CHAPTER 1

INTRODUCTION TO THE PRESENT WORK

1.1 Introduction

In 1975 Wright discovered ionic conductivity in PEO-alkaline metal ion complex. Since then many types of polymer host have been proposed. According to Gray (1991), a criterion for selection of a polymer host is the presence of electron pair donor atoms present in the polymer structure to enable it to form polymer salt complexes.

To date, various types of polymeric systems have been studied. Most of the polymers studied involve synthetic polymers such as PEO, PVdF, PMMA and PVC. Today’s research on electrolytes focuses in developing polymer electrolytes which are environmentally friendlier besides having high ionic conductivity. In the present study chitosan is chosen as it is a natural polymer and can be obtained from renewable resources. Chitosan is derived from alkaline deacetylation of chitin. Chitin is found in crustacean shells, insect exoskeletons, fungal cell walls, microtauna and plankton. It is the second most abundant biopolymer after cellulose. The presence of amine and hydroxyl groups in the structure of chitosan acts as the electron pair donors that enable complexation with lithium ions (Yahya and Arof, 2003; Puteh et al., 2005; Yahya et al., 2005; Amir et al., 2010). Moreover, chitosan has good film forming properties, cheap and biodegradable. Chitosan has very low electrical conductivity which can be improved by addition of suitable salts, plasticizers and fillers. The salts should have high ionic conductivity, non-toxic and non-corrosive. Lithium triflate salt is non-toxic,
highly resistant to oxidation and thermally stable (Ahmad et al., 2006; Ramesh and Wen, 2010). Lithium acetate is soluble in many types of solvent especially acetic acid and cheaper than any other lithium salts. The plasticizers ethylene carbonate (EC) and propylene carbonate (PC) have been added to enhance the conductivity since they have high dielectric constant, low volatility and good miscibility. Incorporation of nano silica fillers can improve mechanical property and electrical conductivity of the polymer electrolyte film.

Many researchers have described that the dielectric parameters and electric modulus values are constant at higher and lower frequencies respectively. The validity of this concept on chitosan based polymer electrolyte system has to be investigated. This is because in samples with high salt content, many types of interactions will take place. If these interactions occur it may not be possible for the dielectric constant and loss to remain constant at high frequencies.

In 1972, Rice and Roth published a theoretical model, a free ion like model, of ionic transport processes in Superionic Conductor (SIC). In this study, an attempt has been made to use Rice and Roth model to determine and analyse the parameters responsible for transport of ions in polymer electrolyte systems.
Chapter 1  

Introduction

1.2  Objectives of the present work

The objectives of the present work are

- To study the effect of anion size on the conductivity of the polymer electrolytes. Lithium acetate and lithium triflate salts will be used as the ion source.
- To analyse the influence of nano fumed SiO\textsubscript{2} filler on the conductivity of the electrolyte system that contains the salt with the higher conductivity.
- To study the effect of filler on the structural, thermal and electrical properties of the electrolyte.

1.3  Scope of thesis

Chapter 2 presents an overview of the background on the development of polymer electrolyte systems. Chapter 3 outlines the details of sample preparation and experimental techniques employed to characterize the material structurally, thermally and electrically.

Chapter 4 deals with electrical studies carried out on the prepared electrolyte films using impedance spectroscopy. Conductivity-temperature studies were carried out to understand the ionic conduction mechanism. The dielectric behaviour of the prepared electrolyte films have been analyzed using dielectric permittivity, electric modulus and loss tangent. The region of high frequency of dielectric permittivity and low frequency of electric modulus of the three electrolyte systems will be probed further.
Chapter 1

Introduction

To investigate the interactions occurring between the various components present in the polymer electrolyte systems, FTIR was carried out and presented in Chapter 5. Chapter 6 presents the X-ray diffraction patterns. This was carried out to examine the effect of addition of the two salts and the filler on the structural properties of the films. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the thermal properties of the polymer electrolytes and the results presented in Chapter 7.

In Chapter 8 the overall results obtained were discussed and Chapter 9 concludes the thesis and suggestions for further work in chitosan-based electrolyte systems are put forward.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Pure polymeric materials are known for their poor electrical conductivity and are often referred to as insulators. Armand and coworkers (1978) suggested that the polymer-salt complex material had potential to be used as an electrolyte in batteries at the Second International Meeting on Solid Electrolytes held in St Andrews, 1978. Polymer electrolytes have since received much attention. The ever growing interest in polymer electrolytes is related their use in a wide variety of advanced electrochemical devices such as fuel cells, batteries, gas separation membranes, chemical sensors and ionic switches (Kim et al., 2009).

In the past three decades, there have been many reports of the physical and electrochemical properties of several types of polymer host, such as poly(ethylene oxide)(PEO) (Nagasubramaniam and Di Stefano, 1990; Borghini et al., 1995; Quartarone et al., 1998; Croce et al., 2000; Kumar and Sunadari, 2010), poly(methylmethacrylate) (PMMA) (Bohnke et al., 1993; Appetecchi et al., 1995; Rajendran and Uma, 2000), poly(acrylonitrile) (PAN) (Singh et al., 1999; Perera et al., 2000; Osman et al., 2010) and poly(vinyl chloride)(PVC) (Ramesh and Arof, 2000; Rahman et al., 2004; Ramesh and Ng, 2009).
Chapter 2

2.2 Polymer Electrolytes

Polymer electrolytes are thin solid film consisting of ionic salts ‘dissolved’ in an appropriate polymer. Although they are like solids, the internal structure and consequently the conductivity behaviour closely resemble that expected of the liquid state (Linford, 1991). The polymer acts as immobile solvent and the salt remains in solution.

A polymer electrolyte has two functions: that of separator and as a medium for the transport charge. It must therefore possess certain desirable properties (Abraham, 1993; Sanchez et al., 1997; Kim and Smotkin, 2002) such as:

- Good ionic conductivity between $10^{-4}$ and $10^{-3}$ S cm$^{-1}$ in the ambient temperature range of –40 to 70°C depending on the application;
- Good dimensional stability in the –40 to 70°C range;
- Good thermal stability in the –40 to 70°C range;
- High electrochemical stability towards metallic lithium and towards cathode materials in order to avoid increase in interfacial resistance which affects the battery performance and shortens its lifetimes;
- Ability to afford Li cycling (recharge) at an efficiency of greater than 99%.

However, since this study does not emphasize on application in any device, our first concern will be the first three properties.

Polymer electrolyte systems can be classified into three broad categories: ‘dry solid systems’, ‘polymer gels’, and ‘polymer composites’.
(a) ‘dry systems’ use the polymer host as the solid solvent and do not include any organic liquids.

(b) ‘polymer gels’ contain organic liquids as plasticizers which with a lithium salt remain encapsulated in a polymer matrix

(c) ‘polymer composites’ include high surface area inorganic solids in proportion with a ‘dry solid polymer’ or ‘polymer gel’ system.

2.2.1 Dry solid polymer electrolytes

Most widely studied dry solid polymer electrolytes are complexes of lithium salt and poly(ethylene oxide) and or poly(propylene oxide). Table 2.1 gives some examples of dry solid polymer electrolyte systems.

