polymer

Structure $\rightarrow$ - (CH$_2$ - CH$_2$ – O-)-n (Fig.3.1), Molecular weight (M.W) = 3 x 10$^5$, Glass transition temperature = -60° C, Melting temperature = 66° C, Alfa- Aesar, U.S.A

![Fig. 3.1 Structure of Polyethylene](image)

Poly ethylene oxide (PEO) is a white powder with no special smell. It is a semi crystalline material with about 70-85% crystallinity and amorphous elastomeric phase at room temperature [1-3]. Due to partial crystallinity in the structure the problem arises both at micro and macroscopical level. Microscopically, it is due to arrangement at atomic level but arrangement of crystalline and amorphous phases in the polymer and/or polymer-salt complex is termed as macroscopically level. The form of the polycrystalline phase is often dendritic or spherulitic crystalline structure with well separated amorphous boundary [2]. The gross morphological structure of PEO-salt complexes may play an
important role in determining the ion transport properties of the material [4]. PEO is a linear polymer and the regularity of the unit is - (CH\textsubscript{2}-CH\textsubscript{2}-O) -. The melting point, \(T_m\), of the crystalline phase is 65\(^\circ\)C and the glass transition temperature, \(T_g\), of the amorphous phase is – 60\(^\circ\)C. In PEO polymer, ether oxygens have sufficient electron donor power to form the coordinate bonds with cations. These electrons also facilitate the multiple intra polymer-ion bonding with low potential barrier for rotation of atoms in the polymer main chains. This makes the high flexibility as well as the good segmental motion of polymer chains in the PEO polymer.

II. Poly (methyl methacrylate) (PMMA) polymer

Structure \(\rightarrow\) - (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2})-n,(Fig.3.2) Molecular weight (M.W) = 3.5 \times 10^5, Glass transition temperature = 108° C, Melting temperature = 170° C, Alfa- Aesar, U.S.A

Poly (methyl methacrylate) (PMMA) is a hard and transparent polymer with good resistance to the effects of light and weathering [5]. It is a synthetic amorphous polymer of methyl methacrylate. The common name for PMMA is acrylic glass because it is a
member of a family of polymers called acrylates. It is a hard thermoplastic with high light transparency and more impact resistant than glass. It has a polar functional group in its polymer chain that exhibits a high affinity for lithium ions and plasticizing solvents. PMMA was polymerized from the monomer methyl methacrylate (Fig.3.3) by free radical initiators such as peroxides and azo compounds via free radical vinyl polymerization. The rigid PMMA is produced due to the substitution of the methyl and methacrylate groups on every carbon of the main carbon backbone chain, providing the steric effects.

III. Poly(ethylene) glycol (PEG)

Structure → \([H(-O-CH_2-CH_2)_n-OH]\) (Fig. 3.4), Molecular weight (M.W.) → 4000, Glass transition temperature → -60° C, Melting temperature → 55° C, Loba Media

Polyethylene glycols (PEGs) are prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol. PEG is also known as the low molecular weight waxy or soft solid PEO which has the end product of the polymerization of ethylene oxide (oxyalkylation) in the presence of Lewis acid or base catalysts. PEG is similar to PEO i.e., semicrystalline and water-soluble polymers that are commercially available in a wide range of molecular weights depending on the number of monomers. While PEG and PEO with different molecular weights find use in different applications and have different physical properties (e.g., viscosity) due to chain length effects, their chemical properties are nearly identical. Polyethylene glycol is produced by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers [6]. The reaction is catalyzed by acidic or basic catalysts. The polymer chains can adopt either a helical or
extended structure depending upon the electrostatic interaction of the oxygen units with either ions or charged surfaces. Lower molecular weight \((M_w < 1000)\) PEGs are viscous and colorless liquids, while PEGs with the molecular weight of 800 to 2000 is pasty or flaky materials with a low melting range, while above a molecular weight of 3000, PEGs are available in solid form with the melting point to an upper limit of about 65\(^{\circ}\)C.

![Chemical structure of Polyethylene glycol (PEG).](image)

**Fig. 3.4** Chemical structure of Polyethylene glycol (PEG).

**IV. Ethylene Carbonate (EC)**

Structure \(\rightarrow C_3H_4O_3\), Molecular Weight \(\rightarrow 88.06\), Melting temperature \(\rightarrow 35^{\circ}-40^{\circ}\)C, Aldrich chemical

Ethylene carbonate is an ester of ethylene glycol and carbonic acid (Fig.3.5). At room temperature (25\(^{\circ}\)C) ethylene carbonate is a transparent crystalline solid, practically odorless and colorless, and somewhat soluble in water. In the liquid state (m.p. 34-37\(^{\circ}\)C) it is a colorless odorless liquid. Ethylene carbonate is used as a polar solvent and it can be used as a high permittivity component of electrolytes in lithium batteries. Ethylene carbonate is also used as plasticizer and as a precursor to vinylene carbonate which is used in polymers and in organic synthesis.

