CHAPTER III

EXPERIMENTAL TECHNIQUES

3.1. Introduction

This chapter describes the experimental techniques used in the present investigation. This includes short description of the experimental setup, materials, procedures etc., the theory behind the techniques and various characterization studies are also explained briefly.

3.2. Properties of the materials used in this study

Poly(ethylene oxide) (PEO)

Polyethylene oxide is the most interesting base material because of its high chemical and thermal stability. PEO is a semi-crystalline polymer, possessing both amorphous and crystalline phases at room temperature. It can solvate a wide variety of salts even at very high salt concentrations. The solvation of salts occurs through the association of the metallic cations with oxygen atoms in the backbone. However, the multiphase nature of PEO is most often regarded as a major problem in real working systems, since the ionic conduction has been shown to take place mainly in the amorphous phase [1]. The properties of PEO are given below:

- **Molecular formula**: \( C_{2n}H_{4n+2}O_{n+1} \)
- **Molecular weight of the polymer used**: \( 8 \times 10^3 \)
- **Nature**: Semi crystalline
- **Glass transition temperature**: -60°C
- **Melting temperature**: 60°C
- **Structure**: ![Structure of PEO](image)
Poly(vinylidene chloride-co-acrylonitrile) (PVdC-co-AN)

PVdC-co-AN is another polymer whose utility in the field of polymer electrolyte is very less but its mechanical and thermal stability are better [2]. Moreover, it is supposed to possess inherent thermal and electrical properties of PVC/PAN [3].

Molecular formula \( : \text{(CH}_2\text{CCl}_2)_{x}[\text{CH}_2\text{CH(CN)}]_y \)

Molecular weight of the polymer used \( : 15 \times 10^4 \)

Nature \( : \text{Crystalline} \)

Glass transition temperature \( : 50^\circ C \)

Structure

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{CN} \\
\text{CH}_2 \\
\text{CCL}_2 \\
\text{CH}_2 \\
\text{CH} \\
\text{CN} \\
\end{array}
\]

Lithium salts

\( \text{Li}^+ \) is the most electropositive cation. Lithium easily gives up electrons to form \( \text{Li}^{+} \) ion which has an ionic radius of 0.6 Å. Lithium is a promising material for high energy density batteries because of its high specific capacity, light weight and high electrochemical reduction potential [4, 5]. Properties of different lithium salts used in this study are listed in Table 3.1.

Table 3.1. Properties of the lithium salts used in the present study.

<table>
<thead>
<tr>
<th>Salt</th>
<th>M.W. (gmol(^{-1}))</th>
<th>Density(gcm(^{-3}))</th>
<th>Lattice energy (kJmol(^{-1}))</th>
<th>( T_m (^\circ C) )</th>
<th>( T_g(\circ C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO(_4)</td>
<td>106.39</td>
<td>2.43</td>
<td>709</td>
<td>236</td>
<td>-24</td>
</tr>
<tr>
<td>LiBF(_4)</td>
<td>93.74</td>
<td>0.852</td>
<td>699</td>
<td>293-300</td>
<td>-30</td>
</tr>
<tr>
<td>LiCF(_3)SO(_3)</td>
<td>156.01</td>
<td>1.9</td>
<td>730</td>
<td>423</td>
<td>-43</td>
</tr>
<tr>
<td>LiN[CF(_3)SO(_2)](_2)</td>
<td>287.09</td>
<td>1334</td>
<td>&lt;700</td>
<td>234-238</td>
<td>&lt;-43</td>
</tr>
</tbody>
</table>
Plasticizers

Plasticizers are low molecular weight non-volatile substances (mostly liquids), which, when added to a polymer, improve its flexibility, processability and hence utility. The plasticizer substantially reduces the brittleness of many polymers because the addition of even small quantities markedly reduces $T_g$ of the polymer.

The plasticizers aid in the ionic transport mainly by reducing crystallinity (including amorphous region), increasing the free volume and the addition of the transit site available in the system. The effect of plasticizer on the polymer segmental, ionic mobility and conductivity depends on the specific nature of the plasticizer including viscosity, dielectric constant, polymer-plasticizer interaction, and ion-plasticizer interaction [6-8]. Properties of the various plasticizers which are used in the present investigation are given in Table 3.2.

