Increasing demand of energy has led to the current wave of research for renewable energy sources. Materials aspect of electrochemical devices can be divided in two branches (i) electrolyte materials and (ii) electrode materials. Present work deals with electrolytes. Liquid electrolytes are the best, from conductivity point of view, but the mechanical problems are associated with them, which forced the scientific community to search for alternatives. Polymer electrolytes, having physique of solids and conductivity comparable to liquids, came as an excellent class of electrolytes. Armand was the first to recognize the technical importance of this class of materials. Since then considerable efforts are continuously being made to improve these materials, and success is achieved in commercialization of polymer based energy devices. Polymer electrolytes, presently used in commercial devices, have small liquid component which are associated with serious problems like volatility, explosion etc. Hence for fabrication of devices along with good electrochemical properties, many other properties such as non-volatility, non-inflammability, electrode electrolyte contact etc are also very important. To address the above mentioned safety concern and to get flexibility in cell design, considerable attention has been given to develop electrolytes having desired features. In this reference, synthesized polymer electrolytes have a good scope, because they have flexibility to combine good conductivity, mechanical and other properties by modifying the synthesis process/crosslinking/gelatinization etc. Hence lab synthesized host matrix are becoming popular to explore the possibilities of new polymer-salt complexes. In same relevance, Ohno et al. reported that polymers having both +ve and –ve charges on same molecular unit may play an important role in electrolyte preparation. In these materials constituent charges on matrix do not move under potential gradient hence better targeted ion transference number is expected. These materials have high dielectric constant which helps salt dissolution.

Besides developing new materials, recently, considerable attention has been diverted to understand the ion dynamics such as salt dissociation pattern, relation of polymer segment and ion movement, temperature dependence of different parameters and nature of ion motion (i.e. hopping or caged movement) etc. These studies are imperative for materials development, as they decide the future protocol for designing of new materials. Impedance spectroscopy and dielectric spectroscopy are excellent tools to get insight details of conducting materials. Investigation of impedance spectroscopy data in different (dielectric,
modulus and conductivity) formalisms reveals information regarding electrical transport behavior. These different formalisms are complementary to each other and are collectively used to analyze ion dynamics in disordered materials. In polymer-salt complexes it is important to understand whether the ion transport mechanism is controlled by polymer lattice or type of salt, their concentration and/or temperature are the deciding factors. Scaling is used to understand the effect of these parameters on conductivity. Hence, in present thesis synthesis and characterization of novel polymer electrolytes with different sodium and ammonium salts are discussed. A method is proposed for accurate estimation of scaling parameters for conductivity data. The present thesis is organized into seven chapters as follows:

Chapter 1: Introduction

Thesis subject area and background of solid polymer electrolytes are introduced here. The chapter deals with classification of ion conducting materials and basics of ion transport mechanism. History of ion dynamic theories, Jonscher power law, subsequent corrections made in them and various available ion dynamics models are discussed in this chapter. Different technological applications of the polymer electrolytes are also discussed.

Chapter 2: Experimental techniques

This chapter describes various experimental techniques which have been used in present work for material characterization. Solution cast technique is used for material preparation. In present work X-ray diffraction (XRD), DC polarization, Impedance spectroscopy, Dielectric and Modulus spectroscopy are used to characterize the prepared materials.

Chapter 3: Effect of anion size on electrical and dielectric properties of sodium based electrolyte systems

This chapter consists a detailed analysis of electrical, dielectric and ion dynamic behavior of 5 different sodium salts at fixed salt concentrations. Polymer electrolyte materials are synthesized by the solution cast technique. Conductivity of the material increases with decrease in the ionic radii. It indicates that in prepared systems, probably anion is the dominating charge carriers. Temperature dependence of conductivity is studied for all the systems and their activation energies are estimated. The conductivity increases with temperature and follows an Arrhenius nature. The activation energy decreases with
decreasing anion size. Dielectric properties of prepared materials are studied with frequency and temperature. High value of dielectric permittivity is observed towards lower frequency region and is associated with electrode polarization. Due to electrode polarization material’s bulk relaxation phenomenon is obscured hence to observe the conductivity relaxation, modulus parameter is studied. Loss tangent is calculated from dielectric parameters. Kohlrausch-Williams-Watts (KWW) exponent (β) calculated from loss tangent is found to be independent of anion size. Scaling of conductivity, dielectric and modulus data has been performed to understand whether type of anion has any influence on underlying ion transport mechanism or only dissociation of salt (and hence number of charge carriers) and mobility are affected by it. A method for estimation of scaling parameters for conductivity data is proposed. Accordingly, after carefully recognizing the JPL region a common frequency range is selected in which all curves follow Jonscher Power Law. Scaling parameter selected by this method resulted in master curve with respect to different salts. Scaled curve obtained, with respect to different salts, is concluded as an indication that ion transport mechanism is governed by host polymer matrix, and salt only affects the number of charge carriers and mobility.