The effect of plasticizer on the polymer electrolyte strongly relies on the specific nature of the plasticizer, including the dielectric constant, polymer-plasticizer interaction and ion-plasticizer coordination. The choice of choosing ethylene carbonate (EC) instead of propylene carbonate (PC) and dimethyl carbonate (DMC) is because it has superior properties when compared to other organic solvents, including a high dielectric constant
(89.1) [7], a high donor number (16.4) and also a high boiling temperature (248°C).

\[
\text{CH}_2\text{CH}_2O + \text{CO}_2 \xrightarrow{[\{\text{C}_6\text{H}_5\text{P}\}_2\text{Ni}]} \text{O} \text{O}
\]

**Fig. 3.5 Production of ethylene carbonate (EC).**

V. Silver Nitrate (AgNO₃)

Molecular Weight $\rightarrow$ 169.87 g mol⁻¹, Melting temperature $\rightarrow$ 212 °C,

\[
\text{Ag}^+ \left[ \begin{array}{c} \text{O} \\ \text{N} \\ \text{O} \end{array} \right] ^- 
\]

**Fig. 3.6 Structure of Silver Nitrate (AgNO₃).**

VI. Common Solvent: Acetonitrile

Acetonitrile is a polar aprotic solvent. It is used for the synthesis of polymer electrolytes by solution cast technique. It has a high static permittivity (36.6 at 30 °C) which promotes the dissociation of alkali metal salt in the solution.

VII. Nano-filler Aluminum Oxide Al₂O₃

Molecular Weight $\rightarrow$ 101.96 g/mol, Melting temperature $\rightarrow$ 35°-40°C, Sigma-Aldrich chemical, Particle size $\rightarrow$ < 50nm

Aluminum Oxide, Al₂O₃, commonly referred to as alumina, is the most cost effective and widely used material in the family of material science. Aluminum oxide possesses strong ionic interatomic bonding giving rise to its desirable material characteristics. It can exist in several crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures. The composition of the ceramic body can be changed to enhance particular desirable material characteristics.
3.3 Various polymer electrolyte systems

Commercially available chemicals of PEO, PMMA, AgNO₃, PEG, EC and nanofiller Al₂O₃ were employed as starting materials and were used as-received. Acetonitrile (MERCK) was used as common solvent for blend polymer films. The inorganic dopant salt silver nitrate (AgNO₃) was used as metal salt. All materials were used without further purification. All the polymer blend electrolytes were prepared by solution casting technique as described below.

3.3.1 First Polymer Blend Electrolytes System (PPS system)

First polymer blend electrolytes system was employed to figure out the most compatible ratio of PEO to PMMA. Solid polymer electrolytes were formed in this system. The compositions prepared were \( [x\text{PEO}-(1-x)\text{PMMA}] \) where \( x = 10-70 \) wt% in steps of 10 with fixed amount of silver nitrate (AgNO₃) salt. The compositions of various polymer blends and their designations are tabulated in table below (Table 3.1).

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Designations</th>
<th>PEO (wt %)</th>
<th>PMMA (wt %)</th>
<th>AgNO₃ (wt%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>PPS-10</td>
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<td>90</td>
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<td>2</td>
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<td>7</td>
<td>PPS-70</td>
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<td>30</td>
<td>5</td>
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3.3.2 Second Polymer Blend Electrolytes System (PPSP system)

From first system, 50 wt% of PEO and 50 wt% of PMMA was achieved the highest ionic conductivity (Chapter 5). In PPSP-system, the effect of addition of plasticizer, poly ethylene glycol (PEG) in highest conducting polymer electrolyte obtained from PPS-system is studied. Thus, the amount of AgNO₃ is kept constant as 5
wt% in this system. The amount of PEG plasticizer added into the polymer blends was ranged from 5 wt% to 15 wt%. The weight fractions of polymer blends electrolytes and their designations are shown in Table 3.2.

**Table 3.2 Designations of second polymer blend electrolytes system.**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Designations</th>
<th>PEO (wt %)</th>
<th>PMMA (wt %)</th>
<th>AgNO₃ (wt %)</th>
<th>PEG (wt %)</th>
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<td>10</td>
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<tr>
<td>4</td>
<td>PPSP-15</td>
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<td>50</td>
<td>5</td>
<td>15</td>
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</tbody>
</table>

### 3.3.3 Third Polymer Blend Electrolytes System (PPSE system)

In this (third) system, the PEG plasticizer has been replaced by ethylene carbonate (EC) plasticizer to study the effect of EC concentration in PEO-PMMA polymer blend which has a higher dielectric constant than that of polymer hosts. The PEO-PMMA blend ratio was kept same as 50-50 wt% with 5 wt% of AgNO₃ salt. In this system, the amount of EC was varied from 5 to 15 wt%.

**Table 3.3 Designations of third polymer blend electrolytes system.**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Designations</th>
<th>PEO (wt %)</th>
<th>PMMA (wt %)</th>
<th>AgNO₃ (wt %)</th>
<th>EC (wt %)</th>
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<td>12</td>
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<td>PPSE-15</td>
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<td>50</td>
<td>5</td>
<td>15</td>
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### 3.3.4 Fourth Polymer Blend Electrolytes System (PPSPA system)

In this system, the effect of addition of nano-filler Al₂O₃ is studied. For this, nano-fillers were dispersed in PEG containing plasticized polymer film with optimum conductivity (obtained from conductivity results of third polymer blend electrolyte system) in the lower concentration range. The range of nano-filler is studied at 1, 2, 3, 4 and 5 wt%. The concentration of PEO–PMMA was kept 50 wt%. PEG and silver salt are
also kept constant as 5 wt% each. As PEG-5 wt% was found to show the maximum ionic conductivity (Chapter 5). Table 3.3 shows the variation of the compositions of polymer blend electrolytes and their designations.

