Chapter II

Experimental
2.1 Methods of Polymer Film Preparation

Various Physical and chemical methods are used to prepare polymer thin films. Some excellent literature [1-4] is available on the preparation of good quality polymer films. Some of the commonly used methods are discussed below:

(a) Hot pressing method

In this technique, the polymer powder is placed between two ferrotype photographic plates and hot-pressed at a temperature 10-15°C above the crystalline melting point under a pressure of 10 to 20 tons/ft. The films are then removed from the press and immediately put in ice water to prevent any crystallization. If necessary, the film is stretched to obtain necessary thickness. This method has also been used to prepare solid polymer electrolyte films [5].

(b) Film blowing

Biaxial stretching by the application of a pressure difference across the film at a high temperature gives rise to thin films. This technique consists of placing the polymer film under a hold down ring that secures the film over a circular opening in the Teflon disk. The entire assembly is placed in vacuum over which heating is allowed under an inert atmosphere or vacuum. Some polymer films were successfully blown to a thickness of 10 to 30 µm. The blowing process is very difficult to control and should be done at a high temperature i.e., near the crystalline melting point.

(c) Gaseous discharge

Thin films of polymers can be obtained when a gas discharge is maintained in the vapour of a monomer. Since the pressure maintained is of the order of 1mm Hg, the discharge is a cold one and no hot cathode emission is necessary. Utilizing a
longitudinal magnetic field to compress the glow discharge in a tube has minimized the problems associated with high gas pressures and substrate heating.

(d) Photolytic process

This method is best suited for thin film formation of dielectric materials. The films are obtained when the surface is irradiated with UV light in the presence of monomer vapour. The films obtained from this method are quite stable and the reliability is also excellent down to 50Å.

(e) Polymerization of monomer

This process probably results in loss of hydrogen by dissociation or breaking up of the carbon chain in a hydrocarbon. This can be done by using high temperature electron bombardment or exposure to ionization radiation such as ultraviolet light. With this technique one can prepare coherent, pinhole free polymer films which are strongly adherent to substrates.

Three different methods of preparation have been in practice based on the polymerization of monomer vapour using glow discharge, electron bombardment and UV radiation. These techniques have attracted, by far, the greatest interest from research workers and from industry. These have been excellently reviewed by Mearns [6].

In glow discharge method, the polymer films are formed on parallel plate electrodes or on substrates in contact with these electrodes when an r.f. discharge is maintained in a low pressure atmosphere of organic vapour. Films have been produced under pressures varying from 0.1 to 10 torr. Depending on the pressure of the monomer vapour, the density of the discharge currents and the time of discharge, films of required thickness are obtained.
In electron beam polymerization, the electron 'gun' and the substrate onto which the film is to be coated are located inside a vacuum chamber which is evacuated to less than $10^{-7}$ torr. A vessel containing monomer vapour at the required vapour pressure is also placed in the vacuum chamber. Monomer pressures in the range of $10^3-10^5$ torr are used. Typical range of electron beam energies used is 0.7 mA/cm$^2$ – 7.5 mA/cm$^2$ at accelerating voltages of 400-2000V [7].

(f) Pyrolysis

It is the thermal decomposition of a compound giving rise to a stable residue and the material is pyrolysed in vacuum at high temperatures. This process spontaneously polymerizes the monomer and yields a deposit onto a substrate maintained at temperature below 30°C. A wide range of substituted poly-p-xyles have been successfully pyrolysed [8, 9]. High molecular weight polymers formed by pyrolysis method, exhibit better electrical, mechanical and optical properties compared to those prepared by thermal evaporation.

(g) Thermal evaporation

In this method, the material is thermally evaporated under extremely clean conditions. The material to be deposited is heated to a very high temperature in high vacuum and the vapour is allowed to condense on a substrate placed above the source. Thermal evaporation is reported to form a wax-like deposit on the substrate together with gaseous fractions and solid residue [10, 11]. Evaporated polymer films are contaminated due to the vigorous boiling action of the molten polymer and rapid evolution of break-down products. However, uncontaminated films can be obtained by choosing a low evaporation temperature and thus a slow rate of deposition [12, 13] and by specially designed thermal evaporation methods like pepper pot [13].
combination of internal baffles and flash evaporation [14]. But the films formed using thermal evaporation was found to suffer from chemical degradation [13,15,16].

(b) Laser evaporation

In this technique, the material is heated by the enormous power of a laser source. The evaporation generally takes place from the surface of the material only. Very thin films can be obtained, as the amount of energy released in each burst is very large. Crystalline polymers evaporated during the laser evaporation retain their crystalline structure with excellent electrical properties [17].

(i) Sputtering

The ejection of atoms from the surface of a material by bombardment with energetic particles is called "sputtering". The ejected or sputtered atoms can be condensed on a substrate to form a thin film. The main advantage of this technique is that the rate of decomposition remains constant. Various sputtering systems such as "glow discharge" and "r.f. sputtering" are based on the fact that free electrons ejected from the evaporant can be accelerated in an electric field to cause further ionization of the residual gas. Such ionization will result in further bombardment on the surface of the target and self sustain the reaction. Some other systems are based on increasing the electron path lengths so that the self-sustained system can work at a relatively low pressure. Such systems are triode and r.f. sputtering. Sputtering is carried out in partial vacuum and some materials are incompatible with good vacuum conditions. Organic solids are generally unable to withstand this process and completely degrade. Polymer films possessing properties comparable with those of bulk polymers have been successfully prepared using r.f. sputtering [18, 19].
(i) Solution – casting method

This is the most commonly used method for the preparation of polymer electrolyte films and has been used by many workers [20-25]. The preparation of polymer films is generally done by a simple casting technique. The polymer is dissolved in suitable solvents (e.g. acetonitrile, methanol, ethanol, triple distilled water, etc.) and the solution is stirred for several hours to achieve complete mixing. Then the solution is cast onto polypropylene dishes and slowly evaporated to obtain a thin film [26, 27]. Polymer films with required thickness can be obtained from this method.

2.2 Synthesis of NaBiF₄, NaFeF₄ and NaLaF₄ Compounds

Sodium Bismuth tetra fluoride (NaBiF₄) salt was prepared by solid-state diffusion method. In this method Bismuth nitrate reacts with Sodium fluoride, forming Sodium bismuth tetra fluoride and sodium nitrate. When dilute nitric acid was passed slowly through this mixture, NO₂ gas is evolved. Finally Sodium Bismuth tetra fluoride precipitate was separated by filterisation and allowed to recrystallize.

\[ \text{Bi(NO}_3\text{)}_3.5\text{H}_2\text{O} + 4 \text{NaF} \rightarrow \text{NaBiF}_4 + 3 \text{NaNO}_3 + 5\text{H}_2\text{O} \]

Similarly Sodium Iron tetra fluoride (NaFeF₄) and Sodium Lanthanum tetra fluoride (NaLaF₄) were also prepared by solid-state diffusion method by the following reactions.

\[ \text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O} + 4 \text{NaF} \rightarrow \text{NaFeF}_4 + 3 \text{NaNO}_3 + 9\text{H}_2\text{O} \]

\[ \text{La(NO}_3\text{)}_3.6\text{H}_2\text{O} + 4 \text{NaF} \rightarrow \text{NaLaF}_4 + 3 \text{NaNO}_3 + 6\text{H}_2\text{O} \]

To confirm the formation of NaBiF₄, NaFeF₄ and NaLaF₄ compounds, X-ray diffraction patterns have been recorded using the SEIFERT X-ray diffractometer.
Chapter-II
Experimental

2.3 Preparation of Technique used in the Present Studies

Films (thickness ~ 150 μm) of polyethylene oxide (PEO) and complexed with Sodium bismuth tetra fluoride (NaBiF₄), Sodium Ferric tetra fluoride (NaFeF₄) and Sodium Lanthanum tetra fluoride (NaLaF₄), were prepared with weight ratios (90:10), (80:20) and (70:30) by solution cast technique using 2-propanol as a solvent. In this method desired amount of PEO is dissolved in a purified 2-propanol using magnetic stirring to form a first solution. A second solution was prepared by dispersing an appropriate amount of NaBiF₄ in a purified 2-propanol. The two solutions were then mixed and vigorously stirred for 10-12 hours. Then the mixed solution was cast onto Polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was dried thoroughly to remove all traces of solvent. The dried composite polymer electrolyte (PEO+NaBiF₄) films were peeled off from the polypropylene dishes and stored inside the dry vacuum box. Similarly (PEO+NaFeF₄) and (PEO+NaLaF₄) films were also prepared. The schematic illustration of the preparation procedure of polymer electrolyte film is shown in Fig. 2.1.

2.4 X-ray diffraction

Since the discovery in 1912 by von Laue, X-ray diffraction has provided a wealth of important information to science and industry. X-ray diffraction studies have proved to be of immense importance in understanding the physical properties of metals, polymeric materials and other solids. The application of X-ray diffraction methods to chemical analysis is primarily in the identification of compounds present in their diffraction patterns, and in the determination of relative concentrations by the
Fig. 2.1 Schematic illustration of the preparation procedure of polymer electrolyte films by solution casting method.
intensities of pattern lines. The arrangement and spacing of atoms in crystalline materials have been directly deduced from diffraction studies.

In a crystalline powder, the tiny crystals are oriented at random. If an X-ray beam strikes such a powder, many planes will be so oriented that Bragg's law is simultaneously satisfied and an X-ray diffraction pattern is obtained. To be certain that all possible planes are exposed to the X-ray beam the specimen is usually rotated by an angle $\theta$ on its own axis during exposure. Most of the X-ray beam passes directly through the sample and the diffracted beam is collected by a detector (scintillation counter), which is rotated by $2\theta$, the output of the detector is processed and then fed to an automatic recorder. The result is a chart, which gives a record of counts per second (proportional to diffracted beam intensity) versus diffraction angle $2\theta$.

In the present study, X-ray diffraction spectra were recorded at room temperature in the range of 5-70° on a SEIFERT X-ray diffractometer. Mo Kα radiation was used along with Zr filter as monochromatic radiation. The block diagram of the Seifert X-ray diffractometer used in the present study is shown in Fig. 2.2.

2.5 Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy has been widely used for the identification of functional groups in organic compounds because of the fact that their spectra are generally complex and provide numerous maxima and minima that can be used for comparison. In fact, the infrared absorption spectrum of an organic compound represents one of its truly physical properties.
From application and instrumentation point of view, the infrared region has been subdivided into three parts.

(i) Near infrared region $14290 - 4000 \text{ cm}^{-1} (0.7 - 2.5 \mu m)$;

(ii) Middle infrared region $4000 - 666 \text{ cm}^{-1} (2.5 - 15 \mu m)$; and

(iii) Far infrared region $700 - 200 \text{ cm}^{-1} (14.3 - 50 \mu m)$.

The schematic diagram of a general infrared instrument is given in Fig. 2.3.

In the present investigation, infrared spectra of polymer electrolyte films were recorded on Perkin-Elmer FTIR spectrophotometer [Model 1605] in the range of $250-4500 \text{ cm}^{-1}$. The optical layout of the spectrophotometer used in the present investigation is shown in Fig. 2.4.

2.6 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) thermo grams of (PEO) and NaBiF$_4$, NaFeF$_4$ and NaLaF$_4$ complexed (PEO) polymer electrolytes were recorded using NETZSCH DSC 204 in the range $40^\circ\text{C}-80^\circ\text{C}$.

2.7 Measurement of D.C. conductivity

The block diagram of the conductivity set up is shown in Fig. 2.5. The specimen was mounted in an experimental jig, which was placed in a non-conducting vessel evacuated to a vacuum of $10^{-3}$ torr. All the connections were perfectly insulated using amphenols throughout the measurements.

Fig. 2.6 shows the sample holder used for conductivity measurements. It consists of two electrodes A and B (blocks of nickel) the lower one being a circular one of diameter $2 \text{ cm}$ and the upper one being a square of $1.2 \text{ cm}^2$ surface area. The lower circular electrode is supported on a single centrally placed ‘vitreosil’ cylinder of $2 \text{ cm}$ length. This vitreosil is a good insulator even at high temperatures. The lower
Schematic diagram of a general infrared instrument.