PEO-based systems were the first solid polymeric electrolyte discovered and extensively studied. The electrolyte low room temperature conductivity is of the order of $10^{-8}$ S cm$^{-1}$. Conductivities of dry solid polymer electrolyte can be increased by (Murata et al., 2000):

- increasing the carrier concentration and/or its mobility
- suppressing crystallinity of the polymer electrolyte
### Table 2.1 Conductivities of some dry solid polymer electrolyte systems

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Polymer electrolyte</th>
<th>Conductivity $\text{S cm}^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>PEO + CF$_3$SO$_3$Li</td>
<td>$7 \times 10^{-8}$</td>
<td>Nagasubramaniam et al., 1995</td>
</tr>
<tr>
<td></td>
<td>PEO + CF$_3$SO$_3$Li</td>
<td>$7 \times 10^{-5}$ at r.t.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PEO + NaI</td>
<td>$5.21 \times 10^{-5}$ at r.t.</td>
<td>Mohamed et al., 1995</td>
</tr>
<tr>
<td></td>
<td>PEO + (NH$_4$)$_2$SO$_4$</td>
<td>$2.7 \times 10^{-6}$ at r.t.</td>
<td>Ali et al., 1998</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA)</td>
<td>PVA + salt (LiCF$_3$SO$_3$, LiBF$_4$, LiClO$_4$, NaBF$_4$)</td>
<td>$10^{-8}$ to $10^{-5}$ at 20$^\circ$C</td>
<td>Yamamoto et al., 1994</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA) and polyacrylonitrile (PAN)</td>
<td>PVA-PAN+3MLiClO$_4$</td>
<td>$3.76 \times 10^{-3}$ at r.t.</td>
<td>Subramania et al., 2006</td>
</tr>
<tr>
<td>Polyvinylidene difluoride (PVdF)</td>
<td>PVdF + AgCF$_3$SO$_3$</td>
<td>$10^{-5}$ to $10^{-3}$ at r.t.</td>
<td>Suthanthiraraj et al., 2006</td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidone) (PVP)</td>
<td>PVP + 20 mol% ammonium thiocyanate</td>
<td>$1.7 \times 10^{-4}$ at r.t.</td>
<td>Ramya et al., 2006</td>
</tr>
<tr>
<td>Polyvinyl Chloride (PVC)</td>
<td>PVC + LiCF$_3$SO$_3$ + LiBF$_4$</td>
<td>$5.2 \times 10^{-5}$ at r.t.</td>
<td>Ramesh and Arof, 2000</td>
</tr>
<tr>
<td></td>
<td>PVC +LiPF$_6$ system</td>
<td>$1.14 \times 10^{-6}$ at r.t.</td>
<td>Subban et al., 2004a</td>
</tr>
<tr>
<td>Polyethylene oxide (PEO) and polyethylenimine (PEI)</td>
<td>[(8:2)PEO:PEI]$\alpha$ + LiClO$_4$</td>
<td>$1.1 \times 10^{-4}$ at r.t.</td>
<td>Tanaka et al., 2001</td>
</tr>
<tr>
<td>poly(N-2-cyanoethyl)ethylenimine (PCEEI)</td>
<td>PCEEI+ LiCF$_3$SO$_3$</td>
<td>$10^{-8}$ at r.t.</td>
<td>Erickson et al., 2003</td>
</tr>
<tr>
<td>Polyvinylidene difluoride (PVdF) and Polyethylene oxide (PEO)</td>
<td>PVDF+PEO$_8$ + LiClO$_4$</td>
<td>$2.62 \times 10^{-5}$ at r.t.</td>
<td>Jacob et al., 1997</td>
</tr>
<tr>
<td>Methylcellulose (MC)</td>
<td>MC + 18% NH$_4$F</td>
<td>$6.4 \times 10^{-7}$ at r.t.</td>
<td>Aziz et al., 2010a</td>
</tr>
</tbody>
</table>
Figure 2.1 shows the segmental motion of the polymer chain in the amorphous state. Lithium cation mobility is regulated by lithium ion–polymer interaction involving cation-ether oxygen coordination bonds. It can be seen that conductivity of the electrolyte is dependant on the local relaxation and segmental motion of the host polymer chains.

![Diagram of ion motion in a polymer host](image)

**Figure 2.1 Cartoon of ion motion in a polymer host (Bruce, 1995; Stephan, 2006)**

One of the approaches to enhance ambient temperature conductivity of PEO-LiX polymers is to use lithium salts (LiX) having large anions which may interfere with and impede crystallization of the polymer to yield primarily amorphous electrolytes (Thokchom *et al.*, 2005). Lithium salts such as LiAsF$_6$, LiBF$_4$, LiClO$_4$ and LiCF$_3$SO$_3$ have low lattice energies that can give rise to better conductivity compared to LiCl and LiBr which have high lattice energies (Abraham, 1993). Salts with low lattice energies can easily dissociate and hence provide more mobile charge carriers that contribute to ionic conductivity. Imide salts are highly desired due to their large anion with delocalized negative charge (e.g. lithium bis(trifluoromethylsulfonyl)imide, LiTFSI) (Geiculescu *et al.*, 2002; Lu *et al.*, 2007). Furthermore, the plasticizing effect of large anion may reduce the glass transition temperature ($T_g$) of the polymer which may
increase the ionic conductivity of the electrolyte (Nagasubramanian et al., 1995). Watanabe et al. (2001) explored the anionic effect on ion transport properties such as ionic conductivity and lithium transference number in solid polymer electrolytes, by using lithium imide salts (LiPPI, LiPEI and LiTFSI). The ionic conductivity of LiPPI systems can reach $10^{-5}$ S cm$^{-1}$ at 30°C and is higher than those containing LiPEI by two orders of magnitude, in spite of their similar structure as shown in Figure 2.2. The dissimilarity in conductivity between the LiPPI and LiPEI systems was caused by the differences in dissociation ability of these imide salts. LiTFSI exhibited the highest ionic conductivity due to its strong electron withdrawing effect of the TFSI$^{-1}$, which promotes dissociation and weakens the interaction with the polymer chain (Watanabe et al., 2001).

Figure 2.2 Lithium imide salts used in the formation of amorphous electrolytes (Dillon and Shriver, 2001; Watanabe et al., 2001).

In attempts to increase ionic conductivity, new structures were synthesized through modification by blending, grafting and cross-linking. Polymer blends such as MEEP-
PEO-LiX was synthesized and characterized by Abraham et al. (1989). Conductivity was reported to be 500-fold better in the polymer blends than that of PEO-based electrolytes. Ikeda et al. (2000) prepared and studied high molecular weight comb-shaped poly(oxy ethylene) with tri(oxy ethylene) side chains. An enhancement in the conductivity was observed with the introduction of tri(oxy ethylene) side chains and this was attributed to the decrease in crystallinity of oxyethylene segments. Chemical cross-linking of polyethylene glycol-salt complexes with 4,4′,4″-methylidyne-tris(phenyl isocyanate) was carried out by Borghini et al. (1996). These electrolytes were found to be promising materials for lithium batteries because of their amorphous state and high mechanical strength.

Niitani et al. (2005 and 2009) studied polymer electrolyte systems using block copolymers. These SPEs exhibit microphase separations. The ionic conductivity at room temperature of the polymer electrolyte system was reported to be greater than $10^{-4}$ S cm$^{-1}$. The formation of micro-domains during phase separation of the block polymer improves ionic conductivity and mechanical property of the polymer electrolyte system.

Noda et al. (2004) explored the properties of semi-interpenetrating polymer network (semi-IPN) polymer alloy electrolyte, composed of high conductivity amorphous poly(dimethyl siloxaneg-oligoethylene oxide), SLX/EO with inadequate mechanical strength and the network phase with good mechanical strength but low conductivity with lithium salt as illustrated in Figure 2.3. The polymer alloy electrolyte was reported by to have high ionic conductivity (more than $10^{-4}$ S cm$^{-1}$ at 25 °C) and good mechanical strength.
Another well established dry solid polymer electrolyte is polyelectrolyte. In polyelectrolyte, the anions are covalently bonded to the polymer backbone, as exemplified in Figure 2.4. The transference number is expected to be close to unity, as the anions are virtually immobile (Snyder et al., 2002). This property deters build-up of resistive layers of high or low salt concentration at the electrode/electrolyte interfaces during charging and discharging in lithium ion batteries. Conductivities in the range of $10^{-5}\text{S cm}^{-1}$ have been established at ambient temperatures with polyelectrolyte systems.

Figure 2.4 Contrast between (a) a polymer electrolyte containing a salt LiX and (b) a polyelectrolyte in which the anion is attached to the polymer backbone via chemical bonds (Song 1999)
Angell et al. (1994) reported another type of solid electrolyte: rubbery electrolytes’ or ‘polymer-in-salt’ electrolytes, which consist of incorporation of a small mole fraction, 5–10% repeat units, of high molecular weight polymer into a supercooled lithium salt mixture of sub-ambient glass transition temperature (Angell et al., 1994; Fan and Angell, 1995; Watanabe, 1996). These electrolytes have shown promising room temperature conductivities of the order $10^{-2}$ S cm$^{-1}$, but unfortunately it incorporates corrosive salts. Improvements in the salt combinations are needed, at the same time retaining the conductivity and mechanical properties.

The performance of electrochemical cells incorporating the ‘dry solid’ polymer electrolytes and lithium metal electrodes were not satisfactory as life cycles were as low as 200 to 300 cycles. Poor performance of the cells was mainly attributed to the low conductivity of the electrolytes, along with the reactivity of the anion of the electrolyte towards the lithium metal electrodes (Dias et al., 2000).

### 2.2.2 Polymer gels

The second category of polymer electrolyte is called “gel polymer electrolyte” or “plasticized polymer electrolyte” which is neither liquid nor solid. The electrolytes are obtained by the addition of a large quantity of liquid plasticizer and/or solvent to a polymer matrix capable of forming a stable gel with the host polymer (Song et al., 1999). Such mixings have resulted in gels with ionic conductivities close to those of the liquid electrolytes, arising from similar conductivity mechanisms taking place in both the systems. The gelled SPE has been developed along the following two concepts: (I) the gelled SPE by physical cross linking, and (II) the gelled SPE by chemical cross-linking (Murata et al., 2000).
Figure 2.5 shows a model of the two types of the gelled SPE. The chemical cross-linking gelled SPE shows thermally stability over time, but the physical cross-linking tends to swell and dissolve with heat ($\Delta H$).

![Figure 2.5 Gelled SPE models (Murata et al., 2000).](image)

Plasticizers are useful for enhancing the ionic conductivity of a solid polymer electrolyte. The plasticizer used should have the following features, such as its dielectric constant should be higher than that of the polymer used, low volatility, good miscibility with polymer and metal salt (MX), low freezing temperature, high boiling temperature and it must be inert towards the electrode materials (Kumar et al., 2002; Kuila et al., 2007). Low molecular weight polar organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and poly(ethylene) glycol (PEG) (Rhoo et al., 1997; Nishi, 2001;
Pradhan et al., 2005) are commonly used as plasticizers in polymer electrolytes. Table 2.2 displays some of the physical properties of plasticizers.

Table 2.2 Physical properties of some organic solvents commonly used in rechargeable lithium batteries (Stephan, 2006)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting point, MP (°C)</th>
<th>Boiling point, BP (°C)</th>
<th>Density, g (cm⁻³)</th>
<th>Dielectric constant, ε</th>
<th>Molecular weight</th>
<th>Solubility parameter (J cm⁻³)¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>2.4</td>
<td>90</td>
<td>1.06</td>
<td>3.12</td>
<td>90.08</td>
<td>20.3</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td>−43.0</td>
<td>126</td>
<td>0.9752</td>
<td>2.82</td>
<td>118.13</td>
<td>18.0</td>
</tr>
<tr>
<td>γ-Butyrolactone (BL)</td>
<td>−43.3</td>
<td>204</td>
<td>1.1284</td>
<td>39.0</td>
<td>86.09</td>
<td>25.8</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td>−48.8</td>
<td>242</td>
<td>1.2047</td>
<td>66.14</td>
<td>102.09</td>
<td>27.2</td>
</tr>
<tr>
<td>Ethylene carbonate (EC)</td>
<td>36.4</td>
<td>248</td>
<td>1.3214</td>
<td>89.78</td>
<td>88.06</td>
<td>30.1</td>
</tr>
</tbody>
</table>

However, when compared to solid polymer electrolytes, polymer gel electrolytes have poorer mechanical properties. Mechanical properties of the gel polymer electrolyte can be improved by adding components which can cross-link or thermoset the gel electrolyte. Various polymeric hosts such as, poly(vinylidene fluoride)-PVdF, poly(vinylidene carbonate)-PVdC) poly(acrylonitrile)-PAN, poly(vinyl chloride)-PVC, poly(vinyl sulfone)-PVS, poly(p-phenylene terephthalamide)-PPTA and poly(vinyl pyrrolidone)-PVP, have been studied and have found to have conductivities ranging between $10^{-4}$ and $10^{-3}$ S cm⁻¹ at 20°C. Table 2.3 lists the conductivities of some of the gel polymer electrolytes.
Table 2.3 Conductivities of some gel polymer electrolyte systems

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Polymer electrolyte</th>
<th>Conductivity $S\ cm^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>PEO + LiCF$_3$SO$_3$+DBP</td>
<td>$6.0 \times 10^{-4}$ at r.t.</td>
<td>Sukeshini et al., 1998</td>
</tr>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>(PEO)$_3$LiClO$_4$+DOP</td>
<td>$9.76 \times 10^{-5}$ at r.t.</td>
<td>Michael et al. 1997</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (PMMA)</td>
<td>PMMA + LiTFSI + EC</td>
<td>$4.34 \times 10^{-4}$ at r.t.</td>
<td>Ali et al., 2007</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (PMMA)</td>
<td>PMMA + LiTFSI + PC</td>
<td>$5.39 \times 10^{-4}$ at r.t.</td>
<td>Uma et al., 2005</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (PMMA)</td>
<td>PMMA + Li$_2$SO$_4$ + DBP</td>
<td>$3.43 \times 10^{-6}$ at r.t.</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl Alcohol (PVA) and polyacrylonitrile (PAN)</td>
<td>PVA- PAN+3MLiClO$_4$</td>
<td>$3.76 \times 10^{-3}$ at r.t.</td>
<td>Subramania et al., 2006</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP)</td>
<td>PVdF-HFP + LiTf : EC (60 : 40)</td>
<td>$1.0 \times 10^{-3}$ at r.t.</td>
<td>Ramesh and Ong, 2010</td>
</tr>
<tr>
<td>Poly(vinyl sulfone) (PVS)</td>
<td>PVS + LiN(CF$_3$SO$_3$)$_2$ + PC</td>
<td>$3.74 \times 10^{-4}$ at r.t.</td>
<td>Choe et al., 1995</td>
</tr>
<tr>
<td>Polyvinyl Chloride (PVC)</td>
<td>PVC + LiTFSI + DOP or DBP</td>
<td>$10^{-4}$ at r.t.</td>
<td>Sukeshini et al., 1996</td>
</tr>
<tr>
<td>Epoxidised natural rubber and Polyethylene oxide (ENR/PEO)</td>
<td>ENR/PEO + EC:PC+LiCF$_3$SO$_3$</td>
<td>$10^{-4}$ at r.t.</td>
<td>Glasse et al., 2002</td>
</tr>
<tr>
<td>Poly[(acrylonitrile-co-3-(bis-carboxymethylamino-2-hydroxy-propyl ester) Poly(AN-co-GMA-ID)]</td>
<td>Poly(AN-co-GMA-IDA)+ LiClO$_4$</td>
<td>$9.75 \times 10^{-4}$ at 30°C</td>
<td>Liang et al., 2009</td>
</tr>
<tr>
<td>Methyl cellulose (MC)</td>
<td>MC-NH$_4$NO$_3$-PEG</td>
<td>$(1.14\pm0.37) \times 10^{-4}$ at r.t.</td>
<td>Shuihaimi et al., 2010a</td>
</tr>
</tbody>
</table>
The improved conductivity on addition of plasticizers can be explained as follows:

i. Better dissociation of the salt due to the high dielectric constant of the plasticizer. This increases the number of free mobile charge carriers (Sekhon, 2003; Rajendran et al., 2010).

ii. Low viscosity of the plasticizer maintains liquid-like state in polymer matrix and increases ionic mobility, and hence, conductivity (Rajendran et al., 2010).

iii. Increase in amorphous content of the polymer matrix (Kumar and Sekhon, 2002; Pradhan et al., 2007).

iv. Lowering of the glass transition temperature $T_g$ (Kumar and Sekhon, 2002) that enables the material to easily enter the amorphous state.

The main drawback of the gel electrolyte systems is their mechanical properties that are insufficient to produce thin films because the impregnation of a liquid electrolyte into a polar polymer results in softening of the polymer (Kim et al., 2000). It has also been reported that PVC-based gels have shown poor stability towards the lithium metal electrode and the anions of the lithium salt are known to decompose at lithium metal electrodes (Dias et al., 2000).

### 2.2.3 Polymer composites

Weston and Steele (1982) found that addition of 10 vol. % α-alumina to lithium perchlorate-poly(ethylene oxide) polymer electrolytes makes a significant improvement in the mechanical stability of the material. Since then, with a view to making dimensionally stable polymer electrolytes for lithium batteries, high surface area particulate fillers such as ZrO$_2$, TiO$_2$, Al$_2$O$_3$, hydrophobic fumed silica, and fiber glass were introduced into polymer matrices to obtain the so-called 'composite
polymer electrolytes’ or ‘composite ceramic electrolytes’. Table 2.4 lists the conductivities of some of the composite polymer electrolytes.

Table 2.4 Conductivities of some composite polymer electrolyte systems

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Polymer electrolyte</th>
<th>Conductivity Scm⁻¹</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>(PEO)₃ + LiTFSI + Al₂O₃</td>
<td>2.2 × 10⁻² at r.t.</td>
<td>Dissanayake, 2004</td>
</tr>
<tr>
<td></td>
<td>PEO + NaClO₄ + PEG + SnO₂</td>
<td>~3 × 10⁻⁵ at 27°C</td>
<td>Pradhan et al., 2005</td>
</tr>
<tr>
<td></td>
<td>PEO + LiCF₃SO₃ + clay</td>
<td>1.4 × 10⁻⁵ at r.t.</td>
<td>Chen and Chang, 2001</td>
</tr>
<tr>
<td>poly(methylmethacrylate) (PMMA)</td>
<td>PMMA + LiClO₄ + DMP + CeO₂</td>
<td>5.36 × 10⁻⁵ at 303K</td>
<td>Rajendran et al., 2002</td>
</tr>
<tr>
<td>polyacrylonitrile (PAN)</td>
<td>PAN + LiAsF₆ + EC:PC + Na₁₂</td>
<td>≥ 10⁻⁷ at r.t.</td>
<td>Slane and Salomon, 1995</td>
</tr>
<tr>
<td></td>
<td>[Al₁₂Si₁₂O₄₈].27H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>PVC + LiCF₃SO₃-SiO₂</td>
<td>1.15 × 10⁻³ at r.t.</td>
<td>Subban et al., 2003</td>
</tr>
<tr>
<td></td>
<td>PVC + LiClO₄ + ZnO</td>
<td>3.7 × 10⁻⁷ at r.t.</td>
<td>Ahmad et al., 2008</td>
</tr>
<tr>
<td></td>
<td>PVC + LiClO₄ + TiO₂</td>
<td>4.4 × 10⁻⁹ at r.t.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVC + LiClO₄ + Al₂O₃</td>
<td>3.4 × 10⁻¹⁰ at r.t.</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)-poly (methyl methacrylate) (PMMA)</td>
<td>PVC + PMMA + LiBF₄ + DBP + ZrO₂</td>
<td>2.391 × 10⁻³ at 304K</td>
<td>Rajendran and Uma, 2000</td>
</tr>
<tr>
<td>poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVDF-HFP)</td>
<td>PVDF-HFP + EC:PC + LiCF₃SO₃ + Lifluorohectorite</td>
<td>4.46 × 10⁻³ at r.t.</td>
<td>Jacob et al., 2003</td>
</tr>
<tr>
<td></td>
<td>PVDF-HFP + EC:DEC + LiDFOB + Sb₂O₃</td>
<td>2.98 × 10⁻⁴ at r.t.</td>
<td>Aravindan and Vickraman, 2007</td>
</tr>
<tr>
<td>poly(acrylonitrile-co-methyl methacrylate) (P(AN-co-MMA))</td>
<td>(P(AN-co-MMA)) + LiClO₄ + EC:PC + SiO₂</td>
<td>1.93 × 10⁻³ at r.t.</td>
<td>Lee et al., 2000</td>
</tr>
</tbody>
</table>
Researchers also found that addition of inorganic fillers enhances the ionic conductivities especially those based on polyether–lithium salt systems. This increase in ionic conductivity is explained by decrease in the degree of crystallinity ($X_c$) of the polymer-salt matrix as well as the $T_g$ value (Wieczorek et al., 1996; Rajendran and Uma, 2000; Qian et al., 2001; Pitawala et al., 2007) and the formation of a new kinetic path via polymer-ceramic boundaries (Rajendran and Uma, 2000; Croce et al., 2006).

It is well known, uncontrolled passivation phenomena affect the cyclability of the lithium electrode (and thus, of the entire lithium battery) and may eventually lead to serious safety hazard (Appetechii et al., 1995). Therefore, it is important for lithium battery to use polymer electrolyte which has favorable interfacial characteristics besides good ionic conductivity. Incorporation of ceramic fillers to polymer electrolyte systems helps improve the lithium metal electrode interfacial stability (Croce et al., 2000; Li et al., 2001; Croce et al., 2006).

Figure 2.6 shows an improvement in the time dependence of the electrolyte with lithium metal by the addition of silica to a gel polymer electrolyte that comprised poly(acrylonitrile-co-methyl methacrylate) (PAN-co-MMA): EC–PC:LiClO$_4$ (Lee et al., 2000). It was suggested that these fillers are capable of trapping impurities such as water and thus prevents them from reacting at the interface. Gentili and coworkers (2007) also reported enhancement in the lithium interfacial properties on addition of surface functionalized fumed silica and alumina, respectively, in PVdF–carbonate solvent–lithium salt systems and they proposed that the surface groups on the fillers may also play a role in the stabilization of the interface.
Kumar and Scanlon (2000) reported that the size of fillers influences the interfacial stability. It is clear from Figure 2.7 the inert particles depending upon the volume fraction would tend to minimize the area of lithium electrode exposed to polymers containing O, OH-species and thus reduce the passivation process. It is also foreseeable that smaller size particles for a similar volume fraction of the ceramic phase would impart an improved performance as compared to larger size particles because they will cover more surface area (Kumar and Scanlon, 2000). The formation of an insulated layer of ceramic particles at the electrode surface will impede electrode reactions. Electrolytes after being assembled into cells are subjected to a dc bias equal to the cell voltage. The ability of the electrolytes to withstand the dc electrical potential is often termed in the literature as ‘electrochemical stability’. Kumar and Scanlon assessed electrochemical stability of ceramic-ceramic composite electrolytes and found that in ceramic-ceramic composite electrolytes, the decomposition potential, $V_d$, was greater, compared to the component members of the electrolyte due to
increased dissipation of energy (Kumar and Scanlon, 2000). If a similar logic was applied to polymer-ceramic composite electrolytes, they suggested that the polymer-ceramic composite electrolytes should have better electrochemical stability compared to polymer electrolytes.

![Schematic diagrams of lithium-composite electrolytes](image)

**Figure 2.7** Schematic diagrams of lithium-composite electrolytes (a) larger size particles, and (b) smaller size particles (Kumar and Scanlon, 2000).

### 2.3 Ion Conduction Mechanism

Knowledge of ion conduction mechanism in polymers is important, as it can help in the design of high ionic conductivity polymer and hence improve the battery performance. Although it is known that ionic association, cation–polymer interaction, and polymer segmental motion play critical roles in ionic conductivity, an in-depth molecular level mechanism of the ionic conductivity is not very much clear (Seneviratne et al., 2003; Anantha and Hariharan, 2005). There are few models that can be used to explain ion conduction mechanism in polymer electrolytes.
2.3.1 Arrhenius

Ion transport of alkali cations in solid electrolytes, polymer electrolytes and super cooled liquids strongly depend on temperature, $T$. Below the glass transition temperature, $T_g$, the conductivity, $\sigma_i$, is an exponential function of temperature and follows the experimental relationship:

$$\sigma_i = \frac{A_i}{T} \exp \left( -\frac{E}{RT} \right)$$

(2.1)

where, $E$ is the activation energy, $A_i$ is the pre-exponential term, $T$ is the absolute temperature and $R$ is the gas constant (Souquet et al., 2004).

Figure 2.8 (Ramesh and Arof, 2001) depicts the Arrhenius plots of logarithmic conductivity versus inverse temperature for samples containing PVC: LiCF$_3$SO$_3$:LiBF$_4$: EC: PC complexes.

![Arrhenius plot](image)

Figure 2.8 Temperature dependence of ionic conductivity for samples PC 5 and PC7 (Ramesh and Arof, 2001).

The increase in conductivity with temperature can be explained in terms similar to ion hopping mechanism in solids. Since the conductivity–temperature data obeys Arrhenius relationship, the nature of cation transport is quite similar to that occurring
in ionic crystals, where ions jump into neighbouring vacant sites and hence increases
the ionic conductivity to a higher value (Souquet et al., 1994; Ramesh and Arof, 2001;
Ramesh et al., 2002). Figure 2.9 (a) shows alkali cation at its normal site jumping to a
neighbouring cationic site that is already occupied to form interstitial cationic pairs
and Figure 2.9 (b) shows the interstitial cationic pair migrates from one interstitial
position to another.

Figure 2.9 Representation of a cationic displacement in a glass below the vitreous
transition temperature. (a) The local perfect structure and interstitial pair formation. (b)
Interstitial pair migration (Souquet et al., 1998; Souquet et al., 2010).

2.3.2 Vogel–Tamman–Fulcher (VTF)

Above $T_B$, amorphous polymer salt complexes have non-Arrhenius temperature
dependence as shown in Figure 2.10. The curve trends can be explained by the Vogel-
Tamman-Fulcher (VTF) equation.

$$\sigma T = A \exp \left( \frac{-B}{R(T - T_o)} \right)$$

(2.2)

where $A$ is the pre-exponential term, $R$ the ideal gas constant and $B$ have the
dimensionality of energy. According to the free volume approach, $T_o$ is the ideal glass
transition temperature.
The free volume model is very useful for explaining the polymer segmental mobility. The basic concept of this model is that sufficient free volume in the polymer system is required before molecular diffusion can occur. When a relatively large amount of free volume exists in the system, the molecules or chain segments can move through the polymer matrix unhindered.

Figure 2.10 The temperature dependence of the conductivity for PMMA–LiClO$_4$–DMP polymer electrolyte with various weight ratios of CeO$_2$: (a), 0; (b), 5; (c), 10; and (d) 15 (Rajendran et al., 2002).

The increase in conductivity with temperature in Figure 2.10 can be explained by free volume theory. It is known that the ionic conduction mainly takes place in the amorphous phase and that the polymeric segmental motion is necessary for ionic motion (Wang et al., 1997). As temperature increases, the polymer can expand easily and produce more free volume and hence the mobility of ions, solvated molecules or polymer segments are increased (Rajendran et al., 2002; Rajendran et al., 2004; Sivakumar et al., 2006).
In VTF relation, ion transport is mainly due to the polymer segmental motion, as illustrated in Figure 2.11.

Figure 2.11. Cationic migration by a free volume mechanism. (a) the local displacement of two solvated cations define two similar cells in which the grey colour represents the free volume; (b) local free volume transfer allowing a displacement to an available neighbouring solvating site; (c) after a cationic displacement and free volume redistribution (Souquet et al., 1996).

2.3.3 Williams–Landel–Ferry (WLF)

According to free-volume considerations, the WLF equation, represented below, can also be applied to the conductivity of amorphous polymer electrolytes.

\[
\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]

(2.3)

where \(\sigma(T)\) and \(\sigma(T_g)\) are the conductivity values at temperatures \(T\) and \(T_g\), respectively, and \(C_1, C_2\) are the WLF parameters for the temperature dependence of the
Chapter 2

Literature Review

Ionic conductivity. Kato et al. (2003) studied the temperature dependence for the ionic conductivity of the polymer electrolytes PEG\(_x\)-B\(_2\)O\(_3\), (\(x = 150, 200, 400, 600\)) + LiN(CF\(_3\)SO\(_2\))\(_2\) (Li:EO = 1:24).

The temperature dependence exhibited a convex-profile in the Arrhenius-type plots as shown in Figure 2.12. The ionic conduction mechanism of the polymer electrolyte samples does not obey the hopping model of carrier ions but obeys the free volume theory of polymers, which is indicative of the temperature dependence for segmental motion of the polymer chains expressed by the William–Landel–Ferry (WLF) relationship. Since \(\sigma(T_g)\) is too low to be measured, Kato et al. (2003) rewrote equation (2.3) as follows:

\[
\log \frac{\sigma(T)}{\sigma(T_o)} = \frac{C_1'(T - T_o)}{C_2 + (T - T_o)}
\]  

\[(2.4)\]

Figure 2.12 Arrhenius plots of ionic conductivity for PEG\(_x\)-B\(_2\)O\(_3\) + LiN(CF\(_3\)SO\(_2\))\(_2\) (Li:EO = 1:24): (○) PEG150, (▲) PEG200, (□) PEG400, (◆) PEG600 (Kato et al., 2003).
From the inverse of equation 2.4, the temperature dependence of the ionic conductivity is plotted as \[\log(\sigma(T)/\sigma(T_0))^{-1}\] vs. \[1/(T - T_0)\] as shown in Figure 2.13. The linearity in the graph shows ionic conductivity for these polymer electrolytes follows the WLF-type equation.

![Figure 2.13 WLF plots for the ionic conductivity of the polymer electrolytes PEGx–B_2O_3 (x = 150, 200, 400, 600) + LiN(CF_3SO_2)_2 (LiEO = 1:24) (Kato et al., 2003).](image)

### 2.3.4 Dielectric relaxation and modulus studies

The dielectric behaviour of polymer materials is of great importance from the point of view of their potential application in electrochemical devices. Dielectric relaxation refers to the relaxation response of a dielectric medium to an external electric field (Ramesh and Wong, 2009). This response is generally described in terms of permittivity as a function of frequency. Dielectric loss is the direct measure of energy dissipated through molecular collisions. Figures 2.14 and 2.15 shows the variations of the real \((\varepsilon')\) and imaginary \((\varepsilon'')\) parts of the dielectric constant as a function of
frequency for samples of the PMMA–LiCF$_3$SO$_3$ polymer electrolytes (Ramesh and Wong, 2009).

![Graph showing variation of the real part of the dielectric constant (\(\varepsilon'\)) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 70:30, b 75:25 and c 95:5.](image1)

**Figure 2.14** Variation of the real part of the dielectric constant (\(\varepsilon'\)) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 70:30, b 75:25 and c 95:5.

![Graph showing variation of the imaginary part of the dielectric constant (\(\varepsilon''\)) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 60:40, b 70:30 and c 75:25.](image2)

**Figure 2.15** Variation of the imaginary part of the dielectric constant (\(\varepsilon''\)) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 60:40, b 70:30 and c 75:25.

The \(\varepsilon'\) and \(\varepsilon''\) for typical polymer electrolytes rise sharply towards low frequency. The sharp rise in dielectric constant of \(\varepsilon'\) and \(\varepsilon''\) is most probably due to electrode polarization. As the frequency increases a nearly constant value of dielectric permittivity is observed (Agrawal *et al.*, 2009; Banarjee and Kumar, 2010; Nayak *et al.*, 2011). This is attributed to at high frequencies the orientational polarization vanishes.
To suppress the effect of electrode polarization, dielectric behaviour are further analysed more successfully by using the formulation of dielectric moduli. Figures 2.16 and 2.17 show the variations of the real ($M'$) and imaginary ($M''$) parts of the modulus as a function of frequency for samples of PMMA–LiCF$_3$SO$_3$ respectively (Ramesh and Wong, 2009).

**Figure 2.16** Variation of the real part of the modulus ($M'$) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 90:10, b 85:15 and c 80:20

**Figure 2.17** Variation of the imaginary part of the modulus ($M''$) as a function of frequency for the PMMA–LiCF$_3$SO$_3$-based electrolyte in the ratio of a 95:5, b 90:10 and c 85:15

The real and imaginary parts of modulus for polymer electrolytes generally show an increase with increasing frequency. At low frequencies, real and imaginary parts of modulus approach to zero indicating the fact that the electrode polarization phenomena make a negligible contribution (Ray et al., 2007; Bhide and Hariharan, 2007; Ramesh et al., 2008) and the long tail is due to large capacitance.
2.3.5 Rice and Roth model

An important characteristic of any electrolyte, in relation to the conductivity is the number density of charge carriers and this quantity is related to the dissociation of doping salt or the ion source. The number of charge density and number of mobile carriers can be determined from the Rice and Roth equation (Majid and Arof, 2005).

According to Rice and Roth (1972), in an ionic conductor there is energy gap $E$ above which conducting ions of mass $m$ can be thermally excited from localized ionic states to free ion-like states in which the ion propagates throughout the solid with velocity, $v$. Such an excited free ion-like state has a finite life time $\tau$. The velocity, $v$ is given by

$$v = \left( \frac{2E}{m} \right)^{\frac{1}{2}}$$

(2.5)

The ‘mean free path’ or distance from one complexed site to another, $\ell$, is given by

$$\ell = v\tau$$

(2.6)

Hence, ionic conductivity, $\sigma$, can be expressed by

$$\sigma = \frac{2}{3} \left( \frac{Ze}{kTm} \right)^2 nE\tau \exp \left( -\frac{E}{kT} \right)$$

(2.7)

The Rice and Roth equation was formulated for superionic conductors typified by cationic disorders, alumina structure and defects. According to Shuhaimi et al. (2010b) the Rice and Roth model can be applied to polymer electrolytes to estimate of the number density of mobile ions that contribute to conduction. This is because the Rice and Roth equation is dependent $E_a$ which can be obtained from the conductivity–temperature relationship and which can be considered as the distance between two
coordinating sites or two atoms with the lone pair electrons across which the ions may hop.

The ionic mobility is defined as

\[ \mu = \frac{\sigma}{nq} \]  

(2.8)

and the diffusion coefficient is given by

\[ D = \left( \frac{kT\sigma}{ne^2} \right) \]  

(2.9)

2.4 Chitosan

Chitin, a naturally abundant mucopolysaccharide, and the supporting material of invertebrates such as crustaceans and insects consist of a homopolymer of β-(1→4) linked 2-acetamido-2-deoxy-b-D-glucopyranose residues (Jayakumar et al., 2007). Chitosan, 2-amino-2-deoxy-b-D-glucopyranosepoly-b-(1,4)-D-glucosamine, can be readily obtained from chitin by deacetylation with alkali. It has been reported that chitin with a degree of 75% or above is known as chitosan (Cervera et al., 2004a). The two polymers, chitin and chitosan have similar chemical structure and are analogues of the homopolymer cellulose as shown in Figure 2.18.

![Figure 2.18 Structures of chitin, chitosan and cellulose (Krajewska, 2005)](image)
Since chitosan is nontoxic, biodegradable and biocompatible, it has been extensively used over a wide range of applications as shown in the Table 2.5.

<table>
<thead>
<tr>
<th>Principal applications for chitosan (Rinaudo, 2006)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
</tr>
<tr>
<td>Defensive mechanism in plants</td>
</tr>
<tr>
<td>Stimulation of plant growth</td>
</tr>
<tr>
<td>Seed coating, Frost protection</td>
</tr>
<tr>
<td>Time release of fertilizers and nutrients into the soil</td>
</tr>
<tr>
<td>Water &amp; waste treatment</td>
</tr>
<tr>
<td>Flocculant to clarify water (drinking water, pools)</td>
</tr>
<tr>
<td>Removal of metal ions</td>
</tr>
<tr>
<td>Ecological polymer (eliminate synthetic polymers)</td>
</tr>
<tr>
<td>Reduce odors</td>
</tr>
<tr>
<td>Food &amp; beverages</td>
</tr>
<tr>
<td>Not digestible by human (dietary fiber)</td>
</tr>
<tr>
<td>Bind lipids (reduce cholesterol)</td>
</tr>
<tr>
<td>Preservative</td>
</tr>
<tr>
<td>Thickener and stabilizer for sauces</td>
</tr>
<tr>
<td>Protective, fungistatic, antibacterial coating for fruit</td>
</tr>
<tr>
<td>Cosmetics &amp; toiletries</td>
</tr>
<tr>
<td>Maintain skin moisture</td>
</tr>
<tr>
<td>Treat acne</td>
</tr>
<tr>
<td>Improve suppleness of hair</td>
</tr>
<tr>
<td>Reduce static electricity in hair</td>
</tr>
<tr>
<td>Tone skin</td>
</tr>
<tr>
<td>Oral care (toothpaste, chewing gum)</td>
</tr>
<tr>
<td>Biopharmaceutics</td>
</tr>
<tr>
<td>Immunologic, antitumoral</td>
</tr>
<tr>
<td>Hemostatic and anticoagulant</td>
</tr>
<tr>
<td>Healing, bacteriostatic</td>
</tr>
</tbody>
</table>

The physicochemical properties of chitosan are influenced greatly by the degree of deacetylation and its molecular weight (Berth and Dautzenberg, 2002; Berger et al., 2004; Cervera et al., 2004b). Other characteristics which affect the chitosan function are viscosity of the solution and the distribution of acetamide groups (Kofuji et al., 2005). Wan et al. (2003) showed that the crystallining degree, mechanical properties
and ionic conductivity of chitosan membranes were influenced by DDA and molecular weight.

2.5 Properties of chitosan

2.5.1 Solubility
Chitosan is generally insoluble in many common solvents, e.g. water, alkali, and organic solvents (Muzzarelli, 1977). The chemical and biological properties of chitosan are unique as a consequence of the presence of both amino and hydroxyl groups in their structure. The presence of amino group makes chitosan a cationic polyelectrolyte (pKa $\approx$ 6.5), due to which chitosan is soluble in aqueous acidic media at pH $<$ 6.5 and when dissolved possesses a high positive charge on $\text{NH}_3^+$ groups (Krajewska, 2005).

2.5.2 Film forming ability
Soluble in acidic solutions and able to aggregate with polyanions impart chitosan with excellent gel-forming properties (Krajewska, 2005). An advantage, as most polymer electrolytes are prepared using solvent cast technique. Higher molecular weight chitosan are reported to have good film-forming properties because of intra- and intermolecular hydrogen bonding (Cervera et al., 2004b). Chitosan films are homogenous and have high mechanical strength.
2.5.3 Glass transition temperature

There are a few communications concerning the relaxation temperature corresponding to the glass transition temperature of chitosan. However, Sakurai et al. (2000) successfully determined the glass transition temperature, $T_g$, of chitosan, to be 203°C by carrying out careful measurements using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

2.5.4 Chelation of metal ions

Numerous studies have shown that chitosan can complex with metallic ions such as that of lead, cadmium, nickel and cadmium. This is important to serve as a polymer electrolyte. According to Rhazi et al. (2002), the chelation process and the stability of the metal–chitosan complex is influenced by the physical state of the chitosan (powder, gel, fibre or film, etc.). But the major parameter influencing complexation process is the degree of acetylation (DA).

2.5.5 Structural studies

Figure 2.19 displays a typical FTIR spectrum for chitosan. Important band assignments for chitosan are shown in Table 2.6. Muzzarelli (1977) reported amine bands will shift to lower wavenumbers when complexation has occurred between metal ions of the salt and amine group.
Figure 2.19 FTIR spectrum for chitosan (Velazquez-Morales et al., 1998)

Velazquez-Morales et al. (1998) used FTIR to prove grafting of propylene oxide onto chitosan. They observed that the relative intensity of bands just below 3000 cm\(^{-1}\) (aliphatic CH, CH\(_2\) and CH\(_3\)) increased considerably after chitosan had reacted with propylene oxide.

Table 2.6 FTIR spectral assignments of chitosan (Ding et al., 2003; Le Tien et al., 2003)

<table>
<thead>
<tr>
<th>Frequency(cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3420</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2860-2930</td>
<td>CH(_2) symmetric and assymetric stretching</td>
</tr>
<tr>
<td>1655</td>
<td>Amide 1 band (C=O stretching)</td>
</tr>
<tr>
<td>1555</td>
<td>Amide II band (N-H bending vibrations)</td>
</tr>
<tr>
<td>1570</td>
<td>Primary amine band</td>
</tr>
</tbody>
</table>

2.6 Chitosan based polymer electrolytes

The presence of lone pair in the polymer structure is an important criteria for a polymer to act as an ionic conductor (Armand, 1994). The amine group and the hydroxyl group have lone pairs of electrons which allow chitosan to act as an ionic...
conductor. Chitosan a natural polymer has shown to be a promising polymer electrolyte by Subban et al. (1996).

Morni and Arof, (1999) showed that molecular weight of chitosan influenced the electrical conductivity. They reported electrolyte system consisting of chitosan + 0.4g EC to LiCF$_3$SO$_3$ of ratio 80:20 gave an ionic conductivity of 3x10$^{-4}$S cm$^{-1}$.

In 2001, Osman et al. studied the conductivity of chitosan, for plasticised and unplasticised film with salt and without salt. They observed the value of conductivity in the plasticised film containing salt increases with EC. The role of plasticizer is to dissociate the salt thereby increasing the number of mobile ions. The film consisting of 0.3g salt and 1.3g of EC gave a conductivity of 4 x10$^{-5}$S cm$^{-1}$.