Table 3.4 Designations of fourth polymer blend electrolytes system.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Designations</th>
<th>PEO (wt %)</th>
<th>PMMA (wt %)</th>
<th>AgNO₃ (wt%)</th>
<th>PEG (wt%)</th>
<th>Al₂O₃ (wt%)</th>
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</thead>
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3.3.5 Fifth Polymer Blend Electrolyte System (PPSEA system)

In the fifth system, the effect of nano-filler Al₂O₃ in EC containing polymer film (optimized from conductivity results of PPSE system) is studied. The PEO-PMMA blend ratio was kept same as 50:50 with 5 wt% of AgNO₃ salt. The amount of EC was also kept constant as 5wt%. Nano-filler Al₂O₃ concentration was varied from 1 to 5 wt% (Table 3.5).

Table 3.5 Designations of fifth polymer blend electrolytes system.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Designations</th>
<th>PEO (wt %)</th>
<th>PMMA (wt %)</th>
<th>AgNO₃ (wt%)</th>
<th>EC (wt%)</th>
<th>Al₂O₃ (wt%)</th>
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<td>5</td>
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</table>

3.3.6 Sample preparation

Sample preparation is carried out by solution cast technique [8, 9]. In this technique, there is a competition between solvent and polymer to interact with the ions. There are five polymer blend electrolyte systems prepared in the present work. The quantity of materials added is expressed as weight percentage (wt%). Appropriate
amounts of materials are dissolved in common solvent acetonitrile. PEO and PMMA are separately dissolved in acetonitrile separately and stirred by using a magnetic stirrer. The stirring of PMMA solution is carried out at 323K for 24 h to dissolve PMMA in acetonitrile. PEO and AgNO₃ are mixed and stirred for 4-5 h at room temperature. Both the solutions are mixed along with the desired amount of plasticizer (PEG or EC) and nano-filler (Al₂O₃). The obtained mixture was again stirred at room temperature for another 10 h for homogenous mixing. Finally, the solution was poured into a Teflon Petri dish and left to evaporate the solvent slowly at ambient temperature. The resulting films are kept in an oven at 313K for 2 days to ensure the removal of the solvent traces. The dried films are peeled off from the Petri-dish and then were stored in dark desiccators to prevent them any contamination from moisture and/or light.

3.4 Theoretical details of different characterization techniques

Different experimental techniques have been used to characterize the prepared polymer films which are discussed briefly in the sub-sections below:

3.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) technique is used to determine the atomic arrangements (i.e., crystal structure) of the material because the inter-planar spacing (d-spacing) of the diffracting planes is of the order of X-ray wavelength [10]. For a crystal of given d-spacing and wavelength λ, the various orders of diffraction peaks, n of reflection occurs only at the precise values of angle, θ which satisfies the Bragg condition

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} \text{…(3.1)}

The accurate determination of inter-planar spacing, lattice parameters etc. provides an important basis for understanding the various physical properties of materials.
X-rays are relatively short-wavelength, high-energy beams of electromagnetic radiation. When an X-ray beam is viewed as a wave, one can think of it as a sinusoidal oscillation of electric field and magnetic field changing with time right angle to each other. Another description of X-rays is as particles of energy called photons. All electromagnetic radiation is characterized either by its wave character using its wavelength \( \lambda \) or its frequency \( \nu \) or by means of its photon energy \( E \). The energy of an X-ray photon is \( E = \frac{hc}{\lambda} \). Insertion of the appropriate values for the fundamental constants gives \( E = 12.398/\lambda \), where \( E \) is in keV and \( \lambda \) in angstroms. As an example the CuK\( \alpha_1 \), K\( \alpha_2 \) doublet has energy of about 8.05 keV, corresponding to a wavelength of 12.398/8.05=1.5402 Å. The X-ray region lies between 0.1 and 100Å (1Å =10\(^{-10}\) m), being bounded by the \( \gamma \)-ray region to the short-wavelength side and the vacuum ultraviolet region to the long-wavelength side.

X-rays are produced from bombarding a metallic target with electrons [11]. The electrons, accelerated by an electrical field, are suddenly slowed down when they come into contact with the target and lose some of their energy which is dispersed in the form of radiation, a process called braking radiation. The resulting X-rays do not have a specific wavelength, the emission spectrum is continuous and its intensity increases with the electron acceleration voltage (Fig. 3.7(a)). The electron bombardment generates a second type of emission. The electrons transmit their energy to the atoms of the target and cause electronic transitions meaning that the atoms reach an excited state. They return to a more stable energy level through a series of electronic transitions and the emission of X photons with non-random energies \( E = h\nu \), equivalent to the energy gaps between the different electron shells of the atom. Therefore, this radiation is comprised of
several wavelengths, but the emission spectrum is totally discontinuous. Fig. 3.7(b) shows an illustration of this type of emission. The emission spectrum still includes a contribution from the braking radiation which causes the continuous background emission.

