DEVELOPMENT AND CHARACTERIZATION OF A SOLID-ION CONDUCTING POLYMER ELECTROLYTE

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Dedicated

to

My Affectionate Parents,

Loving Wife, Adorable Son

and

"The Noble cause of

Education"

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DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

SATYA KRISHNA NIPPANI

Date: May, 2014

Place: Dehradun

THESSIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **"Development & Characterization of a Solid-Ion Conducting Polymer Electrolyte"** submitted by **SATYA KRISHNA NIPPANI** to **University of Petroleum & Energy Studies** for the award of the degree of Doctor of Philosophy is a bona fide record of the research work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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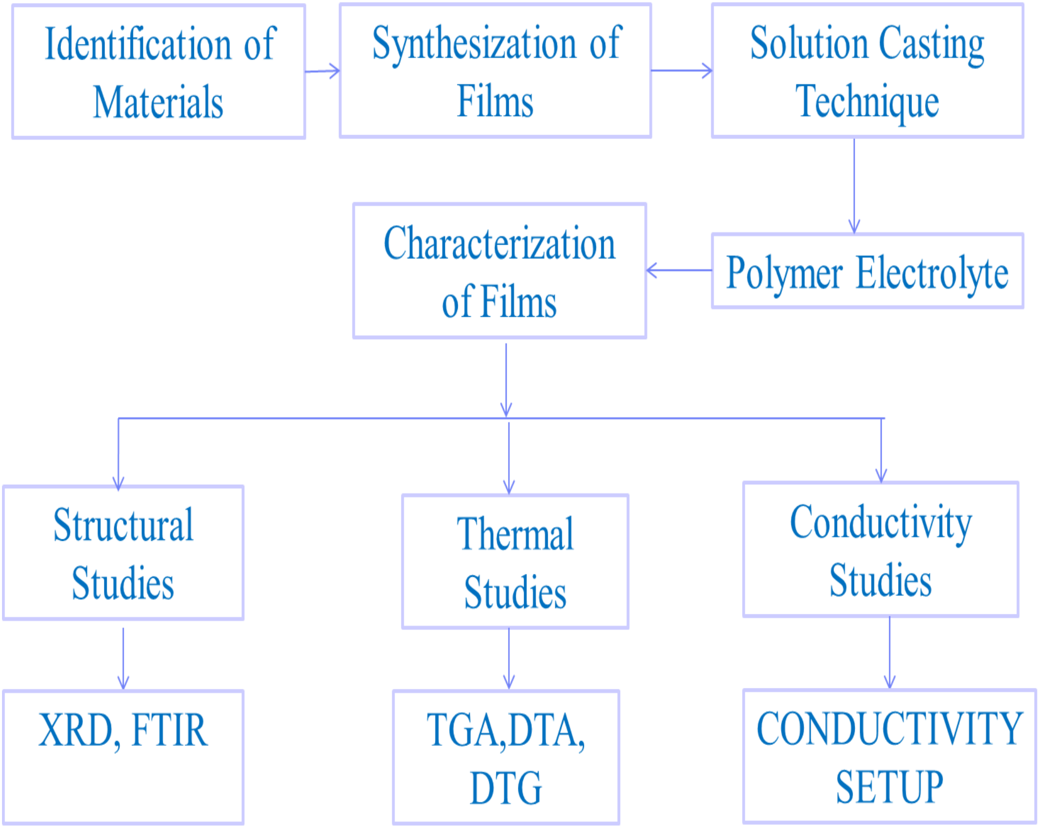
ABSTRACT

Polymer Lithium ion batteries have been fascinating significant thoughtfulness for their prospective solicitations in small portable electronic and electric vehicles (EV), and personal communication equipment. Solid polymer electrolyte, used as both electrolyte and separator between the electrodes, has numerous advantages in contrast to liquid electrolyte, such as no leakage of electrolyte, ease of manufacturing, flexible geometry and improved safety etc.

The polymer electrolytes with various compositions of PAN/N-N DiMethylformamide (DMF) /Lithiumtetrafluoro Borate ($LiBF_4$) are synthesized by solution casting technique. The free standing, clear and transparent 60-80 micron thick films are formed. Different structural, thermal and electrical studies validate hopeful characteristics of the polymer membranes, suitable as electrolytes in rechargeable lithium batteries. The promising conformational/structural changes in polymer electrolytes have been explored by X-ray diffraction (XRD) and Fourier transform infra-red (FTIR) techniques. From the diffractograms, it is observed that there is the formation of a peak at an angle of $2\theta=16.75°$ to $17.5°$ which is in correlation with the results quoted in the literature. This peak signifies the presence of host polymer in the porous polymer electrolyte. FTIR studies show that the polymer salt complexation has taken place which is confirmed by the shifting of peaks and also the formation of new peaks in polymer complexes. FTIR results indicate that the Li^+ cations of dissociated salt are coupled with both the C=O group in DMF and the $\mathrm{C} \equiv \mathrm{N}$ in PAN, along with the dipolar interactions between DMF and PAN through C=O group and $\mathrm{C} \equiv \mathrm{N}$.

The thermal properties of all solid polymer electrolytes (SPE) were studied by Thermo gravimetric Analyzer (TGA) and Differential Thermal Analyzer (DTA). The films were found to be thermally stable. It is observed that there is a gradual degradation in the polymer electrolytes. All the polymer electrolytes are found to be stable up to 194, 138, 89, 91 and 91 °C for 2, 5, 8, 10 and 12 wt. % of salt, respectively with a net weight loss of 10 %. The melting temperature is decreased from 317°C to 279°C upon the addition of the salt. The electrical properties i.e. ionic conductivity of solid polymer electrolytes has been measured as a function of temperature and composition. The temperature dependence of conductivity followed the Arrhenius and Eyeing-Polanyi behaviors. A Polymer membrane for 3 wt. % of salt has a conductivity of 3.06x10^{-4} mScm^{-1} at room temperature and 1.53x10^{-3} mScm^{-1} at 358K. The conductivity values increased with increase in temperature and offered an ionic conductivity of the order of 10^{-3} mScm^{-1} at temperatures 358K. Activation energy, enthalpy and entropy values are determined for all polymer complexes. The conductivity studies reveal that with the increase of salt concentration the conductivity also increased.

The outline of the thesis is elucidated chapter-wise in brief.



For systematic presentation of the whole work, the thesis has been divided into five chapters.

Chapter 1 presents a summary on the subject area of "Solid State Ionics", which includes different materials, designing and comprehensive classification of Solid State Ionic Materials which are commonly referred to as 'Supersonic Solids' or 'Fast Ion Conductors' or 'Solid Electrolytes'. These materials reveals about the ionic conductivity at room temperature close to that of liquid/aqueous electrolytes. These solid state materials are presently grouped broadly into different electrolyte phases such as crystalline/poly-crystalline, glassy/amorphous, composite, polymeric etc. The present work has been mainly focused on polymer electrolyte phase. Hence, this class of materials has been reviewed more extensively. The technological aspects of these materials in variety of all solid-state electrochemical device applications have also been discussed briefly.

Chapter 2 focuses on the literature review, the works carried out on different polymers like Polyethyleneoxide (PEO), Polyaniline (PANi), polyvinyl alcohol (PVA) and the polymer of interest in this work, PAN. Literature from many journal articles, review papers, text books are taken to accomplish the work in a decent way.

Chapter 3 encompasses the different procedures for techniques used to design the solid polymer electrolyte as shown in the flow chart. Synthesis of films is done by employing the solution casting technique. Solid polymer films are developed from different solvents like Dimethyl sulfoxide (DMSO), N-Methyl pyrrolidine (NMP) and combination of two solvents in the volume ratio of 1:1, analyzed and finally found that the membranes of PAN/DMF in the combination of 20:80 in NMP have good stability. Different polymer electrolytes of PAN/DMF/$LiBF_4$ of different compositions are synthesized. Different characterization techniques used are X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Thermogram (DTG), Differential Thermal analysis (DTA) and conductivity measurements. The structural properties of the developed conducting polymer electrolytes are studied by using XRD and FTIR. The thermal properties were analyzed with the help of TGA, DTG and DTA. The temperature dependent ionic conductivity and the composition dependent conductivity are analyzed on dc conductivity setup.

Chapter 4 examines the results and discussions on the different polymer electrolytes. This chapter is divided into three parts that reports the structural properties, the thermal properties and the conductivity studies. Exclusively the curves related to the specific properties are studied and the results are compiled in very part of the chapter.

Chapter 5 hearsays the conclusions and the future scope of the work. Basing on the results obtained and discussed in chapter 4, it is foreseen that there is a wide scope for the work to be extended in different ways to enhance the conductivity in a much better means. All this will be implemented in the future for further improvement.

LIST OF SYMBOLS

2θ	Glancing Angle
a, b, c	Dimensions of the unit cell
d	Interplanar distance between the lattice planes
E_a	Activation Energy
h	Planck’s constant
h, k and l	Indices of the lattice planes
K_B	Boltzmann Constant
R	Ideal Gas Constant
ΔG	Gibb’s Function
ΔH	Enthalpy
ΔS	Entropy
λ	Wavelength of incident radiation
σ	Conductivity

LIST OF ABBREVATIONS

CED	Cohesive Energy Density
DC	Direct Current
DSC	Differential Scanning Calorimetry
DSSC	Dye-sensitized Solar Cells
DTA	Differential Thermal Analyzer
DTG	Differential Thermogram
ECD	Electro Chromic Displays
EV	Electric Vehicles
FIC	Fast Ion Conductors
FTIR	Fourier Transform Infra-Red
FWHM	Full Width Half Maximum
MEA	Membrane Electrode Assembly
PEMFC	Proton Exchange Membrane Fuel Cell
SPE	Solid Polymer Electrolyte
T_g	Glass Transition Temperatures
T_m	Melting Temperature

t_n	Transference Number
TGA	Thermo Gravimetric Analyzer
XRD	X-ray diffraction

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CHAPTER 1

INTRODUCTION ON POLYMER ELECTROLYTES

1.1. BACKGROUND & HISTORIC PERSPECTIVE

1.1.1. BACKGROUND – SOLID STATE IONICS

In the field of Material Science, Solid State Ionics is a thrust area of research. The research in this area of Solid State Ionics focuses on the investigations of the physical and the chemical behavior of the solids. In 1967, the field of Solid State Ionics has come into existence with the discovery of two groups of solids via MAg_4I_5 (where $M = Rb, K, NH_4$) (Owens and Argue, 1967) (Bradley and Greene, 1967) and Na-β-alumina (Yao and Kummer, 1967). Later on, in last four to five decades, many researchers have been exploring this area, that encompasses the investigations on much number of solids that exhibit fast ion transport that involves variety of mobile species. This field mainly deals with the solid materials that exhibit fast ion transport through the materials like polymer electrolytes. The potential use of the polymer electrolytes has stimulated the synthesis of new polymer electrolytes, their structural studies, charge transport and the theoretical modeling of the charge transport process. The work on these polymer electrolytes, has received great interest and thoughtfulness of all the research society in the field of solid state Ionics basing on their applications. The polymer electrolytes may have sufficiently high ionic conductivity depending on the thickness of the solid polymer electrolyte, which is comparable to that of the aqueous electrolytes. Hence, these polymer electrolytes have wide applications in the areas of solid state electrochemical devices such as batteries and electro chromic windows basing on the fast ion movement. These materials which have high ionic conductivity and negligible electronic conductivity are referred to as “Super Ionic Solids” or Fast Ion Conductors” or “Solid Electrolytes” (Polak, 1989).

1.1.2. HISTORIC PERSPECTIVE

The scientific and technological environment highlighted that the work on polymer electrolytes was increased basing on physiochemical and theoretical tools developed. These are ultimate in understanding the structural, mechanical and the transport properties of polymers. Wright in his paper 1998, consolidated the history of family of materials into periods with “Classic Period” in early 1970s, which gave the way to the “period of change” (Noto et al., 2011)**.**

The substantial novel findings in mid 1970s in the arena of macromolecular synthesis were improbable and were not cost effective in the polymer industry for consumer presentations. This made the emphasis shifted towards the innovative fields of research, the composite solid materials and high-performance fibers. At that juncture, the operation of optically active and electro active polymers materialized and assimilated from diverse areas like Physical chemistry, organic chemistry and device engineering that has become multidisciplinary (Noto et al., 2011).

The second decade, 1980s symbolized the development of Polymer electrolytes, was established on the diffusion of micro and portable-electronics. There was a solid mandate for cheap secondary batteries that are very light in weight with high performance. The research and development works on polymer electrolytes during this period has become crucial. To discourse about the crystallinity of materials that hinder the ionic conductivity, new strategies were being developed. New model of dynamic percolation was proposed by Ratner (Ratner, in: MacCallum and Vincent, 1987) (Ratner and Nitzan., 1989), Angell and Torrel's decoupling index (Angell, 1983) (Torell and Angell, 1988) and the WLF equation was studied by Cheredame and Watanabe (Cheredame, in: Benoit and Rempp, 1982) (Watanabe et al., 1987). Aberdeen and St. Andrews (Bruce and Vincent, 1989)(Cameron et al., 1989)(Gordon Cameron, Ingram and Harvie., 1989) (MacCallum, Tomlin and Vincent., 1986) (Xie and Farrington, 1993) addressed the associations concerning the transport numbers and the aggregation of salts in the polymer electrolytes. New applications for Polymer electrolytes in electro chromic displays and "smart" windows were proposed in this 1980s.

1990s, the third decade, witnessed the extensive development of Lithium-ion batteries centered on amorphous polyetheleneoxide (PEO) based polymer electrolytes. Various systems like "salt-rich" or Angell's "Polymer-in-salt" electrolytes and gel electrolytes that contain solvent molecules in polymer matrix were studied and industrialized. Single-ion conducting systems and solvent-free polymer electrolytes for alkali-metal batteries were of great interest. PEO-salt complexes with helical structure by Armand (Armand et al., 1979), the powder X-ray diffraction for spatial alignment by Chatani, helical geometrical structures of polyether chains, ion mobility and the cation coordination geometry that was determined by vibrational and laser luminescence spectroscopes were developed.

In the new millennium, the research on hybrid inorganic-organic polymer electrolytes was a pronounced modernization in polymer electrolytes area. The solid materials synthesized were very favorable in fabrication of high-performance lithium secondary batteries due to their chemical and electrochemical stability, mechanical, thermal, and high ionic conductivity at room temperature (Sanchez et al., 2011) (Sanchez et al., 2005). The potential utility with a specific orientation to devices for the transfiguration and storage of energy such as fuel cells, secondary batteries, sensors, super capacitors, dye-sensitized solar cells (DSSC), actuators and microelectronic devices, divorce range of innovative materials was prompted and proposed for.

Hence, the scientific and technological panorama of the current century will gain importance owing to these polymer electrolytes which are the cornerstones for conversion and storage of energy.

1.2. INTRODUCTION ON SOLID ELECTROLYTES

The making, storage and dissemination of energy are the main apprehensions of modern industry and humanity. Over the past ten years, an exceptional progress has been seen in micro electronic industry but, to-date, the application in integrable power sources has not been still realized. For further integration of the electronic industry, the advancement in novel type of electrical power generators and storage systems are quite essential. The self-reliant power source is an emerging inclination in various fields.

In the existing conventional battery system, a concentrated aqueous solution of potassium hydride or sulphuric acid is employed as a liquid electrolyte. This liquid electrolyte has a very good contact with electrodes and has an excellent high ionic conductivity. But these battery systems with liquid electrolytes often have major drawbacks. Cell leakage or loss of electrolyte, drying out of the cell, self-discharge process or the capability of useful discharge at very low temperatures, corrosion are some of the major shortcomings.

Interest in developing solid polymer electrolytes was motivated with a hope that the above mentioned limitations would be minimized if the liquid electrolyte is substituted by a solid electrolyte. In thin film solid electrolytes, the lone mobile charge carrier is a cation A+ (A = Li, Na, K) linked with an anion which is arrested in crystal lattice. The solid materials which exhibit high ionic conductivity comparable with those of liquid electrolytes are known as “Solid electrolytes”. These materials are also referred as “Fast Ion Conductors (FIC)” or “Super Ion Conductors (SIC)” which are characterized by the following properties for the device applications.

a) Ionic bonding

b) High electrical conductivity (~ 10^{-1} to 10^{-4} $S.cm^{-1}$) and

c) Ionic transport number t_{ion} ~1

The history of super ionic conductors starts with Faraday's work on AgI in 1839 (Faraday, 1989). This field of research has received an additional improvement with the advent of high disordered "soft" super ionic conductors, the polymer-ion conductors. A number of excellent reviews are available (Vincent, 1987) (Armand, 1994). Many researchers worked and attempts were made to enhance the ionic conductivity in the normal ionic solid materials by doping. Major breakthrough was accomplished in the year 1967, year-marked as the beginning or the advent of the field of Solid State Ionics, which is an innovative area of research activity in Materials Science. The solid state ionic resources exposed so far have been grouped into a variety of solid electrolyte phases.

1.3. CLASSIFICATION OF SOLID ELECTROLYTES

Basing on the synthesis methods, microstructure and physical properties of solid state ionic materials, the solid electrolytes are classified into various broad categories of solid electrolyte phases, as mentioned hereunder.

a) Crystalline / polycrystalline solid electrolytes

b) Glassy or Amorphous solid electrolytes

c) Composite solid electrolytes

d) Polymer electrolytes

1.3.1. CRYSTALLINE / POLYCRYSTALLINE SOLID ELECTROLYTES

This class of materials is generally prepared by solid solutions reaction which comprises of two sub-lattices that fundamentally provides a rigid framework with networks through which one of the ionic species of the solid can migrate. The rigid cage like skeleton is one of its kinds. In this structure, the movement of ions is facilitated in a molten sub-lattice i.e. in liquid like regime. The initially developed super ionic materials belong to this category, which are employed as electrolytes in the fabrication of solid state batteries. Thin films made out of these solid electrolytes are used in the development of all solid state electrochemical devices. These materials have been classified into two classes. They are

(a) Soft-framework Materials

These soft materials are generally prepared by the solid solution reaction of double salts. They are characterized by pure ionic bonding, having a sharp order-disorder phase transition, high polarizable heavy ions and exhibiting low Debye temperature.

(b) Hard-framework Materials

These materials are usually made of metal oxides. The properties of these are in contrast with soft-framework materials, and are characterized by covalent bonding, less sharp or absence of order-disorder phase transition, low polarizability of mobile ions and high Debye temperature. One of the examples is the material made of Na-β-Alumina (Yao and Kummer, 1967).

The Ion transport phenomenon involves hopping mechanism from one vacant site to the other. However, all ionic solids exhibit conductivity, but only those materials with very definite structural morphologies are capable of showing conduction mechanism comparable to that of liquid electrolytes. For example, one such solid electrolyte, $RbAg_4I_5$, possess a conductivity of 0.27 S/cm at 25^{o}C comparable to many liquid electrolytes.

1.3.2. GLASSY OR AMORPHOUS SOLID ELECTROLYTES

The systems involving these materials with fast ion conduction exhibited numerous advantages over the first class of electrolytes. Pronounced deal of thoughtfulness was shown towards them in late 70s. High isotropic ionic conduction mechanism, extensive range of compositional variability, simplicity in preparation in desired shapes and absence of grain periphery conditions are important advantages in these materials. The system, made of AgI-Ag_2SeO_4 is a melt-quenched glassy system with fast ion conduction (Kunze and Huber, 1973). This glassy electrolyte exhibited a very high Ag^+ ion conductivity of 10^{-2} S/cm at room temperature. Varieties of techniques are employed in developing these materials. For example, a Li^+ conductivity of 0.16 S/cm at 25^{o}C for a glassy system with the composition 0.7 Li_2S-0.3P_2S_5 has been reported, which compares favorably with the best crystalline Li^+ ion conductors at the room temperature. It appears to be an unforeseen outcome that glasses can support high ionic conductivity.

1.3.3. COMPOSITE SOLID ELECTROLYTES

A number of thought-provoking studies on mixed phase composite electrolytes have been carried out after 1973, which are high ion conducting multiphase solid electrolyte systems, also termed as dispersed solid electrolytes. These electrolytes, comprises of a moderately conducting ionic solid which is the host salt (as Phase

1) and the second either an insulating inert compound or a low ionic conducting solid (as phase 2). Significant enhancement in different physical properties of the host is attained without any change in the structural or chemical environment of the constituent compounds. This is due to the dispersion of submicron sized particles of second phase into the first phase of host salt. In improving the physical properties like conductivity of first phase host salt, the size of the second phase particles dispersed play a very prominent role in the two-phase mixture. These crystalline resources are of high ionic conductivity and are cation conductors. One of the drawbacks of these materials is that they do not possess the flexibility that the polymer electrolytes have. It may consequently be possible to combine the advantageous properties of the two phases. The two important classes of two phase composite solid electrolyte systems are

(i) Inorganic composite electrolytes (crystal crystal composite electrolytes).

(ii) Organic composite polymer electrolytes (conventional solid polymer electrolytes.

1.3.4. POLYMER ELECTROLYTES

Polymer electrolytes form a significant class of materials with high potential to replace normal electrolyte solutions, gaining attention as a new type of ion-containing resources (Fontanella et al., 1986) (Vincent and MacCallum, 1987). These materials are preferred over crystalline solids due to their wide choice of compositions. Some of the important features in the polymer electrolytes are ease of preparation in various forms, control over the properties, good mechanical integrity, good interfacial connections between the electrode and electrolyte, mouldability and ionic conductivity, depending upon the thickness of the film. The polymer electrolytes can be fabricated into soft films of only few microns thickness. Their flexibility supports the interface between the electrodes with solid polymer electrolytes that remains intact, when the cells are charged and discharged. These are electro active polymers in the conductivity range of 10^{-4} S/cm. This marks the progress of all possible electrochemical devices. In recent past, considerable progress has been made to enhance the electrical conductivity, electrochemical and mechanical stability of these polymer electrolyte materials to be utilized for various applications viz. solid state batteries, fuel cells, sensors, super-capacitors, electro-chromic display devices, photo electrochemical solar cells etc. (Chao and Wrighton, 1987) (Gray, 1991).

The first polymer electrolyte membrane was synthesized by Fenton in 1973 by complexing high molecular weight polar polymer with alkali ion salts (Fenton, Parker and Wright, 1973). Many number of polymer electrolytes have been developed after the demonstration of a solid polymer electrolyte thin film battery for the first time by Armand in 1979. Some of the most important characteristics of the polymer electrolyte membranes are

(i) Ionic conductivity

(ii) Ionic Transference Number

(iii) High thermal/electrochemical/chemical/mechanical stability

(iv) Electrode/Electrolyte compatibility.

1.4. CLASSIFICATION OF POLYMER ELECTROLYTES

Solid state polymer electrolytes are broadly classified into various groups based on the methodologies used during the fabrication of membranes. Various polymer electrolytes have been developed with ionic species of H^+, Li^+, Na^+, Mg^{+2}, Zn^{+2} etc. The broad classification of polymer electrolytes is as follows

a) Salt with polymer complexes(Solid Polymer Electrolyte, SPE)
b) Solvent swollen polymers
c) Gel polymer electrolytes
d) Rubbery Polymer electrolytes and
e) Composite polymer electrolytes.

1.5. DEVELOPMENT OF POLYMER-SALT COMPLEXES

A semi crystalline polymer such as Polyacrylonitrile (PAN) and a metal salt such as alkali metal salt are dissolved in suitable solvents. The solvent may be one component or it may be a two-component mixture; alternatively the polymer may be dissolved in one solvent and the salt in another, the two solutions being subsequently mixed, after a substantial stirring period to ensure adequate mixing, the solvent is allowed to evaporate and a thin cast film is formed. The nature of the films formed from given reactants are quite different depending on whether moisture is present or excluded, and on whether the system has been heated or not. There are two energetically significant stages for the electrolyte formation (Vincent, 1987). Initially the lattice energy of the salt is overcome by the process of dissolution in the casting solvent then the salt is transferred from the casting solvent to the polymer, it is helpful to regard the latter as an “immobile solvent”. In the case of PAN-MX (alkali salt) complexes, cation M^+ coordinates with lone pairs of electrons on the heteroatom in the polymer chain. The anion remains in close proximity to preserve local charge neutrality. The most common examples of concern in complexes is electrolytes made of PEO or Polyacylonitrile (PAN) with alkali metal inorganic salts (Armand, 1983).

PAN has the same repeat unit as simple crown ether, i.e. typically about 10^5 repeat units are joined, to give a polymer or relative molar mass ~ $1.5x10^5$ so that the end groups on the polymer chain have a virtually insignificant effect on the chemistry of the system. With some alternative comb and network polymers that are coming into use, the PAN side chains are only two or three repeat units in length and end group effect can be important (Vincent, 1987).

If the interaction between the cation and the polymer chain is strong, then a type of localized “chemical cross–linking” occurs and the material may become highly structurally organized, leading to the formation of a high melting crystalline phase. Weak interactions, especially in dilute systems can lead to the formation of crystalline PAN regions. In some systems, both crystalline complex and crystalline/ semi crystalline PAN may be present (Armand, 1983) (Armand, 1986) (Neat et al., 1985) (Neat, Glasse and Linford., 1986).

Polymer complexes generally have a multiphase nature consisting of salt-rich crystalline phase, pure polymer crystalline phase and amorphous phase with dissolved salt (Robitaille and Fauteux, 1986). If the cation-polymer interaction is too strong, then clearly the cations will have a very low mobility. This is not the only problem that results from over – strong cation – polymer interactions. Typically, a given cation is linked with electronegative atom in the polymer chain; thus, transient ionic cross-links are formed which greatly restrict the local freedom of motion which depends on the length of the polymer chain. Kakihana (Kakihana et al., 1988) showed that ionic motion depends on the ability of the polymer chains to flex, and so the rigidity imposed by the transient cross links (induced by the cations) also impedes the mobility of these anions. In addition, many cations interact with PAN in such a way that crystalline high melting salt-polymer complexes are formed.

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

i) The polymers should be of low glass transition temperatures (T_g) for their flexible backbone, which will ensure the complexation. The low T_g can be attained either by choosing the polymers of low cohesive energy (such as PEO, PPO etc.) or by plasticizing the polymers of high T_g such as PAN.

ii) The lattice energy of the salts should be lower for which, salts of larger anions such as I, CIO_4^-, CIO_3^-, CF_3SO_3, SCN^-, BF_4^- etc. are most suitable.

iii) The concentration of polar groups responsible for complexation of cations, should as large as possible.

Polymer and salts are dissolved in an appropriate solvent. After vaporization, polymer electrolyte was obtained in the solid form. Mechanically it behaves like a solid but the internal structure and consequently the conductivity behavior closely resembles that expected of the liquid state. Being an electrolyte, it must conduct ions but not electrons (or electron/holes) whereas an electrode must conduct both ionically and electronically. A more thorough description of electrochemical transport is given by Linford and Hackwood (1981) and Linford (1988) (Linford and Hackwood, 1981) (Linford, 1988). Most polymer materials on their own are insulators and conduct neither electrons nor ions. Certain polymers act as "immobile solvents" for ionic salts and these solid solution materials are called polymer electrolytes. The most common polymer is poly (ethylene oxide) (PEO) and the electrolytes which are based on PEO are normally described as PEOn: MXz, where n is the oxygen-to-cation ratio[O]:[MZ^+], M is the cation species of valance Z and X is a suitable anion.

A usual feature of most polymer electrolytes when compared with other types of solid electrolytes, is that not only cations (which migrate to the cathode during galvanic discharge but also anions (which go to the anode) are mobile. This causes real problems in polymer batteries, especially those that are designed to be rechargeable.

1.6. APPLICATION OF POLYMER ELECTROLYTES

Ion conducting polymers have a relatively high ionic conductivity and therefore have a potential application as solid electrolytes. These ion conducting polymers are used as electrolytes in different electrochemical devices such as

(i) Electrochemical Batteries

(ii) Electrochemical sensors

(iii) Fuel cells

(iv) Super capacitors

(v) Memory devices

(vi) High-vacuum electrochemistry

(vii) Electro chromic display devices

(viii) Thermoelectric generators and

(ix) Electrochemical switching

(x) Dye-sensitized solar cells.

1.6.1. ELECTROCHEMICAL BATTERIES

The function of the solid polymer electrolyte is to let the migration of the alkali or alkali-earth metal ions from the anode to the cathode during the discharge and the reverse process when the battery undergoes recharging. The polymeric film prevents the short circuit between the terminals and ensures that there is an ionic conductivity in the battery. **Figure 1.1** shows a typical design of the solid state polymer electrolyte cell design with the configuration anode / electrolyte / (I_2+C+electrolyte) cathode. M^+ (metal ion) ions travel across the electrolyte and the electrons leave the anode through a wire, travel through the “load” and then proceed along a wire to a current collector.

