Solid state ionics came into existence in the year 1967 after the discovery of two groups of solids: MAg₄I₅ (M= Rb, K, NH₄I) and Na-β-alumina. Since then, in the last nearly four and half decades, a large number of solids exhibiting fast ion transport involving variety of mobile species such as H⁺, Ag⁺, Cu⁺, Li⁺, Na⁺, K⁺, Mg²⁺, O²⁻, F⁻ etc. have been investigated and their application in devices has been explored extensively.

The research in the field of solid state ionics encompasses investigations of the physical and chemical behaviour of the solids with fast ion movement within the bulk as well as their technological aspects. These materials, widely referred to as ‘Superionic Solids’ or ‘Solid Electrolytes’ or ‘Fast Ion Conductors’, show tremendous scope to develop all-solid-state mini/micro electrochemical devices, viz., batteries, fuel cells, supercapacitors, electrochromic displays, sensors, photoelectrochemical solar cells (PESCs) etc.

For all-solid-state electrochemical device applications, these solids should have the following characteristic properties:

- ionic conductivity should be high (~10⁻¹⁻¹⁰⁻⁴ S/cm⁻¹) and the electronic conductivity should be negligibly small (< 10⁻⁸ S/cm⁻¹),
- activation energy should be low (< 1 eV),
- ions should be the principle charge carriers,
- ionic transference number should be close to unity (i.e., t_ion ~ 1) and
- should be single ion (preferably cation) conducting solids.

The earlier known ionic solids namely, alkali halides, silver halides etc. exhibited very low room temperature conductivity in the range ~10⁻⁶-10⁻⁷ S/cm⁻¹ and were usually considered as insulators. The ion transport in these solids is governed by thermally generated point defects such as Schottky and Frenkel defects. Attempts were made in the past to increase the extent of ionic conductivity in these normal ionic solids by doping but with very limited success. However, a major breakthrough was achieved
after the discovery of MAg$_4$I$_5$ (M = Rb, K, NH$_4$I) and Na-β-alumina. On the basis of physical properties, microstructures and synthesis routes, solid state ionic materials or superionic solids have now been grouped into following broad categories:

- Framework crystalline/polycrystalline electrolytes
- Glassy/amorphous electrolytes
- Gel electrolytes
- Composite electrolytes
- Polymer electrolytes

Composite solid electrolytes, also referred to as ‘dispersed solid electrolytes’, are high ion conducting multiphase solid systems which attracted huge technological attention after 1973 as potential candidates for all-solid-state electrochemical device fabrication. They are mostly two-phase mixtures, containing a moderately conducting ionic solid such as AgI, CuI etc. as I$^{\text{st}}$ phase host and a II$^{\text{nd}}$ phase material, which may be either an inert insulating compound such as Al$_2$O$_3$, SiO$_2$, ZrO$_2$, Fe$_2$O$_3$ etc. or another low conducting ionic solid such as AgBr, AgCl, KCl etc. As a consequence of dispersal of a small fraction of submicron size particles of the II$^{\text{nd}}$ phase into the I$^{\text{st}}$ phase host, a substantial improvement in various physical properties of the host is usually achieved without altering the structural/chemical nature of the constituent compounds. In two-phase composite electrolytes, an enhancement of 1-3 orders of magnitudes could be obtained in the conductivity at room temperature. The size of particles of II$^{\text{nd}}$ phase dispersoid play a significant role in improving the physical properties of the I$^{\text{st}}$ phase host, viz., the conductivity. Hence, the dispersal of nano-size particles would result into a substantial enhancement in the conductivity.

The work presented in this thesis comprises of studies on polymer electrolyte dispersed with various kinds of dispersoids which are detailed chapter-wise later.

Polymer electrolytes are generally prepared by mixing high molecular weight polymers with a salt. The polymer serves as a solid solvent, thus permitting the salt to dissociate into anions and cations. Since the mass of a cation is much smaller than that of an anion, the electrical conductivity is dominated by cation transfer. The transport of cations takes place if there is a relaxation of the polymer segments. Segmental
relaxation requires the presence of free volume in the polymer matrix, a condition that can be attained if the polymer is in an amorphous state.

The polymer electrolytes composites are prepared by dispersing a small fraction of micro/nano size inorganic (ceramic) filler particles into the conventional solid polymer electrolyte which acts as first phase host matrix. The ceramic filler acts as a second phase dispersoid. As a consequence of dispersal, the ionic conductivity, the mechanical strength and the interfacial activity of the composites usually get enhanced substantially. The size of the filler particles and hence, the surface area plays significant role in improving these physical properties.

The present thesis consists of work done on polymer electrolyte (PEO:NH₄I) dispersed with semiconducting (graphene), insulating (SiO₂) and magnetic nanoparticles (Fe₃O₄, NiO, Mn₃O₄ & Co₃O₄).