![Emission spectrum of a molybdenum anode bombarded with an electron beam.](image)

Fig. 3.7 Emission spectrum of a molybdenum anode bombarded with an electron beam.

![Schematic representation of diffraction X-rays by crystal.](image)

Fig. 3.8 Schematic representation of diffraction X-rays by crystal.

XRD is based on the constructive interference of monochromatic x-rays from a crystalline sample. These x-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The
interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s law (Fig. 3.8) \( n\lambda=2d \sin \theta \) [10]. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted x-rays are then detected, processed and counted by scanning the sample through a range of \( 2\theta \) angles. All possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as wavelength. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction [12]. In crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms while for amorphous sample; diffraction pattern shows few diffused halos instead of sharp peaks.

**Fig. 3.9** *Image of XRD instrument.*

**Instrument:** For structural characterization of the prepared samples, the XRD patterns of all samples have been recorded at room temperature using X-ray powder diffractometer (Bruker X-ray diffractometer, Model D8) (Fig. 3.9) with Cu K\(_a\) radiation (\( \lambda = 1.5405 \) Å) in a wide \( 2\theta \) (Bragg angle) range \( (0^\circ \leq 2\theta \leq 60^\circ) \) at a scanning rate of \( 2^\circ/\text{min} \).
3.4.2 Scanning Electron Microscopy (SEM)

In the characterization of solid–state compounds, scanning electron microscopy (SEM) is widely used to investigate their structure, morphology and crystallite size, to examine the surface defects of crystal, and to determine the distribution of elements (EDAX) [13]. In this technique (Figs. 3.10 ((a)-(b)) and Fig. 3.11), an electron beam is produced by heating the tungsten filament and then focused by magnetic fields in a high vacuum. The vacuum prevents the interaction of the beam with any extraneous particles in the atmosphere. The electrons from this finely focused beam are scanned across the surface of a sample in a series of lines and frames called a raster. At any given moment, the specimen is then bombarded with electrons over a very small area. These electrons may be elastically reflected by the surface of the sample with no loss of energy (backscattered electrons), they may be absorbed and emitted secondary electrons of low energy, they may be absorbed and give rise to the emission of visible light, and they may give rise to electric currents within the specimen. All these effects can be detected and hence given a map of the surface topography of samples. Some of the sample may need to be coated with gold or graphite to stop charge building up on the surface of the

Fig. 3.10(a) Principle of SEM.
Fig. 3.10(b) Principle of SEM instrument.

Fig. 3.11 Simplified schematic view of SEM microscope.
specimen. For backscattered electrons, the atomic number of the elements in the sample is used to determine the contrast in the produced image. The image will show the distribution of different chemical phases in the sample. The resolution in the image is not as good as for secondary electrons because of the emission of these electrons from a depth in the sample. Among all the means, the low–energy secondary electron technique is the most common method. The primary electrons enter a surface of the specimen with energy of 0.5–30keV and generate many low–energy secondary electrons. The intensity of these secondary electrons is mainly governed by the surface topography of the sample. The image of the sample can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution can be obtained because the primary electron beam can be focused to a very small spot.

**Fig. 3.12** Image of SEM microscope.  
**Fig. 3.13** Image of the gold/palladium source coating unit for SEM studies.

**Instrument:** The surface morphology/micro structural studies of the prepared polymer film samples is studied by using a computer-controlled Scanning Electron Microscope (JOEL JSM-6380LV) (Fig.3.12) at 20kV with 100 µm resolution and 1000 magnification. The polymer films were gold coated under vacuum by electron beam gold
palladium source (80% Au, 20% Pd) by JEOL coater (Model JFC-1600) (Fig.3.13) to make them conducting and mounted onto circular aluminum stubs with double side sticky tapes.

3.4.3 Differential Scanning Calorimetry (DSC)

Thermal analysis techniques like thermo gravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) etc. are a group of methods which are used to determine the physical and chemical properties of materials as a function of temperature or time [14, 15]. In each method, the sample is subjected to a controlled temperature programme, which may involve heating or cooling or holding the temperature constant. Le Chatelier [16] was the father of thermal analysis.

DSC is widely used to characterize the thermo-physical properties of polymers. DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of the sample and reference are measured as a function of temperature. Basically DSC measures the amount of heat released by a sample as the temperature increased or decreased at a controlled uniform rate [17]. The reference is either an empty pan or a pan with inert material, such as anhydrous alumina. In DSC, the individual heaters are provided to the sample and reference. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well defined heat capacity over the range of temperatures to be scanned. The basic principle is that when the sample undergoes a physical transformation such as phase
transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less, heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions [18].

Fig. 3.14 shows the cross sectional diagram of DSC cell. In the cell, a metallic disc (made of constantan alloy) is the primary means of heat transfer to and from the sample and the reference. The sample contained in a metal pan and the reference (an empty pan) sit on raised platforms formed in the constantan disc. As heat transferred through the disc, the differential heat flowing to the sample and reference is measured by thermocouples formed by the junction of the disc and chromel wafers which cover the underside of the platforms. These thermocouples are connected in series and measure the differential heat flow using the thermal equivalent of ohms written as:

\[
\frac{dQ}{dt} = \frac{\Delta T}{R_D}
\]

\( \text{...(3.2)} \)

where \( \frac{dQ}{dt} \) is heat flow, \( \Delta T \) is the temperature difference between reference and sample \( R_D \) is the thermal resistance of the disc.

