CHAPTER - 3

RESEARCH METHODOLOGY
3.1  Outline

The methodology used in this research work is divided into three sections. The first section deals with the preparation of HPMC test samples that could display a constant performance through a series of tests. Second section deals with irradiating the test samples at various dose of gamma radiation within a standard set of environmental conditions. Lastly, the third section involves the characterization the polymer electrolyte samples before and after gamma irradiation by different experimental techniques like XRD, SEM, FTIR, DSC and DC electrical conductivity. The experimental techniques and procedures described in this chapter are introduced in the sequence they were performed during the experimental process.

3.2  Materials

A series of solid polymer electrolyte thin films are developed through solution-cast technique. HPMC (Hydroxypropyl methylcellulose) is used as the host polymer. HPMC (E15LV), which contained methoxy group (23.8%) and hydroxypropoxy group (8.3%) was purchased from, Loba Chemicals India. Inorganic salts like sodium iodide (NaI), cadmium chloride (CdCl₂) and ceric ammonium nitrate ([NH₄]₂Ce(NO₃)₆) are used as doping filler inorganic salts. NaI and CdCl₂ were purchased from S. D. fine chemicals India, whereas ceric ammonium nitrate (CAN) was purchased from Loba Chemicals India.

3.2.1  Hydroxypropyl methylcellulose (HPMC)

Hypromellose is a short form for hydroxypropyl methylcellulose (HPMC). It appears as a white to off-white granular free flowing powder as shown in figure 3.1. Chemically HPMC is cellulose ether containing methoxyl and hydroxypropyl groups (Greener, I. K., & Fennema O., 1989). A general structure of hypromellose with methyl (CH₃) and hydroxypropyl (CH₂CH(OH)CH₃) is as shown in figure 3.2. Here the R – Group can be a single or a combination of substituents. The substituent group type and distribution affects the physicochemical properties of the polymer. It is strongly affected by the hydroxypropoxy group, methoxy group content and the molecular weight (Ali. R. Rajabi Siahboomi, M.P. Jordan., 2000; Hardy, I. J., Cook, et al., 2006; Honary, S., et al., 2010). The chemical structure of HPMC polymer is shown in figure 3.3 and Table 3.1 shows the physical properties of HPMC.
**Figure 3.1:**  HPMC in powder form.

**Figure 3.2:**  General structure of hypromellose with methyl (CH₃) and hydroxypropyl (CH₂CH(OH)CH₃).

**Figure 3.3:**  Chemical structure of HPMC.

**Table 3.1:**  Physical properties of HPMC.

<table>
<thead>
<tr>
<th>Appearance (Form)</th>
<th>Granular free flowing powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White to off-white</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Soluble</td>
</tr>
<tr>
<td>Molecular Weight (average)</td>
<td>324.28 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>0.5 g/cm³</td>
</tr>
</tbody>
</table>
3.2.2 Sodium iodide (NaI)

Sodium iodide appears as a white crystalline salt (figure 3.4) with the chemical formula NaI. The chemical structure of sodium iodide is shown in figure 3.5. Table 3.2 shows the physical properties of NaI. Research study shows that the sodium ion is used to incorporate as electrolyte material in many sodium batteries (Wang, J., et al., 2007; Kim, J. S., et al., 2008). There also exists some sodium ion conducting polymer electrolytes based on poly-ethylene-oxide (PEO) and poly-propylene- oxide (PPO) complexed with NaSCN, NaI, NaClO₃, NaPF₄, NaYF₄, NaCF₃SO₄, NaN₃ and NaClO₄ (Sreekanth, T., et al., 1999), which has been reported for its application as electrolyte materials in sodium batteries. Sodium is more abundant and cost effective than lithium. The softness of sodium metal promotes the stability of electrode – electrolyte interface in solid state ionic devices (Hunter, C. C., & Ingram, M. D., 1984). Also NaI salt has low lattice energy and large anions which are generally expected to promote greater dissociation of salts, thereby more salts will be dissociated to provide a higher concentration of ions.
**Figure 3.4:** Sodium iodide (NaI) in powder form.