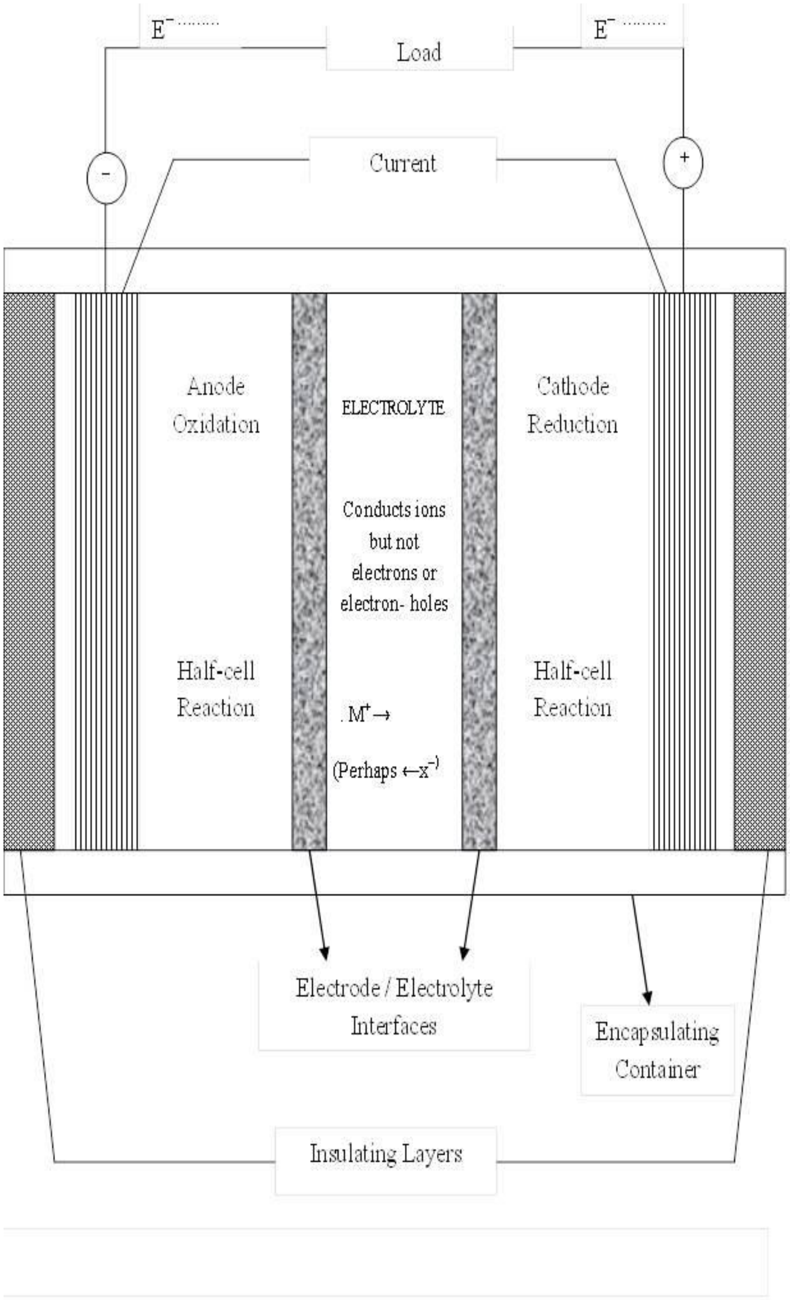


Figure: 1. 1: Schematic diagram of a solid state cell / battery

The ions go between these layers, called intercalation. The cathode material swells during the intercalation process and therefore the solid material surrounding the particles of cathode materials has to be flexible enough to stay in contact even when the particles change size and shape. Consequently, a solid state battery involving an intercalation cathode material requires the particles of cathode material to be embedded in a plastic matrix, which is usually made from the polymer electrolyte materials. In addition, fully intercalated cathode material is usually a poor electronic conductor and is often necessary to add some carbon so that electrons can enter and leave the cathode particles on their way to and from the current collector.

The anions are also mobile in many polymer electrolytes which include PEOn: $LiClO_4$ and PEOn: $LiCF_3SO_3$. Such anions move towards the anode and even react with Li^+ cation at the interface to form a thin layer of polymer conducting lithium salt.

$$Li^+ + X^- \quad \rightarrow \quad LiX$$

This increases the cell resistance, decreases the number of Li^+ ions and reduces the capacity of the battery as it is difficult to dissolve the ions on recharge. This anion migration process is limited by the fact that the cathode does not provide a source of anions to replenish those displaced in the electrolyte and an increase in their concentration on the left hand side means that a concentration gradient opposing the electric field induced migration is setup and the battery becomes concentration polarized with respect to anions.

1.6.2. FUEL CELLS

The solid polymer electrolytes are employed in the fabrication of the fuel cells. These materials are capable of transporting the H^+ ions, produced by the fuel oxidation, from anode to cathode. Membranes are the key components in the development of a proton exchange membrane fuel cell (PEMFC). These polymer electrolyte membranes allow the transport of protons from the anode to the cathode. Also, this membrane at the same instant acts as a separator for electrons and reactant gases. Maximum efficiency and performance of the fuel cell can be obtained if the thickness of the membranes is low. This results in lower ohmic resistance of the membrane electrode assembly (MEA). PEM fuel cell technology is the best widespread technology owing to its potentially multipurpose applications from portable devices, transportation vehicles to stationary power generation.

1.6.3. SUPERCAPACITORS

The electrochemical devices that can store charge electrostatically by developing the reversible absorption of ions supported by the electrolyte onto the electrode materials, characterized by high electrochemical stability and wide surface area are called as “Supercapacitors”. Different kinds of polymer electrolytes viz. solid polymer electrolytes, gel polymer electrolytes, polyelectrolytes and hybrid polymer electrolytes are employed in the application of supercapacitors.

1.6.4. ELECTRO CHROMIC DISPLAYS

The multilayer systems in which atleast one component suffers a colour change due to the application of the electric field are termed as “Electro chromic displays (ECDs)”. The active component will be in the unperturbed state. When the electric field is applied, this active component experiences a reversible colour change, due to oxidation or reduction. Positive or negative ions are to be introduced into the active component to nullify the electrical charges. These ions will be originated from the “ion storage layer” of the electrolyte and they transit through the electrolyte. Various polymer electrolytes can be used in ECDs because they can be fabricated into films of low thickness, have low ohmic losses or high ionic conductivity at room temperature that ensures 10^6 to 10^7 write erase cycles for displays (Noto et al., 2011).

1.7. MOTIVATION FOR THE WORK

1.7.1. NEED FOR ENERGY SOURCES AND STORAGE

The forthcoming energy crisis of the modern developed world raises the fundamental questions to be answered and solved in the field of science as well as in politics. Fossil fuels - oil, coal and gas are the planet’s leading energy sources. The storage of these fuels has recognized drawbacks, not the least influence on the environmental problems of global warming through the “Greenhouse effect”. Oil is the superior part of the fossil fuel is used today (40% of the world’s energy needs, and as much as 90% of its transport fuel). This, at least when it comes to what is economically justifiable to exploit within the next few generations to come, and most of the unexplored resources are in the politically unbalanced areas of the world. Sooner or later, all fossil fuels will run-out (Campbell, 2002) (Campbell and Laherrre, 1998).

It is therefore comprehensible that the researchers in many fields try to develop alternative energy sources. For example, in Sweden today there is an extensive use of water power and additional energy can be generated from wind and waves, or from renewable bio-materials. However, these sources are far from adequate to replace the energy we get from fossil fuels today, and to explore them further often means interfering with the environment. Instead, the main focus of the research community today is on developing solar cells and hydrogen-based fuel cells (Grätzel, 2001) (Steele and Heinzel., 2001). Owing to the framework of finding and using the alternate energy sources, one is often facing a problem of energy storage. One of the most convenient techniques is the electrochemical storage. The work being developed in this thesis is conducted in the development of polymer electrolytes for energy storage in the form of Lithium-ion Polymer Battery. A typical design of the lithium polymer electrolyte battery is shown in **Figure: 1.2.**

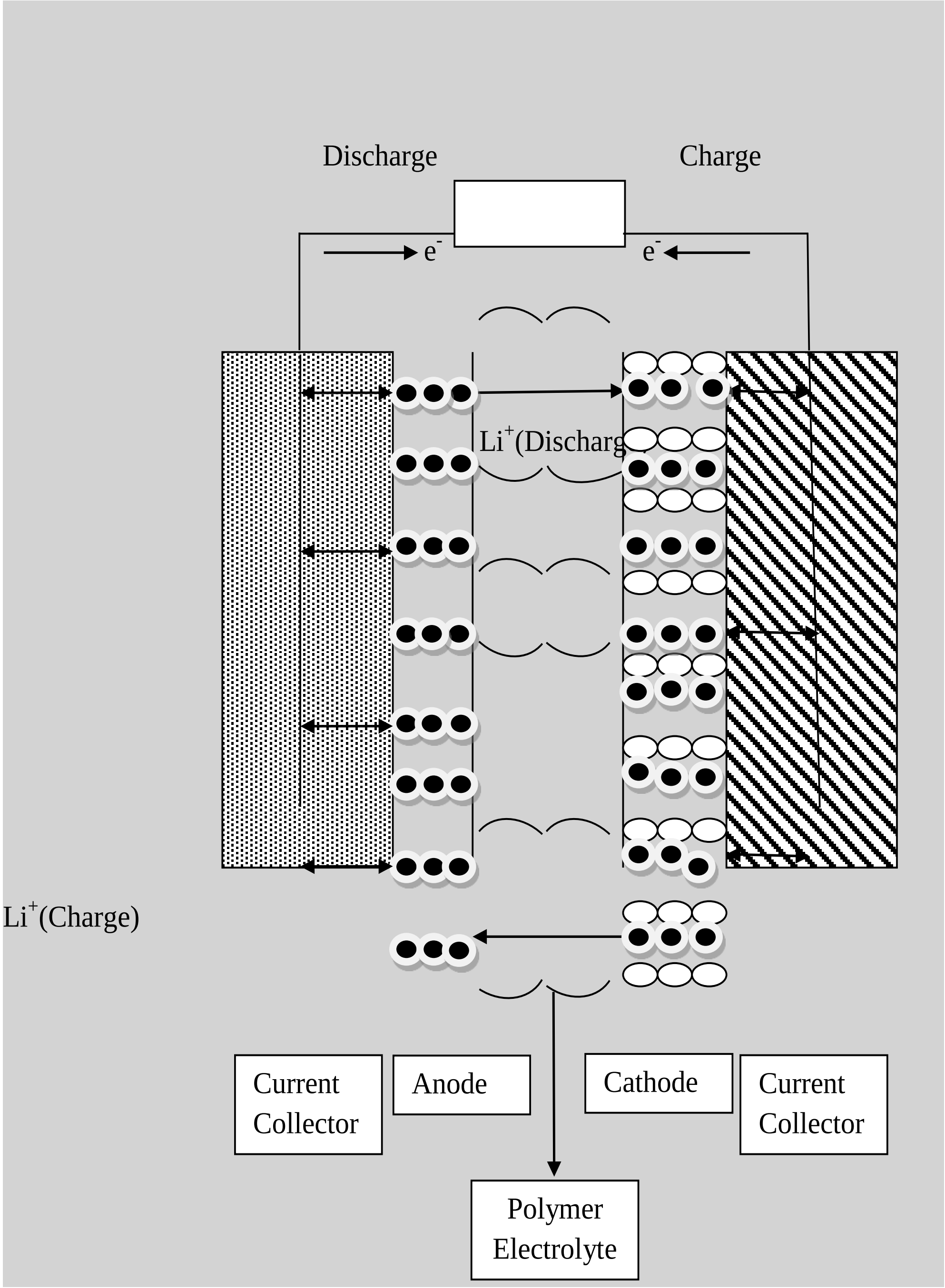


Figure: 1. 2: Schematic representation of a Lithium-ion Polymer Battery

1.7.2. LITHIUM-ION POLYMER BATTERY

The main advantage of a Lithium-ion polymer battery is that it combines a high energy density, a high cell voltage and recharge ability, which means that the energy is stored effectively and efficiently up to its best. The battery can be used in many applications successfully and that it can be used over and over again repeatedly. Above and beyond, the batteries are comparatively reliable and safe (Armand and Tarascon, 2001) (Van Schalkwijk and Scrosati, 2002). Generally, the battery comprises of an Anode, consisting of a Lithium intercalated Graphite with a low electrochemical potential and a transition-metal oxide cathode with high potential (e.g., LiCoC2 or Li(CONi)O_2), which both can reversibly intercalate and release Lithium ions (Winter et al., 1998). Sandwiched between the anode and the cathode there is a polymer electrolyte separator – the focus of the present work. Under Discharge, the electrons pass through from anode to cathode. At the same time, Li^+ ions are extracted from the anode, pass through the electrolyte, and into to the cathode. The task of the electrolyte is merely to facilitate this Lithium transport – not as trivial as it may appear. The ever-increasing demand for the battery systems for mobile electronics and the automotive industry, especially the electric vehicles, has triggered the prosperity of studies aiming at the expansion of the solid electrolytes, meeting the complete property for an application as electrolyte in Lithium Battery systems. This includes a high ionic conductivity, a large electrochemical window, chemical inertness as well as environmental compatibility and safety (Voigt and Wüllen, 2012). The conducting polymers have the ability to switch between the reduced and oxidized states. This fascinated the instantaneous attention of energy technologists who realized the potential to be gained from lighter weight batteries. Bistable polymer devices could be made of any desirable size or shape for applications in electronics. The importance of the switching behavior has been utilized in sensing and membrane separation technologies (Talaie and Wallace, 1994). The research and development of polymer electrolytes for ambient temperature rechargeable Lithium and solid ion batteries were always identifiable. Polymer salt complexes are of technological interest due to their possible applications as solid electrolytes in different devices such as energy conversion units (batteries/fuel cells), electro-chromic displays devices/smart windows and photo-electrochemical solar cells etc. (Vijay Kumar and Suneeta Sundari, 2010).

1.8. AIM AND SCOPE OF THE PRESENT WORK

In the past several years extensive studies have been performed on the ionic conductivity of certain kinds of ion conducting polymers. These ion conducting polymers show a relatively high ionic conductivity and have a potential application as solid electrolytes. Such electrolytes are mainly based on the alkali metal salt systems, with particular attention being focused on Lithium. These may be useful in finding solid electrolytes of sufficiently high conductivity. Polymer electrolytes can be shaped in the form of thin film, thereby reducing the internal resistance leading to high energy density in battery and fuel cell applications.

An encouraging methodology to increase the conductivity of polymer electrolyte is through the use of low molecular weight organic solvents as plasticizers in a host polymer. This method uses the smaller activation barrier for the conducting ions in the plasticizer phase than in a polymer. Furthermore, the low viscosity and high dielectric constant of these plasticizers ensures higher mobility and greater dissociation of ion pairs. Keeping these aspects in view, in the present thesis, the authors report the results obtained on various sets of solid polymer electrolyte thin films based on polyacrylonitrile (PAN) complexed with salt $LiBF_4$.

1.9. SUMMARY

The details of the present thesis entitled "Development and Characterization of a solid-Ion conducting Polymer Electrolyte is summarized below.

[1]. Preparation of polymer electrolyte films of pure PAN and ($PAN+LiBF_4$) by using solution casting technique.

[2]. To select the solvent for the work on polymer electrolytes of $PAN/DMF/LiBF_4$, the following are to be observed.

- (i) Observing the effect of the solvent1
- (ii) Observing the effect of the solvent2
- (iii) Observing the effect of the solvent1+ solvent2 in volume ratio of (1:1)

[3]. To study the polymer electrolytes ($PAN+LiBF_4$+Plasticizer) systems with changing salt concentrations, in low salt polymer ratio.

[4]. To study the structural or complexation of salt with the polymer through X-ray Diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) techniques.

[5]. To study the thermal properties by DTA, TGA and DTG techniques.

[6]. To study the temperature as well as composition dependence conductivity of polymer electrolytes.

[7]. Finally, the future prospects of these solid Ion conducting polymer electrolytes and their applications in different fields.

CHAPTER 2

LITERATURE SURVEY

2.1. REVIEW OF EARLIER WORK ON POLYMER ELECTROLYTES

The polymers are insulating materials, which are having diversified mechanical, chemical and physical properties. The polymers may have good ionic conduction mechanism even though they insulating materials. However, the electrical conduction of a polar polymer in a comparatively low electric field is ionic. Provision for the ionic conduction mechanism can be provided from Faraday's law detected in a gas evolution testing, with an applied voltage and from the dependency of electrical conductivity on pressure, free volume and degree of crystallinity (Saito et al., 1968) (Miyamoto and Shibayama., 1973).

Polymer electrolytes were studied for the first time some four decades earlier (Armand, 1994). Wright developed $(PEO)_n$: Li system (Fenton, Parker and Wright, 1973) and studied about the complexes that were formed between poly (ethylene oxide) and sodium and potassium salts, which was the bench mark data in 1973. Armand et al (Armand, Chabagno and Duclot, 1979) reported poly (ethylene oxide) (PEO) and poly (propylene oxide) (PPO) based solid electrolytes complexes with LiSCN, NaSCN, KSCN and CsSCN alkali salts. The T_g (glass transition temperature) values of PEO has been calculated as a function of temperature. In the temperature range from 40-60^{o}C, the values of conductivity reached 10^{-5} Scm^{-1} approximately. These results made these compounds much more suitable as solid state electrolytes in battery applications.

Poly (ethylene oxide) complexed with alkali salts are very useful for numerous applications such as sensors, batteries, fuel cells, electrochemical display drives, smart windows, photo electrochemical solar cells etc. (Papke, Ratner and Shriver, 1982) (Armand, 1986) (Berthier et al., 1983) (Mark Ratner and Duward Shriver, 1988). The reports recommended that high ionic conductivity is possible in amorphous phase but not in crystalline phase. In particular, Poly (ethylene oxide) (PEO) is an exceptional polymer that dissolves different salts of high concentration to form polymeric electrolytes. This polymer, PEO has high grade of crystallinity. Since the ionic transport in the PEO-salt complexes may be inferred basing on the hopping mechanism between the polymer chains (Armand, Chabagno and Duclot, 1979) (Papke, Ratner and Shriver, 1982) (Armand, 1986) (Berthier et al., 1983) (Mark Ratner and Duward Shriver, 1988) (Weston and Steele, 1981), the conductivity is affected or results in an increase beyond the crystalline-amorphous transition temperature.

The research work in the field of polymer electrolytes developed owing to poly (ethylene oxide) (PEO) based electrolytes using wide variety of alkali salts such as LiSCN (Sørensen and Jacobsen, 1982), $LiSO_3CF_3$ and $LiClO_4$ (Robitaille and

Fauteux, 1986), NaSCN (Lee and Crist, 1986), $LiBF_4$, $LiPF_6$ and $LiB(C_6H_5)_4$ (Rietman, Kaplan and Cava, 1985). Andrew Patrick (Patrick et al., 1986) reported the DSC results on variety of PEO polymeric electrolytes containing Magnesium, Calcium, Strontium and Zinc per chlorates and Magnesium and Calcium thiocyantes. Some other PEO based polymer electrolytes are also studied with the salts of divalent and transition metal cations (Huq and Farrington, 1988) (Huq and Farrington, 1988). Abrantes et al. (Abrantes, Alcacer and Sequeira, 1986) quoted about the electrolytes containing the host polymer PEO complexed with ZnX_2 salts, in which X is Cl, Br, I and ClO_4 above a wide range of compositions.

Blonsky (Blonsky et al., 1984) reported about the complexes of certain Lithium salts and the inorganic polymer poly {bis(methoxy ethoxy ethoxide) phosphazene} known as MEEP that belong to the class of highly conductive polymer electrolytes. The qouted conductivity for MEEP ($LiBF_4$) complexes at room temperature was of 2×10^{-5} S/cm. The MEEP $(LiX)_n$ polymer complexes could not be cast as free standing thin films for application in solid state batteries as they have shown meager mechanical properties.

Abraham et al. (Abraham, Alamgir and Perrotti, 1988) (Abraham, Alamgir and Reynolds, 1989) reported about the mixed polymer electrolyte systems of Li salt complexes of poly {bis-(methyoxy-ethoxyethoxide) phosphazene} (MEEP) and poly (ethylene oxide) (PEO). These complexes exhibited excellent dimensional stability and high ionic conductivity. The conductivity of MEEP / (PEO) – (LiX)n blend polymer electrolytes at $60^{o}C$ was similar to that of the conductivity of PEO

– (LiX)n at 100°C. The higher conductivity values obtained in the mixed polymer electrolytes in comparison to PEO electrolytes was due to the greater degree of amorphous nature introduced by the presence of MEEP.

Chandra et al. (Chandra, Hashmi and Prasad, 1990) and Hashmi (Hashmi et al., 1990) have studied the electrical conductivity properties of proton conducting polymer electrolyte based on poly (ethylene oxide) (PEO) complexed with ammonium per chlorate (NH_4ClO_4) salt along with optical microscopy, X-ray diffraction, differential thermal analysis (DTA), infrared spectroscopy and transference number measurements. The maximum conductivity was of the order of 10^{-5} Scm^{-1} at 30°C, and transference number for H^+ ion, t_n is 0.85. The movement of ClO_4^- ions contributes slightly to the overall charge transport of 0.08.

PEO electrolytes of silver trifluoro methane sulphate were studied for galvanic gas sensor application (Nagashima and Hobo, 1990), in the sequence as $Au/(PEO)_{4.5}$ $AgCF_3SO_3/Ag$. The temperature dependence of ionic transport number of Li^+ were studied by using the complex impedance and potentiostatic polarization measurements (Yoshiki et al., 1990). These studies have shown a dependence on the temperature and $LiClO_4$ proportion to the network of PEO electrolyte.

The polymer electrolytes of PPO-KSCN and PPO-NaSCN have been studied by Watanabe et al. (Watanabe et al., 1985). The conductivity values were found to be higher for cross-linked PPO-KSCN when compared to cross-linked PPO-NaSCN.

Teeters (Teeters and Norton., 1990) reported earlier about thin films of cross-linked poly (propylene oxide) comprising different known ratios of NaSCN and KSCN. Wu and Shen (Wu and Shen, 1990) have studied the conductivity and DSC measurements of poly (EO-CO-PO) – NaSCN complex system. The quoted conductivity at 30°C for the poly (EO-CO-PO) – NaSCN electrolyte system was found to be of the order 5 x 10^{-5} Scm^{-1}.

The ultra-thin modified poly (ethylene oxide) (PEO)-$LiClO_4$ polymer electrolyte film of thickness 50 μm was fabricated by solution –casing technique (Baochen, Li and Xinsheng, 1991). Chandra et al. (Chandra, Srivastava and Chandra, 1992) have reported a composite conducting polymer electrolyte ($PEO+NH_4I +Al_2O_3$) system. Activated as well as inactivated Al_2O_3 powder was employed to study its effect on conductivity and crystallinity. There was a remarkable advantage in the stability of the film by the addition of alumina though there was a marginal decrease in the conductivity and increase in the crystallinity.

Hashmi et al. (Hashmi, Chandra and Chandra, 1992) reported different results that were obtained on ($PEO+NaPF_6$) polymer electrolyte systems. The ion and hole transport in poly (ethylene succinate) + NH_4ClO_4 polymer electrolyte system was reported by Srivastava et al. (Srivastava.P.C., Hashmi.S.A. and Chandra.S, 1992). Lobitz et al. (Lobitz, Reiche and Füllbier, 1993) have studied the mixture of (PEO+LiI) and its transport properties. Martin-Vosshage and Chowdari (Martin and Chowdari, 1993) reported about the polymer electrolyte films of PEO with several concentrations of cobalt bromide ($CoBr_2$). The ionic conductivity of a solid polymer electrolyte based on lithium salt in PEO with the use of plasticizing agents was reported by Walker and Salomon (Charles W. Walker and Salomon, 1993). $Nd(NO_3)_3PEO$ and $Nd(DP_m)_3$ PEO electrolyte systems were reported by Twomey et al. (Twomey et al., 1994) and have studied about complexation and morphology.

The temperature dependence of the conductivity of PEO-$LiCF_3SO_3$ with plasticizer (MC_3) was studied by Andrieu et al. (Andrieu, Vicedo and Fringant, 1995) along with the thermal analysis. The studies revealed an increase in conductivity over the complete complex system. The ionic conductivity of a similar polymer complex PEO-$LiCF_3SO_3$ with modified carbonate (MC_3) as a plasticizer has been studied by Lee (Lee et al., 1994) and Yang (Yang et al., 1995). An acrylate polymer containing a short oligo polymer electrolyte poly (methoxy ethoxy ethylmethacrylate) poly (MEEMA) was studied by Selvaraj (Selvaraj et al., 1995).

Florjanczyk (Florjanczyk et al., 1995) studied the different conducting solid polymer electrolytes comprising random poly (ethylene oxide-propylene oxide) with lithium, sodium, potassium, cesium and rubidium salts. The polymeric electrolytes containing lithium or sodium salts attained conductivity level as high as $10^{-5} – 10^{-4}$ Scm^{-1} at room temperature and at $100^{o}C$ even greater values of the order of 10^{-3} Scm^{-1}. The polymer electrolyte systems based on PEO complexed with silver thiocynate (Sekhon et al., 1995) have also been reported.

An overview of the exploration and expansion of solid polymer electrolyte batteries has been described by Kazuo Murata (Murata, 1995). Solid polymer electrolytes made of alkaline poly (ethylene oxide) and their application to nickel secondary batteries have been reported by Fauvarque (Fauvarque et al., 1995). Clericuzio (Clericuzio et al., 1995) studied the ionic diffusivity and conductivity of plasticized polymer electrolytes. Andrieu et al. (Andrieu, Vicedo and Fringant, 1995) have studied the effect of plasticization of cross-linked polymer electrolytes. Similarly, the effects of network structures and doped salt species on electrochemical properties of polyether –based polymer electrolytes have been investigated by Masayoshi Watanabe and Assushi Nishimoto (Watanabe and Atsushi., 1995).

Structural property relationships in plasticized solid polymer electrolytes have been reported by MacFarlane (MacFarlane et al., 1995). Structural behavior and electrochemistry of polymer electrolytes was reported by Peter G. Bruce (Bruce, 1995). Olsen et al. (olsen, Koksbang and Skou., 1995) (Olsen and Koksbang, 1996) have measured the transference number of different hybrid polymer electrolytes. Grondin et al. (Grondin, Rodriguez and Lassègues, 1995) studied about the proton conducting polymer electrolytes with nylon 6-10/H_3PO_4 blends. Super capacitors by means of a proton conducting polymer electrolytes have been examined by Lassegues (Lassègues et al., 1995). Kaori Ito and Hiroyuki Ohno (Ito and Ohno., 1995) investigated ionic conductivity of poly (ethylene oxide) with charges on the chain end.

The salvation effect of solid polymer electrolytes with salts NaSCN and LiSCN in PEO-400 was observed by Xu et al. (Xu, Eyring and Petrucci., 1996). Melchiors et al. (Melchiors, Keul and Höcker, 1996) investigated the formation of solid electrolytes on the basis of alkali salts e.g.; $LiClO_4$, $LiCF_3SO_3$, NaSCN, NaI, $NaCF_3SO_3$ and KSCN in poly (2, 2-dimethyl trimethylene carbonate) block-poly (ethylene oxide) - block - poly (2, 2-dimethyle methylene carbonate) (PDTC-b-PEO-b-PDTC) and their properties. Johanson et al. (Johansson, Gogoll and Tegenfeldt, 1996) studied the temperature dependence of the diffusion coefficient of solid electrolytes of $Li(CF_3SO_3)$ PEG_{10} and $Li(CF_3SO_2)_2$ PEG_{10} that follow the Arrhenius type behavior whereas the ionic conductivity follow the VTF relation. Analysis of mixed cation belongings in PEO_9 Zn_1xCu_x $(CF_3SO_3)_2$ polymer complexes have been analyzed by Giua et al. (Giua et al., 1996). Senadeera (Senadeera et al., 1996) have carried out ionic conductivity studies on poly (ethylene imine) phosphate. Roger Frech and Sangamithra Chintapalli (Frech and Chintapalli, 1996) (Chintapalli and Frech, 1996) have observed the effect of propylene carbonate (high dielectric constant) as a plasticizer in PEO-$LiCF_3SO_3$ polymer electrolytes.

The preparation of glass-polymer composite electrolytes for lithium batteries and the electrochemical properties have been reported by Jaephil Cho and Melli Liu (Cho and Liu, 1997). Effect of benezenesulfonate group (S) and PEO molecular weight on the bulk ionic conductivity have been analyzed by Kaorilto (Ito, Tominaga and Ohno., 1997).

Acosta and Morales (Acosta and Morales, 1997) studied the synthesis and characterization of polymer complexes for solid state magnesium batteries. Kovac et al. (Kovac, Gaberšcek and Pejovnik, 1998) reported the electrical and electrochemical properties of (PEO)n $M(SO_3CI)_x$ (M=Li, LiAI, Ca) polymer electrolytes. Yoshika Zu Nakai et al. (Nakai, Ito and Ohno., 1998) investigated the ion conduction mechanism in polymer electrolytes prepared by terminal-charged PEO derivatives. Plasticized polymer electrolytes are new versatile receptor materials for the gas sensors (VOC monitoring) and electric noses (odor identification / discrimination) which were reported by Buhlmann (Buhlmann et al., 1998).

Heitner (Heitner, 2000) have inspected the search for getting the better polymer electrolytes. Jacob and Arif (Jacob and Arof, 2000) reported the FTIR studies of polymer electrolytes based on plasticizer polyvinylidene fluoride with DMF as plasticizer. The transport properties and microstructure of gel polymer electrolytes was reported by Capiglia (Capiglia et al., 2000). Polymer complexes of ethylene oxide-epi chlorohydrin copolymers have been analyzed by Gazotti (Gazotti et al., 2000). Maria Forsyth et al. (Forsyth, Jiazeng and MacFarlane, 2000) have reported about the novel high salt content polymer complexes, based on high T_g host polymers. Lithium addition into Sn and SnSbx – based composite electrodes in solid polymer electrolytes was reported by Yang (Yang et al., 2000). Yoichi Tominaga et al. (Tominaga, Takizawa and Ohno., 2000) have described the effect of doped salt species on the ionic conductivity of PEO/sulfonamide salt hybrids.

PEO-carbon complex lithium polymer electrolyte has been studied by Appetecchi and Passerini (Appetecchi and Passerini, 2000). Choi et al. (Choi, Kim and Shin, 2000) have reported about the ionic conductivity in PEO-PAN blend polymer electrolytes.

Naresh Kumar et al. (Naresh Kumar et al., 2001) studied the transport and electrochemical cell features of PVP : $NaClO_3$ polymer electrolyte systems. Various properties viz., Ionic conductivity, electro chemical stability of polymer composites based on PEO hyper-branched polymer, $BaTiO_3$ and Li_n $(CF_3SO_2)2$ have been examined by Takahito Itoh, Yosiaki (Itoh et al., 2003).

Following the initial innovation of Wright (Wright., 1975) (Wright, 1976), countless researchers synthesized PEO based Polymer electrolytes, for the reason that PEO resulted in crystalline complexes with lithium salts, the application of which is pioneered by Armand in batteries. The PAN-based lithium salt complex has many advantages like high ionic conductivity and good mechanical properties at room temperature when compared with PEO-based electrolytes. Abraham et al. reported a conductivity greater than $1x10^{-3}$ Scm^{-1} for PAN-based electrolyte at room temperature. Haung et al. made systematic studies on PAN-PC-EC-$LiClO_4$.The optimum conductivity was $2.5x10^{-3}$ Scm^{-1}, the transference number for a lithium ion is 0.36 and the compatibility with lithium metal is good (Huang et al., 1996).