The result of a DSC experiment is a curve of heat flux versus temperature as
observed in Fig.3.15. In the DSC plot, exothermic peak is due to the evolution of heat from the sample which raises the temperature temporarily above that of the reference material; whereas, endothermic peak is just due to the reverse type of process.

The basic principle of DSC depends on the amount of heat needed to flow in to maintain the samples and reference at the same temperature when the sample undergoes some physical transformation such as phase transition. The amount of less or more heat through the sample depends on whether the process is exothermic or endothermic. Glass transition temperature $T_g$ is a vital characteristic of the amorphous behavior of a polymer during the transition from solid to liquid (or melt) state [19]. The kinetic energy of the molecules increases if an amorphous polymer is heated. As the polymer retains in the
glass–like properties, the mobility of molecules are still restricted even there is a presence of short–range vibrations and rotations. As the temperature is further increased or the polymer matrix is further melted, its glass–like structure will be converted into rubbery state which is soft and elastomeric. This characteristic temperature is known as \( T_g \). At this transition, it is accompanied by more long range molecular motion and thus the degree of rotational freedom increases. As a result, there is more segmental movement among the atoms of the chains. Thus, the space between the atoms will be increased and then results in the increase of the specific volume.

![Image of DSC equipment.](image)

**Fig. 3.16** Image of DSC equipment.

Above \( T_g \), the molecules start to gain the freedom in motion and after reaching a particular stage where they have enough freedom of motion, they will arrange themselves continuously into a crystalline form. At this stage, heat is given out from the system and it is known as crystallization temperature. This result and exothermic peak in DSC thermogram as can be seen from Fig.3.15. As the polymer is further heated, it loses its elastomeric behavior and results in an endothermic dip in DSC thermogram. At this stage, the crystalline melting temperature (\( T_m \)) is reached. In short, DSC plays an
important role to determine the glass transition temperature \( (T_g) \) and crystalline melting point \( (T_m) \).

The main application of DSC is in detection of transitions like melts, glass transitions, phase changes, and curing. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

_Instrument:_ In the present work, the thermal analysis employed, is DSC using model SII EXSTAR-6000 DSC differential scanning calorimeter (from SII SEIKO (Fig.3.16)).

### 3.4.4 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR Spectroscopy is a fundamental technique for chemical identification of a functional group, which provides a useful information regarding structure of molecules [21]. It involves the twisting, bending, rotating and vibrational motions of atoms in a molecule. Upon interacting with IR radiation, portions of the incident radiation are absorbed at particular wavelengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is uniquely characteristic of the functional groups comprising the molecule and of the overall configuration of the atoms as well.

Changes in vibrational and rotational states of the molecules result in absorption in the infrared region. The absorption frequency depends on the vibrational frequency of the molecules, whereas the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule and this depends on the change in the dipole moment that occurs as a result of molecular vibration moment and known as “IR active molecule”. Thus, all those compounds which are IR active can be analyzed by their characteristic infrared absorption.
The block diagram of a typical FTIR-spectrometer is shown in Fig. 3.17. In this, the source of radiation e.g.: heated wire, generates infrared radiation over the entire mid-infrared range [19]. The radiation then enters the Interferometer which consists of a beam splitter, a fixed mirror and a moveable mirror. The beam splitter has the property of transmitting approximately half the radiation falling on it, the remaining half being reflected. The reflected beam passes to the fixed mirror and the transmitted beam passes to a movable mirror. Each of these two mirrors reflects the beam back towards the beam splitter. Here again, half of the radiation is reflected and the other half is transmitted. The radiation reaching the detector thus comprises of beams which can combine...
constructively or destructively. Their recombination depends on the path difference between the upper arm and the right arm of the interferometer as the position of the moving mirror is changed. A cosine wave is detected at the detector when the moving mirror is gradually moved along the beam direction when the source is emitting a single frequency. When a broad band source is used, the interference pattern becomes the sum of the all the frequencies present. This interferogram consists of a strong signal at the point where the path difference is zero, gradually falling away rapidly on either side. A single beam spectrum is obtained when the interferogram is treated by a mathematical process of Fourier transformation. Normally, interferometers operate by first recording the background and then rationing it against the spectrum that is obtained when the sample is inserted in the beam between the interferometer and detector.

IR radiation is passed through the sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

A natural vibrational mode within a molecule will absorb IR radiation, if the following conditions are fulfilled:

1) Those molecules will absorb IR radiation in which the natural frequency of vibration of the molecule is the same as the frequency of the incident radiation. The IR radiation, that is absorbed, causes the molecule to vibrate at increased amplitude (Resonance).

2) Those molecules can absorb IR radiation in which absorption produces some changes
in the electric dipole of the molecules. Such molecules are known as IR active materials.