\[
\text{I} \quad \text{Na}
\]

**Figure 3.5:** Chemical structure of NaI.

**Table 3.2:** Physical properties of sodium iodide (NaI).

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>NaI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (Form)</td>
<td>White crystalline solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Molar mass (average)</td>
<td>149.89 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>3.67 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>661 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>1,304 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>178.8 g/100 mL (20 °C)</td>
</tr>
<tr>
<td>Solubility</td>
<td>soluble in ethanol and acetone (39.9 g/100 mL)</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>0.347 J/Gk</td>
</tr>
</tbody>
</table>
3.2.3 Cadmium chloride (CdCl$_2$)

Cadmium chloride is a white crystalline compound of cadmium and chlorine as shown in figure 3.6. It has the chemical formula CdCl$_2$ having rhombohedral symmetry. It is a hygroscopic solid that is highly soluble in water and is considered to be ionic. The chemical structure of cadmium chloride is shown in figure 3.7. It prefers oxidation state +2 in most of its compounds and shows a low melting point (Lide & David R. 1998). Table 3.3 shows the physical properties of cadmium chloride.

Cadmium is a soft, ductile, divalent metal. It is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals. It is also used for photocopying, dyeing and electroplating. Cadmium electroplating can be found in the aircraft industry due to the ability to resist corrosion. Cadmium was used in batteries, predominantly in rechargeable nickel-cadmium batteries. It is a fast-ion conducting salt and very malleable in a number of crystalline and amorphous materials. Its incorporation in a polymeric system may be expected to allow the more free charges and these free charges contribute to development of the charge transportation mechanism and inter-intra electronic transition (Liu B., et al., 2001).
Figure 3.6: Cadmium chloride (CdCl₂) in powder form.

Figure 3.7: Chemical structure of CdCl₂

Table 3.3: Physical properties of cadmium chloride (CdCl₂)

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>CdCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (Form)</td>
<td>White crystalline solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Molar mass (average)</td>
<td>183.32 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>4.05 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>564 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>960 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>119.6 g/100 mL (25 °C )</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in alcohol, Insoluble in ether, acetone</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>74.7 J/mol·K</td>
</tr>
</tbody>
</table>
3.2.4 Ceric ammonium nitrate (NH4)2Ce(NO3)6

Ceric ammonium nitrate (CAN) is the inorganic compound with the formula (NH4)2Ce(NO3)6. Cerium is a soft silvery metal, belonging to the lanthanide group which is both malleable and ductile. Figure 3.8 shows the orange-red appearance of CAN. This water-soluble cerium salt is widely used as an oxidizing agent in organic synthesis and as a standard oxidant. The chemical structure of ceric ammonium nitrate is shown in figure 3.9 and Table 3.4 shows the physical properties of CAN.

In the past several years, cerium based materials have been intensely investigated as catalysts, structural and electronic promoters of heterogeneous catalytic reactions (Trofarelli, A., et al., 1997; Kilarkaje, S., et al., 2011) and oxide ion conducting solid electrolytes in electrochemical cells (Inaba, H., & Tagawa, H., 1996). Balazs, G. B., 1995, in his article reported the ionic conductivities of materials doped with cerium which showed an increasing trend of conductivity. It has been used extensively as the redox initiator for effecting grafting of a variety of biopolymers. The mechanism by which Ce(IV) interacts with biopolymer to form free radical involves the formation of a coordination complex between the Ce(IV) and the hydroxyl group of biopolymer (Arup Dey, & S. Karan., 2013; Hamdan, K. Z.; Khiar, A. S. A., 2014). At present, ceria based electrolytes appear to be the most promising amongst high ionic conductivity electrolytes.
Figure 3.8: Ceric ammonium nitrate (CAN) in powder form.

Figure 3.9: Chemical structure of Ammonium ceric nitrate.