In 1990, Abraham synthesized Polyacrylonitrile (PAN) based Lithium salt (LiClO4) electrolytes having ionic conductivities of the order of 10^{-5} S/cm and even higher at room temperature. The PAN based polymer electrolytes are ionically conducting and are plasticized-dissolved salt in a polymer matrix. The host polymer gives the mechanical strength and the plasticizer-dissolved salt allows the relatively high conductivity at ambient temperature. These systems combine the mechanical properties of polymers like low density, high flexibility, ease of fabrication etc. and the potential of high conductivity of liquid electrolytes. Many PAN based electrolytes are studied by way of co-complex or plasticizing to promote the ionic mobility. Different PAN based electrolytes with plasticizers like propylene carbonate(PC), ethylene carbonate(EC), dimethylformamide (DMF), dimethylsulfoxide(DMSO), Sulfolane (SL), γ-butyrolactone (BL) and their mixtures were synthesized by Wang and found to have conductivity of 2.5x10^{-3} Scm^{-1} (Wang et al., 1999). The main goal for which many researchers are working on polymer electrolytes for 3-4 decades (already mentioned in the historic perspective) is to develop such an electrolyte with high ionic conductivity at low temperatures. Polymer-in-salt electrolyte, combining good mechanical properties of a polymer and the high conductivity of a solid polymer electrolyte is attractive to the scientists in the R&D sector for the application in polymer lithium ion batteries. In all these polymer based electrolytes, the proportion of the salt is much higher than that of a polymer in a salt-in-polymer electrolyte. After years of research work, it was accepted that high conductivity and efficient transport mechanism associated with high degree of ionic aggregation is observed in polymer-in-salt electrolyte. The enhancement of ionic conductivity reflects on the dynamic connectivity effects in a phaseseparated electrolyte passing through a “smeared” percolation threshold. Wang et al. proposed a model for Polyacrylonitrile (PAN)/$LiCF_3SO_3$ electrolyte showing the connectivity percolation of the ionic clusters decoupled from the segmental motion of the bulk system (Wang et al., 2002). PEO based polymer electrolyte systems which include the solid type, the liquid plasticizer containing the Gel type and the filler containing the composite type were studied. In these electrolyte systems containing PEO-Li-X, the conductivity reached practically to a value of 10^{-4} S/cm only at temperatures from $60\text{-}80^{0}$ C. The highest room temperature conductivity was found to be $2x10^{-3}$ Scm^{-1}, for Gel type. Also, the studies on PAN based polymer electrolytes focused on the liquid plasticizer containing gel type that has a conductivity of 10^{-3} Scm^{-1}. PAN-$LiClO_4$ electrolyte formed at room temperature had a conductivity of $6.5x10^{-7}$ Scm^{-1} (Chen-Yang et al., 2002). Polymer electrolytes received great attention of research centers due to their potential application in energy sources such as lithium and lithium ion batteries. High operating safety, flexibility in cells and low weight of devices is provided by Polymer separators. In complexes of polyether with lithium salts, the lithium ion transport is connected with the segmental motion of polymer matrix. The salt anions do not undergo coordination via the basic centers in polymer matrix and thus their transport proceeds much easier. The main reason for the formation of polarization layers is due to the accumulation of anions in the near-electrode region which is unfavorable from the cell operation point of view. Completely immobilized anions occur in polyelectrolytes by chemical bonding with the matrix. Such salts show too low ionic conductivity for practical applications due to the low degree of dissociation (Monikowska et al., 2006). Solid Polymer electrolytes (SPEs) have their own applications in electrochemical cells and in electrochemical super capacitors. These solid electrolytes have many advantages over liquid counterparts as they are leakage-free, safe, light-weight and easy to synthesize in desirable thickness and area. The PEO-salts are extensively studied polymer electrolytes that show good mechanical properties and low ionic conductivity at room temperature (10^{-6} – 10^{-5} Scm^{-1}). As the conductivity is too low, they are not suitable for practical applications. The reason behind this is the weak interaction of anions. As the cations (Li^+) strongly coordinate with the polymer, they are not as mobile as the anions. The high degree of crystallinity hinders the ionic motion in PEO based electrolytes (Kumar, Hashmi and Pandey, 2011).

The purpose of this work is to investigate the structural, thermal and electrical properties of PAN+$LiBF_4$ based polymer electrolyte which is not taken in the literature as per our best knowledge.

Table: 2. 1: Summary of the literature survey quoting about the conductivity studies of different polymer electrolytes.

S. No	Host Polymer	Salt	Conductivity	Year	Reference
1	PAN blend with PMMA	$LiClO_4$	$5.64x10^{-3}$ Scm^{-1}	2013	(Kuo et al., 2013)
2	PAN blend with PEGME,PC	$LiClO_4$	$5.64x10^{-3}$ Scm^{-1}	2013	(Kuo et al., 2013)
3	PAN	$LiCF_3SO_3$	$8.62x10^{-4}$ Scm^{-1}	2011	(Ahmad, Md. Isa and Osman, 2011)
4	PVDF-HFP	LiTFSI	$1.64x10^{-4}$ Scm^{-1}	2009	(Wu et al., 2009)
5	PVDF, PAN blend	$LiClO_{4-}$ Lithium Cobalt(III) oxide	$7.8x10^{-3}$ Scm^{-1}	2008	(A.Iyenger et al., 2008)
6	PEO	$NaNO_3$	$4.7x10^{-7}$ Scm^{-1}	2005	(Anantha and Hariharan, 2005)
7	PAN	$LiClO_4$, $LiPF_6$,$LiBF_4$	$2.8x10^{-3}$ Scm^{-1}	2003	(Min, Ko and Kim., 2003)

CHAPTER 3

EXPERIMENTAL AND CHARACTERISATION TECHNIQUES

3.1. METHODOLOGY FOR EXPERIMENTATION

The complete methodology involved in the development and the characterization of the polymer electrolytes is represented in **Figure: 3.1.**

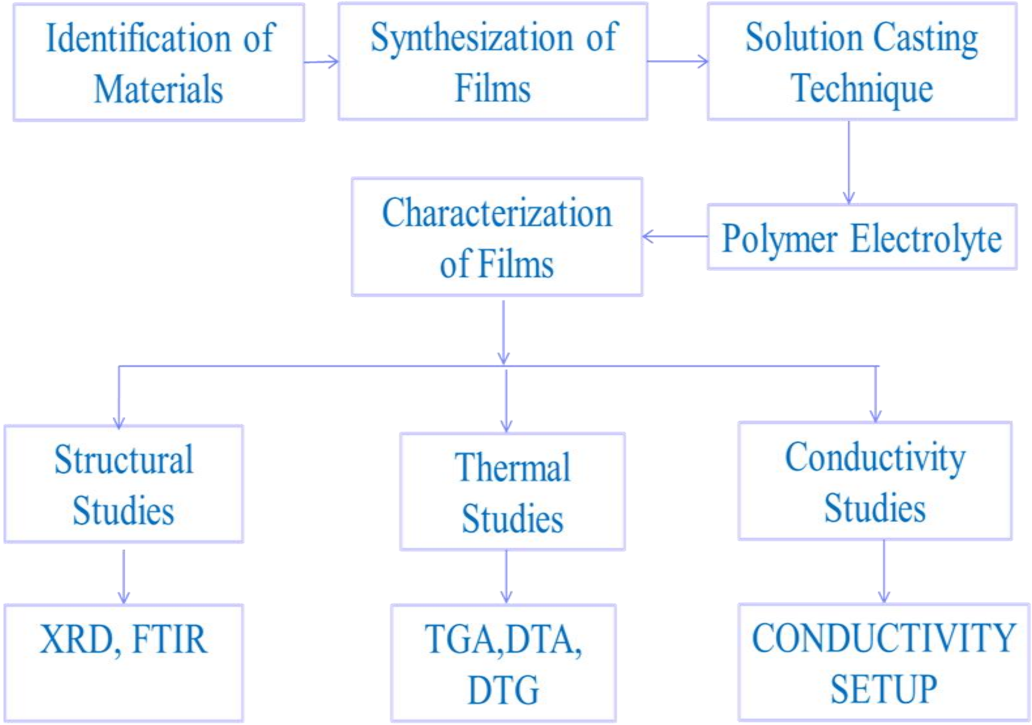


Figure: 3. 1: Flow Chart in the development and Characterization of Polymer Electrolytes.

3.1.1. IDENTIFICATION OF MATERIALS

The materials used in this work are selected basing on the physical properties as well as the basic requirement for the development of Polymer Electrolytes.

3.1.1.1. Basic requirements of polymers and the salt for polymer electrolytes

The basic necessities of the polymer and the salt for the development of polymer electrolytes are

i. Atoms or groups of atoms with adequate electron donor power to form coordinate bonds with cations.
ii. Low hurdles to bond rotation so that segmental motion of the polymer chain can take place freely.
iii. An appropriate distance between coordinating centers for the materialization of multiple intrapolymers ion bonds appears to be important.
iv. Low glass transition temperature to increase the segmental motion.
v. The polymer should be of amorphous phase which lowers the barrier for ionic movement and yields high ionic conductivity.
vi. The lattice energy of the salt should be low.
vii. High electrochemical reduction potential.
viii. The polymer host should have high electron pair donicity (DN) which measures the ability of the solvent to donate electrons to solvate the cations considered as a Lewis acid.

ix. The acceptor number (AN) quantifies the possibility of anion solvation. It should be less for an inorganic salt so that cationic salvation is high compared to anionic salvation.

x. The entropy term depends on the optimal spatial disposition of the solvating units which should be high for the polymer host.

3.1.2. SELECTION OF MATERIALS

3.1.2.1. Selection of Host Polymer

In the last couple of decades, researchers reported abundant work carried with polyethylene oxide (PEO) in the preparation polymer electrolytes. In all polymer electrolytes, the polymer acts as a stiffener for the low molecular weight, high dielectric constant and low viscosity plasticizer that solvate the salt in the conducting medium. Polyacrylonitrile, a homopolymer of acrylonitrile is selected as the host polymer in this study as the attention towards this polymer is not that much praiseworthy as other polymers viz PEO, PANi, PVA etc. The reasons are quoted below.

The fabrication of the polymer electrolyte from this polymer was difficult due to the insolubility of the polymer in common organic solvents that can also dissolve the inorganic Lithium salts. Though difficult, the same material was selected as this is mostly used in development of gel electrolyte studies (Ballard et al., 1990) (Watanabe et al., 1983) (Vincent and MacCallum, 1987), where conductivities are of the order 10^{-3} to 10^{-4} Scm^{-1} at room temperature are reported. The glass transition temperature of Polyacrylonitrile, T_g=85°C is one of the important parameter that signifies the spacing of nitrile groups which has an impact on dipolar interaction which effects the free volume that facilitates the segmental motion of the polymer chain at low temperatures that can promote the ion transport at the ambient temperature.

Most thought-provoking facts that engrossed to work on this polymer are

1. Semi crystalline polymer which is a thermoplastic material.
2. An enhanced ability to trap organic liquid electrolytes.
3. Suppresses the formation of lithium dendrites.
4. High cohesive energy density (CED=220-230 cal per cc).
5. Good mechanical strength.
6. Polar nitrile group that has high dipole moment.
7. Interaction of Nitrile groups results in high melting point, entanglement of chains, large stiffness etc.

3.1.2.2. Selecting the solvent or plasticizer or solvent cum plasticizer

A promising approach to enhance the conductivity of any polymer electrolyte is with the usage of low molecular weight organic solvents as plasticizers in a host polymer. This promising approach employs the smaller activation barrier for conducting ions in the plasticizer phase than in the polymer phase. The following factors are to be taken into consideration when solvents or plasticizers are selected (Sircar et al., 1993).

(i) Freezing point ≤ -40°C

(ii) Boiling point ≥ 175°C

(iii) Non-reactive to Lithium

(iv) Solvate Lithium salts

(v) Low viscosity

(vi) High dielectric constant

The details of the melting and boiling points of the solvent/ plasticizer used in this present work are presented in the **Table: 3.1** (Vincent and MacCallum, 1987)

Table: 3. 1: Physical Constants of DMF and NMP

Organic solvent/Plasticizer	Melting point(°C)	Boiling Point(°C)	Dielectric constant(ε) at 25°C	Viscosity(cP)
DMF	-61	153	36.7	0.80
NMP	-24	81 / 10mm	32.2	1.65

NMP is having higher viscosity when compared with DMF and DMF is having high dielectric constant when compared with NMP. This infers that either of the two can be taken as a solvent or a plasticizer. The dielectric constant and viscosity of DMF is less than that of EC and PC. Lower dielectric constant favors more ion pair formation i.e. lower conductivity while the lower viscosity results in higher ion mobility i.e. higher conductivity.

In the present work, NMP and DMF are chosen as the solvent and plasticizer basing on the conductivity studies quoted for Gel electrolytes.

3.1.2.3. Selection of the salt

The literature reports about the development of many polymer electrolytes with different salts. But Lithium is the promising candidate for high energy density batteries because of the following reasons.

(a) It is the most electropositive among the various cations in the periodic table.

(b) It has high specific current capacity of 3860 Ah/Kg.

(c) It has very light weight and high electrochemical reduction potential. (Scrosati, 1994) (Ulaganathan, Nithya and Rajendran, 2012).

(d) Lithium salt is preferred so as to increase the amorphicity and to introduce conducting moieties into the polymer matrix. (Kuo et al., 2013)

Different inorganic salts employed as electrolytes Lithium tetrafluoroborate ($LiBF_4$), Lithium perchlorate ($LiClO_4$), Lithium hexafluoroarsenate ($LiAsF_6$), Lithium trifluoromethane sulfonate ($LiCF_3SO_3$). H.S. Lee (Lee et al., 1998) (Sun et al., 1998) (Lee et al., 2001) stated that by the addition of borate compounds, particularly those comprising strong electron withdrawing fluorine substituents, it is possible to achieve an increase in ionic conductivity of weakly dissociating salts in aprotic electrolyte solutions. This is one of the main reasons to select $LiBF_4$ as the salt for the present work.

3.1.2.4. List of chemicals

Chemicals used in the work are mentioned hereunder in a **Table: 3.2.**

Table: 3. 2: Details of the chemicals, Molecular weight, Density and Make

Name of the Material	**Chemical Formula**	**Molecular Weight (g/mol)**	**Density (g/cm^3)**	**Make with code number**
Polyacrylonitrile(PAN)	C_3H_3N	Avg MWt1,50, 000 53.06	1.184	ALDRICH (181315)
Dimethyl Sulfoxide (DMSO)	C_2H_6NO	78.13	1.10	RANKEM
1-methyl-2-Pyrollidone (NMP)	C_5H_9NO	99.13	1.03	SIGMAALDRICH (328634)Anhydrous 99.5%
N,N-Dimethyl Formamide (DMF)	C_3H_7NO	73.09	0.944	SIGMAALDRICH (227056)Anhydrous 99.8%
Lithiumtetraflouro Borate	$LiBF_4$	93.75	0.852	ALDRICH (244767)(98%)

3.1.3. SYNTHESIS OF POLYMER ELECTROLYTE FILMS

One of the major efforts in material science is to establish pure materials with well-defined structures where the presence of any defects is suppressed to a minimum. Various synthesis and processing methods are used according to the differences in the nature of the materials. In particular, the preparation of uniform films and crystals without defects is very important from the point of view of precise characterization and physical measurements. The materials thus prepared are characterized by spectroscopy and X-ray diffraction (Hotta, 1997).

Processing and Doping

The purification of polymers is certain and easy by good processability. There may be defects in polymers related to cross linking and networks which are difficult to dissolve. Then select proper or good solvent that softens only the soluble portions and insoluble defects will be left over. When the polymers acquire good solubility, the solution cast films can be synthesized in the conducting or doped form in a very striking method. This is done directly by casting the solution comprising of the doped polymer (Hotta, 1987).

3.1.3.1. METHODS OF POLYMER FILM PREPARATION

Polymer film is an emerging key technology, which will have a tremendous impact on many aspects of our life, environment and economy. Polymer film preparation can be classified as chemical and physical. There are various methods available to prepare polymer films. Some excellent reviews are available in the literature on the methods of preparation of good polymer films (Hass and Thun.,

1966) (Jackson, 1970) (Mana and Durow, 1987) (White, 1973). The preparation methods are given below.

i. Solution – casting method
ii. Thermal evaporation method
iii. Flash evaporation method
iv. Hot pressing method
v. Pyrolysis
vi. Film blowing
vii. Polymerization of monomer
viii. Gaseous discharge
ix. Sputtering

3.1.3.2. Solution-casting method

The best way to achieve the desired doping standard precisely is to go through the direct process casting of the doped polymer solution only as preferred quantity of dopant is involved in the process. Hence a homogeneous clear and transparent solution of the doped polymer confirms systematic or uniform doping in the subsequent cast films. The solution casting method is used as it is the best convenient method for the polymer electrolytes. Different methods have been employed to synthesize the films but found the solution casting method is the best suitable method for the polymer electrolytes.

Polymer electrolyte films are generally obtained by simple casting procedure. The polymer PAN is the host and $LiBF_4$ inorganic salts are dissolved in adequate reciprocate compositions in suitable solvents (e.g. NMP, Acetonitrile, Methanol, Ethanol, double distilled water, etc.). A small magnetic stirring bar (size: 1inch) was placed in a 50 ml round-bottom wide mouth flask. PAN and $LiBF_4$ both were dried under vacuum for 4-5 hours before stirring so that no moisture content will be present. Appropriate amounts of salt, polymer, solvents are weighed and introduced into the flask. Appropriate amounts of salt and PAN were separately dissolved in DMF and NMP respectively. During the stirring process, each flask was covered with a para film and heated up to 50°C for 24 hours approximately. Then the two solutions are mixed and further stirred at a temperature of 40°C for 24 hours until a homogeneous mixture was obtained. The homogeneous mixture was allowed to cool and was carefully put under observation for any un-dissolved, deposited or suspended particles. Then the solution was taken onto the glass petri dishes. Solvent was allowed to evaporate slowly at room temperature in a vacuum oven for a couple of weeks (Scrosati, 1988). Later on, the polymer film was carefully removed from the glass petri dishes without stretching and rupturing and further dried in a vacuum oven at 50°C for 48 hours. The thickness of the cast films was varying between 50 μm to 60 μm. As all these salts are highly hygroscopic, samples are stored in desiccators so as to avoid the films from the absorption of moisture. The schematic illustration of the preparation procedure of polymer electrolyte film is shown in **Figure: 3.2** and the flow chart for solution casting method is represented in **Figure: 3.3**.

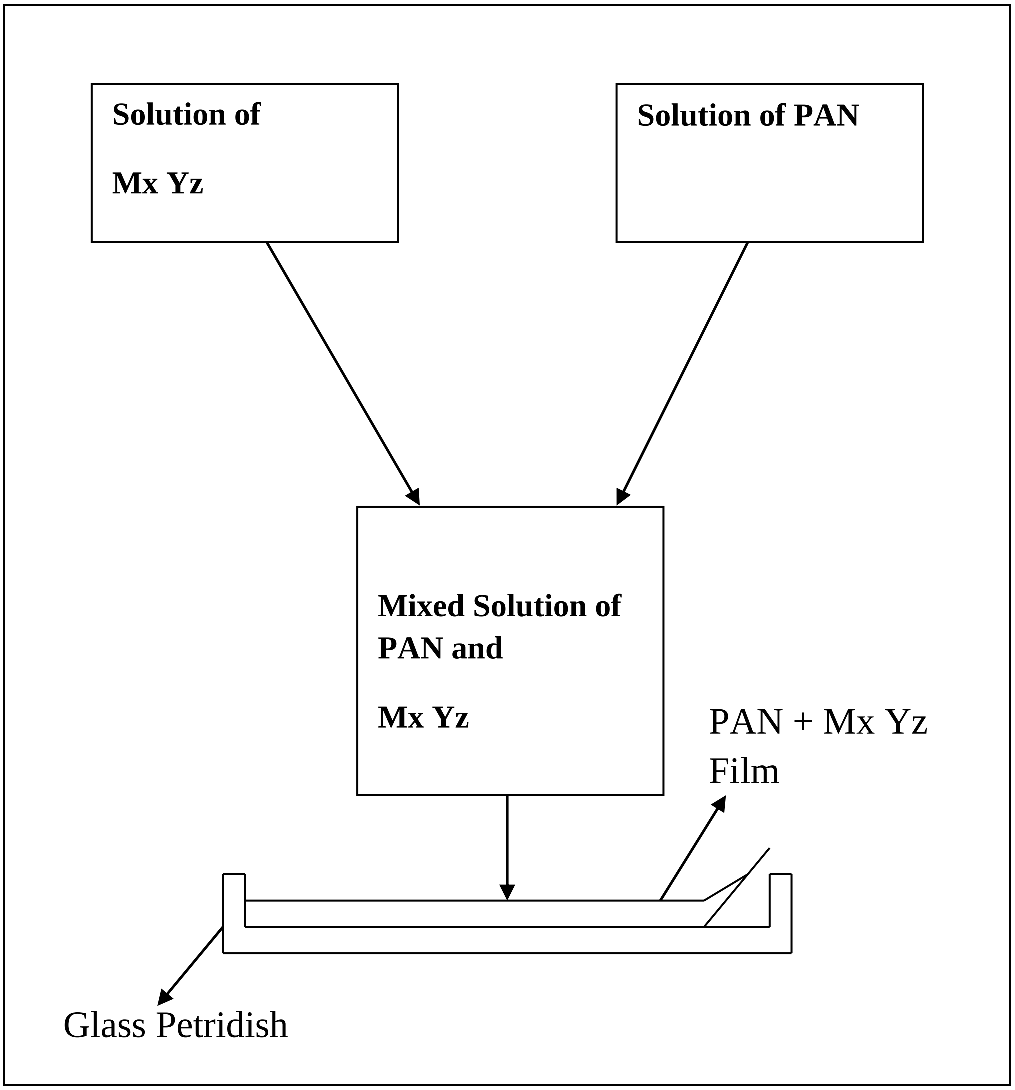


Figure: 3.2: Schematic design of the preparation procedure of polymer electrolyte film by solution casting method.

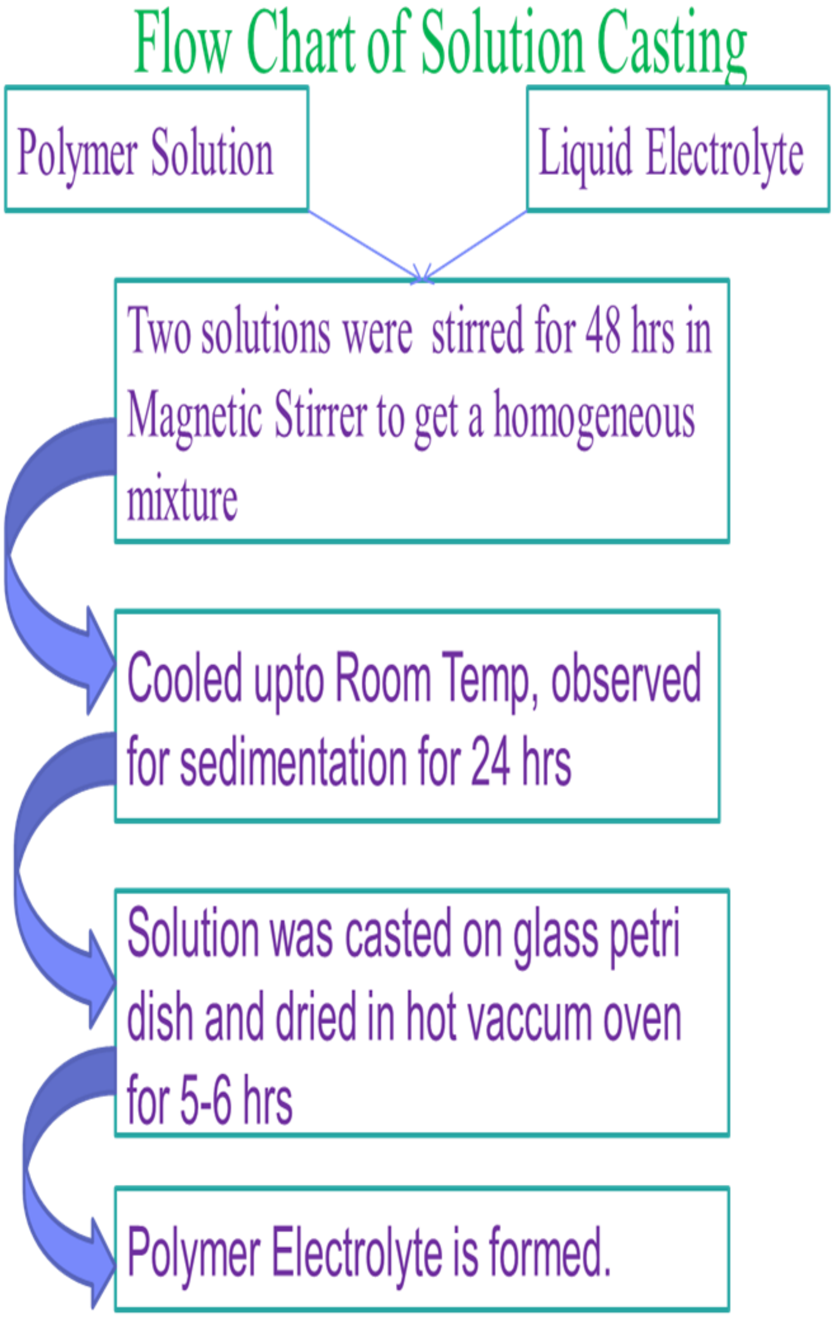


Figure: 3. 3: Flow Chart for the preparation procedure of polymer electrolyte film by solution casting method.

3.1.3.3. Characteristics of the Film

Abraham and Alamgir proposed the fundamental requirement of films (Abraham and Alamgir, 1993). The polymer electrolyte should be processed into a free standing thin film that can withstand the physical manipulation during the cell construction and cycling of secondary Lithium batteries. The strength requirement of these thin membranes is based on thickness which is a typical parameter that should be of the order of 50 to 60 μm. Thirty films of PAN/DMF/$LiBF_4$ were synthesized which were of different proportions. All the films are synthesized at the normal room temperature. The first set of six films was prepared by considering the host polymer and the solvent DMSO along with DMF as the plasticizer. The second set of other six films were synthesized with host polymer in solvent NMP along with plasticizer DMF. The third set of next six films was synthesized by taking the combination of the two solvents NMP and DMSO in the volume ratio of 1:1. The stability and the strength of the films were observed and basing on this, it was concluded that the mechanical strength of films with NMP as solvent and with polymer plasticizer (PAN+DMF) ratio 20:80 are relatively better. Hence the same combination is taken for characterization studies. The composition of different films synthesized for characterization purpose is quoted in **Table: 3.3**. The synthesized polymer electrolyte film obtained after drying the film for a couple of weeks. The film appears to be clear, transparent and flexible as shown in **Figure: 3.4.** It was observed that the mechanical strength of the films was not much remarkable due to the brittle nature.

Table: 3. 3: Polymer electrolytes with various compositions

Film	Composition
	PAN:DMF:SALT
A	20:80:0
B	19 : 78 : 3
C	19 : 76 : 5
D	18: 74 : 8
E	18 : 72 : 10
F	18 : 70 : 12

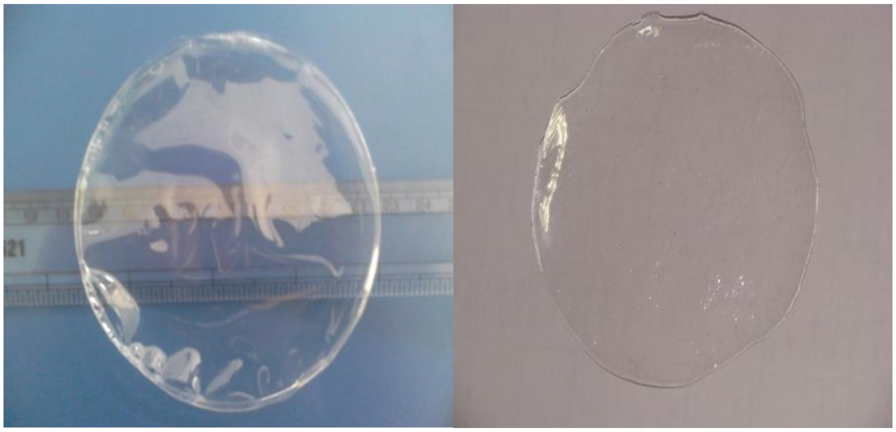


Figure: 3.4: PAN - $LiBF_4$ polymer composites synthesized in the Nanotechnology laboratory, University of Petroleum & Energy Studies (UPES), Dehradun.(Photograph of the Thin Polymer Films).

3.2. CHARACTERIZATION TECHNIQUES

All the samples synthesized are to be characterized using different experimental techniques to study about the structural, thermal and conductivity studies. The prepared materials are characterized for spectroscopic and structural features by FTIR and X-ray diffraction respectively that are closely connected with the electronic properties. The samples for different physical measurements regarding thermal (TGA, DTG and DTA) and conductivity studies are described subsequently. The flowchart demonstrating the characterization techniques is shown in **Figure: 3.5**.