The dipole moment is determined by the positions of the centers of gravity of the positive and negative electrical charges. When a molecule having electric dipole is kept in the electric field, it exerts a force on the electric charges in the molecules, which gives rise to decrease or increase of a separation. Change in the electric field of IR radiation causes a change in polarity periodically. It means that the spacing between the charged atoms of the molecule also changes periodically and vibration of these charged atoms causes the absorption of IR radiation. In symmetrical stretching vibration, the centers of gravity of the charges coincide in every vibrational position, no dipole moment is created and the absorption characteristic of this mode is not observed in IR. Such vibrations are said to be IR inactive. However, in asymmetrical stretching vibration, a dipole moment is produced and the vibration is IR active and is observed in IR spectrum.

The position of atoms in a molecule is not fixed; they are subjected to a number of different vibrations and rotations. Two atoms are joined by a covalent bond which may undergo stretching vibrations. The atoms can undergo a variety of stretching and bending vibrations. Energy of a vibration depends on (1) the mass of the atom present in the molecule, (2) strength of the bond and (3) the arrangement of various atoms in the molecule. The position of IR band is described in terms of wavelength \( \lambda \) (usually measured in microns, \( \mu \)) or wave number, \( \tilde{\nu} \). Both these units are related to each other by the relation

\[
\tilde{\nu} \text{(in } cm^{-1}) = \frac{10^4}{\lambda} \text{ (in } \mu) \quad \text{ ...(3.3)}
\]

The positions of absorption bands, as determined from the mechanical theory of harmonic oscillators, are given by
\[ \bar{v} \text{ (in cm}^{-1}\text{)} = \frac{1}{2\pi c} \sqrt[4]{\frac{k(m_1 + m_2)}{m_1 m_2}} \]...

(3.4)

where \( m_1 \) and \( m_2 \) are the masses of two adjacent atoms in a molecule and \( k \) is the restoring force per unit displacement and can be expressed as

\[ k = aN \left( \frac{\chi_1 \chi_2}{d^3} \right)^{3/4} + b \]

...(3.5)

where \( N \) is the band order (i.e., effective number of covalent or ionic bands), \( \chi_1 \) and \( \chi_2 \) are the electro negativities of the atoms, \( d \) is the internuclear distance in angstroms and \( a = 1.67 \) and \( b = 0.30 \) are constants. From the above relations, it is clear that the bond length can be a good guide to the direction of a shift of band resulting from a change in chemical group- the greater the length, the lower the frequency. Bending modes usually produce lower frequency absorption bands than fundamental stretching modes.

**Stretching vibrations:**

![Fig. 3.18](image1.png)  
**Symmetric stretching vibrations:**  
(a) diatomic molecule (b) triatomic molecule.

![Fig. 3.19](image2.png)  
**Asymmetric Stretching Vibrations:**  
(a) and (b) triatomic molecule.
It arises due to stretching and contracting of bond without producing any change in the bond angles, which are of two types namely, symmetric and asymmetric stretching. If the movement of atoms with respect to a particular atom in a molecule is in the same direction, it is called symmetrical stretching vibrations as shown in Fig. 3.18. If one atom approaches the central atom whereas the other approaches away from it in a triatomic system, it gives unequal movement of the outer atom with respect to central one, as shown in Fig. 3.19. Because of this, the change in electric dipole takes place. Therefore, asymmetric stretching gives it vibrational frequency at higher wave number than for symmetric system.

**Bending vibrations**

It gives rise to deformation of bond angle but there is no change in bond lengths. In diatomic molecules, most of the bond angles are found to be in two categories i.e.; linear or $180^0$ bond angle and bond angle in a neighborhood of $120^0$ to $110^0$.

In triatomic molecules, the two atoms are the same and are bound to the middle atom by two equal bonds with two different frequencies symmetric or asymmetric.

$$v_{\text{sym}} (cm^{-1}) \approx \left( \frac{1}{2\pi c} \right) \left[ k \left( \frac{1}{m_{\text{end}}} + \frac{(1 + \cos \alpha)}{m_{\text{mid}}} \right) \right]^{1/2} \quad \text{...(3.6)}$$

where $\alpha$ is a bond angle, $V$ is a frequency in cm$^{-1}$, $k$ is the force constant in dyne/cm, $m_{\text{end}}$ and $m_{\text{mid}}$ are the masses of one end and middle atom respectively. The above Eqn. 3.5 and 3.6 can also be written as.

$$v_{\text{asym}} (cm^{-1}) \approx \left( \frac{1}{2\pi c} \right) \left[ k \left( \frac{1}{m_{\text{end}}} + \frac{(1 - \cos \alpha)}{m_{\text{mid}}} \right) \right]^{1/2} \quad \text{...(3.7)}$$
\[
\nu_{\text{sym}} \approx \left( \frac{1}{2\pi c} \right)^{1/2} \left[ k \left\{ \frac{1}{M_{\text{end}}} + \frac{(1+\cos \alpha)}{M_{\text{mid}}} \right\} \right] \quad \ldots (3.8)
\]

\[
\nu_{\text{asym}} \approx \left( \frac{1}{2\pi c} \right)^{1/2} \left[ k \left\{ \frac{1}{M_{\text{end}}} + \frac{(1-\cos \alpha)}{M_{\text{mid}}} \right\} \right]^{1/2} \quad \ldots (3.9)
\]

where \( M_{\text{end}} \) and \( M_{\text{mid}} \) are the atomic weights of end atom and middle atoms.