**Chapter 4: Electrical transport and dielectric study of sodium salt based systems**

This chapter reports salt concentration dependent behavior of sodium salt based systems. Here, based on anion size, three different sodium salts are chosen, namely NaCl (Cl\(^-\) = 0.133nm), NaI (I\(^-\) = 0.22nm) and NaPF\(_6\) (PF\(_6^+\) = 0.33nm). Salt concentration of all the three systems have been varied from 10 to 50%. Conductivity as a function of salt concentration followed the typical polymer-salt complex behavior. XRD pattern indicated that as salt concentration increases, system transform from semicrystalline to amorphous state. Increasing amorphosity makes the system flexible which assists the relaxation process. This has been confirmed by shifting of minima in \(\partial\log\varepsilon'/\partial\log\omega\) vs. \(\log\omega\) curve. Different parameters like fractional number of dissociated charge carriers, number of charge carriers, mobility, KWW exponent (β) are estimated to understand the ion transport in these systems. Applicability of the conductivity power law to the present data has been analyzed. The study indicated that in present case, below MHz frequency ion exhibites three different types of movement (i) free hopping (ii) correlated hopping (iii) caged movement of ions within the experimental frequency range. Temperature dependent study has confirmed this conclusion.
Dielectric and Modulus studies have been carried out to understand the relaxation process and their dependence on salt and temperature. $\tan\delta$ vs logω curves have been deconvoluted to determine the relaxation time. Two relaxation times ($\tau_1$ and $\tau_2$) are observed in all the systems. In case of NaPF$_6$ and NaCl both $\tau_1$ and $\tau_2$ inversely follow the conductivity data with salt concentration. Two $\tau$’s are associated with cation and anions. In case of NaI system one $\tau$ is inversely following $\sigma_0$ but the other one does not. A new and fast relaxation appeared at 50% NaI concentration which is associated with direct diffusion of ions. Hence it is expected that in this system, decoupling of polymer-salt interaction is taking place at high salt concentration. Conductivity data, are successfully scaled by estimating the scaling parameters exclusively in a common frequency range as per our proposed method discussed in chapter 3.

**Chapter 5: Electrical transport and dielectric study of ammonium salt based systems**

This chapter deals with ammonium salt based systems. Here also, same three anions have been chosen, i.e. Cl$^-$, I$^-$ and PF$_6^-$ . These systems also followed the similar trend as discussed for sodium salts. In these systems, also, salt plasticizing effect is observed and system acquires amorphous nature on higher salt concentration. Here also the deconvolution of $\tan\delta$ vs logω peak indicated two relaxation times. In case of NH$_4$Cl and NH$_4$PF$_6$ based systems they followed the inverse trend with salt concentration and hence they are associated with cation and anion movement and hence here also a strongly correlated ion segment motion is expected. $\tau$’s of NH$_4$I system follows the similar trend as discussed for NaI system hence here also the fast relaxation observed at 50% NH$_4$I concentration is associated with direct diffusion of ions and it is concluded that at this salt concentration, ion and segment motions are decoupled. Estimation of scaling parameters as per our proposed method resulted in good master curve and it has been concluded that in these systems also, salt concentration and temperature do not affect ion transport mechanism.

**Chapter 6: Ion dynamic behavior of polymer-salt complexes**

The comparative ion dynamic studies of 7 different systems are discussed in this chapter. Based on the variation of power law exponent ‘n’ with salt concentration and temperature it has been observed that systems can be divided into three classes- (1) where exponent ‘n’ and fractional number of dissociated charge carriers ($N/N_0$) follow inverse trend with varying salt concentration. In these systems ‘n’ follows inverse trend with temperature. - (2) Where ‘n’ and $N/N_0$ have same relation when studied as a function of salt concentration.
In these systems ‘n’ follows the temperature. (3) In third category of materials no clear trend is observed. From these observations we propose that these different trends are manifestation of different caging phenomena. In case (1) it is concluded that caging is dominantly by neighboring lattice charge whereas in case (2) caging due to neighboring mobile charge is dominating and case (3) represents the systems where both caging due to lattice and mobile charge are having equal control. The concept is further supported by the observation that in case (1) dc region (frequency range where $\sigma$ is independent of frequency) increases with increasing conductivity whereas in case (2) it decreases with increasing conductivity.

**Chapter 7: Summary**

Finally, this chapter summarizes the overall results, focusing the important findings of the thesis.