Chitosan, palmitic acid and lithium acetate was studied by Yahya and Arof, 2002. Palmitic acid is a non-toxic fatty acid found in palm oil. It is used as a plasticiser. They reported the film containing 0.80g lithium acetate and 0.15g of plasmatic acid gave a conductivity of 5x10$^{-6}$S cm$^{-1}$.

Majid et al. (2005) prepared chitosan-NH$_4$NO$_3$-Al$_2$O$_3$. The authors reported that addition of filler to the chitosan-NH$_4$NO$_3$ greatly enhanced conductivity. The maximum conductivity obtained for chitosan-NH$_4$NO$_3$-Al$_2$O$_3$ was 2.10x10$^{-5}$S cm$^{-1}$.

Winie et al. (2006) worked on modified chitosan as polymer electrolyte. They reported room temperature conductivity of 1.1x10$^{-4}$ S cm$^{-1}$ for hexanoyl chitosan-LiCF$_3$SO$_3$ system plasticized with mixture of PC: EC composition of 50:50 (wt. %).
Another group of researchers, Ng and Mohammad (2006) studied plasticized chitosan-proton conductor polymer electrolyte film. The film containing 8 wt. % chitosan-12 wt. %NH₄NO₃-70 wt. % EC had a conductivity of \((9.93 \pm 1.90) \times 10^{-3} \text{ S cm}^{-1}\).

### 2.7 Summary

Since Wright discovered ionic conductivity in PEO complexed with sodium ion in 1975, the research and development on solid polymer electrolyte (SPE) has been active, in particular for improvement of the ionic conductivity (Murata et al., 2000). Some common polymer host used as solid polymer electrolyte has been briefly mentioned. The field of polymer electrolytes has gone through three stages of development which can be classified as dry solid systems, polymer gels, and polymer composites. Different types of salts, plasticizers and fillers and their influence on ionic conductivity were discussed. Polymer modification by blending, grafting and cross-linking also effects conductivity. Borghini et al. (1996) suggested chemically cross-linked polyethylene glycol-salt complexes with 4,4',4"-methylidyne- tris(phenyl isocyanate) are promising electrolyte for lithium batteries because of their amorphous state and mechanical strength. Also reviewed in this chapter are various models that can be used to describe ion conduction mechanism in polymer electrolytes. The models mentioned are Arrhenius, VTF, WLF and ‘Rice and Roth’. Some properties of chitosan and work done by previous researchers on chitosan electrolyte were discussed in detail.
3.1 Introduction

In this study, films of chitosan based polymer electrolytes were prepared using a single solvent by means of solution cast technique. Chitosan used in the present investigation was obtained from Fluka. Lithium triflate (LiCF$_3$SO$_3$) and lithium acetate (LiCH$_3$COO) were used as doping salts. Lithium triflate is used, as it is nontoxic, highly resistant to oxidation and thermally stable (Ahmad et al., 2006; Ramesh and Wen, 2010). According to Ismail et al. (2009) LiCH$_3$COO is highly soluble in many types of solvent and is cheaper than other lithium salts. In order for a plasticizer to play the role as a conductivity enhancer, it should have a high dielectric constant to dissociate ions and low viscosity to facilitate the ion transport (Winie and Arof, 2006a). Since it is impossible for a single organic solvent to satisfy all these requirements, a mixed solvent of EC and PC was used as plasticizers. Fumed silica (SiO$_2$) was selected to serve as filler. SiO$_2$ is a loose white powder with particle size of 7 nm. A report by Ramesh and Liew (2010) showed ionic conductivity of PMMA-LiCF$_3$SO$_3$ system increased with addition of nano-sized fumed silica. Ethanoic acid was selected as the solvent on the basis of its efficacy for dissolution of chitosan.

3.2 Electrolyte Preparation

1 gram of chitosan was dissolved in 100 ml of 1% ethanoic acid and was continuously stirred at room temperature for several hours. The solution was then added with
40 wt. % lithium salt. This was followed by the addition of 30 wt % of plasticizers PC and EC (1:1) to the mixture and further stirred for 24 hours. After complete dissolution, fumed silica of different weight percentages was added to the mixed polymer solution. The mixture was stirred vigorously until a homogeneous solution was obtained. The solutions were cast in glass petri dishes and allowed to evaporate slowly at room temperature for two weeks to form films. The resulting films were then kept dry in a desiccator. Figure 3.1 shows the schematic preparation of the electrolyte film and table 3.1 lists the composition of the prepared films.

![Figure 3.1 Schematic diagram of electrolyte preparation](image)

**Table 3.1. Compositions of the prepared films**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Chitosan (g)</th>
<th>Lithium Triflate (wt. %)</th>
<th>Lithium Acetate (wt. %)</th>
<th>EC:PC (wt. %)</th>
<th>Silica (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLA</td>
<td>1.0</td>
<td>-</td>
<td>40</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>CLT</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>CLTS1</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td>CLTS2</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>CLTS3</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>1.5</td>
</tr>
<tr>
<td>CLTS4</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>CLTS5</td>
<td>1.0</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.3 Impedance Spectroscopy

All matter is made up of charged entities. The effect of an externally applied field on the charge distribution is specific to the material; the dielectric properties are a
measure of that effect; they are intrinsic properties of matter used to characterize materials (Gabriel, 2006). Dielectric spectroscopy is an important tool for characterization of the dielectric materials. The dielectric properties measured in response to the applied field is the relative permittivity or dielectric constant. Its real part ($\varepsilon_r$) represents the polarisability of the material, while the imaginary part ($\varepsilon_i$) represents the energy losses due to polarization and ionic conduction (Saltas, 2005).

There are four main types of polarization, namely electronic, atomic, orientation and ionic. Dielectric materials usually exhibit one of these of polarization.

In polymeric materials two major types of polarization mechanism are studied by dielectric spectroscopy: 1) polarization due to charge migration, and 2) polarization due to orientation of permanent dipoles (Mijovic and Fitz, 1998). Charge migration gives rise to conductivity. Many polymeric materials have permanent dipoles and when these materials are placed in an electric field, the dipoles would align in the direction applied field to give a net polarization (orientation polarization). The orientation of permanent dipoles involves cooperative motion of molecular segments in a viscous medium with time scales measureable by dielectric spectroscopy. The response of dipoles to changes in electric field from their equilibrium position is known as dipole relaxation. The time required for the dipoles to reach the new equilibrium position is called the relaxation time.

In dielectric spectroscopy, the alternating voltage applied is given by

$$V(t) = V_0 \sin(\omega t)$$

That results in a current response

$$I(t) = I_0 \exp(j\omega t - j\Phi)$$
Where $\omega=2\pi f$, $\Phi=$ phase difference between voltage and current, $V_o=$ maximum voltage and $I_o=$ maximum current. Hence, impedance can be written as

$$Z = \frac{V}{I}$$

$$= Z_o \cos \Phi + j Z_o \sin \Phi \quad (3.3)$$

The impedance can be written into two parts, a real part $Z_r = Z_o \cos \Phi$ and the imaginary part $Z_i = Z_o \sin \Phi$.

If the real part of impedance is plotted on the x-axis and the imaginary part on the y-axis, Nyquist plot is obtained. The Nyquist plot is also known as Cole-Cole plot or complex impedance plot. Figure 3.2 is an example of Cole-Cole/Nyquist plot. In the Bode plot, the absolute value of impedance and phase shift are plotted on the y-axis and log frequency on the X-axis respectively.

![Figure 3.2 A Typical Cole-Cole / Nyquist plot.](image)

Figure 3.3 is an example of Bode plot. Each point on both plots corresponds to impedance at a particular frequency.

![Figure 3.3 A typical Bode plot.](image)
A typical complex impedance diagram for polymer electrolytes is shown in Figure 3.4. The figure shows an arc followed by a slanted spike, which represents the high frequency semi circular region can be attributed to the electrolyte resistance. The intercept of the curve on the real axis gives the bulk resistance of the electrolyte ($R_b$).

![Impedance plot](image)

**Figure 3.4 Impedance diagram of: (a) PVdF (80)–PVC (20)–8% of LiBF$_4$ and (b) PVdF (80)–PVC (20)–8% of LiClO$_4$ at 304 K (Rajendran et al., 2007)**

Other related functions which are used in impedance spectroscopy are complex admittance, $Y(\omega)$, complex permittivity $\varepsilon(\omega)$ and complex electric modulus $M(\omega)$. The four basic impedance response quantities can be denoted by a general term called immittance, $I=I_r+jI_i$. Table 3.2 shows the relationship between the four basic immittance functions.