Bending vibrations are classified into four types i.e.; scissoring (Fig. 3.20 (a)), rocking (Fig.3.20 (b)), wagging (Fig.3.21.(a)) and twisting (Fig.3.21(b)) bending. In scissoring bending vibrations of the bonds, the two atoms approach each other in the same plane as shown in Fig. 3.20 (a).

**Fig. 3.20** (a) Scissoring bending (in plane bending with lower frequency of vibration) (b) Rocking bending (in plane bending with lower frequency of vibration).

In rocking bending of bond vibration, the movements of atoms occur in the same direction and also in the same plane as shown in Fig.3.20(b). Wagging bending of bond vibrations is due to the two atoms move up and down below the plane with respect to the central atom as shown in Fig.3.21(a). In twisting bending vibrations, one of the atoms
moves up the plane and the other moves down the plane with respect to the central atom as shown in Fig. 3.21(b). Here (+ve) and (–ve) sign represents motion above and below the plane of the paper respectively. The energy required to stretch a spring is more than that needed to bend it so the stretching absorption of the bond will appear at higher frequencies than the bending absorption of a bond. Thus IR spectroscopy is widely used for molecular structural studies of various materials.

Fig. 3.21 (a) Wagging bending (out of plane having high frequency of vibration). (b) Twisting bending (out of plane bending with high frequency of vibration).

Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for the following reasons:

➢ **Multiplex Advantage:**
An interferometer in an FT-IR instrument does not separate energy into individual frequencies for measurement of the infrared spectrum. Each point in the interferogram contains information from each wavelength of light being measured whereas; every wavelength across the spectrum is measured individually in a dispersive spectrometer.
This is a slow process, and typically only one measurement scan of the sample is made in a dispersive instrument. The multiplex advantage results in faster data collection of an FT-IR spectrum.

➢ **Precision Advantage:**
   Accuracy and precision in infrared spectra are much higher when collected on an FT-IR due to maintaining of internal precision and accuracy of the wavelength positions by laser which controls the velocity of the moving mirror and to time the collection of data points.

➢ **Throughput Advantage:**
   There are less reflection losses in FT-IR spectrometer than in a dispersive spectrometer. This means that the signal-to-noise ratio of an infrared spectrum measured on an FT-IR is higher hence, the sensitivity of small peaks will be greater, and details i.e., high-resolution in a spectrum will be clearer and more distinguishable in the FT-IR spectrum than the dispersive spectrum of the same sample.

**Instrument:** FTIR spectra of prepared polymer electrolyte system are carried out using FT-IR 4100 JASCO model (Fig.3.22).

![Image of FTIR instrument.](image-url)
3.5 Complex Impedance Analysis

Complex impedance analysis is a powerful technique to characterize the electrical properties of the solid electrolytes [20]. The complex impedance measurement were carried out using a computer-interfaced impedance analyzer (Impedance Gain/Phase Analyzer, Solartron 1260) in the frequency range of 100 Hz to 1MHz at a.c. signal of 100 mV at 303-373K temperatures (Fig.3.23). The polymer electrolyte film is sandwiched between two stainless silver block electrodes used as cell for the electrical measurement.

![Image of setup of impedance measurement (Impedance analyzer interfaced with computer).](image)

The complex impedance spectrum data is used to evaluate the conductivity and other related electrical properties e.g.; ac conductivity, dielectric permittivity and modulus. The real, $Z'$ and imaginary, $Z''$ parts of complex impedance $Z^*$ are directly measured from the instrument. The impedance plot of prepared polymer electrolyte films is obtained by plotting the real, $Z'$ on x-axis and imaginary, $Z''$ on y-axis, parts of complex impedance $Z^*$. The bulk resistance, $R_b$ was determined by extrapolating the
complex impedance plot curve to intercept at the real axis (Z'-axis). The obtained impedance plots can be fitted using “Zview2 program” (developed by Solartron Analytical). Then the ionic conductivity can be calculated from bulk resistance with the dimension of polymer electrolyte sample using the formula given below:

\[
\text{Ionic conductivity } \sigma = \left( \frac{t}{A} \right)^* \left( \frac{1}{R_b} \right)
\]

The complex conductivity can be given as,

\[
\sigma^*(\omega) = \frac{t}{A} \left( \frac{Z^*(\omega)}{Z'^2 + Z''^2} \right)
\]

\[= \sigma'(\omega) + \sigma''(\omega) \quad \ldots (3.10)
\]

where, \(\omega\), \(t\) and \(A\) are the angular frequency, thickness and cross sectional area of the sample, respectively. The real part, \(\sigma'\), of \(\sigma^*\) is called the AC conductivity.

The complex dielectric function \(\varepsilon^*\) is given as [21]

\[
\varepsilon^*(\omega) = j \omega C_0 Z^* = \varepsilon'(\omega) - i \varepsilon''(\omega) \quad \ldots (3.11)
\]

where, \(C_0\) is the vacuum capacitance and is expressed as \(C_0 = \varepsilon_0 A t\). \(\varepsilon_0\) is the permittivity of free space (constant). The real part of complex dielectric function is called the dielectric constant, \(\varepsilon'\) and the imaginary part, \(\varepsilon''\) is considered to be the loss occurring due to conduction process.