Table 3.4: Physical properties of ceric ammonium nitrate (CAN).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>(NH₄)₂Ce(NO₃)₆</td>
</tr>
<tr>
<td>Appearance (Form)</td>
<td>orange-red crystals</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Molar mass (average)</td>
<td>548.26 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>107–108 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>141 g/100 mL (25 °C)</td>
</tr>
</tbody>
</table>
3.3 Preparation of samples

3.3.1 Solution-cast technique

HPMC hosted, three polymer electrolyte systems (HPMC:NaI, HPMC:CdCl$_2$, and HPMC:CAN) were prepared using solution-cast technique. Prior to the preparation of the polymer electrolytes, HPMC and all inorganic doping salts are dried at 50 °C for overnight to eliminate any trace water in the material. The quantity of materials integrated was expressed in weight percentage (wt %). Double distilled water is used as solvent. Here, HPMC in weight ratio (wt %) was dissolved in double distilled water and stirred continuously using a magnetic stirrer at room temperature for 8-10 hrs. The completely soluble homogeneous solution was filtered through Whatmann No. 41 filter paper and degassed to remove foam and any undissolved impurities. Then the desired amount of inorganic salt (wt %) as a dopant, was added and stirred continuously for 3 - 4 hrs. The clear solution of HPMC complexed with different salts was poured on to a clean and leveled glass plates (30 cm X 40 cm) to evaporate at room temperature for 5 days and peeled off from the glass plate. The final films were vacuum dried thoroughly and stored in desiccators to avoid the absorption of moisture.

In the initial stage of the preparation of polymer electrolyte films, HPMC polymer was blended with inorganic salt of NaI. The weight of HPMC was fixed as 5g, while for NaI, it varied from 1% - 4% (wt%). After HPMC:NaI (5:1, 5:2, 5:3, and 5:4) polymer samples with the best ionic conductivity was determined, the sample with HPMC:NaI (5:4) system showed the highest ionic conductivity. Therefore, this ratio is being fixed in this system and the sample preparation with same (wt%) ratio process was then repeated for another inorganic salt CdCl$_2$ to prepare HPMC: CdCl$_2$ (5:1, 5:2, 5:3, and 5:4) systems. In the last stage of the sample preparation, ceric ammonium nitrate (CAN) is used as inorganic filler to obtain the HPMC:CAN (5:0.5, 5:1, 5:1.5, and 5:2) polymer electrolyte systems. The preparation method, pure HPMC solution, HPMC blended with different salt concentration and the polymer sample are depicted in figure 3.10. All the prepared polymer electrolyte films which are generated from the solution-cast technique were gamma irradiated at different doses in air and will then be characterized by XRD, SEM, FTIR, DSC and DC electrical conductivity before and after gamma irradiation.
Figure 3.10: Sample preparation.
3.4 Gamma irradiation

Gamma radiation is located near the high energy end within the electromagnetic radiation spectrum. The radiation energy emitted from a gamma source (for example, gamma rays emitted by cobalt-60) is able to break the molecular bonds and ionize atoms, but it is not high enough to affect the structure of atomic nucleus, hence it avoids the induction of radioactivity for irradiated material. Gamma radiation may, therefore, modify physical, chemical, or biological properties of the irradiated material. Cobalt-60 gamma source has relatively high energy. Cobalt-60 is the most commonly used and most suitable gamma radiation source for radiation processing because of the relatively high energy of their gamma rays and fairly long half-life (5.27 years for cobalt-60.)

Here the sample is placed in a sample holder on a rotating stage at the center of the lead chamber with approximately 28,000 cm$^3$ internal volume. The source is a cobalt-60 source (661 keV) and is introduced into a corner of the chamber. The chamber allows radiation to reflect from the walls and interact with the sample from all directions. The system is equipped with an automated calibration to deliver a specific radiation dose to the sample present in the chamber. The samples were irradiated by exposure to the cobalt-60 source applied at a dose rate of 2.5 kGy / hour for time required to obtain total radiation doses of 20 kGy, 60 kGy and 100 kGy for all polymer electrolyte systems. In this present research work, films of pure HPMC and various compositions of HPMC based polymer electrolyte samples has been gamma irradiated in air by $^{60}$Co source at the doses of 20, 60 and 100 kGy. As the mechanical properties and wear resistance of the polymer saturate at above 100 kGy irradiation (Muratoglu, O. K., 2009), the proposed study was carried out upto 100 kGy dose level, which was performed at M/s Microtrol sterilization private limited, Bangalore, India.