Table 3.2. Characteristics of different plasticizers used in the present study.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>EC</th>
<th>PC</th>
<th>DMC</th>
<th>DEC</th>
<th>DBP</th>
<th>GBL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$_3$H$_4$O$_3$</td>
<td>C$_4$H$_6$O$_3$</td>
<td>CHO</td>
<td>C$<em>5$H$</em>{10}$O$_3$</td>
<td>C$<em>{16}$H$</em>{22}$O$_4$</td>
<td>C$_4$H$_6$O$_2$</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>1.3210</td>
<td>1.205</td>
<td>1.069</td>
<td>0.975</td>
<td>1.05 at 20°C</td>
<td>1.1286</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>34-37</td>
<td>-55</td>
<td>2-4</td>
<td>-43</td>
<td>-35</td>
<td>-43</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>260.7</td>
<td>240</td>
<td>90</td>
<td>126-128</td>
<td>340</td>
<td>204</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>89.6</td>
<td>64.4</td>
<td>3.087</td>
<td>2.82</td>
<td>5.8</td>
<td>39.1</td>
</tr>
<tr>
<td>Viscosity(Kg ms$^{-1}$)</td>
<td>1.85</td>
<td>2.53</td>
<td>0.664</td>
<td>0.75</td>
<td>15 at 25°C</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Barium Titanate(BaTiO$_3$)

Barium Titanate is an oxide of Barium and Titanate. It is a ferroelectric ceramic material, with piezoelectric properties. It has five phases as a solid, listing from high temperature to low temperature: hexagonal, cubic, tetragonal, orthorhombic
and rhombohedral crystal structure. All the structures exhibit the ferroelectric effect except cubic.

Molecular Formula : BaTiO$_3$

Molar mass : 233.192 g mol$^{-1}$

Density : 6.02 g cm$^{-3}$

Melting point : 1625 °C

3.3. Preparation of Polymer Blend Electrolyte

The flow chart for the preparation of electrolyte films is shown in Fig.3.1.

![Flow chart for the preparation of Polymer Blend Electrolyte](image)

Fig.3.1. Flow chart for the preparation of Polymer Blend Electrolyte.
Materials Purification

It is impossible to get a chemical substance of hundred percent pure. Every chemical substance may be having a small amount of moisture, dust and other foreign elements. Hence the chemical substance should be purified before use.

The polymer host and inorganic salt were purified by a heating process using vacuum heating arrangement LOGITECH, DTC 5050, fitted with a vacuum pump of $10^{-3}$ torr capacity made by Vacuum technique Pvt. Ltd., Bangalore. The vacuum heating arrangement used in the present study is shown in Fig. 3.2.

![Fig.3.2. Photograph of vacuum heating arrangement.](image)
Mixing

Methanol was used as the common solvent for the polymer and salt. The basic constituent polymers were dissolved in methanol separately. After their dissolution, they were mixed together in a conical flask.

Stirring

The conical flask which contains polymer-salt complex was placed on the top of the magnetic stirrer arrangement. The mixture was stirred for about 24 hours at room temperature.

Casting technique

Thus the obtained slurry was cast onto finely polished Petri dishes and the solvent was allowed to evaporate slowly at room temperature for 48 h. Finally, solvent free polymer electrolyte films were obtained. Chemical storage, film casting and cell assemblies were performed under vacuum.

3.4. Characterization techniques

Material properties like structure, surface morphology, thermal, electrical, mechanical, optical etc. should be studied in detail in order to understand the Chemistry and Physics of materials. These experimental characterization techniques also provide useful guideline on the suitability of the material for possible device applications. Among the various techniques available for characterizing the materials, some appropriate technique for charactering the solid ionic/ fast ionic conductors are

- X-ray Diffraction
- FTIR spectral studies
- ac Impedance spectroscopy
- Thermal analysis (TG/DTA)
- DSC studies
- SEM analysis
- AFM analysis
- Photoluminescence studies
- Cyclic voltammetric studies
- Linear sweep voltammetric studies

3.4.1. X-ray diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that has been used for the fingerprint characterization of natural and manufactured materials and the determination of the structure. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound using XRD.

**Basic Theory**

- When X-rays interact with a single particle, it scatters the incident beam uniformly in all directions.
- When X-rays interact with a solid material, the scattered beams can add together in a few directions and reinforce each other to yield diffraction.

The regularity of the material is responsible for the diffraction of the beams. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distributions of atoms. Measuring the diffraction pattern therefore allows to deduce the distribution of atoms in a material.

From the diffraction patterns one can find the crystal structure of an unknown material. In addition, one can also determine factors such as the orientation of single
crystals, or measure the size and shape of crystalline regions. Based on the above principle, X-ray diffraction studies can be carried out in two different manner i.e.

**Single crystal X-ray diffraction**

Single crystal X-ray diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles and details of site-ordering.

**Powder X-ray diffraction**

Powder XRD is perhaps the most widely used X-ray diffraction technique for characterizing materials. The technique is useful for the immediate determination of the nature of the sample, phase identification, quantitative analysis of the mixture of phases, particle size analysis, characterization of physical imperfections etc.

**XRD for polymers**

All XRD studies were carried out at room temperature to know the structural details of the polymer complex. However, the exact structure cannot be determined from XRD analysis due to the presence of multiple phases. The various phases present in polymer complexes include crystalline phase, amorphous phase and combinations of the above phases.

In the case of polymer blends the X-ray diffraction provides valuable information. In polymer blends, phase separation may occur if one or both of the phases crystallize which may be indicated by X-ray diffraction. For example, poly ethylene and poly propylene do not co-crystallize and diffraction peaks from both poly ethylene and poly propylene crystals can be expected from a blend if phase separation occurs, as happens in most compositions.

If a polymer is polymorphic, X-ray diffraction may be used to show which type of polymorphism is present. This may relate to the crystallization, including
processing conditions in fabricated polymer or to a post-crystallization modification. For example, orthorhombic poly ethylene may be transformed to the monoclinic modification by determination and this may be detected by X-ray diffraction.

In the present work, X-ray diffraction studies were carried out for the prepared polymer electrolytes to know the information about the material such as crystalline or amorphous nature, complex formation etc. The photograph of the X-ray diffractometer used in the present study is shown in Fig.3.3.

Fig.3.3. PANalytical ‘X’Pert PRO Powder X-ray Diffractometer.
3.4.2. FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule. The infrared region constitutes three parts viz. near infrared, middle infrared and far infrared. The near infrared corresponds to a wave number of 13, 300-4000 cm\(^{-1}\); the middle infrared is between 4000-200 cm\(^{-1}\). The far infrared lies between 200-10 cm\(^{-1}\). Spectroscopy in the region 4000-200 cm\(^{-1}\) is very important for organic compound analysis. The region 4000-600 cm\(^{-1}\) is called a functional group region and that between 1600-200 cm\(^{-1}\) is called the fingerprint region. The patterns of absorption in the fingerprint region are unique to any particular compound as a person’s fingerprint.

FTIR for polymers

IR spectroscopy is a versatile and widely used technique for the detection of functional groups in pure compounds and mixtures and for compound comparison. Utilization of laser light sources has greatly decreased experimental difficulties in this technique and the method has now become one of the standard tools for polymer analysis. The great majority of the functional groups present in polymers give characteristic bands in the IR spectral region thus facilitating their identification.

IR has been used to characterize the chain structures of polymers and has led the way in interpreting the reaction of multifunctional monomers including rearrangements and isomerizations. Conformation of polymer chains in the polymer-salt complexes and also the position of metal-ions in the polymer chain can also be identified using IR spectroscopy.

Thus the value of IR spectroscopy is considerably enhanced by its ability to provide detailed information on the microstructure of polymers [9, 10]. This includes the way in which successive monomer units add onto the existing chain, both in the
case of homo and co-polymers, the configurational and conformational structure of the chain-end groups. This type of information is becoming increasingly important in gaining a fuller understanding of the properties of polymers and in improving their long-term stability in commercial usage.

The photograph of Fourier Transform Infrared Spectrophotometer which is used in the present study is shown in Fig.3.4.

![FTIR spectrophotometer](image)

**Fig.3.4.** Photograph of FTIR spectrophotometer.

FTIR spectrometers offer speed and sensitivity impossible to achieve with earlier wavelength-dispersive instruments. This capability allows rapid analysis of micro-samples down to the nanogram level in some cases, making the FTIR unmatched as a problem-solving tool in organic analysis.
3.4.3. a.c Impedance Analysis

Ac impedance spectroscopy is a strategic analytical method employed in basic and applied electrochemistry as well as in the field of materials science. The purpose is to explore the electrical behavior of materials and their interfaces with electronically conducting electrodes as a function of an alternating current (ac) with a variable frequency. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid materials: ionic, semiconducting, electronic and even insulators.

The reason for using AC measurement is due to the effect of the interfacial impedance of the grain boundary of the electrode. As an interface, physical properties, particularly electrical charge precipitously and polarization reduces overall electrical conductivity of a system. Each interface will polarize in its own way when the system is subjected to an applied potential difference. The rate at which a polarized region will change when the applied voltage is reversed is the characteristic of the type of interface.

Conductivity is a very important property for electrolytes. The conductivity of an electrolyte is measured using a test cell, in which the electrolyte is sandwiched between a pair of contacting electrodes. In such a cell system, the electrode/electrolyte interfacial impedance, such as double layer capacitance and charge-transfer resistance, must be taken into consideration in addition to the bulk electrolyte impedance. The electrochemical behaviour of electrode and/or electrolyte materials is usually made with cells having two identical electrodes applied to the faces of the sample in the form of a circular cylinder or rectangular parallelepiped. Thus impedance behaviour is dependent on frequency and is therefore obtained from a.c measurement over a wide range of frequencies.
In general, in test cells involving polymeric electrolytes it is often possible to ignore the inductive components and to represent the data in the form of a plot of real (X-axis) against imaginary (Y-axis), where the real contributions arise from the resistance and the imaginary terms from the capacitances and its corresponding plot with equivalent circuit is shown in Fig. 3.5. It is explained that the plot consisting of a semi-circle followed by a spike in terms of the simple equivalent circuit and the electrolyte resistance can be obtained by extrapolating the spike to the point of intersection with the x-axis.

**Fig. 3.5.** Schematic representation of complex impedance plot.
**Electrical conductivity set up**

The essential parts of the conductivity cell arrangements are

- A cell to hold the thin film
- A heating furnace
- A thermocouple
- A temperature controller/ programmer.

**Cell design**

In the present study, the bulk conductivity as a function of composition and temperature is evaluated from complex impedance plots. The experimental arrangement used for the conductivity measurement is shown in Fig. 3.6.

![Conductivity cell diagram for polymer electrolyte thin films.](image)

**Fig. 3.6.** Conductivity cell diagram for polymer electrolyte thin films.
The cell consists of two stainless steel rods of 1 cm diameter and 30 cm length was gas-welded to the two top edges of the inner hole of the rigid block. Of these, one rod was used as a current carrying lead. A rod of 30 cm length and 1 cm diameter was used as a second electrode. The second electrode was held through a spring load arrangement so as to keep the thin film of polymer electrolyte under an optimum stress condition and to ensure good electrical contact between the sample film and the electrodes. A flat portion of 20 mm diameter has been welded at one end of the rods, which serves as blocking electrodes for ions. The upper portion of the current carrying electrodes is held in place with a circular Teflon lid. A small hole is made on one side of the stainless steel block at the area exactly where the film would be placed for measurement. A chromel-alumel thermocouple was used for measurement. Care was taken to place the tip of the thermocouple close to the film to measure as accurately as possible the temperature of the sample environment. The thermocouple was connected to temperature controller-cum-programmer for controlling the sample temperature within ±1 ºC. During the conductivity measurement the sample was kept in a vacuum chamber (using continuous pumping) to avoid contact of the polymer membrane with the atmosphere. Conductivity measurements were carried out on the thin films using computer controlled micro Autolab Potentiostat/Galvanostat type III model (Fig.3.7). Measurements were taken between room temperature and 80ºC (303–353K).
3.4.4. TG/DTA Analysis

Thermogravimetry is a technique used to measure the variation in mass of a sample when it undergoes temperature scanning in a controlled atmosphere. This variation in mass can be either a loss of mass (vapour emission) or a gain of mass (gas fixation).

Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize the materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. TG technique is very popular in polymer research, in particular to study the thermal stability of polymeric systems.
Differential thermal analysis is a technique used to measure the difference in temperature between a sample and a reference (a thermally inert material) as a function of the time or the temperature, when they undergo temperature scanning in a controlled atmosphere. Any transition, which the sample undergoes, will result in liberation or absorption of energy by the sample with the corresponding deviation of its temperature from that of the reference. This differential temperature ($\Delta T$) versus the programmed temperature ($T$) at which the whole system is being changed tells the analyst the temperature of transition and whether the transition is exothermic or endothermic. The DTA method enables any transformation to be detected for all the categories of materials.

For DTA measurements, the sample is placed in first identical and symmetrical chamber, which is located in furnace environment and the reference sample such as $\alpha - \text{Al}_2\text{O}_3$ is placed in the other chamber. The furnace and sample block temperature are then increased at a linear rate, most often 5 to $12^\circ\text{C min}^{-1}$, either by increasing the voltage through the heater element by a motor – driven variable transformer or by a thermocouple actuated feedback type of controller. The difference in temperature between the sample and reference thermocouples, connected in series opposition, is continuously measured. After amplification by a high gain, low noise, dc-amplifier for the micro volt-level signals, the difference signal is recorded on the Y-axis of a millivolt recorder. The temperature of the furnace is measured by a separate thermocouple, which is connected to the X-axis of the recorder, frequently through a reference junction or the room temperature compensator. Because the thermocouple is placed directly in the sample or attached to the sample container, the DTA technique provides the highest thermometric accuracy of all the thermal methods.
Thermogravimetry (TG) provides the analyst with quantitative measurements of any weight change associated with a transition. For example, the TG can directly record the loss of weight with time or temperature due to dehydration or decomposition. Thermogravimetric curves are characteristics of a given compound or systems because of the unique sequence of physicochemical reactions, which occur over definite temperature ranges and at rates that are a function of the molecular structure. A thermal behaviour of the thin films was analyzed using Perkin Elmer, Pyris Diamond thermal analyzer at the heating rate of 10ºC min\(^{-1}\) from room temperature to 700ºC. The photograph of thermal analyzer used in this study is shown in Fig.3.8.

![Photograph of the Thermal analyser.](image)

**Fig.3.8.** Photograph of the Thermal analyser.

### 3.4.5. DSC analysis

The DSC technique is an ever-widening field of application, including the polymer and pharmaceutical industries, food science and forensic studies. Differential scanning calorimetry is a technique used to determine the variation in the heat flow given out or taken in by a sample when it undergoes temperature scanning in a
controlled atmosphere. With heating or cooling any transformation taking place in a material is accompanied by an exchange of heat; DSC enables the temperature of this transformation to be determined and the heat from it to be quantified.

Polymers have a higher heat capacity above the glass transition temperature than they do below it. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymer’s glass transition temperature. DSC defines the glass transition as change in the heat capacity as the polymer matrix goes from the glassy state to the rubbery state. Since the mechanical behavior of polymers changes markedly at the glass transition temperature, it is an important characteristic of every polymer. In the DSC experiment, \( T_g \) is manifested by a drastic change in the baseline, indicating a change in the heat capacity of the polymer. This is a second order endothermic transition (requires heat to go through the transition). So in the DSC, the transition appears as a step transition and not peak such as might be seen with a melting transition. A typical DSC plot of a polymer is shown in Fig.3.9.

It is important to recognize that not all polymers will show \( T_c \) and \( T_m \). \( T_c \) and \( T_m \) will only show up for polymers that can form crystals. Completely amorphous polymers exhibit only \( T_g \). However, polymers with both crystalline and amorphous domains will show all the features as shown above. In addition, it can also be used to measure the percentage of crystallinity which is a measure of how much of a polymer is crystalline and how much is amorphous.
3.4.6. **Scanning electron microscope (SEM)**

The analysis of micro structure of the polymer electrolyte plays an important role in determining the structure, spatial arrangements of atoms or molecules in the electrolytes. Also, it provides particle size, shape, orientation and phase identification of an atom or molecules. The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the micro structural characteristics of solid objects. The scanning electron microscope is a microscope that uses electrons to form an image. The combination of higher magnification, larger depth of field, which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample, greater resolution and compositional and crystallographic information, makes the SEM one of the most heavily used instruments in research areas and industries.

A beam of electrons is produced at the top of the microscope by an electron gun. The SEM column and sample chamber are at moderate vacuum to allow the electrons to travel freely from the electron beam source to the sample and then to the detectors. The beam travels through electromagnetic fields and lenses, which focus...
down the beam towards the sample. A finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons and characteristic X-rays.

The emitted electrons are detected for each position in the scanned area by an electron detector which converts them into a signal that is sent to a screen. This produces the final image.

The SEM can be operated in many different modes and the choice of operating mode depends on the properties of the sample and on what features one wants to investigate. The most commonly used mode is the secondary electron mode. Secondary electron imaging shows the topography of the surface features. Scintillation type detectors are used for secondary electron imaging. This detector is charged with a positive voltage to attract electrons towards the detector. Materials are viewed at useful magnifications up to 100KX without damaging the sample.

High resolution imaging is done by the chamber at high vacuum, typically from $10^{-5}$ to $10^{-7}$ torr. Imaging of non conductive, volatile, and vacuum-sensitive samples can be performed at high pressures. Scanning electron microscopy can be applied to the study of (1) the morphology of polymer blends, co-polymers (2) polymer networks (3) rough surfaces (4) fractured surfaces (5) foamed polymers etc. In the present study JEOL, JSM-840A scanning electron microscope is used to depict the sample surface morphology. The photograph of SEM is shown in Fig. 3.10.
3.4.7. Atomic force microscopy

The polymeric membrane has three important structural level, (i) the molecular, which is equivalent to the chemical nature of the polymer, is characterized by polar, steric and ionic factors, and is also responsible for the membrane’s microcrystalline nature; (ii) the microcrystalline, which affects both the transport and mechanical properties of the membrane; and (iii) the colloidal, which is concerned with the aggregation of macromolecules and governs the statistics of pores. It is desirable to develop new characterization methods at each level to achieve a more rigorous understanding of the polymeric structure in the membrane.

Different approaches can be used to characterize the membranes, and there are various well-established methods for such characterization. There are also newly developed methods, especially for surface morphology. Standard methods for the investigation of membranes are scanning electron microscopy (SEM) [11], scanning force microscopy [12], and atomic force microscopy (AFM) [13]. Among these, AFM allows the surface study of non-conducting materials down to the scale of nanometers.

Fig.3.10. Photograph of Scanning electron microscope.
**AFM instrumentation**

A more recent microscopic technique, termed atomic force microscopy (AFM), has become a popular method for characterizing specific features of polymer blend morphology. AFM has been shown to have the ability to identify surface phase separation mechanisms of polymer blends. AFM is also referred to as scanning force microscopy (SFM) or scanning probe microscopy (SPM).

Atomic force microscopy can be described as high-resolution profiling of surfaces with a sharp probe. In general, the sharper the probe, the higher is the resolution of the image. In an AFM, a constant force is maintained between the probe and sample while the probe is scanned across the surface. By monitoring the motion of the probe as it is scanned across the surface, a three dimensional image of the surface is constructed. The contact force is maintained by measuring the force with the “light lever” sensor and using a feedback control, electronic circuit to control the position of the Z piezoelectric ceramic. The motion of the probe over the surface is generated by piezoelectric ceramics that move the probe and the force sensor across the surface in the X and Y directions. For the present study, AFM (A100SGS) model AFM instrument is used to analyze the surface of the membrane. The photograph of AFM instrumentation is shown in Fig.3.11.
3.4.8. Photoluminescence Spectrophotometer

Photoluminescence (PL) spectroscopy in the band edge emission region is one of the versatile techniques to study the lattice defects in thin film samples. Usually, higher energy radiation such as UV is used to irradiate the sample which gives light in the lower energy region.

Luminescence is the emission of light from a material due to the transition from an excited electronic state to a state of lower energy. PL is a type of luminescence where the excited electronic state is created by the absorption of a photon or photons from incident radiation. Electromagnetic radiation from an ultraviolet-visible source passes through a wavelength selector and through the cell as in a spectrophotometer. Unlike the measurement of absorption in a spectrophotometer, however, a portion of the emitted radiation that exists from the cell is measured. Because the luminescent radiation is emitted in broadband that are centered at different wavelengths, a second wavelength selector is required on the path of the emitted radiation between the cell and the detector. The emitted radiation is not usually measured in-line with the exciting radiation, because of possible spectral
interference from the exciting radiation. PL signal has been measured in many angles relative to the incident radiation. The most common practice is to measure the emitted radiation at 90° from the path of exciting radiation and at the center of the cell. The signal from the detector is amplified, if required and routed to a readout device. High pressure Xenon lamps emit a continuum of radiation that is useful throughout the ultraviolet-visible and into the near-infrared spectral regions. In order to emit constant intensity radiation at a particular wavelength, a lamp requires a stable power supply. Nevertheless, lasers have proved to be useful radiative sources. In addition, spectrophotometers are required, whenever it is necessary to scan the wavelength of either exciting radiation or the luminescent radiation. Scanning instruments must be capable of recording both the excitation and emission spectrum. In the present work, the intensity of the emission spectrum corresponding to the change in local viscosity of the medium is identified.

Varian Cary Eclipse Photoluminescence spectrophotometer (Fig.3.12) employing 15W Xe flash lamp was used for the photoluminescence studies of electrolyte films.

![Fig.3.12. Photograph of Varian Cary Eclipse Photoluminescence spectrophotometer.](image-url)
3.4.9. Cyclic voltammetry

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired. The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution.

Experimental method

![Typical diagram of a cyclic voltammogram.](image)

The typical diagram of a cyclic voltammogram is shown in Fig.3.13. The rate of voltage change over time during each of these phases is known as the experiment's scan rate (V/s). The potential is applied between the working electrode and the reference electrode while the current is measured between the working electrode and the counter electrode. These data are plotted as current ($i$) vs. applied potential ($E$, often referred to as just 'potential'). During the initial forward scan an increasingly
reducing potential is applied; thus the cathodic current will, at least initially, increase over this time period assuming that there are reducible analytes in the system. At some point after the reduction potential of the analyte is reached, the cathodic current will decrease as the concentration of reducible analyte is depleted. If the redox couple is reversible then during the reverse scan the reduced analyte will start to be re-oxidized, giving rise to a current of reverse polarity (anodic current) to before. The more reversible redox couple is, the more similar the oxidation peak will be in shape to the reduction peak. Hence, CV data can provide information about redox potentials and electrochemical reaction rates.

### 3.4.10. Linear sweep voltammetric studies

Linear sweep voltammetry (LSV) is a voltammetric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced. The region between the oxidation peak and reduction peak currents is assumed to be the electrochemical stability window of the polymer electrolyte. In the present work, we have applied the sweep potential from cathodic voltage of -4 V and anodic voltage of +4 V. A computer controlled micro Autolab type III Potentiostat/Galvanostat was used to study both the CV and LSV studies (Fig.3.7).
References