The modulus formalism is used to analyze the relaxation processes in solids [22]. The complex modulus function can be given as,

\[
M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = j \omega C_0 Z^* = M' + i M'' \quad \ldots (3.12)
\]

The complex dielectric analysis provides information about the electrode polarization while the modulus formalism gives the conductivity relaxation effects as these effects
become prominent in modulus formalism due to suppression of electrode-electrolyte interface polarization effects [23].

3.6. Transference number measurement

Solid polymer electrolytes are solutions of salts in polymers, both of cation and anion have a chance to move [24]. It is of great importance to clarify the ionic transport number in terms of the understanding of the ion-conduction mechanism and of their practical applications. The ionic transference number has been measured in certain kinds of the polymer electrolytes using various methods including Wagner’s polarization technique, PEFG-NMR measurements, EMF measurements, potentiostatic polarization, Tubandt method and DC polarization technique [25-30]. The data obtained are somewhat distributed. The transference number measurement of solid materials signifies the contribution of ionic conductivity to the total conductivity. Therefore, it is one of the key factors to be considered while choosing the system as an electrolyte (in super ionic system) or to be used as a cathode material (in mixed conducting system) for battery application. Normally, the transference number measurement can be carried out through different methods namely, Tubandt’s method [30], Hebb-Wagner’s polarization method [25] and electrochemical (EMF) method [27]. The electronic contribution to the total conductivity can be obtained from Wagner polarization technique, whereas the other techniques brief about ionic nature of the conducting species.

*The transference number of a moving charged particle is defined as the ratio of the conductivity due to itself and the total conductivity.*

There are many methods to ensure the transference number, few of these described below in brief:
3.6.1 Wagner Polarization technique

The Wagner's polarization method, which is generally used to determine ionic and electronic transference numbers, is schematically shown in Fig.4.2. In this technique, the sample is placed between two electrode one blocking and the other non-blocking for the mobile ionic species. The sample was polarized under dc bias of constant voltage. Current versus time is monitored for a fixed applied dc potential. The initial current is the total current ($i_T$), due to the ions ($i_i$) and electrons ($i_e$). As the polarization builds up the $i_i$ is blocked and the final current is only the electronic current. The initial total current decreases with time due to the depletion of ionic species in the samples and becomes constant in the fully depleted situation. At this stage, the residual current is only electronic current.

![Experimental arrangement of Wagner's polarization method for determining transference number.](image)

The electronic transference number $t_e$ and the ionic transference number $t_i$ respectively are given by

$$t_e = \frac{\sigma_e}{\sigma_T} = \frac{i_e}{i_T} \quad \ldots(3.13)$$
and \( t_i = 1 - t_e \) \( \text{...(3.14)} \)

where \( \sigma_e \) and \( \sigma_t \) are the electronic conductivity and total conductivity respectively while \( i_e \) is the electronic current and \( i_t \) is the total current.

### 3.6.2 EMF method

Transference number can also be measured by EMF method \([33]\). In this method the ionic conductor is placed between a pair of electrodes of different chemical potentials \( \mu_1 \) and \( \mu_2 \). The potential difference (emf) developed across the electrodes is given by \([34]\):

\[
E_{\text{emf}} = \frac{-1}{|Z|F} \int_{\mu_1}^{\mu_2} t_i d\mu = \frac{t_i (\mu_1 - \mu_2)}{|Z|F} = \frac{t_i \Delta G}{F|Z|} \text{...(3.15)}
\]

where \( t_i \) is the ionic transport number, \( \mu_1 \) and \( \mu_2 \) are chemical potential of the electrodes, \( \Delta G \) is the change in free energy involved for a given pair of electrodes, \( |Z| \) is the valence of mobile ion and F is the Faraday’s constant. For an ideal electrolyte with \( t_i = 1 \), the emf generated is given by

\[
E_{\text{theo}} = \frac{\Delta G}{F|Z|} \text{...(3.16)}
\]

From the above relations, \( E_{\text{obs}} = t_i E_{\text{theo}} \). Thus the transport number of the mobile ion can be calculated from the ratio of observed emf \( (E_{\text{obs}}) \) to the theoretical value of emf \( (E_{\text{theo}}) \) for a given pair of electrodes.

### 3.6.3 DC polarization technique

This method was proposed by Evans \textit{et.al.} \([27]\). According to this technique, Na-Hg \( \mid \) polymer electrolyte film \( \mid \) Na-Hg cells are polarized by applying a voltage
$\Delta V = 20\text{mV}$ for 2h. The initial and final currents are subsequently recorded. Further, as a part of this method, the cells are subjected to ac impedance measurements prior to and after the polarization, and the values of the electrode-electrolyte contact resistances are estimated from the impedance plots. The ionic transference number values are calculated using the expression:

$$t_{Na} = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)}$$

where $I_0$ and $I_s$ are the initial and final current; $R_0$ and $R_s$ are the cell resistance before and after polarization.

Out of these different methods for obtaining the transference number, in the present investigation, Wagner’s polarization technique is used. Keithley model 6514 electrometer was employed for the accurate measurements of current as a function of time.
References: