CHAPTER ONE

INTRODUCTION

Dry solid polymer electrolytes (SPE) have been attracting interest as safer alternatives to liquid electrolytes [Itoh et al., 2009]. The pioneering work in the field of solid polymer electrolytes (SPEs) was carried out by Wright and co-workers who reported ionic conductivity of the order of 10^{-5} S/cm at 330 K in highly crystalline PEO–NaSCN complexes [Singh and Bhat, 2003].

Solid polymer electrolytes (SPE) are formed by dissolving salts in a polymer matrix. They have been receiving considerable attention as solid electrolyte materials for advanced applications, such as high energy density batteries, sensors and fuel cells [Zang et al., 2010]. The main advantages of the polymeric electrolytes are their good mechanical properties, ease of fabrication into thin films of desirable sizes, and the ability to form good electrode/electrolyte contact [Hema et al., 2009a]. Recent challenge is to find a low-cost membrane with good ionic conductivity, good dimensional and mechanical stabilities.

Although SPEs have many advantages like mechanical flexibility and corrosion resistance, they also have some disadvantages like low ionic conductivity and high crystallinity. Ionic conduction in SPEs is known to take place in the amorphous fraction of the polymer matrix, but the polymers used as hosts in polymer electrolytes are often semi-crystalline [Borgohain et al., 2010]. Thus, to overcome the disadvantages and improve conductivity of SPEs, the method mostly applied is to add plasticizer to improve the ambient ionic conductivity. Plasticizers can increase the amorphous content of polymer electrolytes and dissociate ion aggregates present in polymer electrolytes and thereby improve electrical conductivity of SPE [Pradhan et al., 2009]. It is important to note that the conductivity and mechanical stability of plasticized polymer electrolytes are properties that have reciprocal effect to each other, i.e., the ionic conductivity in plasticized polymer electrolytes increases at the expense of reduced mechanical strength, and vice versa [Deka and Kumar, 2011]. In addition to high conductivity and a wide electrochemical stability window, polymer electrolytes must exhibit a high thermal and mechanical performance. These performances can be obtained by dispersing nano size fillers in polymer electrolyte. Since the original work of Weston and Steele (1982), who reported the improvement of polymer electrolyte conductivity and mechanical stability by adding Al_2O_3 particles, nanocomposite polymer electrolytes have been extensively studied, i.e., the nano filler dispersion is a popular approach to overcome the shortcoming such as mechanical strength. The understanding of the impact of the inorganic filler on conduction, thermal, mechanical and electrochemical properties of polymer electrolytes is still in progress. The best performances were obtained with Al_2O_3 and TiO_2 [Alloin et al., 2010].

The study of dielectric relaxation in ion conducting polymer electrolytes is a powerful approach for obtaining information about the characteristics of ionic and molecular interactions. [Singh and Gupta, 1998]. Recently Malathi et al., (2010) and Prajapati et al., (2010), have considered complex permittivity parameters in explaining ionic conductivity of PVA based solid polymer electrolytes. Pradhan et al., (2008a, 2009), and Sengwa et al., (2010), have also used dielectric analysis to understand the conductivity behavior in nano-composite solid polymer electrolytes. The extensive and intensive survey of literature indicated that very little work has been done on dielectric properties of ion conducting solid polymer electrolytes and nano-composite electrolytes. Even the mechanism of ion conduction in SPEs is still not well understood. Hence, it becomes important to understand the ion transport behavior in solid and composite polymer electrolytes.

The ion transport property depends upon several factors like salt concentration, degree of salt dissociation, dielectric constant of host polymer, degree of ion aggregation and mobility of polymer chains. Further, ion association in a heterogeneous system is directly related to the presence of dipoles due to solvent dipoles/ion pairs [Agrawal et al., 2009]. The dielectric parameters associated with relaxation processes are of particular significance in ion conducting polymers where the dielectric constant plays a fundamental role which shows the ability of a polymer material to dissolve salts [Singh and Gupta, 1998]. Recently Petrowsky and Frech (2009, 2010), hypothesized that the DC conductivity is not only a function of temperature, but is also dependent on the dielectric constant for low salt concentration in organic liquid electrolytes. They have also interpreted the non-Arrhenian behavior of DC conductivity as a result of dependence of pre-exponential factor, σ_o , on the dielectric constant, $\sigma_{(T,\varepsilon')} = \sigma_{o(\varepsilon'(T))} \exp^{(-\frac{E_a}{K_B T})}$.