The objective of the work presented in this thesis is to obtain polymer electrolyte composites using dispersoid particles of different nature and size. A wide variety of techniques have been used to characterize the electrical, structural and thermal properties of the polymer electrolyte composites.

The thesis consists of six chapters and the chapter-wise description of the work is given below:

**Chapter 1** consists of the literature review on solid state ionics, polymer electrolytes and polymer electrolyte composites. This chapter gives a brief introduction of the broad research field of ‘Solid State Ionics’ in general and polymeric electrolyte materials in particular. Different types of ionic conductors have also been discussed. Different conductivity models to understand the ion conduction phenomena in composites have been given. Brief description of the applications of polymer electrolyte materials like solid state batteries, fuel cells, super capacitors, electrochromic display devices has also been given.

**Chapter 2** deals with the experimental part of the work which includes the synthesis of polymer electrolytes and their composites by solution cast technique. A description of the impedance spectroscopic technique has been given which is used for
the evaluation of bulk electrical conductivity of the composites. Wagner's polarization method has been described for transport number measurements. Techniques like X-ray diffraction (XRD), Raman spectroscopy, positron annihilation lifetime spectroscopy (PALS) and scanning electron microscopy (SEM) have been given which have been used to study the structural and morphology of the polymer electrolyte composites. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) have been described which have been used to study the thermal properties of the polymer electrolyte composites. A brief description about transmission electron microscopy (TEM), Fourier transform infra-red spectroscopy (FTIR), magnetic measurements using vibrating sample magnetometer (VSM) and shielding measurements using vector network analyzer (VNA) have also been given in this chapter.

**Chapter 3** deals with the mixed conductors. Results on composites of polymer electrolyte (PEO:NH₄I) with dispersed graphene have been discussed. The composites have been prepared by solution cast technique. Graphene dispersal introduces partial electronic conductivity in the ion conducting polymer electrolyte. Electrical and transport number studies has been done for the mixed conductor composites. Graphene is important in fundamental studies and technological applications due to its unique structure and a wide range of unusual properties. Total electrical conductivity has been found to be a function of the amount of dispersed graphene. Conformational and structural changes have been investigated by Raman spectroscopy, differential scanning calorimetry (DSC) and positron annihilation lifetime spectroscopy (PALS). Graphene dispersal leads to conformational changes in the nature of the host polymer as well as that of and the dispersed graphene sheets. Conductivity studies give evidence of two-percolation thresholds for the charge carriers which are supported by thermal and structural studies. Peaks in the conductivity have been explained on the basis of changes in crystallinity of the host polymer and establishment of percolation paths.

**Chapter 4** deals with the particle size effects of the dispersoid on the percolation threshold and the extent of maximum conductivity enhancement for the composites. Silica particles of different diameters (0.007, 0.014 and 44 µm) have been dispersed in polymer electrolyte (PEO: NH₄I), to form composites and their electrical and thermal behaviour has been studied. The role of degree of crystallinity/amorphicity
of the composites in modifying the conductivity of the composites is discussed and a phenomenological explanation is suggested. The conductivity variation shows that there are two peaks in the conductivity versus composition of SiO₂. The two peaks in the conductivity have been attained for different wt. % of SiO₂ in the composites, i.e., at lower wt.% of SiO₂ for smaller SiO₂ particles. Also, the maximum conductivity has been found to decrease as the SiO₂ particles size increases. The peaks in the conductivity have been explained in terms of degree of crystallinity in the polymer composites which is evidenced in the thermal and XRD studies of the composites. The restriction in polymer chain flexibility (due to the wrapping of the polymer around the dispersoid particles) leads to the generation of additional interfacial charge carriers giving conductivity modification of the polymer composites.

**Chapter 5** deals with studies on polymer electrolyte (PEO:NH₄I) in which transition metal oxides (TMOs) Fe₃O₄, NiO, Mn₃O₄ & Co₃O₄ nanoparticles have been dispersed. Magnetic nanoparticles of transition metal oxides give unique response to magnetic fields. They have a saturation magnetization much lower than that of corresponding bulk materials. Transition metal oxide nanoparticles have been synthesized by known chemical methods. Iron oxide as well as iron oxide dispersed composites show superparamagnetic behavior. Iron oxide dispersed composites give the best conducting composites possessing saturation magnetization (Ms) value of ~3 emu/g with conductivity of 1.6 E-5 S/cm. Crystallite size determination and morphological study of the TMO nanoparticles has been done. The chapter also contains the magnetic field dependence of conductance of the iron oxide dispersed composites. Shielding effectiveness has been measured for Fe₃O₄ dispersed composites. The combination of polymer electrolyte and magnetic particles forms a composite having electromagnetic properties. The Fe₃O₄ dispersed composites have the potential to be used as medium field magnetic sensors.

Finally, **chapter 6** gives the summary of the overall work done and the conclusions. The scope of future work has also been given in the last part of this chapter.