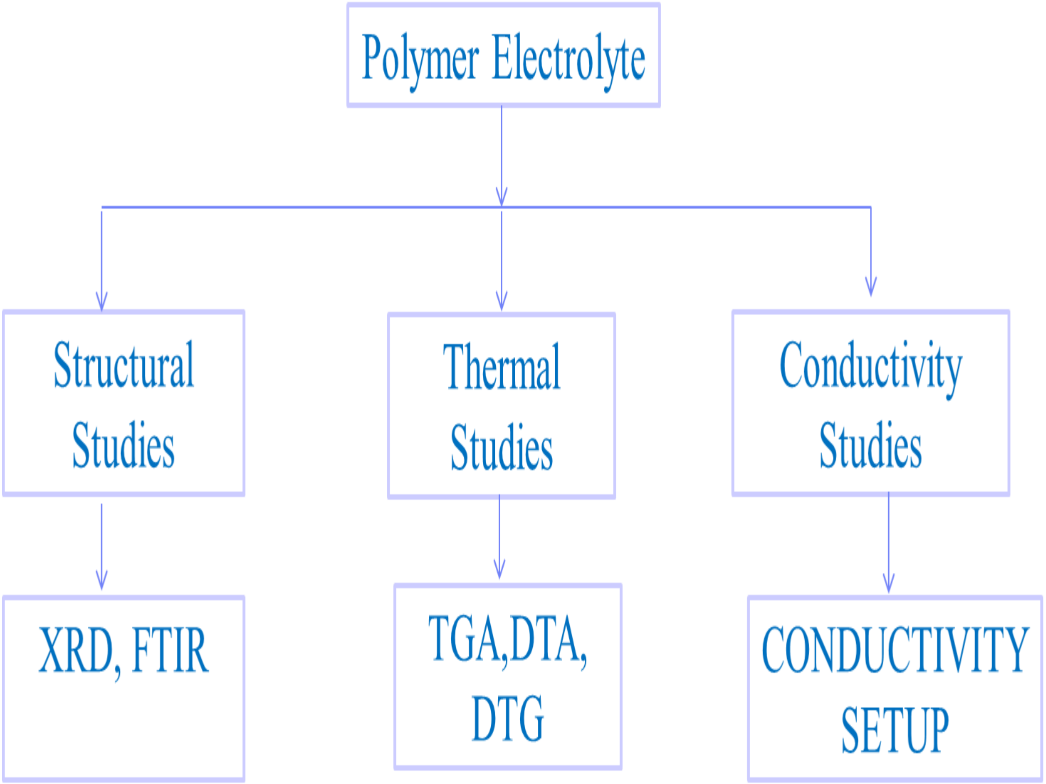


Figure: 3. 5: Flow Chart for the Characterization of Polymer Electrolytes**.**

3.2.1. X-RAY DIFFRACTION (XRD)

X-ray diffraction is the most powerful tool for determining the structure of solid matter and it finds wide ranging applications in material characterization particularly for

i. Identification of unknown substances
ii. Trace analysis
iii. Determination of crystal structure
iv. Phase analysis
v. Detection of crystal imperfection
vi. Layer thickness determination
vii. Determination of preferred orientation and crystallite size

X-ray diffraction is a non-destructive technique. The basic principle of the XRD is based on the Bragg's law which describes the condition for constructive interference for X-rays scattered from atomic planes of a crystal. The angle between the diffracted beam and the incident beam is always 2θ, and it is this angle, rather than θ, which is usually measured experimentally

$$2d\sin\theta = n\lambda \qquad \text{Eqn. } 3.1$$

Where λ is the wavelength of incident radiation and d is the interplanar distance between the lattice planes which is given by

$$d = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]^{-1/2} \qquad \text{Eqn. } 3.2$$

Where *h, k* and *l* are the indices of the lattice planes and *a, b, c* are the dimensions of the unit cell. From the above relations one can easily evaluate the lattice parameters when the values of d and corresponding values of θ (for fixed value of λ) are known (Cullity and Stock, 2001). We have used X-ray diffractometer, Bruker D8 Advance diffractometer as shown in **Figure :3.7**. The radiation (Cu Kα) emanating from the X-ray tube is diffracted at the specimen and recorded by a detector.

The specimen is rotated at constant angular speed in such a way so that angle of incidence of primary beam changes, while detector moves about the specimen at twice the angular speed. The diffraction angle (2θ) is thus always equal to double the glancing angle (θ). The beam path is shown in the **Figure: 3.6**. Whenever the Bragg's condition $2d\sin\theta = n\lambda$ is satisfied, the incident X-ray beam is diffracted at the specimen and reaches the detector. The detector converts the X-ray quanta into electron pulses, which are recorded by recorder. Monochromators are used to suppress the undesired portions of radiation. To restrict the irradiated specimen area, aperture diaphragm is arranged between the tube and the specimen as shown in **Figure: 3.6**. The second aperture diaphragm shields the strong scattered radiation of the first aperture diaphragm. The resolution depends upon the detector diaphragm. The undesired scattered radiations are suppressed by scattered radiation diaphragm.

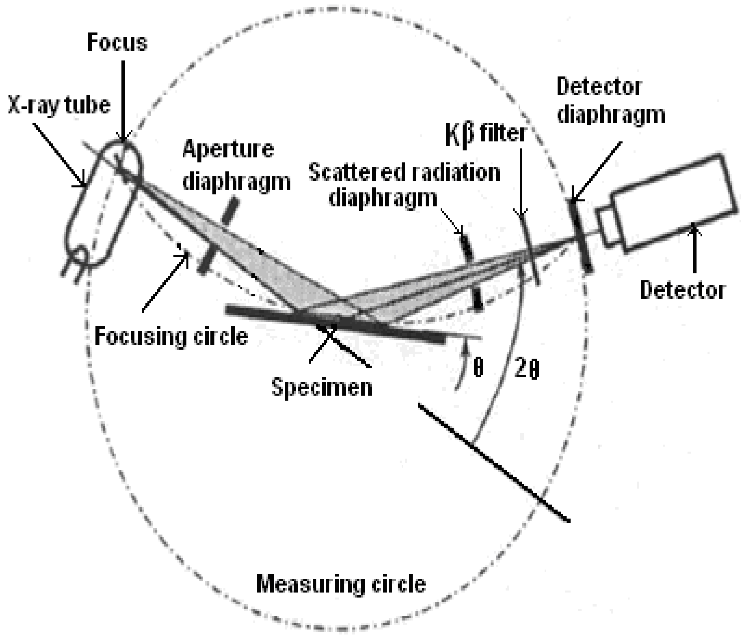


Figure: 3. 6: Schematic diagram of beam path.

The crystallographic information is obtained by evaluating d values and indexing of reflections. The characteristics diffraction pattern of a given substance can always be obtained whether the substance is present in pure state or as one constituent in a mixture of several substances. This fact is the basis of the diffraction method of chemical analysis. X-ray diffraction pattern is characterized by a set of line positions (2θ) and a set of relative intensities (I). The angular position of lines depends on the wavelength of the incident ray and spacing (d) of the lattice planes.

The technique can be used for quantitative analysis in which the concentration of phases are calculated by determining the area of the peak, since the intensity of diffraction lines due to one constituent of a sample depend upon the concentration of that constituent in the sample specimen. The qualitative analysis for a particular substance is accomplished by identification of the pattern of that substance. For nano crystalline materials, the crystallite size is an important parameter, which can be determined from the width of the Bragg reflection and is given by the Scherrer formula, Eqn. (3.3) (Cullity and Stock, 2001).

$$l = \frac{0.9\lambda}{B\cos\theta_b} \qquad \text{Eqn. (3.3)}$$

where '*l*' is the length of the crystal in the direction perpendicular to the reflecting planes, '*B*' is the full width at half maximum (FWHM) of the Bragg reflection in the radians on the 2θ scale and 'θ_b' is the Bragg reflection angle. It is important to subtract the instrumental line width from the observed line width to get a correct estimate of broadening due to small particle size. X-ray diffractograms of different polymer electrolytes were recorded at room temperature using an X-ray powder diffractometer (Bruker D8 Advance diffractometer) with Cu-K_α radiation (λ=1.5406 A°). The radial scans on the SPEs were performed in terms of 2θ (Bragg angles) range ($10° \leq 2\theta \leq 100°$) at a scan speed of 0.5° minute^{-1}**. Figure: 3.7** shows a Bruker D8 Advance diffractometer that uses NaI scintillation counter as a detector. It can detect the diffracted radiations in the wavelength ranging from 0.5 to 3 Å. The results are reported and discussed in chapter 4.

Figure: 3. 7: Photograph of Bruker D8 advance X-ray Diffractometer

3.2.2. INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy has widely been used for the identification of the functional groups in organic compounds because of the fact that their spectra are generally complex with numerous maxima and minima that can be used for comparison purpose. In fact, the infrared absorption spectrum of an organic compound represents one of its truly physical properties. The schematic diagram of a general instrument is shown in **Figure: 3.8**.

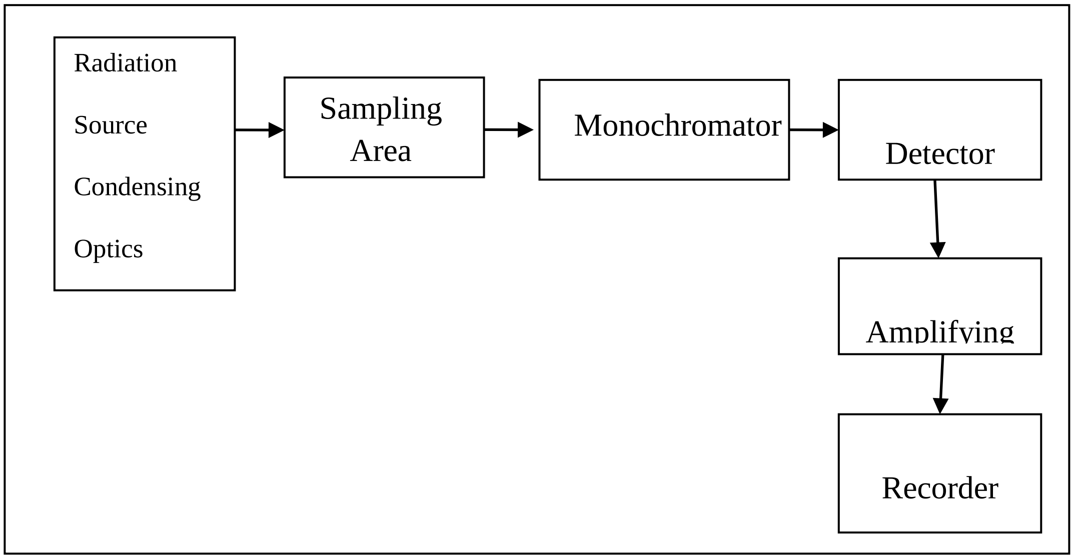


Figure: 3. 8**: Schematic diagram of a general infra-red instrument.**

From application and instrumentation point of view, the infrared region has been subdivided into three parts.

(i)	Near infrared region	14290 – 400 cm^{-1}	(0.7 – 2.5 μm)
(ii)	Middle infrared region	4000 – 666 cm^{-1}	(2.5 – 15 μm)
(iii)	Far infrared region	700 – 200 cm^{-1}	(14.3 – 50 μm)

In the present investigation, the infrared spectrum of polymer electrolyte films was recorded on a Perkin Elmer USA spectrum Two spectrophotometer in the wavenumber range from 450-4000 cm^{-1}. The experiments were performed in a dynamic nitrogen atmosphere, keeping an optical resolution of 0.2 cm^{-1} by averaging 64 scans per sample. The results obtained are reported and discussed in chapter 4.

The optical layout of Perkin Elmer spectrophotometer diagram is as shown in **Figure: 3.9.**

Figure: 3. 9: Perkin Elmer, USA spectrum Two spectrophotometer.

3.2.3. THERMAL PROPERTIES

The thermal analysis is the best method employed to study the thermodynamic parameters which are vital to understand the behavior of a material under different heating and cooling rates. This is performed under inert, reduction or oxidation atmosphere or under different gas pressures. The thermal analysis consists of group of techniques in which a physical property of a substance is measured with respect to a controlled temperature program. To determine the thermo-physical properties several commonly used methods are Differential Thermal Analyzer (DTA), Thermo gravimetric Analysis (TGA) and Differential Thermo gravimetry (DTG) (Klancnik, Medved and Mrvar, 2010). The thermal properties define about the thermal transitions of a polymer. The thermal transitions are the changes in the polymer when the polymer is heated. This thermal transition involves the phase transitions under different atmospheric influences, temperatures. The examples of the thermal transitions are glass transition temperature and the melting temperature of the crystalline polymers.

The TG, DTA and DTG measurements were implemented with EXSTAR TG/DTA 6300 at Institute Instrumentation Centre, IITR, Roorkee, as shown in **Figure: 3.10.** The thermal analysis was performed at a scanning rate of 10°C/min in a flux of Nitrogen gas at a rate of 200ml/min and in the temperature range from room temperature to a maximum of 800°C. The analysis was performed by taking Alumina powder as a reference material.

Figure: 3. 10: **EXSTAR TG/DTA 6300.**

3.2.3.1. Thermo gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is an analytical technique to determine a material’s thermal stability and its fraction of volatile components. This is done by monitoring the weight change that happens when the specimen is heated. The measurements are generally carried out in air or an inert atmosphere such as Helium or Argon, and the weight is recorded as a function of increasing temperature. At times, the measurements are made in lean Oxygen atmosphere (1 to 5% O_2 in N_2 or He). In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans(in DTA) or the heat flow into the specimen pan with that of the reference pan(in DSC).

3.2.3.2. Differential Thermal Analyzer (DTA)

Differential Thermal analysis (DTA) is one of the methods employed in thermal analysis that uses a reference. The specimen and the reference are heated in one furnace. The difference of the sample temperature and the reference material temperature are recorded during programmed heating and cooling cycles. DTA curve is a curve of temperature variation between the sample and the reference material versus time. DTA is mostly used for qualitative measurements like enthalpy measurements. DTA measures the deviations in temperature between the reference and sample and is transformed to enthalpy through a conversion factor. As DTA allows the sample mass loss during the measurement, this is considered to be best useful method for the materials with intensive decomposition (elastomers, exothermic materials etc) (Hohne, Hemminger and Flammersheim, 2003).

DTA curves can record the transformations where the heat is either absorbed or released (dehydration, decarbonation, burning of materials, ordering). DTA is useful for better understanding of results given by XRD, chemical analysis and microscopy (Rowland, 1952).

3.2.3.3. Differential Thermogravimetry (DTG)

DTG is used to analyze the major wt. loss% represented by the first peak, called as the maximum decomposition peak. This is the sharpest peak which indicates about the maximum weight loss at a particular temperature.

3.2.4. D.C. CONDUCTIVITY MEASUREMENTS

Block diagram of the conductivity set up is shown in **Figure: 3.11**.

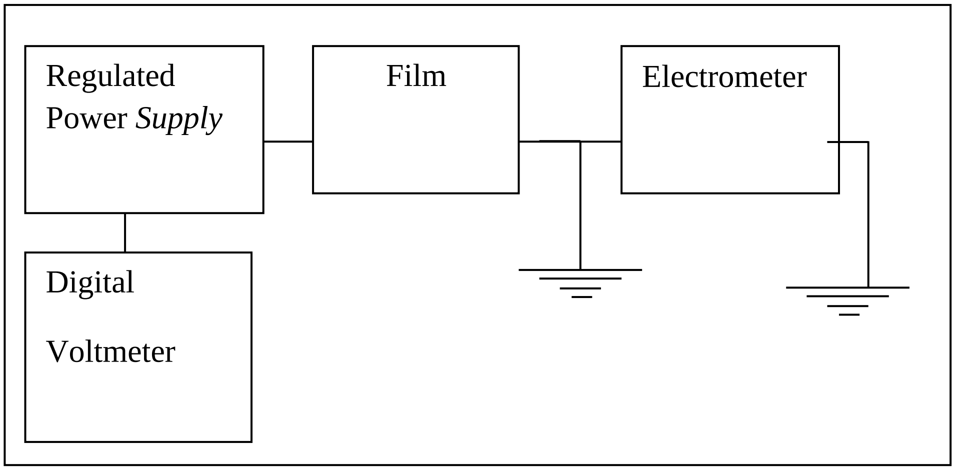


Figure: 3. 11: Block diagram of experimental setup used for conductivity.

Figure: 3.12 shows the sample holder fabricated and used for the conductivity measurements. It consists of two electrodes A and B (blocks of nickel), the lower one being circular one of diameter 2cm and the upper one being square of 1.2 cm^2 surface area. The lower circular electrode is supported on a single centrally placed “viterosil” cylinder of 2cms length. This viterosil is a good insulator even at high temperature. The lower end of the viterosil cylinder is fixed to the steel frame F. the upper electrode B is also fixed to the viterosil cylinder of length 2cms. The other end of the viterosil cylinder is inserted in a socket which sis the end point of a steel rod “R” of about 8cms length. This rod is arranged such 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 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. Two flexible chromyle wires are brazed into two nickel electrodes and are brought out of the furnace. The two leads are fixed to amphienel connections J_1 and J_2. 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 earthen and acts as a shield. The furnace is a resistance type furnace and consists of an alumina muffle of 30cm long and 10cm in diameter.

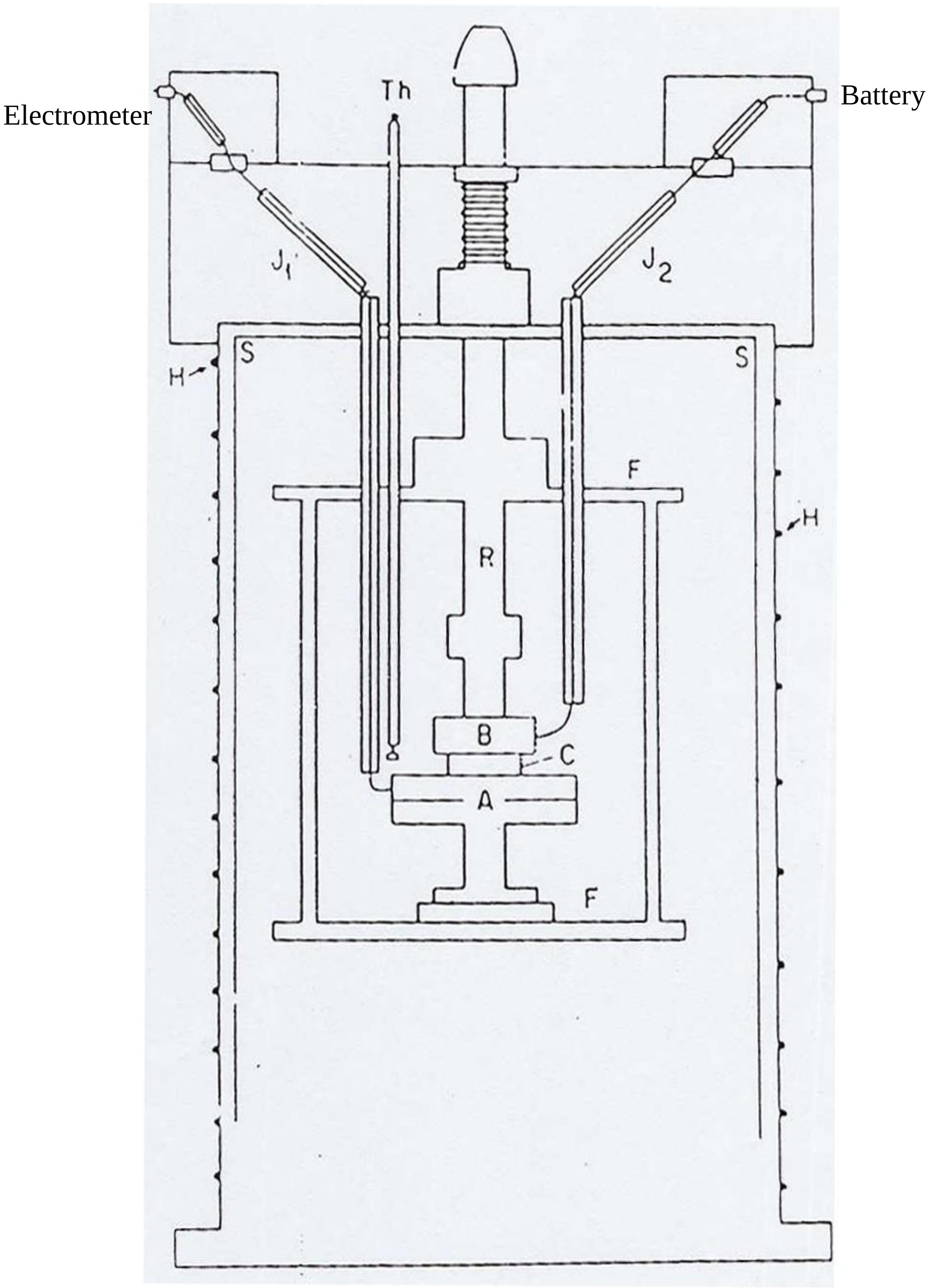


Figure: 3. 12: Ionic conductivity apparatus along with the conductivity cell.

The heating element is super kantholribbon, that is in the muffle furnace. The windings are such that the numbers of windings are maximum at the place where the sample is situated. The temperature of furnace has been controlled by a temperature controller. The outer surface of the furnace is covered with a metallic sheet which in turn is earthen in order to avoid pick up currents.

The stainless steel frame “F” hangs into the muffle furnace over a steel rod support. The points, which are connected to the electrometer is fixed to a perspex box as shown in the **Figure: 3.12**. The battery is arranged in a separate box. The box is thermally insulated. The temperature of the sample is measured by means of choromel /alumel 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. The polarizing effects during the measurements of D.C. conductivity were minimized by applying smaller voltages for a short interval of time and short-circuiting after every reading. The ion transport is measured by using this dc polarization technique, in which a voltage of 0.5 volts was applied across the cell configuration SS| polymer electrolyte|SS and the resulting current was monitored. The temperature of the sample was controlled by varying the ac current through the heater coil of the furnace. An earthened brass sheet is placed inside the muffle furnace around the conductivity cell, so that the temperature distribution around the sample is uniform. It also acts as a shield for strong pickups. The samples were heated slowly so as to avoid any thermal strains or shocks. The heating rate

Figure: 3. 13: Photograph of dc conductivity measurement setup at KL University, Vijayawada.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. STRUCTURAL STUDIES

4.1.1. XRD ANALYSIS

XRD studies provides a wide range of information on crystal structure, orientation, crystallinity and phase variations in materials including polymers, salts and complexes. This study is used in a perspective to identify or confirm amorphous, semi crystalline or crystalline nature of the material and the complex formation (Rajendran, Babu and Usha Rani, 2011).

The membrane morphology or the structural elucidation of the solid polymer electrolytes (SPEs) is accomplished by X-ray diffraction studies. The ionic conductivity of polymer separators is mainly determined by the amorphous nature of the polymer electrolytes. It is vital to define the phase of the polymer electrolyte either crystalline or semi crystalline or amorphous to study about the ionic conductivity. X-ray diffractograms of different polymer electrolytes were recorded at room temperature using an X-ray powder diffractometer (Bruker D8 Advance diffractometer) with Cu-K_α radiation (λ=1.5406 A°). The radial scans on the SPEs were performed in terms of 2θ (Bragg angles) range (10°≤2θ≤100°) at a scan speed of 0.5° minute^{-1}. The XRD pattern for all the polymer electrolytes doped with different concentrations is as shown in **Figure: 4.1.**

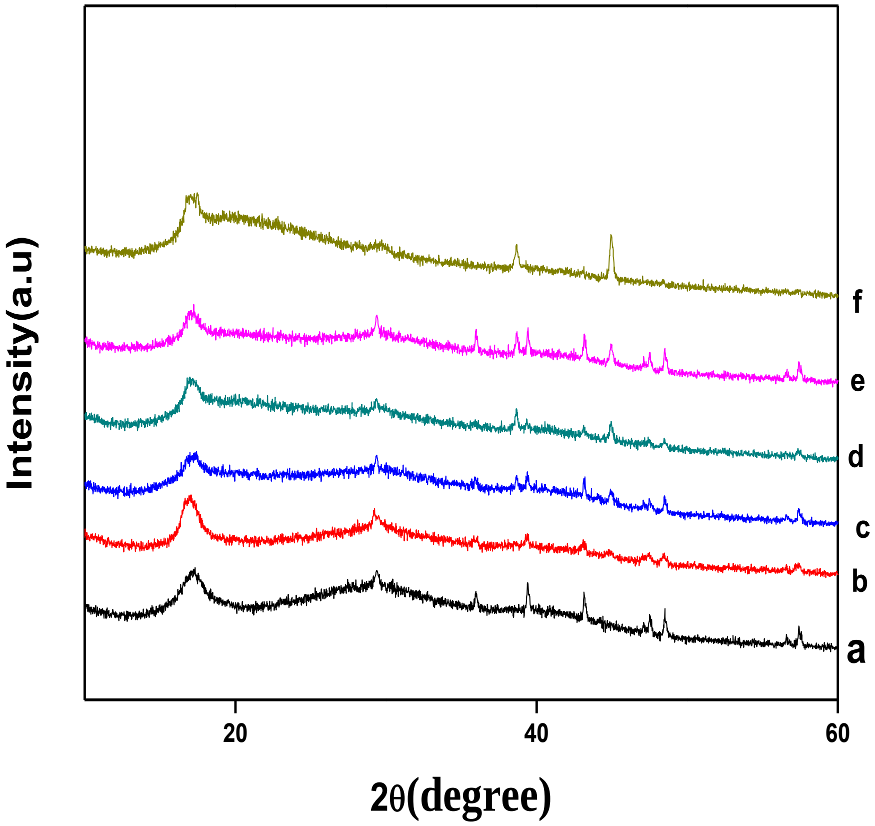


Figure 4. 1: X-ray diffractograms for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

The prominent diffraction peaks of pure PAN were observed at 2θ = 16.43 and 29.24° (Helan Flora, Ulaganathan and Rajendran, 2012). The diffractogram of PAN powder, exhibits a reflection peak at an angle approximately 2θ=17° corresponds to orthorhombic PAN [110] reflection with interlayer spacing, d=5.30 A° and d=3.05 A° for 2θ=29.5° respectively (Sawai et al., 2000) (Zhang et al., 2001) (Rajendran, Kannan and Mahendran, 2001). These two peaks corresponding to the respective spacing is associated with the hexagonal polymorph (Bashir, Church and Price, 1993). The XRD pattern of pure salt is taken from the standard XRD where the diffraction peaks are observed at 2θ = 14°, 21°, 23°, 26°, 28°, 32°, 39°, 44° and 55° (Ahmad et al., 2011) (Fahmi et al., 2012). The peaks pertaining to pure salt are not present in polymer complexes which indicate the complete dissolution of the salt in the polymer matrix. The complexes so formed are semi crystalline or amorphous as complexation is confirmed by the XRD studies (Ahmad, Md. Isa and Osman, 2011). The most prominent peaks in combined XRD pattern is summarized in **Table: 4.1.** Details of the films of different compositions are quoted in **Table :3.3**.

From the diffractograms, it is observed that there is the formation of a peak at an angle of 2θ=16.75° to 17.5° which is in correlation with the results quoted in the literature. This peak signifies the presence of host polymer in the porous polymer electrolyte. The intensity of this peak is revealing the crystalline nature. Hodge et al. defined a relationship between the height of the peak and the degree of crystallinity (Hodge, Edward and Simon., 1996).

Table 4. 1: Position of most prominent XRD peaks

Polymer electrolyte sample	Diffraction peak(P_1) 2θ (in °)	Diffraction peak(P_2) 2θ (in °)
a	17.33	29.08
b	16.93	29.50
c	17.33	29.08
d	17.33	29.50
e	17.06	29.43
f	17.46	38.6

It is observed that the intensity of the peaks is in general decreasing upon the incorporation of the salt. The crystalline regions are disturbed and there is an increase in the semi crystalline or amorphous nature in plasticized polymer electrolytes due to the addition of the salt. The diffractogram corresponding to 5 wt. % of salt concentration is broader and less prominent which confirms the semi crystalline nature (Helan Flora, Ulaganathan and Rajendran, 2012). With the addition of salt into the polymer, it is observed that the intensity of this peak is increasing and decreasing i.e. there is a fluctuation observed in the formed peak at 2θ=16.75° to 17.5°. The sharp peak is becoming a broad hump or flattened when the salt concentration is increasing. This indicates the semi crystalline nature of the membranes. The peak intensity is increasing for 3 wt. % salt concentrations salt which may be due to the undissolution of lithium salt. This infers that the degree of crystallinity is increasing. For 5 wt. % salt concentration, there is a decrease in the intensity of the peak. Followed by this, there is a small increase in intensity but the peak appears to be broadened. For 8 wt. % salt concentration, the curve appears to be totally flattened with a small peak and a broad hump. This indicates that the crystallinity is decreased. But due to the availability of a peak, it is confirmed that the polymer complex is showing semi crystalline nature. Subban et al. (Subban and Arof, 2003) inferred that there is a decrease of crystalline phase when the intensity of peak decreases along with broadening takes place. This suggests the existence of multiphase systems having crystalline complexed and uncomplexed polymer along with amorphous phase. Andreev (Andreev et al., 2005) clearly described that the polymer electrolytes can be crystalline or amorphous, not necessarily in amorphous phase above the glass transition temperature for enhancing the ionic conductivity. The XRD observations are not new and are quoted in PAN based literature (Kuo et al., 2013).

The sharp peaks and the relative intensity calculations clearly establishes about the semi crystalline nature of polymer salt complexes. Basing on the relative intensity studies from XRD patterns, it is inferred that there are no remarkable structural changes. The small peaks between $2\theta = 38\text{-}50°$ may be due to the noise present during the experimentation.

4.1.2. FTIR ANALYSIS

With the advent of Lasers, the accurate spectroscopic technique used to observe the vibrational modes of conjugated polymers (i.e. C=C) is Raman Spectroscopy. The material can be of any form like solution, powder or thin film (Kuzmany, 1990) (Zerbi et al., 1989). The alternate technique which is very close to Raman spectroscopy is Fourier Transform Infrared Spectroscopy (FTIR) (Potts, 1963). When there is an interaction between the molecular vibrations and infrared light, the infrared light gets absorbed. FTIR depends upon the interaction of the molecules oscillating dipole moment and the infrared beam's oscillating electric field vector (Conley, 1966).

One of the important parameters to attain high conductivity is the structural orientation, which leads to increase the hopping of cations. There are different methods to obtain orientation in the polymer chains. There is a factor called "f" which denotes the degree of orientation, which is given by Eqn 4.1(Shindo, Read and Stein, 1968)

$$f = 3\{(cos^2\,\theta)\text{av} - 1\} \qquad \text{Eqn 4.1}$$

Where "θ" is the angle between the axis of the chain and the direction of stretch and $(cos^2\,\theta)_{\text{av}}$ gives the mean value of all$(cos^2\,\theta)$, which is taken over all the chains in the samples. The calculation of average values of cosine from the line shape analysis was not possible due to uncertainties in the line shape intensity distribution at high angles 'θ'.

Fourier Transform Infrared Spectroscopy (FTIR) is an effective tool that analyses about the local structural changes in polymers. The infrared spectra of these materials change in accordance with the structure and confirms the complexation among the polymer matrices and interaction between different elements (Starkey and Frech., 1997) (MacFarlane et al., 1995) (Frech and Chintapalli, 1996) (Wang et al., 1996) (Forsyth, Meakin and MacFarlane, 1997) (Quist, Bates and Boyd, 1971).

FTIR is also used to identify the nature of bonding and different functional groups in the polymer complex by observing the vibrational energy levels of the molecules, which are the fingerprint of different molecules (Kuo et al., 2013). IR spectra were recorded with the help of a Perkin Elmer, USA spectrum Two spectrophotometer in the wavenumber range from 450-4000 cm^{-1}. The experiments were performed in a dynamic nitrogen atmosphere, keeping an optical resolution of 0.2 cm^{-1} by averaging 64 scans per sample.

Figure: 4.2. shows the IR spectra of all the polymer electrolytes in the wavenumber from 500-4000 cm^{-1}. The strong bonds were observed at 1450 cm^{-1}, 1720 cm^{-1}, 2245 cm^{-1} and 2945 cm^{-1} for C-H bending, C=O stretching, $C \equiv N$ stretching and C-H stretching respectively for pure PAN. The C=O peak was observed at 1650 cm^{-1} for DMF (Kim and Park., 2005). For $LiBF_4$, the vibrational peaks are observed at 1980 cm^{-1},1769 cm^{-1} and 1545 cm^{-1} respectively (Ramesh Prabhu, Sudalaimuthu and Rajendran, 2013). All the observed peaks are as per described in the literature.

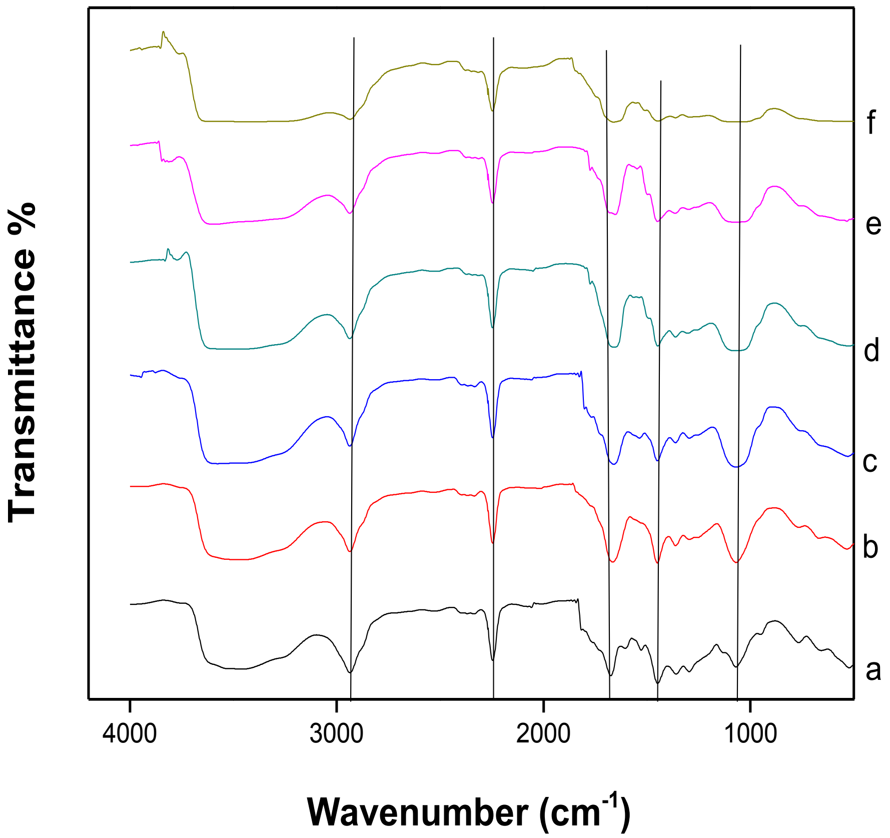


Figure 4. 2: IR spectra of polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

There are quite a few ways of interaction of Li$^+$ cations with $-\mathrm{C}\equiv\mathrm{N}$ groups.

(a) At least two $-\mathrm{C}\equiv\mathrm{N}$ groups in the same polymer chain can be coordinated with Li$^+$ cations or (b) The Li$^+$ cations may be intermingled by $-\mathrm{C}\equiv\mathrm{N}$ clusters of different polymer (PAN) chains or forms dissimilar micro crystallites. In these two, the former interactions are dominant as the Li$^+$ cations are coordinated by the solvent molecules partially and also partially by the $-\mathrm{C}\equiv\mathrm{N}$ groups in the same

PAN chain. In the latter, significant cross-networking effect is resulted, which results in the increase of viscosity (Park, Hong and Oh., 1996).

Figure: 4.3 shows the IR spectrum for Nitrile group for all polymer electrolytes. In the IR spectrum, the C≡N stretching band is the most important characteristic feature of the nitrile group that appears at 2245 cm^{-1} for pure PAN (Helan Flora, Ulaganathan and Rajendran, 2012) (Ramesh and Ng, 2011).

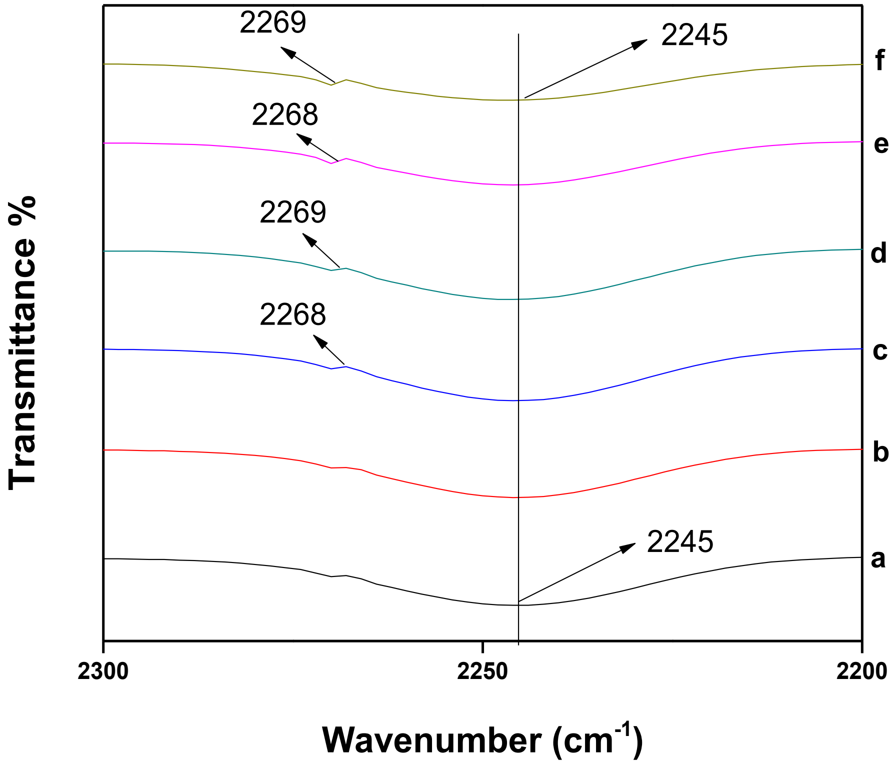


Figure 4. 3: IR spectra (**C ≡ N** stretching) of polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12

By the addition of salt of increasing concentration, a new hump is observed at 2268cm^{-1} in all the SPEs which is due to the inductive effect created by the interaction or coordination of N atom in $-\mathrm{C}\equiv\mathrm{N}$ with Lithium cations (Ramesh and Ng, 2011) (Osman et al., 2010). The most prominent feature was the presence of a weak but convinced bump at 2268 cm^{-1} on the higher frequency side of the symmetric $\mathrm{C}\equiv\mathrm{N}$ stretch mode observed at 2245 cm^{-1}. This represents the interaction between the salt and the polymer. This also shows that there is no interaction between the BF_4^- anion and PAN molecules (Huang et al., 1996). The superposition of the new shoulder at 2269 cm^{-1} reflects the interaction between Li^+ cations and $\mathrm{C}\equiv\mathrm{N}$ group which is in agreement with the analysis of the chemical structure of PAN. Li^+ cation has an empty orbital and nitrogen atom has a pair of unbound electrons. Therefore it is possible for Li^+ cation to form a bond with nitrogen atom of nitrile group to form an associate (Wang et al., 1999). It is also observed that the intensity of the absorption band at 2245 cm^{-1} is changing (especially with the SPE with maximum concentration, which is high) on the addition of salt with increasing concentration. This clearly shows the complexation of Polyacrylonitrile with that of $LiBF_4$. Appreciable change in intensity is not observed for all the SPEs. But the peak intensity is decreased for polymer electrolyte with 12 wt. % concentration when compared with other polymer electrolytes (Ahmad, Md. Isa and Osman, 2011). On addition of the salt, the relative peak intensity is increasing which is clearly observed in the higher concentration films. This is mainly due to the increase in the number of carrier ions (Kuo et al., 2013). At low salt concentrations, the characteristic frequency at

2269 cm^{-1} is not prominently observed. This can be attributed to the interaction between the Li^{+} cation and the plasticizer decrease the bonding chance between Li^{+} cation and the nitrile group of PAN (Kuo et al., 2013). **Figure: 4.4** shows the IR spectra for carbonyl group C=O of polymer electrolytes of PAN/DMF/LiBF$_4$. The C=O peak was observed at 1650 cm^{-1} for pure DMF and is observed at 1643 cm^{-1} as C=O stretching peak for a plasticized polymer electrolyte.

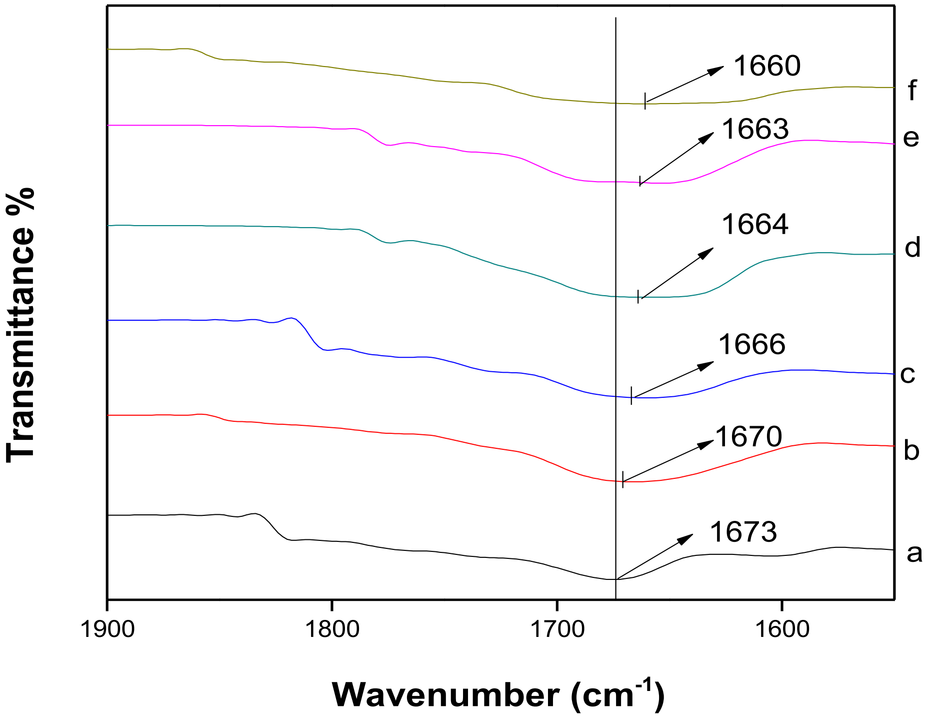


Figure 4. 4: IR spectra (C=O stretching) of polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

With the addition of salt into SPEs, it was observed that the there is a shift in wavenumber towards the lower frequency side. There was a decrease in the wavenumber from 1673 cm^{-1} to 1670 cm^{-1} with the addition of the salt and this decrease was continuous from 1670 cm^{-1} to 1660 cm^{-1} with the increase in the salt concentration from 2 wt.% to 12 wt. %. This shows the interaction of Li$^+$ cations with C=O molecules. The vibrational peak at 2935 cm^{-1} is assigned to asymmetrical stretching of C-H bond in PAN as represented in **Figure: 4.5.**

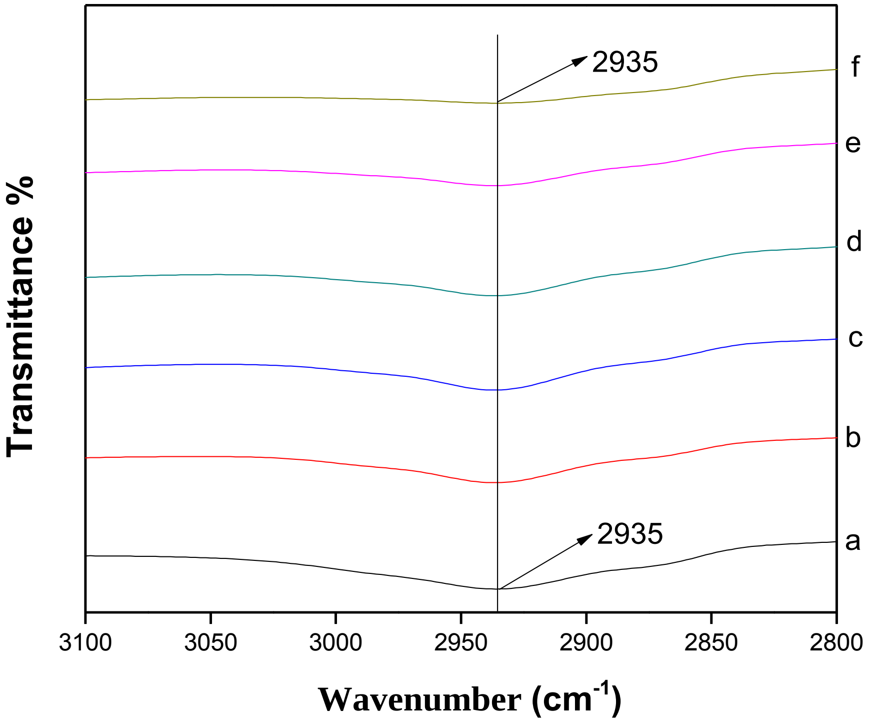


Figure 4. 5: IR spectra(C-H stretching) of polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Figure: 4.6 shows the IR spectra of polymer electrolytes with different weight ratio of PAN/DMF/$LiBF_4$ for C-H stretching and bending. Due to the change in the environment of BF_4^- anions, there is a shift in the frequency from 1450 cm^{-1} to 1448 cm^{-1} (Rajendran, Babu and Usha Rani, 2011).

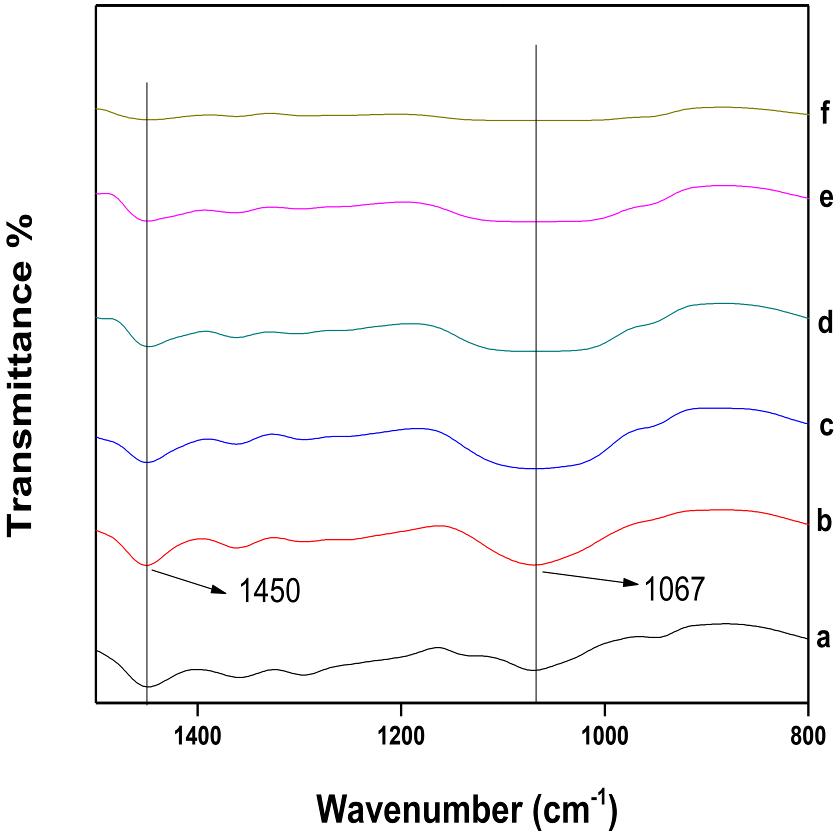


Figure 4. 6: IR spectra(C-H Stretching and Bending) of polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

The peak observed at 1067cm^{-1} is assigned to BF^{-} anion present in the plasticized polymer complexes. This peak serves as an indicator for the dissociation of the salt (Rajendran and Uma, 2000). The peak intensity doesn't exhibit considerable variation as the dopant concentration is increasing, which infers that certain quantity of salt was dissolved in the polymer matrix. This dissolution may lead to a limitation of the number of ions generated in the electrolyte (Noor et al., 2010).

FTIR studies show that the polymer salt complexation has taken place which is confirmed by the shifting of peaks or and also the formation of new peaks in polymer complexes. FTIR results indicate that the Li^{+} cations of dissociated salt are coupled with both the C=O group in DMF and the $\mathrm{C} \equiv \mathrm{N}$ in PAN, along with the dipolar interactions between DMF and PAN through C=O group and $\mathrm{C} \equiv \mathrm{N}$.

4.2. THERMAL STUDIES

4.2.1. INTRODUCTION

The Exstar TG/DTA 6300 Simultaneous Thermal Analyzer combines the flexibility of DTA with the abilities of the TG measurement technology, providing property evidence for a diversity of specimens. Both temperature and weight signals are measured simultaneously. Thermogravimetric Analysis (TGA) analyses about the weight changes in the material basing on temperature (or time) under a controlled atmosphere. The principal uses of TGA include the measurement of a sample's thermal stability and composition.

Differential thermal analysis (DTA) encompasses heating of a sample at a controlled rate up to a pre-determined temperature and matching any chemical emissions of heat (exothermic) or absorptions of heat (endothermic) from the specimen in comparison with passive material such as alumina. This is most suitable for defining the precise temperature at which a reaction occurs or recognizing a reaction product or phase change. The thermograms taken on the experimental setup are shown in **Figures 4.7-4.12.**

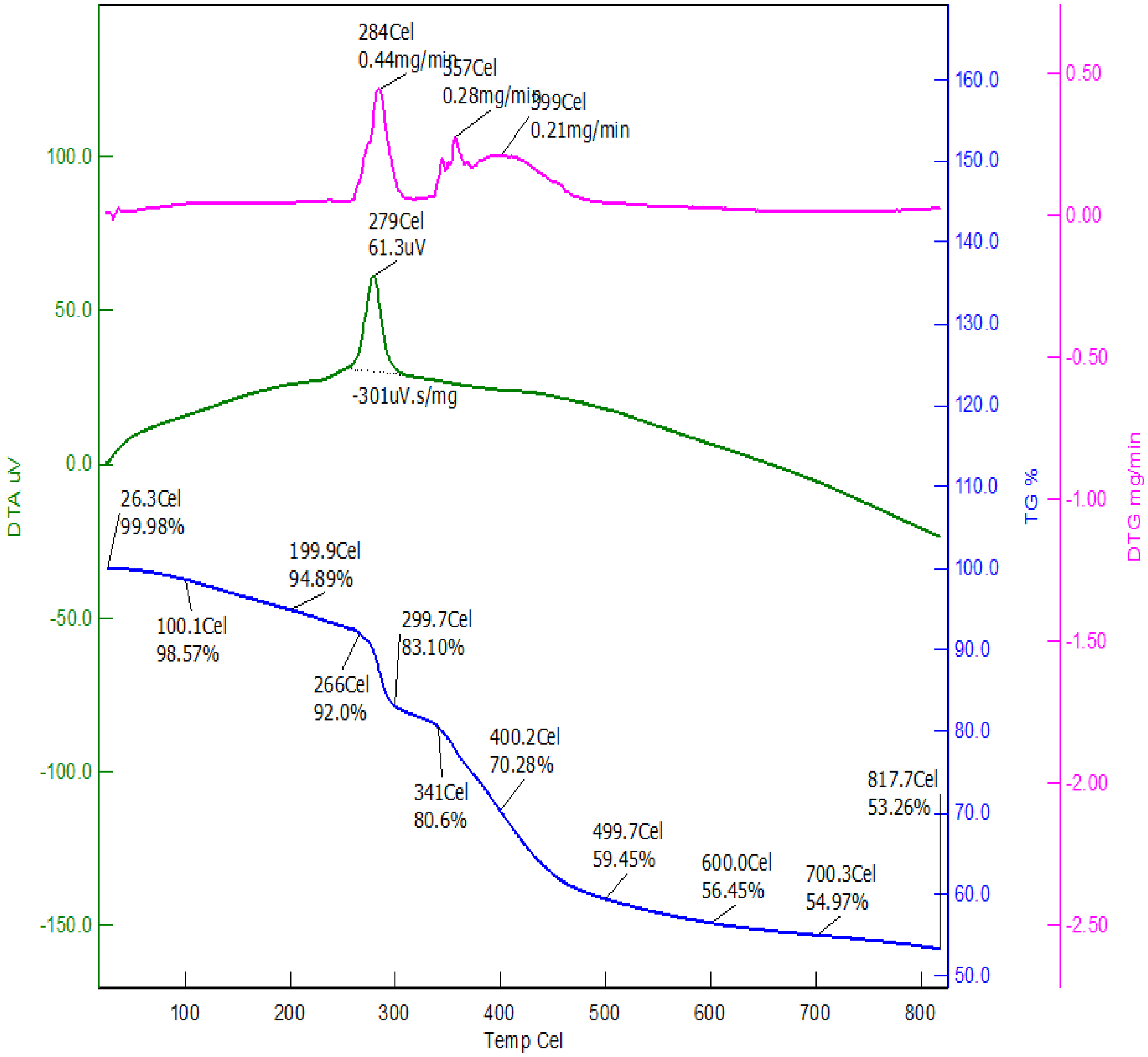


Figure 4. 7 : Thermogram for polymer electrolyte of PAN/DMF/LiBF$_4$ of weight ratio 19: 80: 00.

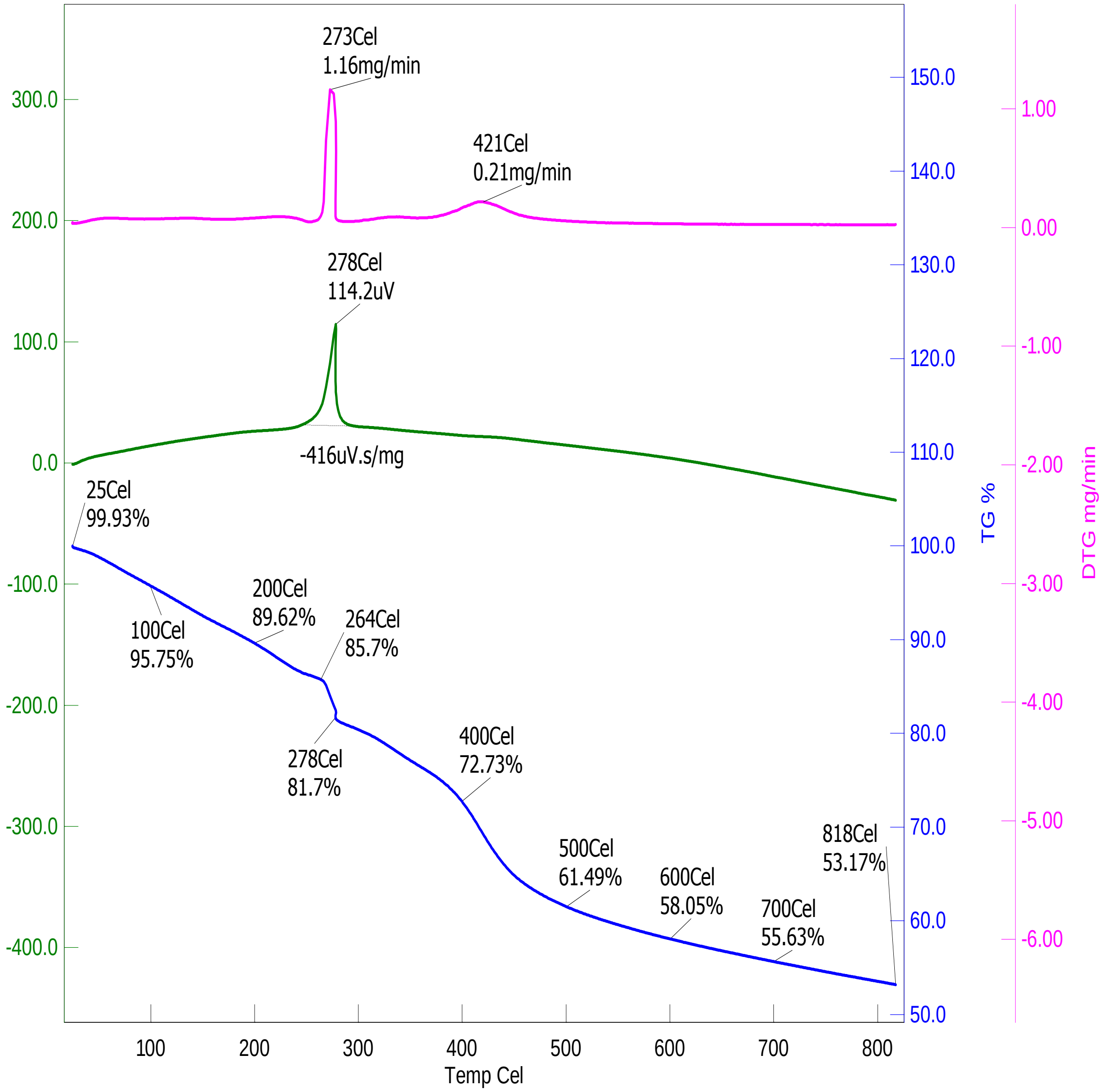


Figure 4. 8 : Thermogram for polymer electrolyte of PAN/DMF/LiBF$_4$ of weight ratio 19:78:03.

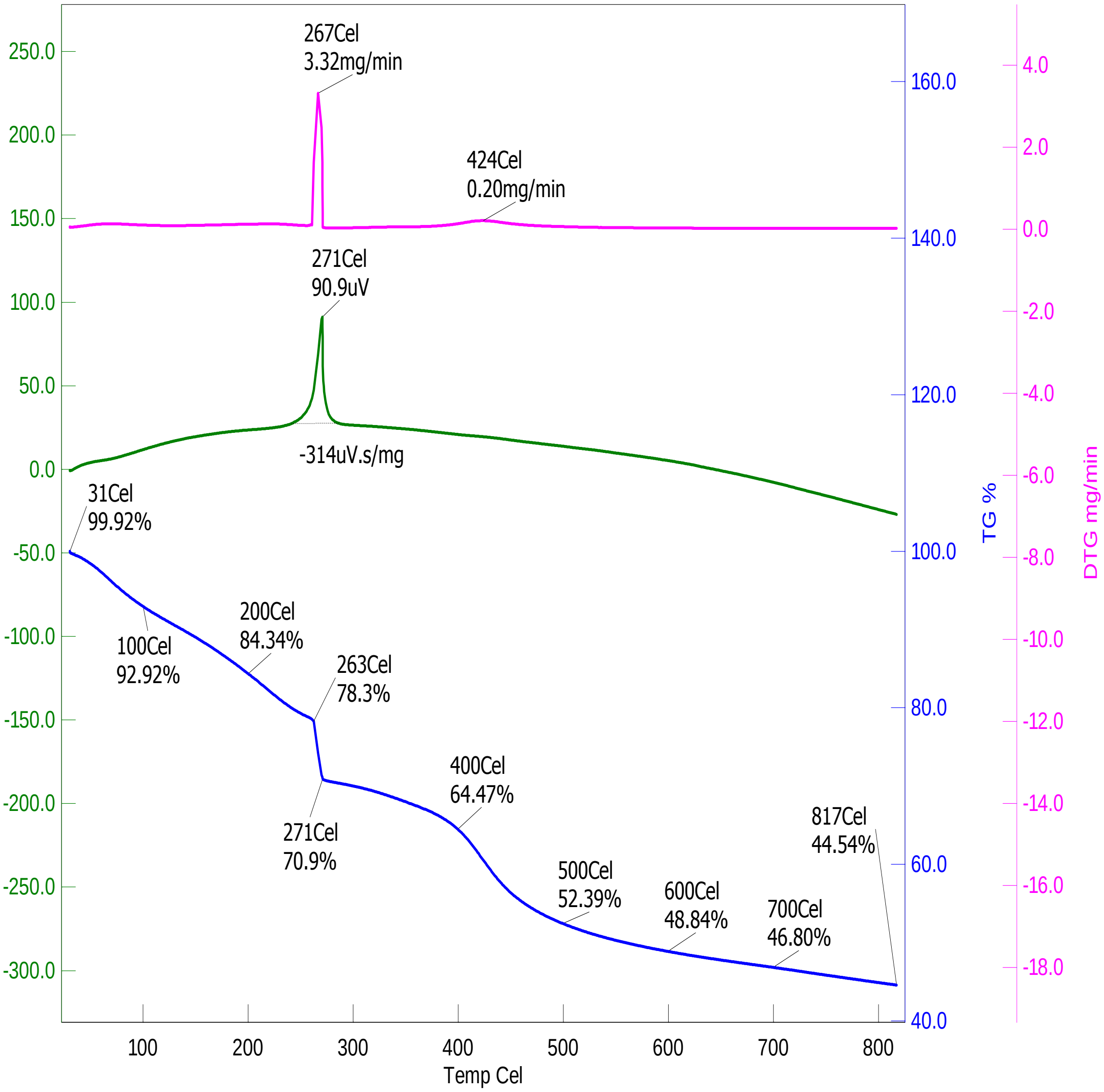


Figure 4. 9: Thermogram for polymer electrolyte of PAN/DMF/LiBF$_4$ of weight ratio 19:76:05.

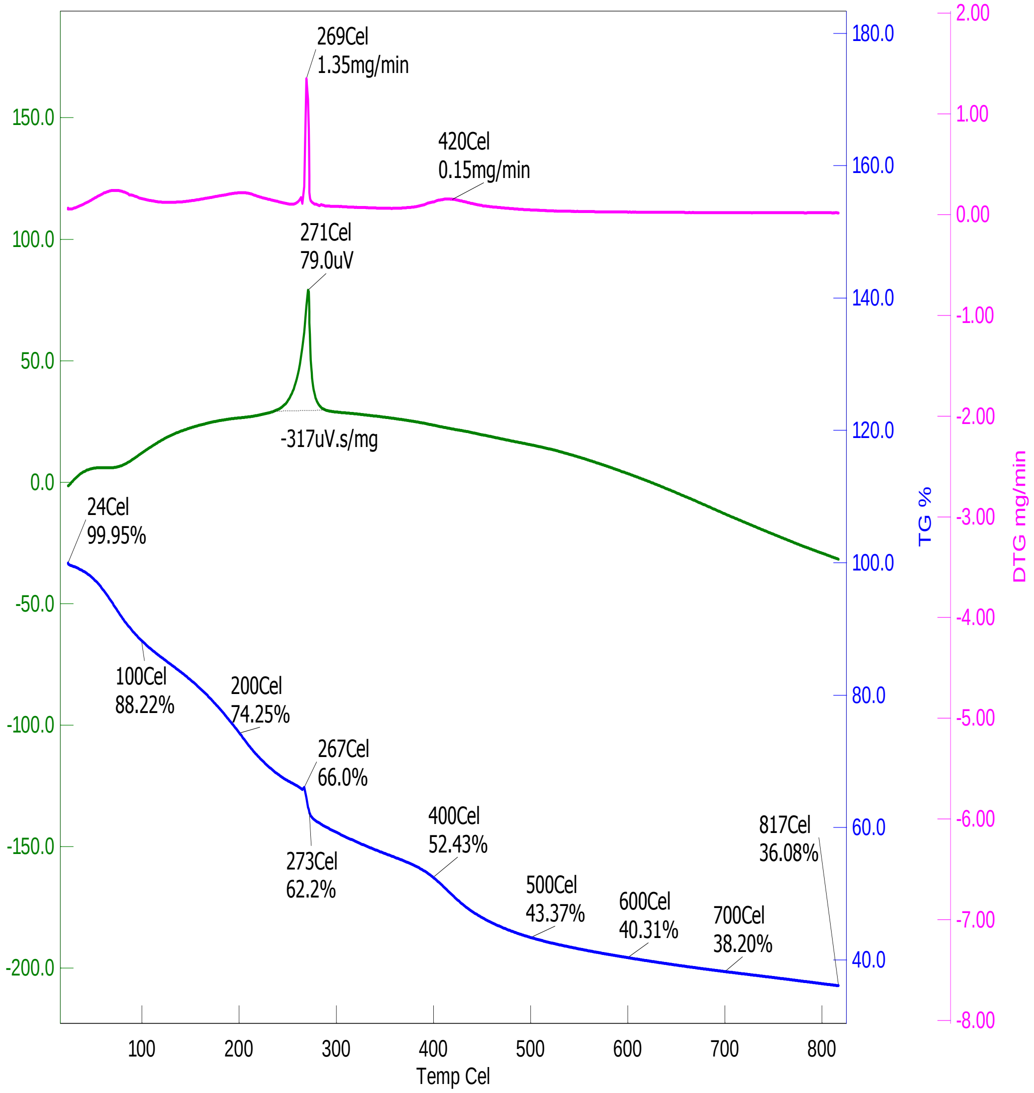


Figure 4. 10: Thermogram for polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:74:8.

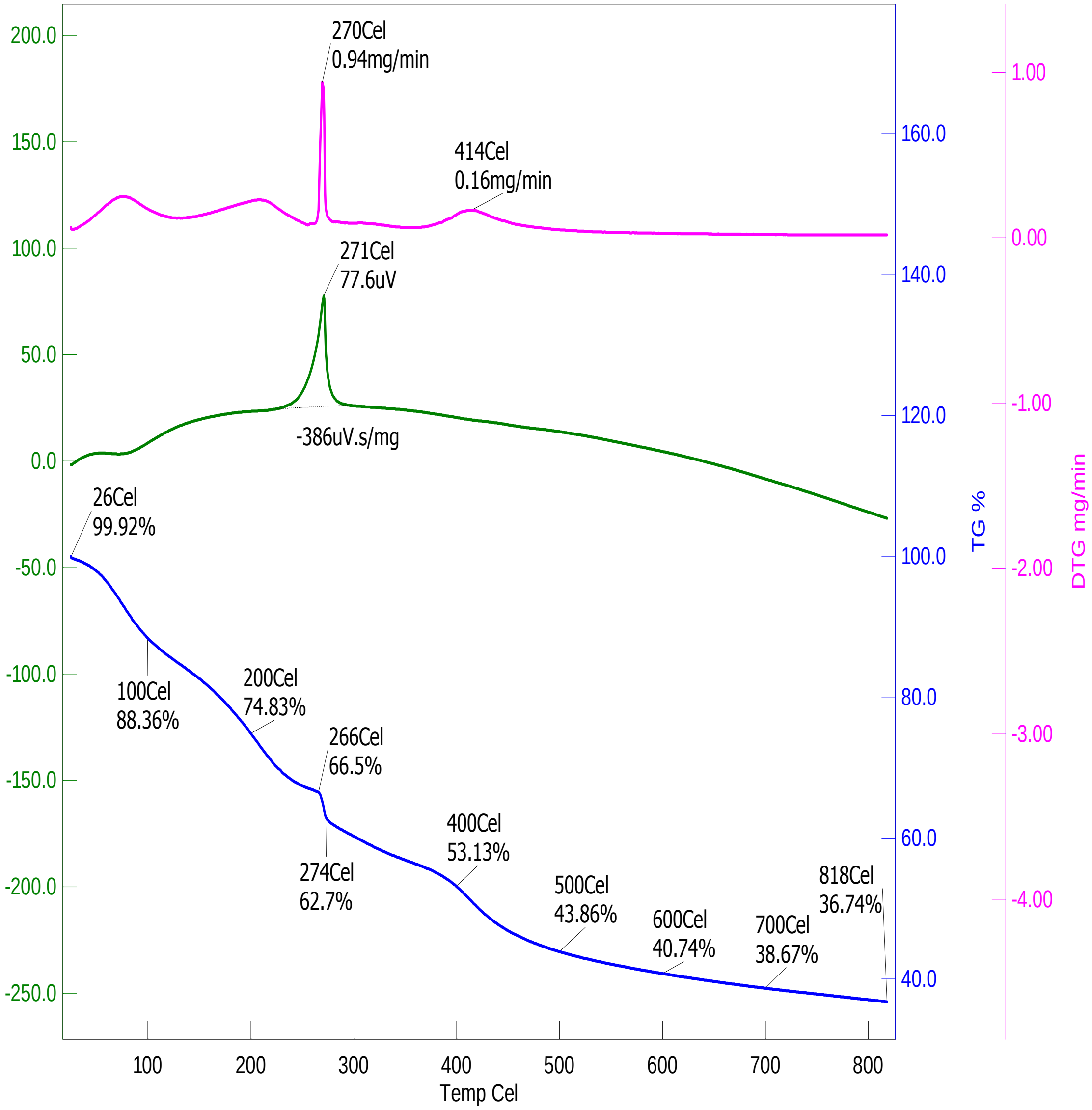


Figure 4. 11: Thermogram for polymer electrolyte of PAN/DMF/LiBF$_4$ of weight ratio 18:72:10.

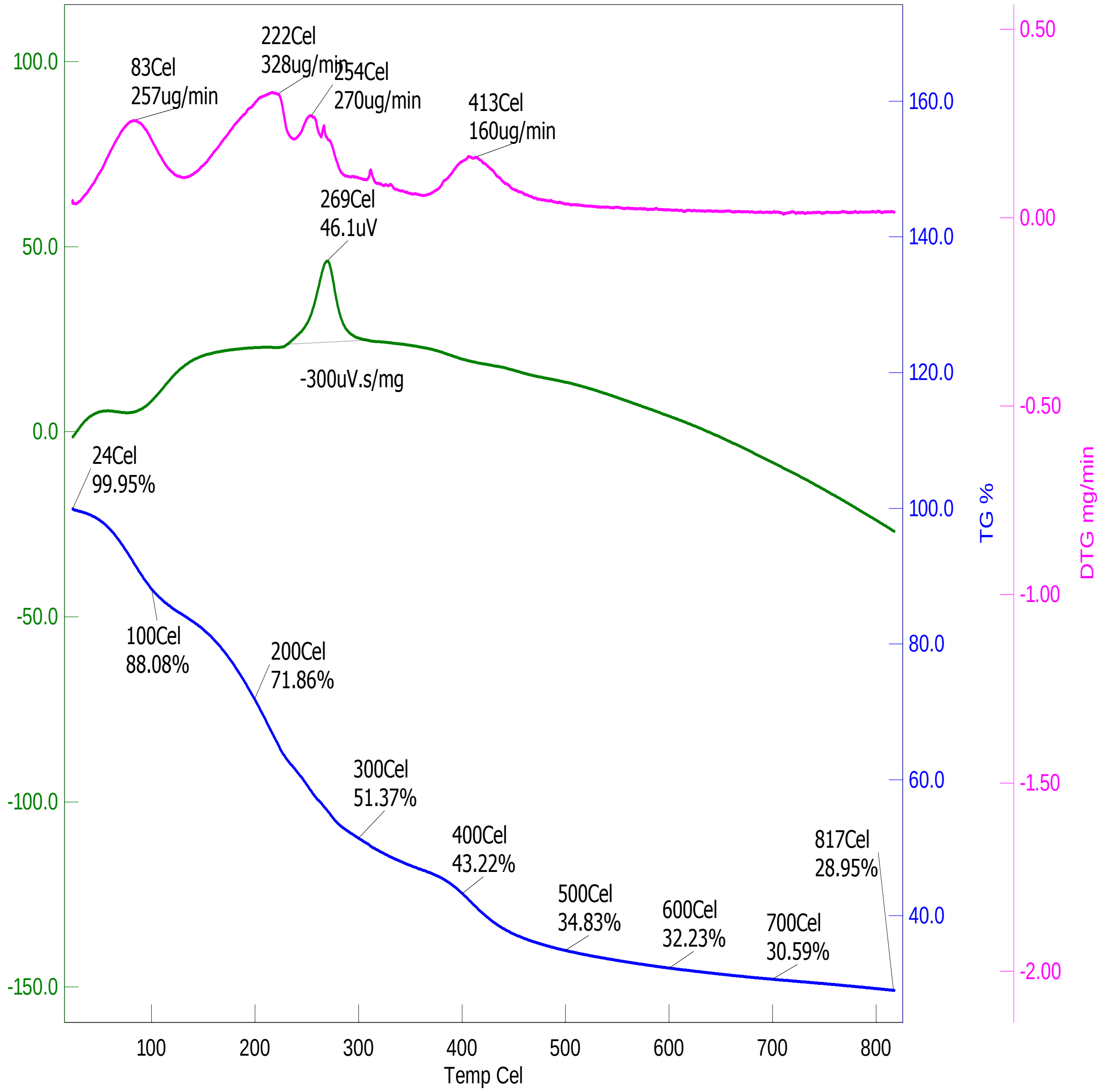


Figure 4. 12: Thermogram for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio 18:70:12.

4.2.2. TG ANALYSIS

Thermo gravimetric (TG) technique is used to study the variations in the physical changes come across in the polymer electrolytes. In TG, the initial present 100% decreases or undergoes degradation with increase in temperature. This is used to study about the thermal stability of the given polymer electrolyte. Thermo grams obtained for various polymer electrolytes with different doping percentages of $LiBF_4$ are shown in **Figure: 4.13.**

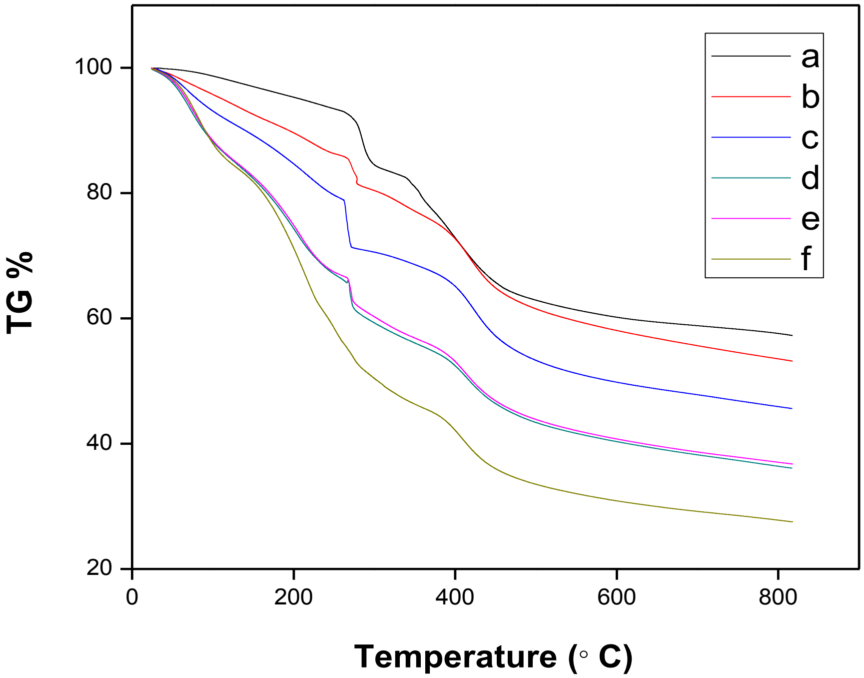


Figure 4. 13: TG curves for polymer electrolytes of $PAN/DMF/LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Thermo grams show that there is a gradual weight loss with temperature and it becomes 10 % when the sample reaches a temperature of 279°C when no salt is added. Further, the temperature by which 10 % weight loss occurred decreases with doping concentration i.e. for a SPE with 3 wt. % doping concentration, there is a 10 wt. % loss when the temperature is 194 ° C. All the temperature values corresponding to wt. loss % are tabulated in **Table 4.2**.

Table 4. 2: Variation of Temperatures vs. wt. loss % for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Film	Salt Conc (wt. %)	Temperature(in degree)				
		10 wt. % loss	20 wt. % loss	40 wt. % loss	50 wt. % loss	60 wt. % loss
a	0	279	345	486		
b	3	194	308	538		
c	5	138	241	427	559	
d	8	89	167	291	418	615
e	10	91	170	303	422	634
f	12	91	164	247	314	423

This may be due to the evaporation of the solvent present in the sample. From the variation in wt. % vs. temperature curves as shown in figures **4.14- 4.15**, it is found that all the films are thermally stable. Thermal Stability is represented by determining the weight loss % of the sample after heating over temperature from 30-800 °C using TGA.

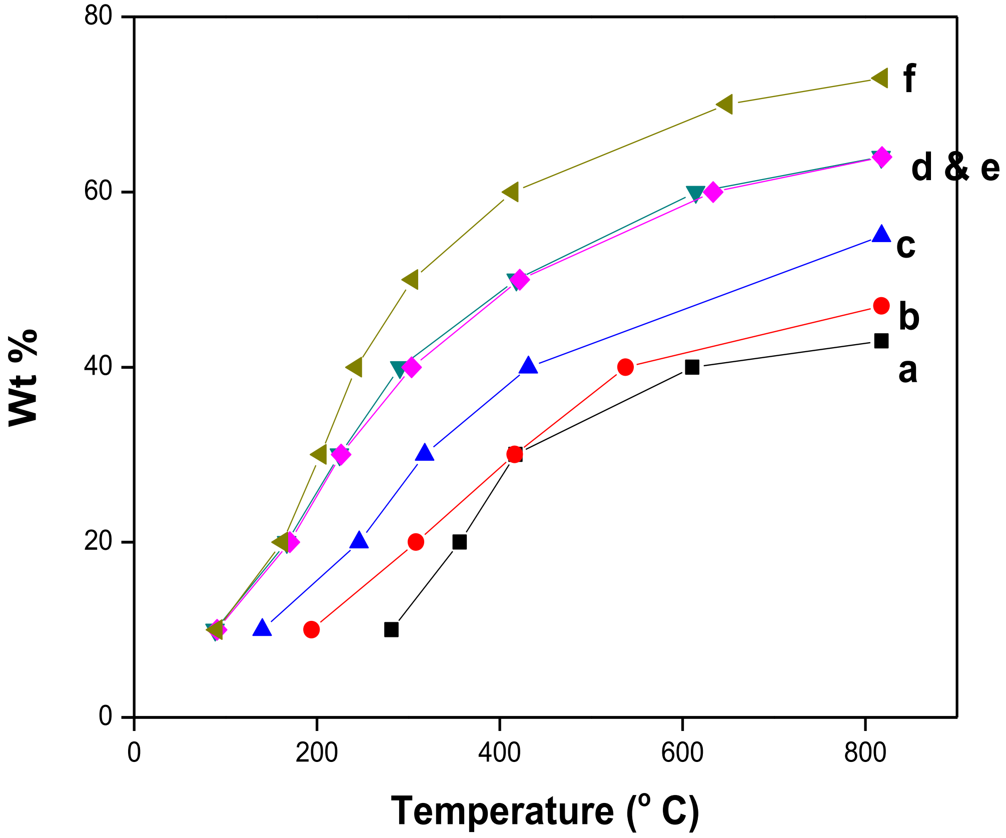


Figure 4. 14: Yield percentages from TG curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

It is observed that there is a gradual degradation in the polymer electrolytes. All the polymer electrolytes are stable up to 194, 138, 89, 91 and 91 °C with a net weight loss of 10 % as mentioned in **Table: 4.2** which implies that the films exhibit good thermal stability.

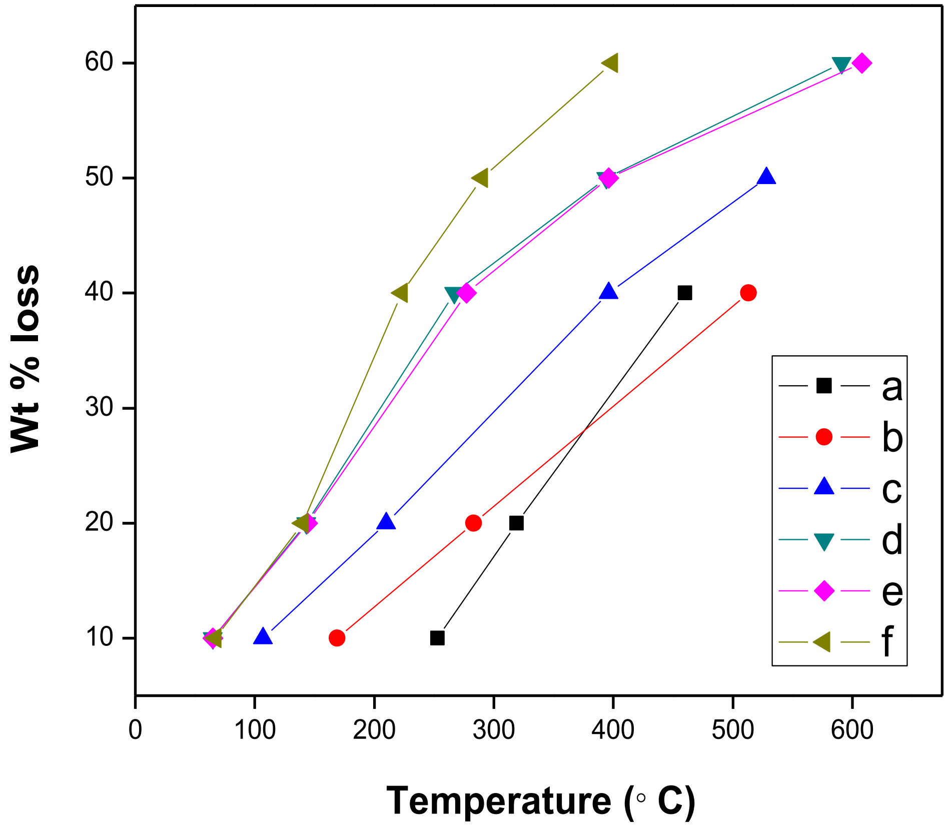


Figure 4. 15: Wt. % loss vs. Temperature curves for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

With the increase in doping weight percentages, it is observed that the temperatures corresponding to 10, 20, 40 wt. loss% (or 90, 80, 60 wt. % remaining) are decreasing up to 8 Wt. % of salt concentration. There is an increase in temperature for a salt concentration of 10 wt. % from 10 to 60 wt. loss %, then followed by a decrease for a concentration of 12 wt. % of salt from 20-60 wt. loss % but remains the same at 10 wt. loss%. The Residue or the Characteristic Yield is decreasing at temperatures approximately at around 800 °C. The temperatures corresponding to residual yield are given in **Table 4.3.**

Table 4. 3: Residue or Characteristic Yield with Temperatures for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Film	Salt Concentration	Residue or Characteristic Yield (In %)	Temperature(°C) Exact(approx.)
a	0	53	818
b	3	53	818
c	5	45	817
d	8	36	817
e	10	37	817
f	12	29	817

The polymer electrolyte with 8 wt. % of salt has low thermal stability when compared with other films. The films are stable up to 194, 138 and 89 ^{o} C for 2, 5 and 8 wt. % respectively with a gradual weight loss of 10 %. As the temperature at which 10 wt. % degradation happens is low, the thermal stability is low.

4.2.3. DT ANALYSIS

Different methods are to be mentioned when thermal stability is to be studied. The materials can also be classified as Thermosetting and Thermo plastic basing on these methods which are

1. Integral procedure decomposition Temperature (IPDT)
2. Thermal Kinematics(curing Kinematics)
3. Activation Energy or Decomposition of host polymer.

The materials that cannot be recycled are called as “thermosetting” and “thermoplastic” are the materials which can be recycled where curing Kinematics can be used. This happens during the thermal excitation which gives the idea of the nature of variations that the polymer electrolyte undergoes in different working atmosphere. This process encompasses the change in weight attributed to the moisture uptake and the corresponding thermal stability of the polymer electrolyte.

The thermo setting materials don’t have the melting temperatures as they are basically amorphous materials. But it is evident from melting temperature values observed from DTA studies that the host polymer, Polyacrylonitrile is a thermoplastic material. The melting temperature values of different polymer electrolytes are mentioned in **Table: 4.4.**

Table 4. 4: Glass Transition and Melting Temperatures from DTA curves for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Film	Salt Concentration (in wt. %)	Glass Transition Temp(°C)	Melting Temperature(°C)
a	0	-	279.57
b	3	-	278.38
c	5	56.58	270.72
d	8	62.10	271.38
e	10	66.89	271.21
f	12	67.94	269.84

From DTA curves shown in **Figures 4.16– 4.17**, it is difficult to observe the crystallinity peak because the crystalline hump will be formed well before the melting peak. If crystallinity is present then there could have been the formation of the peak in the downward (exo) direction, which is not observed in DTA curves. As the crystalline peak is not observed and it is not amorphous, the host material is found to be semi crystalline in nature which is even confirmed from the XRD studies.

The temperature at which the last bond of the polymer structure breaks is called as the melting temperature (T_m). This melting temperature can be defined from the DTA curves as shown in **Figure: 4.16**.

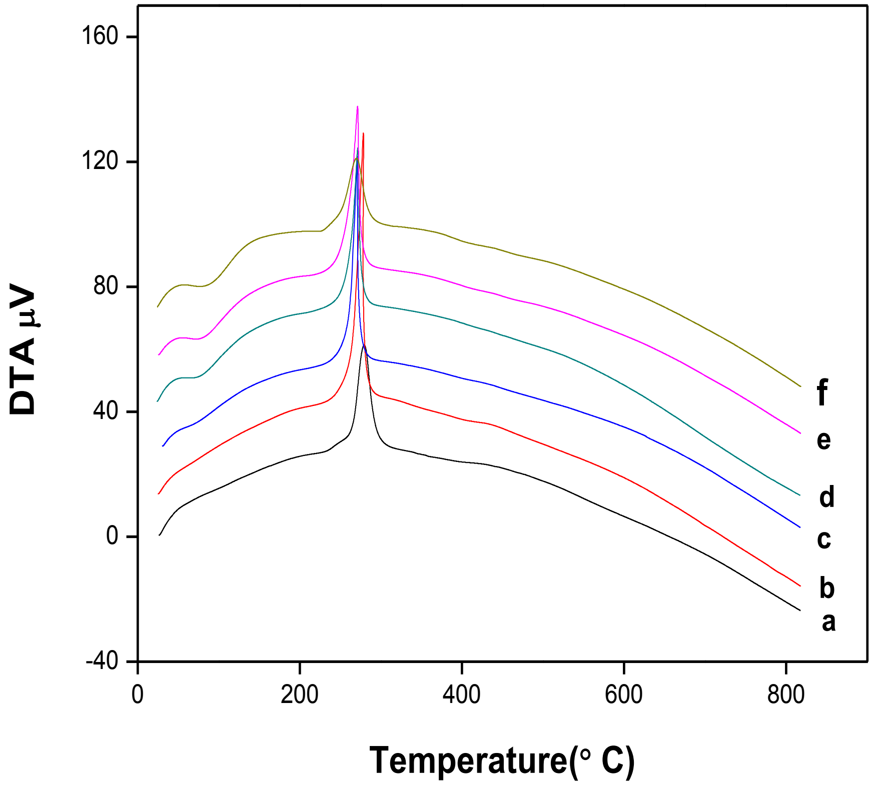


Figure 4. 16: DTA curves for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

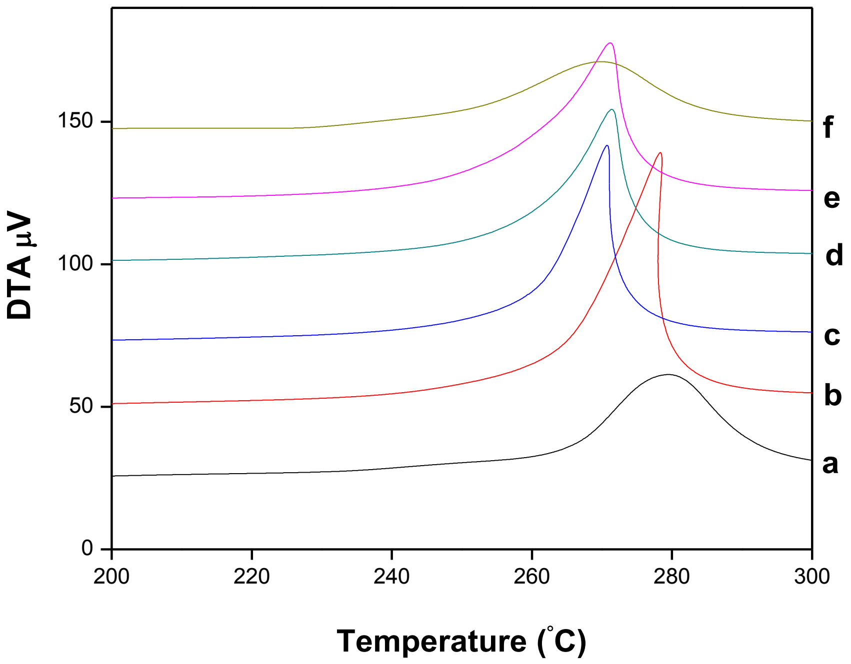


Figure 4. 17: Extended DTA curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

The temperature that corresponds to the sharp peak formed is the melting temperature. The melting temperature of the polymer complex without salt is decreased from the standard value of 317 °C to 279 °C. The melting temperature of the polymer electrolytes is further decreased with the addition of salt into the polymer. The addition of salt may be helping the decomposition process and may be activating the degradation, which infers that the thermal stability is decreasing as inferred from TGA, inturn implies that the thermal conductivity will also decrease accordingly.

The Glass transition temperature can be defined from DTA, but can be measured much more precisely from DSC. Pure PAN exhibits a glass transition temperature of 88.1°C (Jayathilakaa et al., 2003). The glass transition temperature is determined from DTA curves as shown in **Figure: 4.18**.

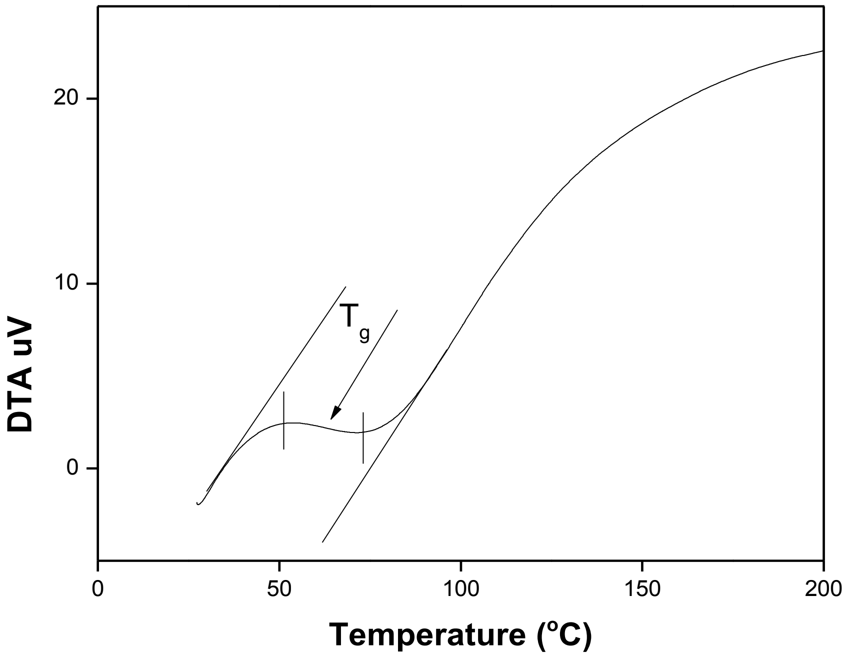


Figure 4. 18: Measurement of Glass Transition Temperature from DTA curve

It is observed from DTA curves that the glass transition temperature of the cast film decreased for the host polymer. From the **Table: 4.4**, it is observed that the glass transition temperature of the polymer- salt complexes decreases with the introduction of salt. This may be due to the presence of the plasticizer and interaction of plasticizer with the salt. The spacing of Nitrile groups decreases dipolar interactions which increases the free volume which intern decreases the glass transition temperature. When salt concentration is further increased, the glass transition temperature is increased from 55-70 °C for concentrations from 5 wt. % to 12 wt. % of salt. The increase in glass transition temperature with increasing salt content indicates the decrease in free volume of the material (Chen-Yang et al., 2002). One value for T_g exhibited by polymer electrolytes, indicates the homogeneous behavior. Decrease in glass transition temperature upon incorporation of salt may be due to the interaction of PAN with $LiBF_4$. Beyond this transition temperature from glassy state to rubbery state, a long range molecular motion takes place and hence the degree of rotational freedom increases. This increase may be due to the high polarity of closely spaced nitrile groups. This may be ascribed to the solvation of Lithium salts to produce free ions that increases conductivity by immobilization of chain segments.

