CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

The interest in solid materials with ionic conduction properties has become important due to their application in solid state batteries and electrochromic devices [Armand, 1994; Bruce, 1995; Quartarone et al., 1998]. Among the most studied polymer as host for electrolyte system is poly(ethylene oxide), PEO. This is due to its ability to solvate many types of salt. In order to improve the mechanical properties and ionic conductivity of polymer electrolytes, different approaches such as blending with other polymers [Quartarone et al., 1998], adding filler to form composite polymer electrolytes (CPE), and plasticization have been proposed.

2.2   Composite polymer electrolyte

Composite electrolyte is a subset of polymer electrolytes with an idea of incorporating electrochemically inert fillers into the matrix of the electrolyte [Croce et al., 1998; Krawiec et al., 1995; Weston et al., 1982; Wieczorek et al., 1998]. Generally, high surface area particulate fillers such as ZrO_2, TiO_2, Al_2O_3 and hydrophobic fumed silica used [Golodnitsky et al., 1997; Dai et al., 1998].

Polymer composites have attracted the attention of researchers due to their interesting electrical and electronic properties. It has the potential application in integrated decoupling capacitors, angular acceleration accelerometers, acoustic emission sensors and electronic packaging and etc. [Chahal et al., 1998; Dias et al., 2004].

Organic/inorganic composite materials constitute a family of isotropic, flexible, amorphous nanocomposite materials, that have been widely studied for structural and biomedical applications. Apart from these, organic-inorganic composite membranes have been used in fuel cell studies [Park et al., 2005]. High ionic conductivity, adequate chemical and mechanical strength, extended thermal stability and low price are the favorable characteristics of polymer electrolyte membranes. These pre-requisites of polymer electrolyte membranes were obtained by combining both organic and inorganic materials. The prepared hybrid materials possess enhanced properties compared with the single organic or inorganic material. The organic-inorganic composite membranes exhibit a specific interaction between the components and influence the electrochemical stability [Kumar et al., 2009].

It is widely known from the literature that the addition of the nonconductive (passive) filler like alumina or silica to the electrolyte based on the PEO matrix will enhance its electrical properties [Choi et al., 1996]. For example, a maximum in ambient temperature conductivity equal to 10^{-5} S cm^{-1} was achieved for samples containing 10% by weight of the dispersoid which is about 2-3 orders of magnitude higher than for the unmodified polymeric electrolyte. This increase is due to a decrease in the crystalline phase concentration and thus an increase in the amorphous phase of the polymer host. The effect observed is opposite to both dilution effect by the dispersed grains causing the decrease in charge carrier concentration and amorphous phase

stiffening (glass transition temperature increase) effect caused by the addition of hard filler causing the lowering of the charge carriers mobility and therefore conductivity. Higher concentrations of the inorganic filler result in an abrupt decrease in ionic conductivity.

In some composite electrolytes however, the additives such as α-Al_2O_3 lithium borosulfate glass and γ-LiAlO, have been found to have a negligible or a small depressing effect on the polymer electrolyte conductivity [Weston and Steele, 1982; Panero et al., 1992; Kumar et al., 1994].

2.3   Aluminum Titanate

Aluminum titanate or tialite, exists in two allotropic forms, α and β. The low-temperature phase, β-Al_2TiO_5, has two temperature ranges of stability, the first from room temperature up to around 750 ^{o}C, and the second from 1280 ^{o}C up to the inversion temperature at 1820 ^{o}C. The high-temperature phase, α-Al_2TiO_5, is stable from 1820 ^{o}C up to the melting temperature, 1860 ^{o}C. Below 1280 ^{o}C, aluminum titanate decomposes, into α-Al_2O_3 and rutile titania. The decomposition process is very slow below 900 ^{o}C, whilst in the range 900-1200 ^{o}C it accelerates with a maximum decomposition rate at 1100-1150 ^{o}C, a range in which full decomposition is observed after annealing from 5 to 50 h [Innocenzi et al., 2005].

Tialite is a compound with orthorhombic structure and the following lattice parameters: a = 3.591, b = 9.429 and c = 9.36 Å. The density determined by X-ray diffraction is 3.70 g cm^{-3}[Zaharescu et al., 1998].

According to Fukuda et al., (2002) aluminum titanate ceramics are important for high-temperature employable product. They have been used as articles for high-temperature portions of an automotive engine and parts for high-temperature portions in electric and electronic devices. In nuclear reactors aluminum titanate ceramics are used as shielding materials. However, the high temperature application of aluminum titanate ceramics is limited by the low fracture strength caused by the microcracking phenomena and the thermodynamic decomposition that occur over a given range of temperature. It has been proven that a reduced grain size (0.5 – 1 μm) help reduce the microcracking problem [Parker et al., 1989; Lee et al., 1997]. The phase equilibrium diagram shows that 1200 ^{o}C is the temperature below which tialite becomes thermodynamically unstable [Thomas and Stevens, 1989]. Below 1280 ^{o}C, metastable Al_2TiO_5 undergoes a eutectoid decomposition to α-Al_2O_3 and TiO_2 (rutile) within the temperature range 900-1280 ^{o}C [Kato et al., 1980]. It is generally agreed that the decomposition rate peaks at 1100 ^{o}C. The kinetics of decomposition is poorly understood and it is still unclear whether the process of phase decomposition is a reversible or irreversible process. If the process is reversible, it may be possible for the decomposed Al_2TiO_5 to undergo self-recovery or 'reformation' when it is reheated to elevated temperatures (i.e. > 1300 ^{o}C) [Low et al., 2008]. The easy tendency to decompose follows the reaction [Kato et al., 1980]:

$$Al_2TiO_5 \rightarrow \alpha\text{-}Al_2O_3 + TiO_2 \text{ (rutile)} \qquad\qquad (2.1)$$
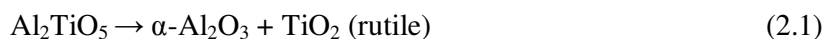
2.4   Filler

Though polymer membranes have many advantages such as high performance, size, safety, environmental aspects, they still suffer from some critical drawbacks which should be overcome prior to their use in practical applications. One of the major drawbacks which have limited the market penetration of these systems is the cost of the polymer electrolyte membranes. Commercially available polymer electrolyte membranes such as Nafion contributes a significant extent to the cost of the entire device. Nafion membranes suffer a conductivity drop beyond 80 $^{\circ}$C, which results in reduction of the fuel cell performance [Arico et al., 2003]. This limitation has prompted research in composite membranes.

One of the most promising ways to improve the morphological and electrochemical properties of polymer electrolytes is addition of ceramic fillers [Croce et al., 1998; Appetecchi et al., 2000; Itoh et al., 2003]. The highly conducting ceramic fillers, zeolites [Skaarup et al., 1980], ionites [Wieczorek, 1992] as well as electrically neutral ceramic fillers [Capuoano et al., 1991] have been investigated. It has been well established that the addition of ceramic fillers improves the conductivity of polymer hosts and their interfacial properties in contact with the lithium electrode. This increase in ionic conductivity is explained by enhanced degree of amorphousness of the polymer chain or hindered recrystallization formation [Appetecchi et al., 2000].

Electrical properties such as dielectric permittivity can be suitably adjusted by controlling the type and amount of ceramic inclusions. Ceramic materials are typically brittle, possess low dielectric strength and in many cases are difficult to produce

because of the requiring high temperatures process. On the other hand, polymers are flexible, can be easily processed at low temperatures and exhibit high dielectric breakdown fields [Bai et al., 2000]. Many polymers have been proven suitable matrices in the development of composite structures since they are easy to produce and process. Polymers have good adhesion with reinforcing elements, high resistance to corrosive environment, light weight and in some cases ductile mechanical performance. Furthermore, polymers are basically insulators with low dielectric permittivity and often high dielectric strength [Patsidis et al., 2008].

The advantages of incorporating fillers are two-fold. One is the enhancement in ionic conductivity at low temperatures and the other one is to improve the stability at the interface with electrodes [Borghini et al., 1995].

Since the first introduction of a ceramic filler (γ-Al_2O_3) into a polymer electrolyte by Weston and Steel (1982) to improve the mechanical strength of PEO–$LiClO_4$ polymer electrolytes, several researchers have reported that the incorporation of a ceramic filler in polymer electrolytes improves the interfacial properties by lowering the interface resistance [Appetecchi et al., 2000; Li et al., 2001].

Ceramic fillers reduce the crystalline character as well as promote thermal behavior of the membranes. Among the various fillers utilized in polymer electrolyte membranes, SiO_2 supports ionic mobility by its starburst shape which effectively disturbs the order packing tendency of the host polymer chains [Liu et al., 2007]. The particle size and shape of ceramic fillers also have a tremendous influence on the electrochemical properties of polymer electrolyte membranes. In lithium battery studies,

nanometer-size filler particles exhibited higher ionic conductivity than the micrometer-size filler particles [Krawiec et al., 1995].

Although there are many reports, in which addition of fillers reduces conductivity [Weston and Steele, 1982; Croce et al., 1989; Panero et al., 1992], it must be realized that conductivity depends on many factors that include salt species, salt concentration, particle size, temperature, thermal history, and preparative methods.

In general, the ceramic fillers can be classified into two categories: active and passive. The active component materials participate in the conduction process e.g. Li_2N, $LiAl_2O_3$ while passive fillers such as Al_2O_3, SiO_2, MgO do not involve in the lithium transport process. The selection of fillers between active and passive components is quite arbitrary [Stephan et al., 2006].

It can be concluded that, ceramic fillers not only facilitates ionic conductivity but also interacts with the polymer phase and the nature of interaction depends upon size of the particles [Kumar et al., 2001].

2.5   Chitosan as a host polymer

Ever since the discovery by Wright (1975) that poly(ethylene oxide) (PEO) – salt complexes [Frech et al., 1996] can support ionic conductivity many other polymeric materials have been tested and found to support ionic conductivity. Rapid development in ion conducting polymers probably took place when Armand realized the technological importance of such materials several years later [Armand, 1987].

The characteristics of the polymer host chains play a key role in the ionic transport process of polymer electrolytes. Poly(ethylene oxide) (PEO) is the most popular polymer host for electrolytes because of its exceptional ability to solvate ionics salts [Paulmer et al., 1992]. To date, several polymer hosts have been developed and characterized that include poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP), etc., Table 2.1 displays some of the physical properties of polymer hosts generally studied [Song et al., 2000]. The electrolytes commonly exhibit conductivities which range from 10^{-8} to 10^{-4} S cm^{-1} at temperatures between 40 and 100 ^{o}C.

In the effort to find alternative polymers with good mechanical and electrical properties to act as an electrolyte in polymer batteries, chitosan was studied (Mohamed et al., 1995, Subban et al., 1996 and Subban et al., 1996a).

Table 2.1: Physical properties of polymer hosts.

Polymer host	Repeating unit	Glass transition temperature, T_g (^{o}C)	Melting point, T_m (^{o}C)
Poly(ethylene oxide)	$-(CH_2CH_2O)_n-$	-64	65
Poly(propylene oxide)	$-(CH(-CH_3)CH_2O)_n-$	-60	a
Poly(acrylonitrile)	$-(CH_2-CH(-CN))_n-$	125	317
Poly(methyl methacrylate)	$-(CH_2C(-CH_3)(-COOCH_3))_n$	105	-
Poly(vinyl chloride)	$-(CH_2-CHCl)_n-$	85	-
Poly(vinylidene fluoride)	$-(CH_2-CF_2)_n-$	-40	171
Poly(vinylidene fluoride-hexafluoropropylene) P(VDF-HFP)	$-(CH_2-CH)$	-90	135

^{a} Amorphous

An important criterion for the choice of a successful polymer host is the presence of heteroatoms such as O and N that possess lone pairs electrons [Gray, 1991; Soquet et al., 1997; Sekhon et al., 1995]. These atoms are present in the polar groups of chitosan as shown in Fig. 2.1.
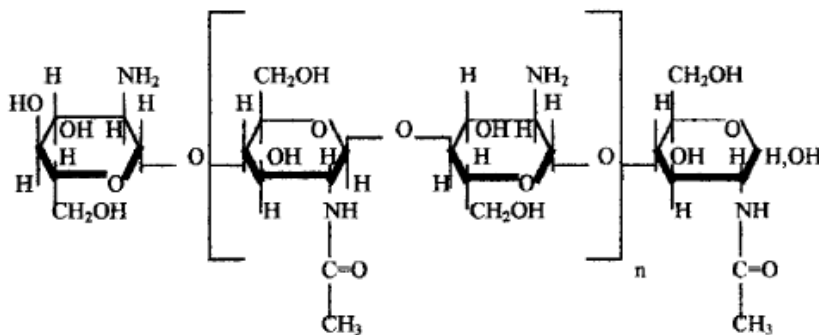

Fig. 2.1: Structure of chitosan [Yahya et al., 2002]

Chitosan is another polymer which has been shown to be a promising polymer electrolyte for solid-state cells [Mohamed et al., 1995; Morni et al., 1997; Kamaruddin et al., 1994; Subban et al., 1996]. This biopolymer has a variety of uses [Muzarelli, 1977]. It has several polar groups (OH and NH_2) in its structure that can act as electron donors and thus interact with inorganic salts. Interaction between a lithium-cation and a nitrogen donor has been proven by X-ray photoelectron spectroscopy [Arof et al., 1998]. X-ray diffraction has shown that a chitosan film is partially crystalline and its glass transition temperature, T_g is also quite high (~ 200 ^{o}C). In polymers, the addition of salt at levels higher then required for the optimum conductivity is known to increase the T_g values [Mellander et al., 1996].

Chitosan has increased a lot of interest in view of its applications in the industrial and biomedical sectors [Wan et al., 2003]. It is also the first natural polymer-chelating membrane and does not possess any pores. Chitosan films are homogeneous

with high mechanical strength [Muzarelli, 1973]. In its actual state, a chitosan film has very low electrical conductivity.

Chitosan is a biopolymer derived from chitin. Its monomer is almost similar to chitin with the exception of the $HNCOCH_3$ functional group which is replaced by the NH_2 functional group in chitosan [Bolker, 1974]. The nitrogen atom in the amine group has a lone pair electron just as in the case of the oxygen atom in the poly(ethylene oxide) or PEO polymer. In PEO, polymer-salt complexes form when the salt bonds with the lone pair electron of the oxygen atom of the polymer. Likewise, chitosan-salt complexes are expected to form when the metallic salt bonds with the lone pair electron of the nitrogen in the amine group of the chitosan polymer [Morni et al., 1997].

Chitosan is a biopolymer that may be considered as a binary heteropolysaccharide that contains residues of (1-4) linked 2-acetamide-2-deoxy-β-D-glucopyranose (GlcNac, A) and 2-amino-2-deoxy-β-D-glucopyranose (GlcN, D) [Varum et al., 1992]. Although the structure of chitosan monomer contains three hydrogens, the atoms are strongly bonded to the structure and cannot be mobilized under the action of an electric field to make it a proton conductor [Mohamed et al., 1995].

Chitosan is virtually a non-toxic polymer with a wide safety margin [Jumaa et al., 1999]. Moreover, chitosan is a biodegradable, biocompatible, positively charged polymer, which shows many interesting properties, such as a biodegradable edible coating or film in food packaging [Butler et al., 1996], a dietary fibre [Arvanitoyannis et al., 1998], a biomaterial in medicine either on its own or as a blend component, a

medicine against hypertension because of its scavenging action for chloride ions [Muzarelli, 1996] and a membrane filter for water treatment [Kawamura, 1995].

Chitosan can be dissolved in solvents such as acetic acid and formic acid [Subban et al., 1996]. According to Mohamed et al., (1995) if chitosan is dissolved in acetic acid and the resulting solution is cast into a thin film, then the H^+ or H_3O^+ and CH_3COO^- ions in the 'acetylated chitosan' film will be dispersed in the immobilized chitosan solvent and these ions can be mobilized under the influence of an electric field. If H^+ or H_3O^+ ions are more mobile than the CH_3COO^- ions the film becomes a proton conductor. Further, if the electrical conductivity of this films increases, then it should be possible to produce a more ionically conducting film by dissolving chitosan in acetic solutions of increasing concentration since more H^+ (or H_3O^+) will be contributed by the acetic acid [Mohamed et al., 1995].