3.5 Characterizations

The HPMC based polymer electrolyte films before and after gamma irradiation were characterized by different experimental techniques. X-ray diffraction (XRD) is used to determine the nature of the sample, phase identification, quantitative identification of the mixture of phases, percentage of crystallinity analysis etc. Scanning electron microscopy (SEM) is used to study the compatibility between the
various components of the polymer electrolytes through the detection of phase separation and interfaces. Fourier transform infrared spectroscopy (FTIR) is used to identify the interaction between molecules and the structural changes. Differential Scanning Calorimetry (DSC) used to study the thermal transitions of polymer matrix. The dc electrical conductivity (σ) measurements were done using Keithley Programmable Electrometer (Model 617).

3.5.1 X-Ray Diffraction (XRD)

XRD is a useful method in the identification of compounds for qualitative analysis. It is also widely been probed to provide a rough check of the purity of sample, percentage of crystallinity, particle size etc. (Smart, L. & Moore, E. A., 2005). In general, X–ray is an electromagnetic radiation of wavelength ~1 Å (10⁻¹₀ m) and lies between γ – ray and the ultraviolet in the electromagnetic spectrum. A filament, usually tungsten, is electrically heated and thus a beam of electrons are emitted. These electrons are accelerated by a high potential difference (20–50 kV) and then allowed to strike a metal target (often copper Cu). These incident electrons have got sufficient energy to knock out or ionize electrons from the innermost K shell (n =1) which in turn creates vacancies. An electron from an outer orbit (2p or 3p) immediately drops down to occupy these vacancies releasing the energy as radiation, as shown in figure 3.11. The electrons descending from the L shell (n =2 or 2p) produce Kα lines with a wavelength of 1.5418 Å, whereas the electrons from the M shell (n =3 or 3p) will give rise to Kβ lines with wavelength of 1.3922 Å. Kα transition occurs more frequently than Kβ transition. Kα line is usually selected and Kβ line is filtered out by using a filter made of nickel metal foil. In XRD, monochromatic radiation, which defined as single wavelength or a very narrow range of wavelengths, is required (West, A.R., 1999; Smart, L. & Moore, E. A., 2005).

Figure 3.12 illustrates the Bragg condition for of X–ray reflection by a crystal. Ray 1 and Ray 2 are the X–rays beams reflected from adjacent planes. ‘d’ is the spacing between these atomic planes. Ray 1 reflects from the upper atomic plane with an angle θ which is equal to its incident angle. Similarly, ray 2 reflects from the lower atomic plane with an angle θ. Ray 2 has to cover an extra path xyz (or distance of 2a) as compared to ray 1. For these two reflected rays to emerge as a single beam of reasonable intensity, they must be in phase with one another undergoing constructive
interference. Constructive interference occurs if the interfering two rays (ray1 and ray 2) must differ by an integral number of wavelengths (nλ). The perpendicular distance between pairs of adjacent planes (d_{hkl}) and the angle of incidence, or Bragg angle (θ) are related to the distance xy by equation 3.1.

\[ xy = yz = d_{hkl} \sin \theta \tag{3.1} \]

The difference in path length between the two beams is given by:

Difference in path length = xy + yz

Thus, difference In path length = 2 \( d_{hkl} \sin \theta \)

This must be equal to an integral number, n, of wavelengths. If the wavelength of the X–rays is λ, then we have equation 3.2.

\[ n\lambda = 2 d_{hkl} \sin \theta \tag{3.2} \]

Where \( d_{hkl} \) is the interplanar distance between crystallographic planes for a set of miller indices hkl.

λ is the wavelength of the incident beam, and

θ is the scattering angle at which diffraction intensity can be observed.

This is known as the Bragg equation. At angles of incidence other than Bragg angle, the reflected beams are out of phase and destructive interference or cancellation occurs.

The technique consists in exposing a target material to an X-ray beam which is diffracted as a result of the interaction with the electrons of the material. The diffraction will occur at specific angles (θ) with intensities (I) producing an absorption spectrum with peaks of area (A). A scintillation detector is used to record the angle and the intensity of diffracted beams, which are plotted as intensity against 2θ. The increase in the width of the diffraction peak indicates the decrease in the crystallite size. The crystallinity was determined by the ratio of the sum of the areas of the crystalline peaks over the total area of the spectrum.

In the current research, the XRD characterization study is done with an X-ray source with CuKα radiation of wavelength 1.5406 Å (Make/Model: Bruker AXS D8 Advance) diffrator with a range which varies from 3° to 80°. Besides that, the scan speed was 2.5° 0/20 per minute and step size was 0.02° 0/20. After that, the polymer electrolyte sample is placed in the path of a monochromatic X-ray beam, the
planes in the crystallites will orient at the correct angle to fulfill the Bragg condition and hence form the diffraction. The diffraction beam makes an angle of \(2\theta\) with the incident beam and the diffraction pattern is performed by automatic diffractometers. Figure 3.13 shows the experimental setup for XRD diffratrometer model. The XRD analysis for all the prepared samples were done at the Sophisticated Test and Instrumentation Centre (STIC), Kochi University, Kerala, India.

**Figure 3.11:** Generation of \(K_{\alpha}\) and \(K_{\beta}\) transitions.

**Figure 3.12:** Derivation of Bragg’s law.
Figure 3.13: Experimental setup of XRD diffractometer
3.5.2 Scanning Electron Microscope (SEM)

The magnified image of the sample in a raster scan pattern can be obtained by using a scanning electron microscope. SEM consists of an electron gun assembly fitted with a tungsten filament cathode inside. During the operation of SEM, electron gun emit an electron beam, which is focused by one or two condenser lenses to a spot about 1 nm to 5 nm in diameter. The beam passes through pairs of deflector plates in the electron column which deflect the beam so that it scans in a raster fashion over a rectangular area of the sample surface. The electrons incident on the sample are called primary electrons. Out of these, some of them will be scattered by the sample and some of them knock out the electrons from the atoms in the specimen. Those which are scattered from the sample are called back scattered electrons and the ones which are knocked off from the atoms are called secondary electrons. When the primary electron beam interacts with the sample, the electrons lose energy by the repeated random scattering or absorption within a teardrop-shaped volume of the specimen, which extends from less than 100 nm to around 5 µm into the surface. They may be absorbed and emit secondary electrons of low energy. They may also be absorbed and give rise to the emission of visible light, and also 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.

The scanned image of the sample will show the distribution of different chemical phases. The spatial resolution of the SEM images depends on the size of the electron spot which in turn depends on both the wavelength of the electrons and the electron-optical system (magnetic electron-optical system) which produces the scanning beam. The resolution is also limited by the size of the interaction volume which is very large as compared to the distances between atoms, so the resolution of the SEM is not high enough to image down to the atomic scale. However, SEM has the ability to image a comparatively large area of the specimen, to image bulk materials and the variety of analytical modes available for measuring the composition and nature of the specimen.

Here the surface morphology of all the polymer electrolyte films before and after irradiation were observed using JEOL 840 scanning electron microscope operated at 20 kV, 10 nm scanning electron microscope (SEM) with a magnification about 500X and 2000X. The samples were gold coated with a thin layer of gold to prevent electrostatic charging using the sputter coater at 10 mA current under $10^{-2}$
torr vacuum for 3 minutes before imaging. Once the scanning is ready, the chamber is vacuumed to prevent the interaction of the beam with any extraneous particles in the atmosphere. The experiments were done at the Materials Science and Engineering department, IISc., Bangalore, India. Figure 3.14 shows the JEOL 840 Scanning electron microscope which was used to obtain different magnified SEM images of all polymer samples before and after gamma irradiation.
Figure 3.14: Experimental setup of the JEOL 840 Scanning Electron Microscope.
3.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique to obtain an infrared spectrum of emission and absorption of a solid such as metal, powder and thin film (Rajendran, S., & Shanker Babu, R., 2009). When infrared light passes through a sample of an organic compound, some of the frequencies are absorbed and some other frequencies are transmitted. The variation of infrared absorbance against frequencies gives the infrared spectrum. IR spectrum has the best feature of absorption bands of specific functional groups in specific frequency regions that can be correlated with specific stretching and bonding motions of these groups. Thus it is possible to interpret the presence or disappearance of certain functional groups. IR spectroscopy has been used to enumerate the inter- and intra-molecular interactions of the components of the polymer-salt complexes. Such interaction could induce changes in vibrational modes of the atoms or molecules in the material, which in turn changes the physical and chemical properties of the constituents of the complex.

Working of FTIR spectrometer

The operation of the FTIR is shown in Figure 3.15. The IR spectrometer consists of two mirrors which are placed at right angle to each other and oriented perpendicularly. A beam splitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors. From the beam splitter, 50% of the light is reflected towards the fixed mirror and 50% is transmitted towards the moving mirror. The reflected light from the two mirrors reaches back to the beam splitter and 50% of the original light passes into the sample. Once the infrared beam is passed through the sample, the molecules absorb the infrared radiation and are then excited to a higher energy state. Therefore, the energies associated with these vibrations are quantized within a molecule. The amount of energy absorbed at each wavelength was recorded. The frequencies which have been absorbed by the sample are determined by a detector and the signal is amplified.

In the present research work the FTIR spectra of the polymer electrolyte samples before and after irradiation were recorded using Thermo – Nicolet 6700 module as shown in figure 3.16. The FTIR experiments were carried out in the Spectroscopy / Analytical / test facility, Entrepreneurship center, SID, IISc. Bangalore. The measurements were taken over a wave number range of 400 – 4000 cm⁻¹.
Figure 3.15: Operation of the FTIR spectroscopy.

Figure 3.16: FTIR experimental set up.
3.5.4 Differential Scanning Calorimetry (DSC)

DSC is mainly applied to study phase transitions such as melting temperature ($T_m$), glass transition temperature ($T_g$), or exothermic decompositions of the sample. These transitions involve energy changes or heat capacity changes which can be detected by DSC with great sensitivity. In this technique the difference in the amount of heat required to increase the temperature of the sample and reference are measured as a function of temperature. The result of a DSC experiment is a curve of heat flux versus temperature and the exothermic reaction of the sample appears as a positive peak whereas endothermic reaction appears as a negative peak as shown in Figure 3.17. In endothermic reaction, energy absorption is in the form of heat, whereas in exothermic process, heat will be released. So, the endothermic process such as melting process will require more heat flowing into the sample to increase its temperature same as that of reference temperature. On the other hand, the heat required is lesser to raise the temperature of sample, if it undergoes an exothermic phase transition such as crystallization from matrix polymer to liquid state. Therefore, throughout the experiment the temperature of both the sample and reference are maintained nearly same. Here the peak areas of thermograms are directly related to the enthalpy changes in the sample. Therefore, the data obtained can be used in the measurements of heat capacities, heats of fusion and enthalpies of reactions (Dean, J. A. 1995; Malcolm, Stevens, P., 1999b; West, A.R., 1999).

In general, DSC analysis is designed to ensure that, the temperature of the sample holder increases linearly as a function of time. As the temperature increases the amorphous solid will become less viscous and at some point and the molecules may obtain enough freedom of motion to spontaneously arrange them into a crystalline form. This is known as crystallization temperature ($T_c$). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a positive peak in the DSC curve. As the temperature increases the sample eventually reaches its melting temperature ($T_m$). The melting process results in an endothermic process resulting in a negative peak in the DSC curve as shown in figure 3.17. $T_g$ is a vital characteristic of the amorphous behavior of a polymer during the transition from solid to liquid (or melt) state. 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. 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. It is less commonly known as second–order transition temperature because it is associated with a change in heat capacity but no latent heat is involved in this process. If the heating is continued, the polymer will be degraded and it is known as decomposition temperature $T_d$.

Hence DSC plays an important role to determine the glass transition temperature ($T_g$), crystallization temperature ($T_c$), crystalline melting point ($T_m$) and the decomposition temperature ($T_d$) can also be obtained as well. In this present research work the DSC measurements for the un-irradiated and gamma irradiated polymer samples have been taken in the temperature range of 30 $^0$C – 200 $^0$C with the help of differential scanning calorimeter Model: METTLER-TOLEDO DSC1 thermal analysis system at a heating rate of 10 $^0$C per minute. The DSC characterizations for all polymer electrolyte samples were performed at the Spectroscopy / Analytical / test facility, Entrepreneurship centre, SID, IISc. Bangalore. The experimental set up for DSC thermo grams are shown in figure 3.18.

![Figure 3.17: A schematic DSC thermogram demonstrating the appearance of several common features, which are glass transition, crystallization and melting process.](image)

**Figure 3.17:** A schematic DSC thermogram demonstrating the appearance of several common features, which are glass transition, crystallization and melting process.
Figure 3.18: Experimental set up for DSC measurements.
3.5.5 DC Electrical Conductivity Measurements

The widespread use of electrical conductivity measurements is in industrial applications that involve the measurement of electrical conductivity on materials such as metals, amorphous materials, crystals, etc. The unit of conductivity is Siemens/cm (S/cm), which is identical to the older unit of mhos/cm. In this section, method for obtaining conductivity data on polymer electrolyte is described. The conductivity of a material is measured in terms of its resistivity. Resistance is most often measured with a digital multimeter. Resistance in giga ohm and higher ranges can be measured accurately by using an electrometer, which can measure both very low current and high impedance voltage.

There are two methods to measure high resistance, one is the constant voltage method and the other one is constant current method. In the constant voltage method a known voltage is kept constant and resulting current is measured. Where as in constant current method, a constant current is applied and the voltage drop across the sample is measured. The basic configuration of the constant voltage method is shown in figure 3.19. In this method a constant voltage is applied in series connection with the sample and an electrometer. Here all voltage appears across the sample as the voltage drop across an electrometer is negligible. An electrometer is used to measure the resulting current, and resistance is calculated using the Ohm’s law. The resistivity is calculated from the geometry of the electrode and the thickness of the sample.

The temperature dependent dc conductivity of the reported polymer electrolyte samples before and after gamma irradiation were measured in the temperature range of 313–383 K using Keithley Programmable Electrometer (Model 617). The thickness of the polymer electrolytes was measured by using a micrometer screw gauge. The ionic conductivity varies with the thickness of corresponding sample therefore the measurement of thickness was repeated on the polymer electrolyte sample in order to obtain an average thickness. The disk sample (13 mm in diameter) was sandwiched between the finely polished stainless steel electrodes. Silver paste is deposited on both sides of the sample for good electrical contact.

Figure 3.20 shows the sample holder which consists of four small threaded rods with plates fixed to these rods using nuts. The sample is placed in between two electrodes, well insulated from the outer chamber. The sample along with electrode is held in between two glass plates with help of a spring-loaded arm fixed at the top of the sample holder. The change in the resistance with temperature was noted. Figures
3.21 and 3.22 shows the photographs of the dc conductivity measurement setup and a close up view of the Keithley electrometer used. The dc electrical conductivity ( $\sigma_{dc}$ ) is calculated using the formula

$$\sigma = \left( \frac{1}{R} \right) \left( \frac{t}{A} \right)$$  \hspace{1cm} (3.3)

Where ‘t’ is the thickness of the sample in mm, ‘R’ is the resistance in MΩ and ‘A’ is the area of the sample in $mm^2$.

**Figure 3.19:** Resistivity measurement method.

**Figure 3.20:** A typical sample holder. Enlarged portion illustrates the sample mounted between two electrode plates.
Figure 3.21: DC conductivity measurement setup.

Figure 3.22: Close up view of Keithley electrometer.