**Fig. 2.3** Schematic diagram of a general infrared spectrometer.

Optical layout of PERKIN ELMER FTIR - Spectrophotometer

**Fig. 2.4** Optical layout of PERKIN ELMER FTIR - Spectrophotometer
Fig. 2.5  Block diagram of experimental setup used for conductivity measurements.
Fig. 2.6 Ionic conductivity apparatus along with the conductivity cell.
end of the vitreous cylinder is fixed to the steel frame F. The upper electrode B is also fixed to the vitreous cylinder. The other end of the vitreous cylinder is inserted in a socket, which is the end point of a steel rod R of about 8 cm length. This rod is arranged in such a way that it can move up and down through a groove made in a steel frame. The steel frame consists of a circular steel plate supporting the lower electrode and another circular plate at the top as shown in figure. The two plates are held in their position by three steel rods. At the end of steel rod R a spring is provided so that a well pressed contact is given to the sample C. This spring is just outside the furnace and retains the spring action even though it acquires certain temperature. Flexible copper-constantan wires are brazed into two nickel electrodes and are brought out of the furnace. The two leads are fixed to amphenol connectors J1 and J2. The two wires are shielded by fine bored alumina tubes, which prevent the wires from touching the steel frame. S is a thin copper foil, which is earthed and acts as a shield. The furnace is a resistance type furnace and consists of an alumina muffle of 30 cm length and 10 cm diameter. The heating element is a super kanthal ribbon, wound on the muffle. The windings are designed such that their number is maximum at the place where the sample is situated. A temperature controller can control the temperature of the furnace. The outer surface of the furnace is covered with a metallic sheet, which, in turn, is earthed in order to avoid pick up currents.

The stainless steel frame F hangs onto the muffle of the furnace over a steel rod support. The points, which are connected to the electrometer, are fixed to a Perspex box as shown in the figure. The battery is arranged in a separate box that is thermally insulated. The temperature of the sample is measured by means of a copper-constantan thermocouple arranged very close to the sample and the output of
the thermocouple is fed to the digital temperature controller. The currents are measured by means of the Keithley electrometer (Model 604). The polarizing effects during the measurements of DC conductivity were minimized by applying smaller voltages for a short interval of time and by short-circuiting after every reading [28].

2.8 Measurement of transference numbers

The nature of the conductivity in a material is expressed by the transference number, which denotes the fraction of current carried by anions and cations (or) electrons in the material in terms of the total conductivity. To measure the ionic and electronic transference numbers, Wagner’s polarization technique [29] has been employed. The Wagner’s polarization method is schematically shown in Fig. 2.7 In this method, the polymer electrolyte under investigation is sandwiched between two electrodes; one is the blocking electrode and the other the non-blocking electrode. It is then polarized using a constant DC voltage. The currents observed are monitored as a function of time using Keithley electrometer (Model-604).

2.9 Dielectric properties

Dielectric and Impedance measurements were made using Hioki 3532-50 LCR Hi-Tester in the frequency range 100 Hz- 1MHz and temperature range 300-370 K. From the impedance data frequency dependent conductivity, activation energy, relaxation time values were determined.

2.10 Optical absorption

The optical absorption spectra of undoped and NaBiF₄, NaFeF₄ and NaLaF₄ doped (PEO) polymer films were recorded at room temperature in the wavelength range 200-600 nm using JASCO spectrophotometer, model V-570. From this data
Fig. 2.7 Experimental arrangement of Wagner's polarization method of determining transference numbers.
the optical constants such as band edge, optical band gap (both direct and indirect) were determined.

(PEO+NaBiF₄) films were peeled off from the polypropylene dishes and stored inside the dry vacuum box. Similarly (PEO+NaFeF₄), (PEO+NaLaF₄) and (PEO+NaLaF₄+DMF) films were also prepared.

2.11 Fabrication of polymer batteries

Polymer batteries were prepared using (PEO+NaBiF₄), (PEO+NaFeF₄), (PEO+NaLaF₄) and (PEO+NaLaF₄+DMF) solid polymer electrolytes in the configuration “anode/polymer electrolyte/cathode”. For the battery fabrication, Sodium metal was used as anode material and for cathode, several materials such as iodine (I₂), iodine + carbon (I₂+C) and (iodine carbon + electrolyte) (I₂ + C + electrolyte) were used in the form of thin pellets. The complete geometrical structure of the cell and the circuit diagram for studying discharge characteristics are shown in figs. 2.8 and 2.9 respectively. Various cell parameters like open circuit voltage (OCV), short circuit current (SCC), power density and energy density of the device were evaluated and reported.

2.12 Thickness of the film

A number of methods are available for the measurement of thickness of a thin film. Among them a few methods like mechanical stylus method, gravimetric method and capacitance method are suitable for the measurement of thickness of the polymer thin films. In the present investigations, mechanical stylus method was used to determine the thickness of the films.

In mechanical stylus method, German made ‘Perthometer’ was used to determine the thickness of the films and it was found to be approximately 150 μm.
Fig. 2.8 Fabrication diagram of an electrochemical cell

Fig. 2.9 Discharge characteristic circuit diagram of an electrochemical cell.
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