With further increase in salt doping percentage, T_g is increased which shows that the crystallinity of the complexes is increasing confirmed from XRD as well. This may be due to the presence of salt in excess. This increase in T_g signifies the hardening of polymer backbone as doping concentration is increasing (Kuo et al., 2013). Glass transition temperatures are in range from 55 -70 °C. Watanabe (Watanabe et al., 1983) observed that the salts producing the largest increase in T_g also gave complexes with higher conductivities than those showing weaker interactions, indicated by lower T_g. This is ascribed to the solvation of Lithium salts to produce free ions which increases conductivity but tends to increase T_g by immobilization of chain segments. An ionic-cross-link network is assumed where the cross link density increases with salt concentration (Watanabe et al., 1983). It is also found that the polymer salt complexes start melting at around 270°C which is in agreement with the results from TGA.

4.2.4. DTG ANALYSIS

DTG is used to analyze the major wt. loss% represented by the first peak, called as the maximum decomposition peak. This is the sharpest peak which indicates about the maximum weight loss at a particular temperature. It is observed from DTG curves shown in **Figure: 4.19** that there is a variation in the temperature values with increasing salt concentration.

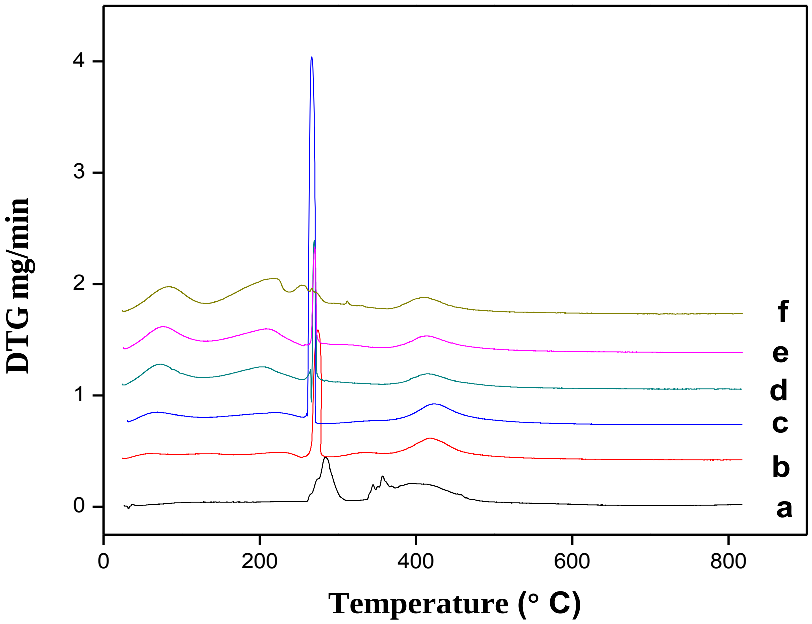


Figure 4. 19: DTG curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Temperatures corresponding to the peak values are shown in **Table 4.5** are decreasing from initial reading to highly doped polymer electrolyte. Approximate range of temperature is at around 270-285°C. The results obtained from DTG and DTA are found to be similar.

Table 4. 5: First peak Temperatures from DTG curves for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

Film	Salt Concentration (In wt. %)	First Peak Temp(°C)
a	0	284
b	3	273
c	5	267
d	8	269
e	10	270
f	12	271

4.3. CONDUCTVITY STUDIES

4.3.1. ION TRANSPORT THEORY

Conductivity is a vital property to be well thought-out to produce a better polymer electrolyte. The resulting conductivity is determined by the concentration of cations, anions and their mobilities. The concentration of cations and anions depend on the dissociation of salt MX which is further determined by the dielectric constant of the plasticizer. The mobility of ions depends on the interaction of M^+ ions with host polymer, plasticizer and free ions available in the electrolyte. Moreover the overall mobility of ion is determined by the free volume which leads to an increase in ionic and segmental mobility that will assist ion transport and practically compensates the retarding effect of the ion clouds (Mahendran and Rajendran, 2003). FTIR studies on the PAN based electrolytes demonstrate that there are at least two states of Li^+ ions in solid polymer electrolytes: (i) Lithium ions associated with nitrile group of PAN and (ii) Lithium ions associated with the plasticizer. One more state is also possible in which lithium ions are thought to be present in gel state. The motion of Li^+ in solid polymer electrolyte, based on the state, may be characterized as long range movement and short range movement. The motion of the Li^+ along the PAN chain through jumping from one site to next and polymer segmental chain movement both are regarded long range movement while the movement of Li^+ in liquid type medium is strongly affected by the Brownian motion of solvent molecules and thought as a short range one. The movement of Li^+ in gel state is in between the long range one and the short range one. Since the segmental chain motion is slow in PAN at room temperature, the motion of Li^+ is faster in gel state and hence Li^+ moving in the gel contribute the most to the ionic conductivity at room temperature. But the movement of segmental chain becomes faster as the temperature increases (olsen, Koksbang and Skou., 1995). On the above transport mechanism, the plasticizer helps to increase the conductivity by decreasing the glass transition temperature of the polymer and hence free volume which lead to increase the mobility of segmental chain. Apart from that, it also helps to increase the concentration of charge carriers.

In general the ionic conductivity, σ of the polymer electrolyte is the given by Eqn (4.2) (Shriver and Bruce, 1995)

$$\sigma = nq\mu \quad \text{or} \quad \sigma = \Sigma\,(n_i\, q_i\, \mu_i) \qquad \text{Eqn (4.2)}$$

Where 'n' or 'n_i' represents the number of ionic carriers per unit volume of type 'i', q or 'q_i' defines the charge of the charge carrier of type 'i', and μ or 'μ_i' corresponds to the mobility of charge carrier of type 'i'. With the increase of 'n_i' and/or 'μ_i', the conductivity will be enhanced.

The experimental setup used for studying the ionic conductivity has already been described in Chapter-II. The photograph of the setup used to study the conductivity studies is shown in **Figure 3.13**. The measurements of conductivity were carried out on films, the surfaces of the films being coated with silver for good electrical contact. The conductivity was measured by using dc polarization technique. The polymer electrolyte was sandwiched between the two stainless steel electrodes. This spring loaded cell is introduced into the muffle furnace. The temperature in the furnace is controlled by the constant current fixed in the dimmerstat. The polarizing effects during the measurements of D.C. conductivity were minimized by applying smaller voltages for a short interval of time and short-circuiting after every reading. The ion transport is measured by using this dc polarization technique, in which a voltage of 0.5 volts was applied across the cell configuration SS| polymer electrolyte| SS and the resulting current was monitored. The dc conductivity was measured in the temperature range of 313 - 358K. The whole experiment was repeated for each and every sample.

The investigation of conductivity variations were studied as a function of

(1) Concentration/composition dependence of D.C. conductivity

(2) D.C. conductivity measurement as a function of temperature

The dependence of conductivity and its variation is discussed in detail as follows.

4.3.2. CONCENTRATION/COMPOSITION DEPENDENCE OF IONIC CONDUCTIVITY

The ionic conductivities of SPEs as a function of different wt. % of salt over the temperature 313-358K are reported in **Table 4.6** and are shown in **Figure: 4.20**. The conductivity of the pure PAN at room temperature is of the order of 10^{-11} Scm^{-1} (Ahmad, Md. Isa and Osman, 2011). From the **Figure: 4.20**, it is clear that the ionic conductivity increases gradually in entire wt. % range of salt.

Table 4. 6: conductivity values of PAN/DMF/$LiBF_4$ Polymer electrolytes of weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12

Temp(°C)	1000/T (/kelvin)	Conductivity values (at different wt. % of salt),σ (x 10^7 S/cm)				
		a	b	c	d	e
40	3.19	3.05732	3.21019	3.51592	4.12739	4.43312
45	3.14	3.36306	3.66879	4.12739	4.58599	4.89172
50	3.10	3.97452	4.12739	4.43312	4.89172	5.35032
55	3.05	5.04459	5.35032	5.80892	6.11465	6.42038
60	3.00	5.80892	6.26752	6.72611	7.33758	7.79618
65	2.96	7.49045	7.94904	8.56051	9.32484	10.3949
70	2.92	8.86624	9.63057	10.3949	11.0064	11.6178
75	2.87	11.3121	12.6879	13.4522	13.9108	14.9809
80	2.83	13.758	14.9809	16.5096	17.4268	18.3439
85	2.79	15.2866	16.8153	18.3439	20.6369	21.4013

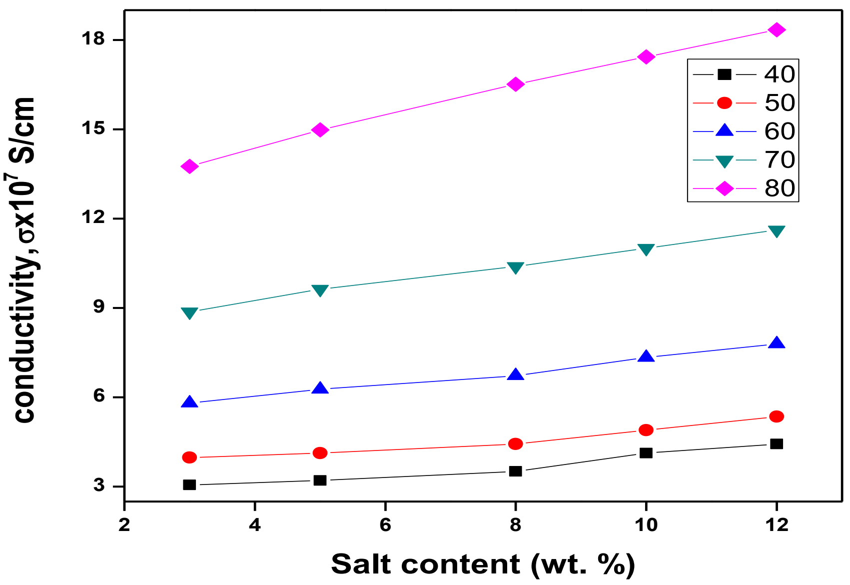


Figure 4. 20: variation between conductivity vs. wt. % of $LiBF_4$ content in polymer electrolytes of PAN/DMF/$LiBF_4$ at different temperatures.

When the concentration of $LiBF_4$ is low in $LiBF_4$-solvent (plasticizer) system, most of the salt gets dissociated, due to which the conductivity increases (Wang et al., 1999). The conductivity of the solid polymer electrolyte is of a very low value of the order of 10^{-7} Scm^{-1}. Most of the dissolved Li^+ ions coordinate to the oxygen in the carbonyl group in DMF as clear from FTIR study in section 4.1.2. This result may be due to the formation of a cross link between the chain segments which reduce the mobility of the charge carriers and tend to decrease the conductivity (Othman, Chew and Osman, 2007) (Ali et al., 2008). In addition to that, the appearance of shoulder near to 2260 cm^{-1} as shown in **Figure 4.3** indicates the coordination of some Li^+ with $C \equiv N$ of PAN which contributes in conductivity through segmental chain motion which is more prominent at high temperatures. **Figure 4.20** witnessed that the conductivity is increasing in entire concentration range of study at all temperatures. At 313 K, it is observed that the conductivity increased from 3.05x10^{-4} mScm^{-1} for 3 wt. % to 4.43x10^{-4} mScm^{-1} for 12 wt. % of $LiBF_4$.

When the salt concentration is low, $LiBF_4$ is completely dissociated. The increase in conductivity in entire salt proportions may be attributed to the development of charge transporters or decrease in the crystalline environment. The conductivity increases even when the free volume decreases as confirmed from FTIR studies which indicate that the hopping of Li^+ ions is dominating other mechanisms.

The conductivity of the polymer electrolytes is increased with weight % of salt due to the increase of the charge carriers or the increase in concentration of mobile ions (Kuo et al., 2013). This increasing trend in conductivity of polymer complexes is observed irrespective of salt content at any constant temperature and is in agreement with Armand et al. (Armand et al., 1979). When the temperatures are approaching towards the higher side i.e. at 358K, the conductivity values increased from 1.52x10^{-3} mScm^{-1} for 3 Wt.% to 2.14x10^{-3} mScm^{-1} for 12 wt. % of $LiBF_4$.

4.3.3. TEMPERATURE DEPENDENCE ON IONIC CONDUCTIVITY

The temperature variations of conductivity are shown in **Figure. 4.21**. From the curves shown in **Figure 4.21**, it is clear that the present work follows Arrhenius relation for ion transport i.e., the major ions movement happen by an activated hopping, decoupled with the polymer matrix at elevated temperatures.

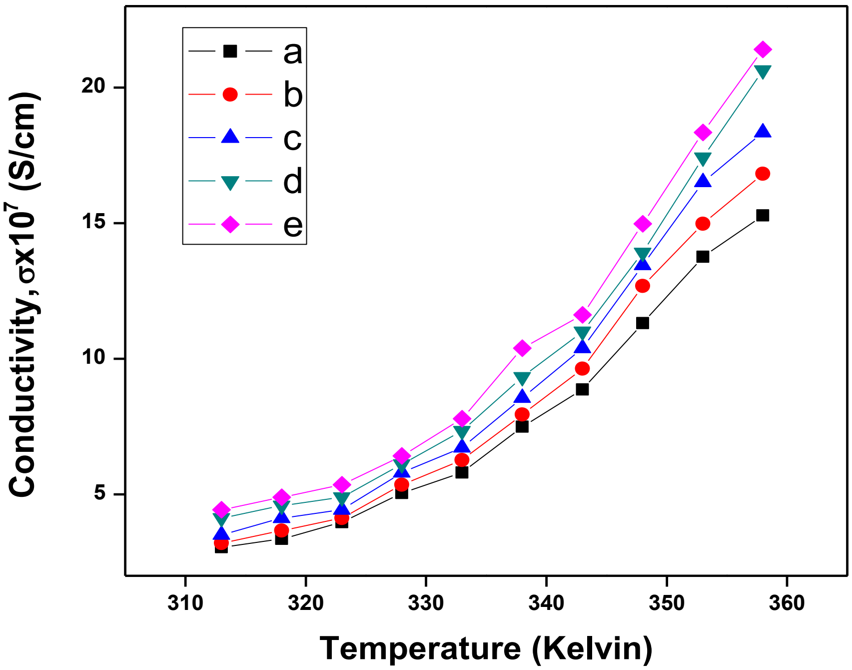


Figure 4. 21: Arrhenius plot of ionic conductivity vs. Temperature for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

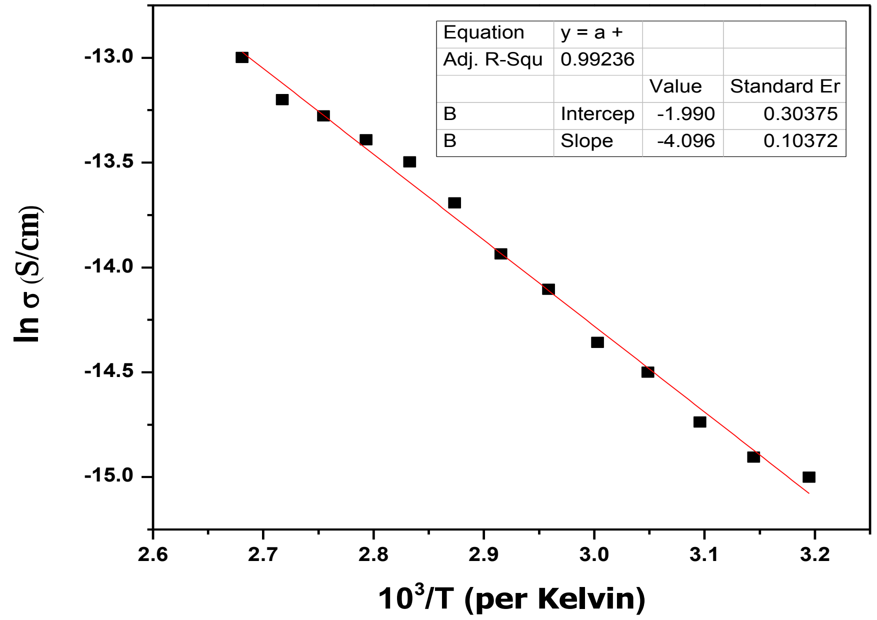
In addition to above mechanism, the ionic conductivity of a SPE increases with temperature is due to the higher segmental motion of the polymer chain (Kuo et al., 2013) which is in the semi-crystalline phase as confirmed from the XRD studies. Also, the higher conductivity at elevated temperatures may be due to the motion of Li^+ along the segmental chain.

4.3.4. ACTIVATED PROPERTIES OF SOLID POLYMER ELECTROLYTES

The temperature dependent conductivity for all polymer electrolytes may be given by the Arrhenius type relation given by Eqn (4.3).

$$\sigma(\mathrm{T}) = \mathrm{A}\exp\left(\frac{-E_a}{K_B\,T}\right) \qquad \text{Eqn (4.3)}$$

where ‘A’ is the pre-exponential factor, proportional to the number of carrier ions, ‘E_a’ is the activation energy for electrical conduction (energy required for an ion to jump to a free hole).The Arrhenius plots of the polymer electrolytes are shown in **Figures 4.22 – 4.26**.



Equation	y = a +		
Adj. R-Squ	0.99236		
		Value	Standard Er
B	Intercep	-1.990	0.30375
B	Slope	-4.096	0.10372

Figure 4. 22: Arrhenius plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/ $LiBF_4$ of weight ratio 19:78:3.

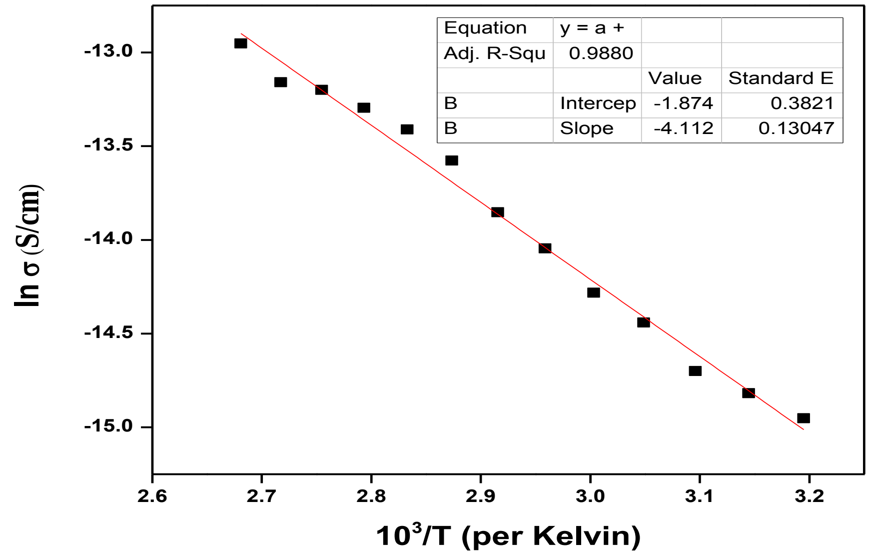


Figure 4. 23: Arrhenius plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/ $LiBF_4$ of weight ratio 19:76:5.

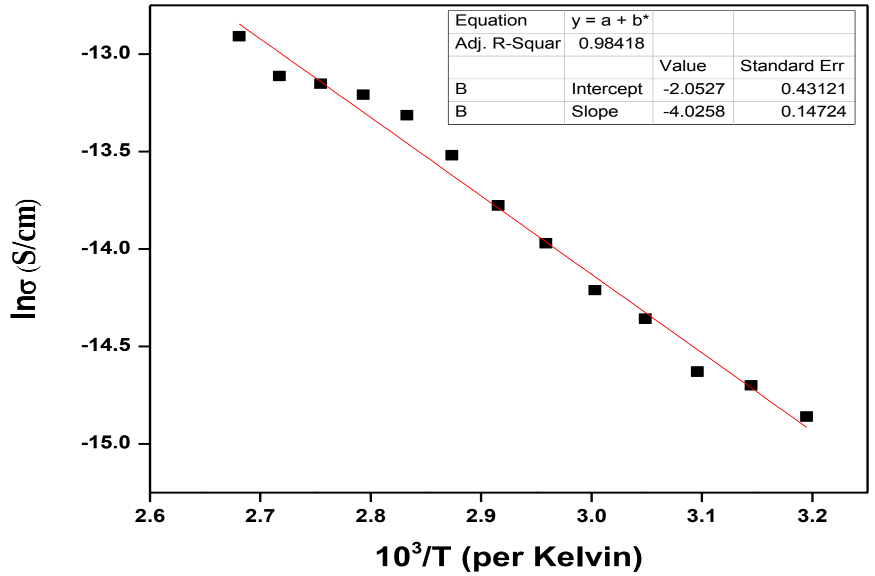


Figure 4. 24: Arrhenius plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:74:8.

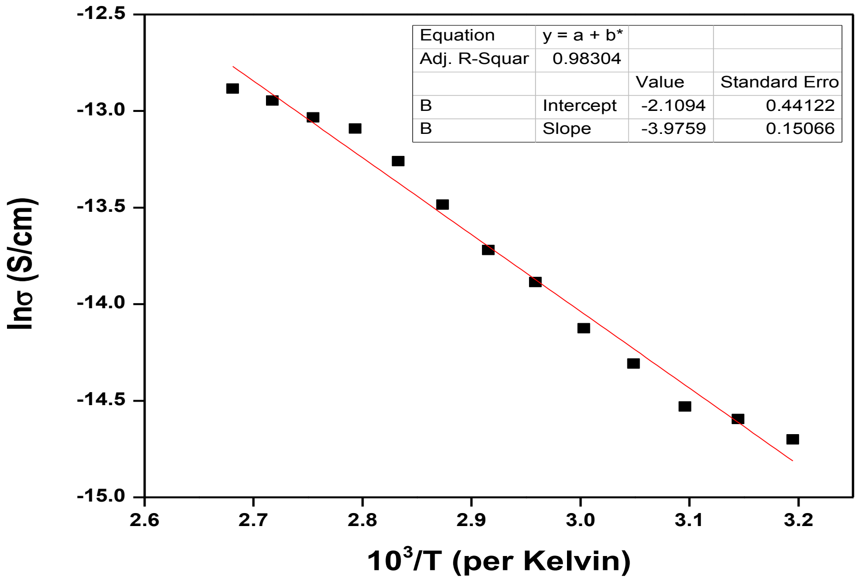


Figure 4. 25: Arrhenius plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:72:10.

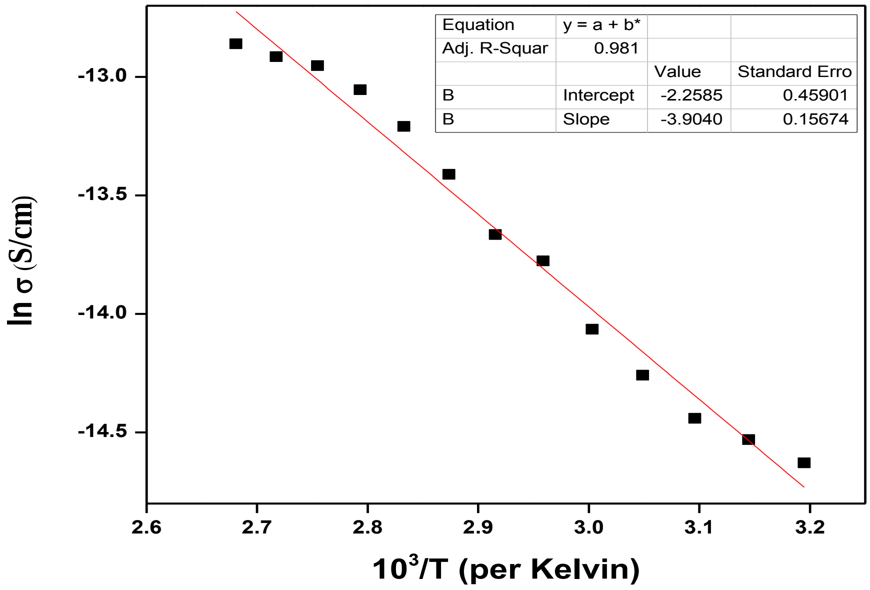


Figure 4. 26: Arrhenius plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:70:12.

The activation energy values from Arrhenius relation are summarized in **Table: 4.7.**

Table 4. 7: Activation Energy values of different Polymer Electrolytes of PAN/DMF/$LiBF_4$ weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

Film	Intercept	slope	R^2	E_a (KJ/Mole)
a	-1.99016	-4.09657	0.99236	34.05
b	-1.8742	-4.11229	0.98805	34.18
c	-2.05277	-4.02583	0.98418	33.46
d	-2.10948	-3.97591	0.98304	33.05
e	-2.2585	-3.90402	0.981	32.45

It is observed that there is an increase in conductivity and decrease in activation energy with the increase in dopant concentration. This can be explained basing on the mixed phases, either amorphous or semi-crystalline nature present in polymer films. These results illustrates that the conductivity in such films may be dominated by the amorphous phase which may be due to the formation of charge complexes in the host lattice (Ramu, Naidu and Sharma, 1994). These charge transfer complexes increase the additional charges in the lattice which results in

an increase in conductivity and decrease in Activation energy (Chandra Sekhar, Naveen Kumar and Sharma, 2012).

The complexes exhibited a single value for T_g. With the incorporation of $LiBF_4$ into the polymer complex, the glass transition temperature decreased and then increased as the salt concentration is further increased as discussed in section 4.2.3. This shows the semi-crystalline nature of polymer electrolytes because of the presence of the salt in excess. The conductivity studies also reveal the same, with the increase of salt concentration the conductivity also increased.

If conductivity is result of thermal activation process, Enthalpy (ΔH) and Entropy (ΔS) are determined from the Eyring equation, a linear relation obtained as a plot of $\ln(\sigma h/K_B T)$ vs 1000/T, given by Eqn (4.4).

$$Rln\left(\frac{\sigma h}{K_B T}\right) = -\frac{\Delta H}{T} + \Delta S \qquad \text{Eqn (4.4)}$$

Where "h" is the Planck's constant and "K_B" is the Boltzmann constant.

The another general linear form of Arrhenius-like expression is given by Eyring-Polanyi equation, that relates the conductivity with the Gibb's function to determine the values of Enthalpy (ΔH) and Entropy (ΔS), given by Eqn (4.5).

$$\sigma = \left(\frac{K_B T}{h}\right) \exp\left(\frac{-\Delta G}{RT}\right) \qquad \text{Eqn (4.5)}$$

This can be written in the form of y=mx+c as given by Eqn (4.6).

$$ln\left(\frac{\sigma}{T}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + ln\left(\frac{K_B}{h}\right) \qquad \text{Eqn (4.6)}$$

Where slope determines Enthalpy of activation,–ΔH(m=–ΔH/R) and the intercept gives entropy of activation, ΔS[Intercept = (ΔS/R) + ln(k/h)]. The Eyring-Polanyi plots for all the polymer electrolytes are drawn as shown in **Figure 4.27-4.31.**

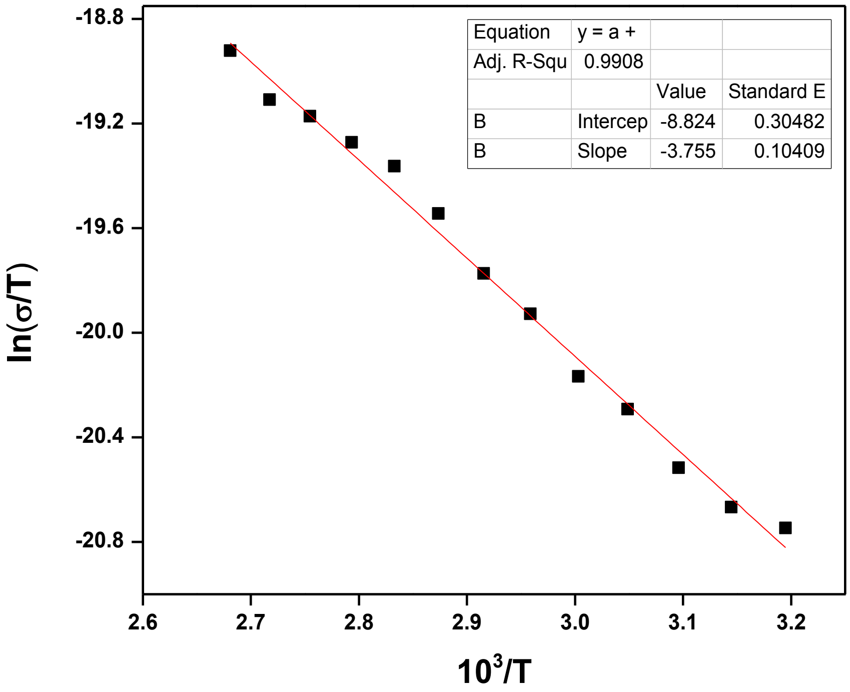
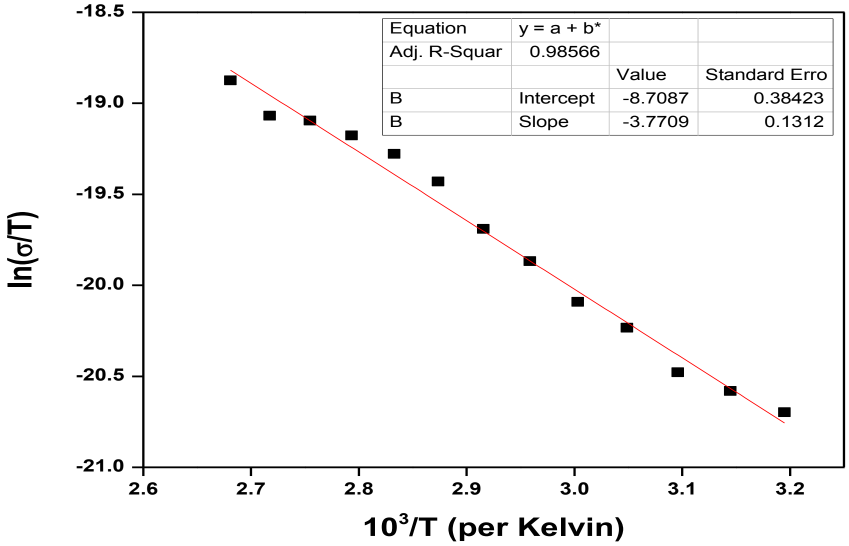
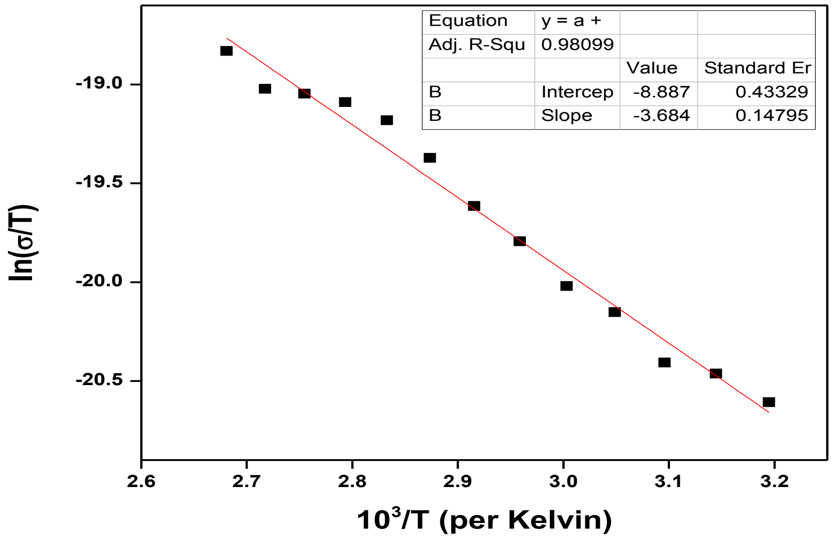


Figure 4. 27: Eyring-Polanyi plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/ $LiBF_4$ of weight ratio 19:78:3.