It has been reported [Muzzarelli, 1977] that in solution, the periodic table group IA metals do not interact with chitosan. These metal ions or their salts do not form dative bonds with the nitrogen electrons. The nitrogen atoms come from the amide group that is abundant in chitosan. One of the criteria for a polymer to become a successful electrolyte is that it must form coordinate bonds with cations of the added inorganic salt [Gary, 1991]. Therefore it is necessary to prove that such interactions do occur between the cation of the doping salt and chitosan, as the polymer host material. Among the group IA element is lithium (Li). Lithium salts such as $LiClO_4$ and $LiCF_3SO_3$ have been used as the ion providing salt in polymer electrolytes that have potential commercial value. Conventional polymers that have successfully acted as polymer hosts include poly(ethylene oxide), poly(propylene oxide), poly(ethylene succinate), etc. One of the criteria that has made these polymers successful polymer

electrolytes is their ability to solvate many inorganic salts. This ability is afforded by the presence of an electron donor atom. In poly(ethylene oxide), poly(propylene oxide) and poly(ethylene succinate), the electron donating atom is oxygen. In poly(ethylene imine), the atom is nitrogen and in poly(ethylene sulfide), it is sulfur. The electron donor atom in chitosan is the nitrogen atom in the amine group [Arof et al., 1998]. According to Armand (1987), the presence of such electron donor atoms and the possible interaction between the cation of the ion providing salt and these electron donor atoms is the basic principle for the preparation of polymer electrolytes.

Previous studies have proven that chitosan can be used as a polymer matrix for ionic conduction [Mohamed et al., 1995; Arof et al., 1998; Osman et al., 2001; Subban et al., 1996; Subban et al., 1996a]. Thus chitosan satisfies one of the criteria as pointed out by Armand (1987) and Gray (1991) for the chitosan to act as a polymer host for the solvation of salts. Table 2.2 and 2.3 show the general properties, and sources of chitin and chitosan respectively.

Table 2.2: Sources of chitin and chitosan [Mathur et al., 1990].

Sea animals	Insects	Microorganisms
Annelida	Scorpions	Green algae
Mollusca	Spiders	Yeast (β-type)
Coelenterata	Brachiopods	Fungi (cell walls)
Crustaceans:	Ants	Mycelia Penicillium
Lobster	Cockroaches	Brown algae

Table 2.2 contliued….

Crab	Beetles	Spores
Shrimp		Chytridiaceae
Prawn		Ascomydes
Krill		Blastocladiaceae

Table 2.3: General properties of chitin and chitosan [Pillai et al., 2009].

Property	Chitin	Chitosan
Molecular weight	$(1\text{-}1.03) \times 10^6$ to 2.5×10^6	10^3 to 5×10^3
Viscosity of 1% solution, in 1% acetic cid, cps	-	200-2000
Moisture content		6-7
Solubility / solvent	DMAc-LiCl/TCA-Mc	Dilute acids TCA-MCA

When chitosan is dissolved in acetic acid and the solution is cast, a water-soluble chitosan acetate film is formed. If a plasticizer is dissolved together, a chitosan acetate-plasticizer film will be obtained after drying [Arof et al., 1998].

One of the important classes of polymer electrolyte is "polymer-salt complexes" in which some polar polymers like poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(vinyl alcohol) (PVA), etc. are incorporated with alkali-metal salts, ammonium salts, silver salts, acids, etc., to develop alkali, silver, copper, H^+, etc., ion conducting polymers. There were efforts taken to incorporate polymers like PEO [Chandra, 1992] with different ammonium salts for example, ammonium chlorate (NH_4ClO_4), ammonium hydrogen sulfate (NH_4HSO_4), ammonium sulfate (($NH_4)_2SO_4$), ammonium iodide (NH_4I), etc. In most polymer electrolytes the anions as well as

cations are found to be mobile. It is in this context that Chandra [Chandra et al., 1994] have recently considered polymer electrolytes as natural framework for growth of large size fractals due to random walk of free anions (or cations) and they successfully grew 2-3 cm large iodine fractals in PEO: NH_4I polymer electrolyte matrix, in which the mobile I^- aggregates.

As in all polymer-salt complexes, conductivity can be attributed to both anions and cations. The mobility of each of these ions is known to be quite comparable [Srivastava et al., 2000].

2.6   Summary

Many researchers have investigated the conductivity behavior of chitosan and its blend as polymer electrolytes [Reddy et al., 1999; Lewandowski, 2001]. Addition of ceramic fillers is one of the commonly used approaches to enhance ionic conductivity of solid polymer electrolytes and has been proven to be effective. In this work, chitosan has been chosen as polymer host, NH_4SCN as doping salt and Al_2TiO_5 as filler.