Thus, the correlation of dielectric properties with electrical conductivity is important in understanding the conduction mechanism in solid and nano-composite based polymer electrolytes. The electrode polarization (EP) in polymer electrolyte is one of the most undesired effects in low frequency dielectric spectroscopy, which occurs due to the blocking of charges at the sample/electrode interface [Senwa and Sankhla, 2008a]. In polymer electrolytes containing low salt concentration a high frequency semicircle and a spike region can be observed. The electrical properties associated with the high frequency semicircle are important because they represent the bulk and intrinsic property of the material. One of the main advantages of frequency dependent measurements are that the contributions of the bulk materials (high frequency region) and the electrode polarization (low frequency spike region) effects can easily be represented [Bassiouni et al., 2003]. Thus electrical impedance spectroscopy (EIS) technique becomes very efficient and easy because in frequency dependent measurements the bulk and interface has different polarization properties and therefore can be separated.

Thesis Organization

The research organized in this thesis is divided into 8 chapters. Chapter Two introduces an overview of the current state of SPEs and NCPEs. Basic equations are derived for dielectric function, electric modulus and electrical conductivity with a brief theory of polarization.

Chapter Three provides a detail description of the preparation of solid polymer electrolytes (SPEs) and nanocomposite solid polymer electrolytes (NCSPEs) in this work, using the solution cast method. The effect of low salt concentration of silver triflate, sodium triflate and lithium triflate as a doping salt is investigated. To the sample with the highest conductivity and highest dielectric constant in the solid polymer electrolytes, nano size Al_2O_3 will be added and the effect of filler investigated. The results of the characterizing methods for SPEs and NCPEs such as X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive x-ray (EDX), transmission electron microscope (TEM) and ultraviolet visible (UV-Vis) are given in Chapter Four. XRD analysis can estimate a wide range of information on crystallinity and complex formation in the prepared SPE and NCPE samples. The filler distribution and surface morphology of NCPEs have been investigated using SEM and EDX technique. TEM and UV-vis methods are used to detect the silver nanoparticle formation in chitosan:silver triflate system. These structural analyses are crucial in understanding structure-electrical property relationship.

Chapter Five provides in detail the results for DC conductivity, dielectric constant, normal and compensated Arrhenius relations with temperature, loss tangent and real and imaginary parts of electric modulus. The impedance plots and AC conductivity spectra at different temperatures are also displayed. From the AC conductivity spectra at various temperatures, the frequency exponent (s) was calculated. Chapter Six provides electrical and dielectric properties of NCPEs. Chapter Seven discusses results presented in the thesis and Chapter Eight concludes the thesis with some suggestions for future work.

Objective of the present work

In the present thesis the electrical/dielectric properties of all SPEs and NCPEs are represented in terms of complex dielectric function $\varepsilon^*(\omega)$, electrical modulus function $M^*(\omega)$, electrical conductivity function $\sigma^*(\omega)$, and complex impedance function $Z^*(\omega)$. The purpose and main objectives of the present work can be expressed as follows:

- To study the structural and morphological properties of SPEs and NCPEs based on chitosan.

- To reveal the dependence of bulk DC conductivity on bulk dielectric constant and temperature ($\sigma_{(\varepsilon',T)} = \sigma_o \exp(-E_a / K_B T)$) in SPEs and NCPEs based on chitosan for the first time.

- To demonstrate the constant behavior of pre-exponential factor (σ_o) in Arrhenius equation in solid and nano-composite polymer electrolytes based on chitosan.

- To study the relaxation processes in terms of loss tangent and electric modulus (Argand plot) in SPEs and NCPEs.

- To demonstrate the correlation between impedance plots and AC conductivity plots and the electrode polarization effect at high temperatures on AC dispersion.

To the authors knowledge the present work reveals for the first time the relationship between DC conductivity and dielectric constant in solid and nano-composite polymer electrolytes based on chitosan. The effect of electrode polarization on bulk AC conductivity dispersion and bulk dielectric constant is also specified.