Equation	y = a + b*		
Adj. R-Squar	0.98566		
		Value	Standard Erro
B	Intercept	-8.7087	0.38423
B	Slope	-3.7709	0.1312

Figure 4. 28: Eyring-Polanyi plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/ $LiBF_4$ of weight ratio 19:76:5.



Equation	y = a +		
Adj. R-Squ	0.98099		
		Value	Standard Er
B	Intercep	-8.887	0.43329
B	Slope	-3.684	0.14795

Figure 4. 29: Eyring-Polanyi plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:74:8.

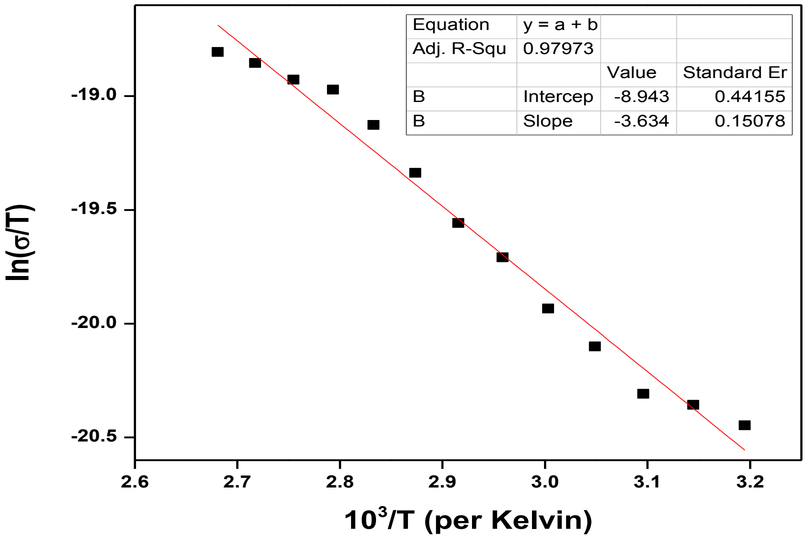


Figure 4. 30: Eyring-Polanyi plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:72:10.

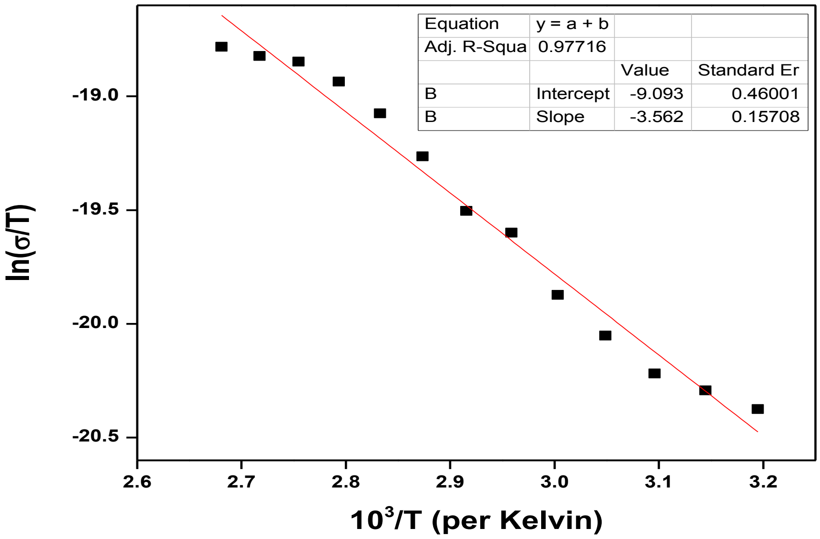


Figure 4. 31: Eyring-Polanyi plot of ionic conductivity vs. T for a polymer electrolyte of PAN/DMF/$LiBF_4$ of weight ratio 18:70:12.

The values of Enthalpy and Entropy so determined and reported in **Table: 4.8**. A decrease in activation energy and Enthalpy are observed with increase in salt concentration which can be attributed to the lithium ion hopping mechanism in polymer backbone (Wen, Kuo and Gopalan., 2002).

Table 4. 8: Enthalpy and Entropy values of different Polymer electrolytes of PAN/DMF/$LiBF_4$ weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

FILM	SLOPE	INTERCEPT	R^2	ΔH(J/mol/kel)	ΔS(J/mol/Kel)
a	-3.75519	-8.82466	0.99086	31.2206497	-270.907
b	-3.77091	-8.7087	0.98566	31.3513457	-269.943
c	-3.68445	-8.88726	0.98099	30.6325173	-271.428
d	-3.63453	-8.94397	0.97973	30.2174824	-271.899
e	-3.56264	-9.093	0.97716	29.619789	-273.138

CHAPTER 5

CONCLUSIONS AND FUTURE SCOPE

5.1. SYNTHESIS

The details of the present thesis entitled “Development and Characterization of a Solid-Ion conducting Polymer Electrolyte” is briefly summarized as follows.

All the chemicals were dried under vacuum and then homogeneous viscous solution of polymer electrolyte was prepared by using a magnetic stirrer. Different sets of films were synthesized by solution casting method. Thin films were casted on the glass petri dishes. Petridishes were then shifted into vacuum oven and the solvent was allowed to evaporate slowly at room temperature. Then the sample was dried for 48 hours at a temperature of 323 K to remove all traces of excess solvent. Clear and transparent films of thickness around 50-60 microns were obtained. Six films were synthesized with NMP as solvent in the first set of six films. The same procedure was adapted in developing six other films with Dimethyl sulfoxide (DMSO) as the second solvent. The next set of films was prepared by taking the combination of two solvents NMP and DMSO in the volume ratio of 1:1. From the films so prepared, it was observed that the solid polymer electrolytes with NMP as solvent were stable and free standing when compared with films made of DMSO. Different films of PAN/DMF/$LiBF_4$ with increasing salt concentration were synthesized that were stored in a vacuum desiccator. Utmost care has been taken to prevent the films from the moisture effects. It was observed that the polymer electrolyte films so formed were free standing, clear and transparent with less mechanical and dimensional stability and were not flexible. Details of polymer electrolytes of different compositions were quoted in **Table: 3.3.**

Table: 3.3: Polymer electrolytes with various compositions.

Film	Composition
	PAN:DMF:SALT
a	20 : 80 : 0
b	19 : 78 : 3
c	19 : 76 : 5
d	18: 74 : 8
e	18 : 72 : 10
f	18 : 70 : 12

5.2. CHARACTERIZATION

These membranes so synthesized were characterized by various experimental techniques. The structural characterization was studied by X-ray diffraction on Bruker D8 Advance diffractometer. The complexation studies for all the polymer electrolytes were analyzed by performing FTIR on Perkin Elmer, USA spectrum

Two spectrophotometer. The thermal properties and related parameters were studied by using TGA, DTA and DTG that were implemented on EXSTAR TG/DTA 6300. The ionic conductivity was studied basing on dc polarization technique employing a two electrode conductive cell comprising of a polymer electrolyte, sandwiched between two stainless steel electrodes.

Some of the graphical representations and tables are repeated to summarize all the results obtained in the structural, thermal and conductivity studies.

5.2.1. STRUCTURAL STUDIES

The films showed the semi crystalline nature from the XRD patterns as there was a variation in the intensity of peaks with the doping of salt of increasing concentrations as depicted in **Figure: 4.1.** The sharp peaks and the relative intensity calculations establish the semi crystalline nature of polymer salt complexes. Basing on the relative intensity studies from XRD patterns, it was inferred that there were no remarkable structural changes. This was also confirmed from the complexation studies of FTIR as shown in **Figure 4.2** with reference to the interactions between Li^+ ions and the nitrile group of the host polymer. FTIR studies showed that the polymer salt complexation has taken place which is confirmed by the shifting of peaks or and also the formation of new peaks in polymer complexes. This was proved by the formation of new shoulder at 2269 cm^{-1} as represented in **Figure: 4.3**. Also, the complete complexation was established from the shifting of peaks corresponding to the Carbonyl group. FTIR results indicated that the Li^+ cations of dissociated salt are coupled with both the

C=O group in DMF and the $C \equiv N$ in PAN, along with the dipolar interactions between DMF and PAN through C=O group and $C \equiv N$. XRD and FTIR studies determine about the possible conformational changes in crystal texture of solid polymer electrolytes.

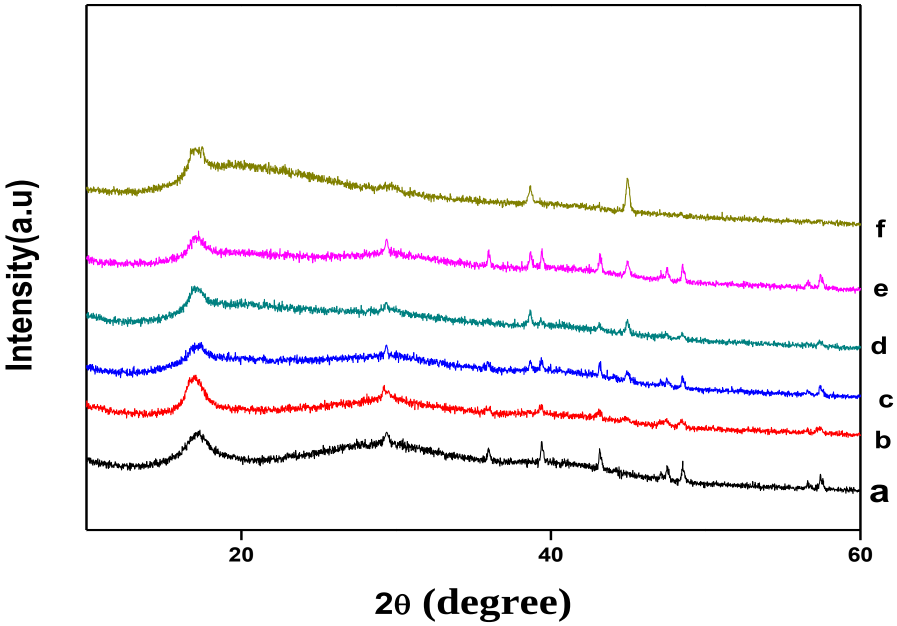


Figure 4.1: X-ray diffractograms for polymer electrolytes of PAN/DMF/$LiBF_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

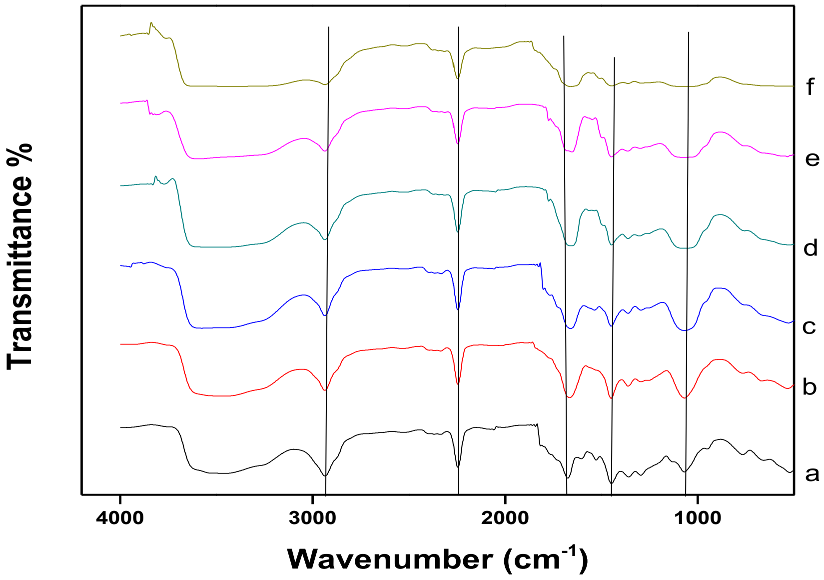


Figure 4.2: IR spectra of polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

5.2.2. THERMAL STUDIES

The thermal properties studied from TGA shown in **Figure 4.13** indicate the stability of the polymer electrolytes with gradual degradation or weight loss of 10 % as salt is added. The films are stable up to 194, 138 and 89 ^{o} C for 2, 5 and 8 wt. % respectively with a gradual weight loss of 10 %. As the temperature at which 10 wt. % degradation happens is low, the thermal stability is low.

DTA studies as symbolized in **Figure 4.16** were strongly showing the semi crystalline nature of the polymer electrolytes as confirmed from XRD studies. The melting temperatures decreased from 317 °C to 279 °C by the addition of the salt in the polymer. DTG curves are as shown in **Figure 4.19.** With further increase in salt doping percentage, T_g is increased which shows that the crystallinity of the complexes is increasing confirmed from XRD as well.

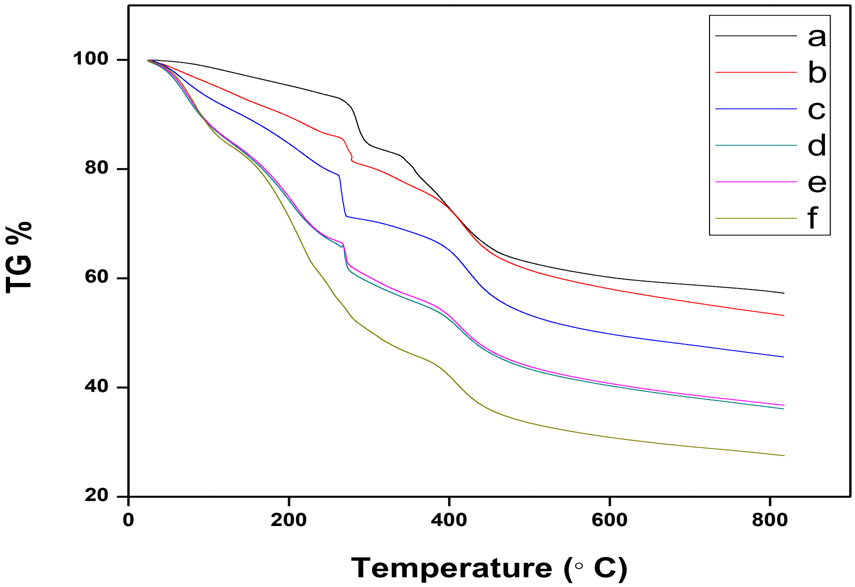


Figure 4.13: TG curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

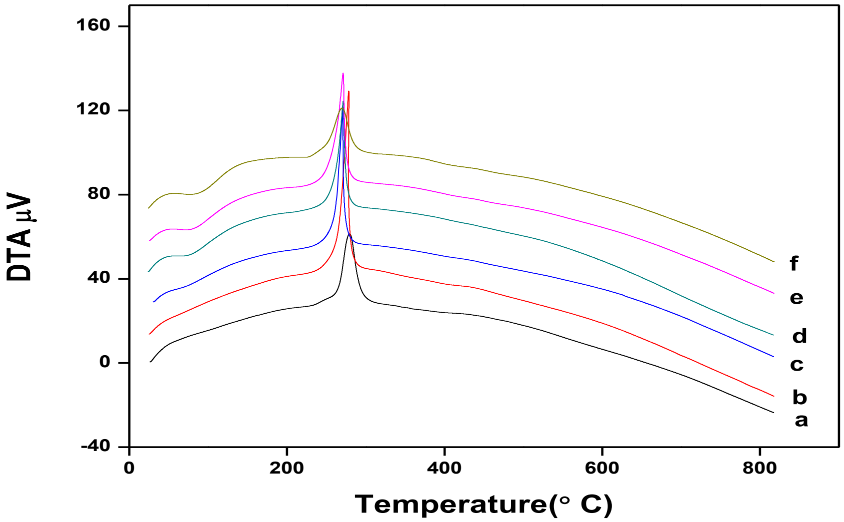


Figure 4.16: DTA curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

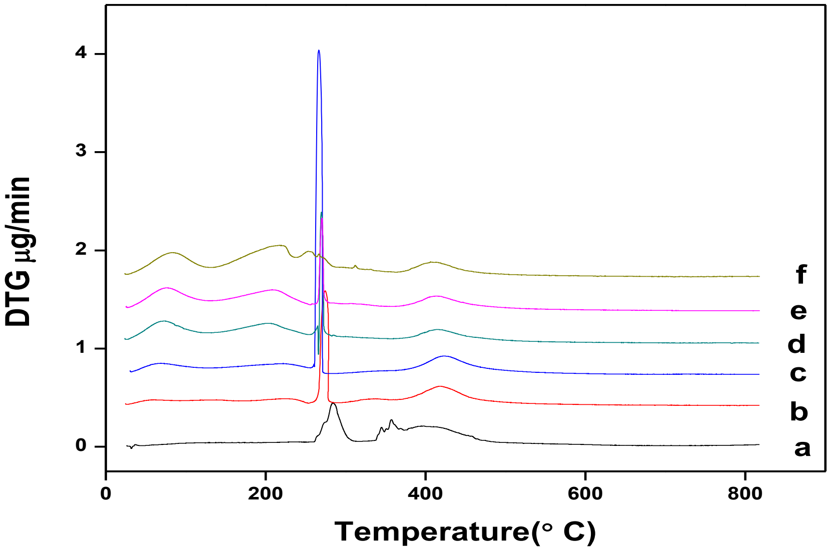


Figure 4.19: DTG curves for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 20:80:0 (b) 19:78:3 (c) 19:76:5 (d) 18:74:8 (e) 18:72:10 (f) 18:70:12.

5.2.3. CONDUCTIVITY STUDIES

Temperature dependence as well as the composition dependence conductivity studies, shown in **Figure 4. 20 & Figure 4. 21** were studied and were observed to follow the Arrhenius and Eyring- Polanyi equations. The conductivity values of solid polymer electrolytes obtained were very low, of the order of 10^{-4} $mScm^{-1}$. This poor result may be because of most of the dissolved Li^+ ions coordinated to the oxygen in the carbonyl group in DMF as clear from FTIR study in section 4.1.2. This result may also be due to the formation of a cross link between the chain segments which reduce the mobility of the charge carriers and tend to decrease the conductivity. It was observed that the conductivity increased from $3.05x10^{-4}$ $mScm^{-1}$ for 3 wt. % to $4.43x10^{-4}$ $mScm^{-1}$ for 12 wt. % of $LiBF_4$ at 313K. At 358K, the conductivity values increased from $1.52x10^{-3}$ $mScm^{-1}$ for 3 Wt. % to $2.14x10^{-3}$ $mScm^{-1}$ for 12 wt. % of $LiBF_4$. The order of ionic conductivity of polymer complexes increased from 10^{-4} $mScm^{-1}$ to 10^{-3} $mScm^{-1}$, which was not a considerable increase. The conductivity studies reveal that there was an increase in conductivity with increase in temperature. Similarly, the conductivity values showed an increase with the increase in the wt. % of the salt concentration. The activation energies, enthalpy and the entropy values are also determined. It was observed that there is an increase in conductivity and decrease in activation energy with the increase in dopant concentration. **Table 4.6** reveals about the conductivity values obtained. A decrease in activation energy and enthalpy were observed with increase in salt concentration as quoted in **Table 4.8**.

The conductivity of the solid polymer electrolyte is of a very low value of the order of 10^{-4} mScm^{-1}.

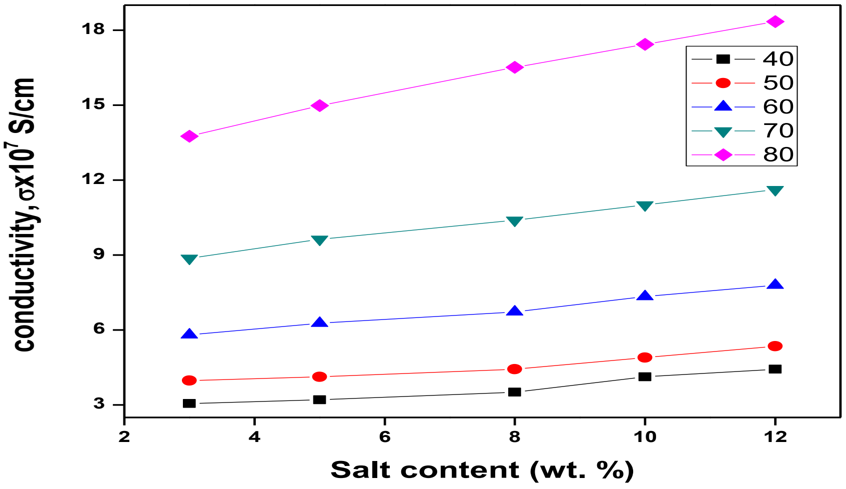


Figure 4.20: variation between conductivity vs. wt. % of LiBF$_4$ content in polymer electrolytes of PAN/DMF/LiBF$_4$ at different temperatures.

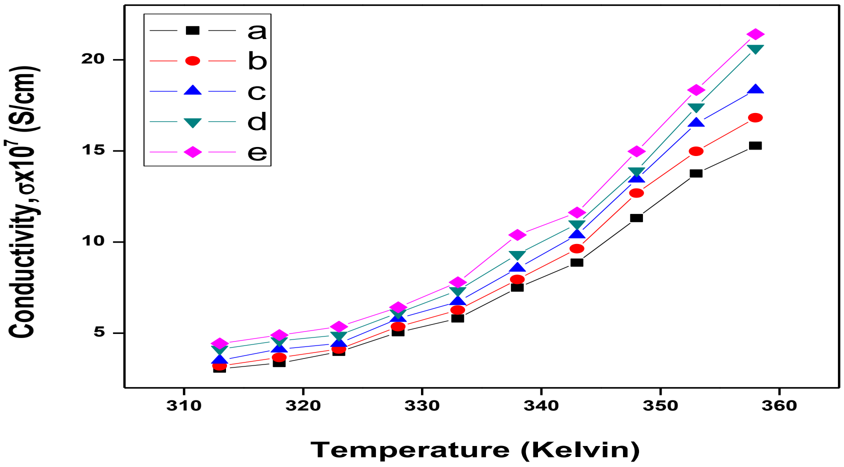


Figure 4.21: Arrhenius plot of ionic conductivity vs. Temperature for polymer electrolytes of PAN/DMF/LiBF$_4$ of weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

Table 4. 6: conductivity values of different Polymer electrolytes of PAN/DMF/$LiBF_4$ weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

Temp(°C)	1000/T (/kelvin)	Conductivity values (at different wt. % of salt), σ (x 10^7 S/cm)				
		a	b	c	d	e
40	3.19	3.05732	3.21019	3.51592	4.12739	4.43312
45	3.14	3.36306	3.66879	4.12739	4.58599	4.89172
50	3.10	3.97452	4.12739	4.43312	4.89172	5.35032
55	3.05	5.04459	5.35032	5.80892	6.11465	6.42038
60	3.00	5.80892	6.26752	6.72611	7.33758	7.79618
65	2.96	7.49045	7.94904	8.56051	9.32484	10.3949
70	2.92	8.86624	9.63057	10.3949	11.0064	11.6178
75	2.87	11.3121	12.6879	13.4522	13.9108	14.9809
80	2.83	13.758	14.9809	16.5096	17.4268	18.3439
85	2.79	15.2866	16.8153	18.3439	20.6369	21.4013

Table 4. 8 : Enthalpy and Entropy values of different Polymer electrolytes of PAN/DMF/$LiBF_4$ weight ratio (a) 19:78:3 (b) 19:76:5 (c) 18:74:8 (d) 18:72:10 (e) 18:70:12.

FILM	SLOPE	INTERCEPT	R^2	ΔH(J/mol/kel)	ΔS(J/mol/Kel)
a	-3.75519	-8.82466	0.99086	31.2206497	-270.907
b	-3.77091	-8.7087	0.98566	31.3513457	-269.943
c	-3.68445	-8.88726	0.98099	30.6325173	-271.428
d	-3.63453	-8.94397	0.97973	30.2174824	-271.899
e	-3.56264	-9.093	0.97716	29.619789	-273.138

5.3. FUTURE SCOPE

In the present work carried out, it was observed that the conductivity values are not meeting the requirements for the development of Lithium ion polymer batteries.

The main reasons attributed for this are the host polymer, solvents and plasticizers considered. The effect of moisture and humidity conditions are other important factors that influenced the low conductivity values quoted in the result. The considered host polymer being a semi crystalline nature did not yield a good conductivity value. The conductivity value could be increased if a polymer blend is formed i.e. if the polymers like PEO, PVA, PMMA, PVDF etc. are blended with the host polymer. Considerable increase in conductivity may be possible, which may be due to the amorphous phase of the polymer blend. The work can be extended by considering other solvents like Acetonitrile and Tetrahedrafuron, based on their cohesive energy density values and solubility parameters. Many other parameters related to mechanical stress and strain can be studied. The conductivity values could have been enhanced if propylene carbonate and ethylene carbonate are introduced as plasticizers. The conductivity studies can be done along with other lithium salts for comparison. By the addition of nanoparticles, the conductivity of the nano polymer composite can also be enhanced. Addition of fillers can improve the conditions of the polymer electrolyte that supports the stability and the mechanical strength of the films. Similarly, with the introduction of Nano ceramic additives, such as e.g. Al_2O_3 or TiO_2 permits to achieve a growth in ionic conductivity.

LIST OF PAPERS PRESENTED IN CONFERENCES

1. **Electrical Conductivity studies of a new Conducting Nano Polymer Composite based on (PAni-TiO_2) and (PAni-PVA) Blend system for High Energy Rechargeable Battery Applications**

Kambila Vijaya Kumar*, G.Suneetha Sundari** **N.Satya Krishna**[+], V.N. Mani***

Paper Presentation.

International Conference on Nano Science and Technology (ICONSAT-2012)

January 20-23, 2012.

Hyderabad, India.

2. Charactersiation and Conductivity studies of PAN based thin film polymer electrolyte for application in Lithium polymer batteries

Satya Krishna Nippani[1], Kambila Vijay kumar[2], Piyush Kuchhal[3]

Poster Presentation, Poster Code: N – 28

Nanotechnology in Conventional and Alternate Energy

A Global Status and Pathway-2013 Nano-Energy Seminar

August 12-13, 2013

UPES, Dehradun, India.

3. Structural and a.c conductivity studies of lithium ion conducting pan based polymer electrolyte system

Satya Krishna Nippani*, Piyush Kuchhal*, Kambila Vijay Kumar[#]

N. Krishna Jyothi [#], G. Sunita Sundari[#], J. Ramesh Babu[#]

Poster Presentation, Reference id: ICA2013-0001174

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DEC 16-20, 2013.

I.I.SC., Bangalore, India.

4. Structural and Conductivity studies of PAN based thin film Polymer Electrolyte

Satya Krishna Nippani[**1**],Kambila Vijay kumar[2],Piyush Kuchhal[3]

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GLOSSARY

Ag_2SeO_4	Silver Selenate
$AgCF_3SO_3$	Silver trifluoro methane sulphate
AgI	Silver Iodide
Al_2O_3	Aluminium oxide
$BaTiO_3$	Barium Titanate
BL	γ- butyrolactone
$CoBr_2$	Cobalt Bromide
CsSCN	Cesium Thiocyanate
DMF	N-N DiMethylformamide
DMSO	Dimethyl sulfoxide
EC	Ethylene Carbonate
H_3PO_4	Phosphoric Acid
KAg_4I_5	Silver Potassium Iodide
KSCN	Potassium Thiocyanate
$Li(CF_3SO_2)_2$	Lithium bis(trifluoromethylsulfonyl)amide

$Li(CONi)O_2$	Lithium intercalated Graphite
Li_2S	Lithium Sulfide
$LiAsF_6$	Lithium hexafluoroarsenate
$LiB(C_6H_5)_4$	Lithium tetraphenylborate
$LiBF_4$	Lithiumtetrafluoro Borate
$LiCF_3SO_{3,}$	Lithium Triflate
$LiClO_4$	Lithium perchlorate
LiCoC2	Lithium Cobaltite
LiI	Lithium Iodide
$LiPF_6$	Lithium hexafluorophosphate
LiSCN	Lithium Thiocyanate
LiTFSI	Lithium trifluoromethanesulfonimide
MEEMA	Poly Methoxy Ethoxy Ethyl Meth Acrylate
MEEP	Poly bis(methoxy ethoxy ethoxide) phosphazene
$NaCF_3SO_3$	Sodium Triflate
$NaClO_3$	Sodium chlorate
NaI	Sodium Iodide
$NaPF_6$	Sodium hexafluorophosphate

NaSCN	Sodium Thiocyanate
$Nd(NO_3)_3$	Neodymium(III) nitrate hexahydrate
NH_4ClO_4	Ammonium perchlorate
NH_4ClO_4	Ammonium perchlorate
NH_4I	Ammonium Iodide
NMP	N-Methyl pyrrolidine
P_2S_5	Phosphorous Pentasulfide
PAN	Polyacrylonitrile
PANi	Polyaniline
PC	Propylene Carbonate
PDTC	Pyrrolidine dithiocarbonate
PEGME	Polyethyl glycol methyl ether
PEO	Polyethyleneoxide
PMMA	Poly(methyl methacrylate)
PPO	Poly Propylene Oxide
PPO	Polypyrrole
PVA	Polyvinyl Alcohol
PVDF-HFP	Poly(vinylidene fluoride-hexa fluoropropylene)

PVP	Polyvinylpyrrolidone
$RbAg_4I_5$	Rubidium Silver Iodide
SL	Sulfolane
THF	Tetrahedrafuron
TiO_2	Titanium dioxide

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