**Table 3.2 Relationship between the four basic immittance functions (Macdonald, 1987)**

<table>
<thead>
<tr>
<th></th>
<th>$M$</th>
<th>$Z$</th>
<th>$Y$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>$\mu Z$</td>
<td>$\mu Y^{-1}$</td>
<td>$\varepsilon^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$Z$</td>
<td>$\mu^{-1} M$</td>
<td>$Y^{-1}$</td>
<td>$\mu^{-1} \varepsilon^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$Y$</td>
<td>$\mu M^{-1}$</td>
<td>$Z^{-1}$</td>
<td>$\mu \varepsilon$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>$M^{-1}$</td>
<td>$\mu^{-1} Z^{-1}$</td>
<td>$\mu^{-1} Y$</td>
<td></td>
</tr>
</tbody>
</table>
Converting the impedance data of an electrolyte into complex other immittance response quantities can provide an understanding of the conductivity mechanism in the electrolyte (Subban et al., 2000).

The equations for the dielectric constant, $\varepsilon_r$, the dielectric loss, $\varepsilon_i$, the real electrical modulus $M_r$ and the imaginary electrical modulus $M_i$ can be shown as (Khiar et al., 2006).

\[
\varepsilon_r = \frac{Z_1}{\omega C_0 \left( \frac{Z_R^2 + Z_i^2}{Z_R^2} \right)} \quad (3.4)
\]

\[
\varepsilon_i = \frac{Z_R}{\omega C_0 \left( \frac{Z_R^2 + Z_i^2}{Z_R^2} \right)} \quad (3.5)
\]

\[
M_r = \frac{\varepsilon_i}{\left( \frac{\varepsilon_R^2 + \varepsilon_i^2}{\varepsilon_R^2} \right)} \quad (3.6)
\]

\[
M_i = \frac{\varepsilon_R}{\left( \frac{\varepsilon_R^2 + \varepsilon_i^2}{\varepsilon_i^2} \right)} \quad (3.7)
\]

Here, $\mu = j\omega C$, where $C = A\varepsilon_0/\tau$, $\varepsilon_0$ is permittivity of free space, $A$ is electrolyte-electrode contact area and $t$ is the thickness of the electrolyte.

In this study, the impedance of the polymer film was measured with a HIOKI 3531-01 LCR bridge interfaced with a computer for data acquisition over a frequency range between 50 Hz to 1 MHz as shown in Figure 3.5. The thin polymer electrolyte film was sandwiched between two stainless steel disc electrodes. A micrometer screw gauge was used to measure the thickness of the film and the diameter of film was with a vernier caliper to calculate the area $A$. The conductivity measurements for each sample were carried at from 298K to 373 K. Prior to each impedance measurement, the samples was equilibrated for 10 minutes at constant temperature. The variation of
the dielectric properties with frequency and temperature were studied to get a better insight into the conduction mechanism and the relaxation processes that takes place inside the prepared polymer electrolyte systems.

![Figure 3.5 Experimental setup for dielectric spectroscopy studies](image)

### 3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by chemists. It is mainly used for identification of substances or the determination of structures. Infrared spectra can reveal both the specific functional groups present and their general location in a molecule (Harris and Kratochvil, 1981). If the frequency of the radiation absorbed matches the vibrational frequency of the molecule, this will cause a change in the amplitude of molecular vibration. The major types of molecular vibrations are stretching and bending as illustrated in Figure 3.6. Several researchers have used FTIR to study the interactions existing between the different components in the system such as polymer and salt, polymer and plasticizer, plasticizer and salt and polymer and filler (Rajendran *et al.*, 2005; Kumutha and Alias, 2006; Reddy *et al.*, 2006; Ramesh *et al.*, 2007; Ramesh and Chai, 2007).
In all these work, the complexation is confirmed by the appearance of new peaks, frequency shifts, changes in intensities or shape of existing peaks in the FTIR spectra. Figure 3.7 shows the FTIR spectra of (i) the pure components and (ii) PVdF-HFP+LiTf:EC with different compositions of EC (Ramesh and Ling, 2010).

Figure 3.7 FTIR spectra (i) The FTIR spectra for (a) pure PVdF-HFP; (b) pure LiTf; (c) pure EC
According to Ramesh and Ong (2010) complexation of the LiCF$_3$SO$_3$ salt with polymer PVdF-HFP was confirmed by the presence of new peaks at 1032 and 640 cm$^{-1}$ corresponding to free SO$_3^-$ ions. The addition of EC caused the C=O peaks to shift to slightly higher frequencies due to interaction between the hydrogen in the methylene group of PVdF-HFP and the oxygen in EC. In the present work, IR studies were done using FTIR Thermoscientific Nicolet iS10 as shown in Figure 3.8 in the region between 4000 cm$^{-1}$ to 400 cm$^{-1}$ at a resolution 1 cm$^{-1}$.
3.5 X-ray diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. The technique is based on when X-rays hit a sample, the rays are diffracted creating waves of scattered X-rays that intensity each other in certain directions. From such considerations, Bragg derived the famous equation

\[ n\lambda = 2d \sin \theta \]  

(3.8)

\( \lambda \) = wavelength of radiation  
\( n \) = an integer  
\( d \) = perpendicular spacing between lattice planes  
\( \theta \) = angle of incidence

XRD technique is used to determine whether a material is amorphous or crystalline by observing the characteristic pattern from X-ray diffractogram. Crystalline materials tend to give sharp distinctive peaks, whereas amorphous materials have broad peaks. Examples of the two types of diffractograms are shown in Figures 3.9 (a) and (b).

![XRD patterns for: (a) pure PVC (b) pure LiAsF₆ (Rajendran and Uma, 2000)](image_url)

Figure 3.9 XRD patterns for: (a) pure PVC (b) pure LiAsF₆ (Rajendran and Uma, 2000)
XRD can also be used to show whether complexation between salt and polymer host has taken place. This is observed by the absence of certain peaks of the salt and polymer host or shifts in peaks of the salt and polymer host. An example of this behaviour is observed in XRD patterns for PVAc and LiClO$_4$ complexes as shown in Figure 3.10 (a–e) (Baskaran et al., 2007). The incorporation of salt into the polymer matrix causes the appearance of a broad peak.

This behavior demonstrates that complexation between the salt and the polymer takes place in the amorphous region. The absence of peaks for the concentrations of the salt ranging from 10 to 15 wt. %, indicates the complete dissolution of salt in the amorphous region of network polymers and inhibits the crystallization of PVAc–LiClO$_4$ complexes. The amorphous nature produces greater ionic diffusivity leading to high ionic conductivity (Frech and Chintapalli, 1996).

![Figure 3.10 XRD patterns of pure PVAc, LiClO4 and PVAc–LiClO4 polymer electrolytes of various compositions (Baskaran et al., 2007)](image)
In this work, X-ray diffraction patterns were recorded using Siemens D-5000 X-Ray Diffractometer, shown in Figure 3.11, using Cu-Kα radiation of wavelength $\lambda = 1.5418 \times 10^{-7}$ mm in the 2θ range 5° to 60°. The films were scanned using slit width 0.05 and receiving slit 0.2.

Figure 3.11 Siemens D-5000 X-Ray Diffractometer at University of Malaya

3.6 Thermal Studies

Thermal analysis techniques are used for obtaining qualitative and quantitative information about the various effects of heat treatment on materials. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of material being studied (Brown, 2001). Differential scanning calorimetry (DSC) and thermal gravimetric instrumentation (TGA) are used to analyze these properties.

3.6.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyzes thermal transitions occurring in polymer samples when they are heated and cooled in a controlled environment. Melting temperature, heat capacity, crystallization temperature, glass transition
temperature, identification, thermal stability, decomposition temperature and purity of a polymer can be determined using DSC.

DSC compares differences between the heat flow rate of the test sample and known reference material. In the DSC instrument, two aluminium pans are placed on a pair of identically positioned platforms connected to a furnace as shown in Figure 3.12. The sample to be tested is placed in one pan and the other pan is used as a reference. The two pans are heated up at a specific rate, usually 10°C per minute. The heat flow to the sample is adjusted in such a way that the temperature of the sample and reference pan is equal. Since the sample pan has the extra material, it will take more heat to keep the temperatures of the sample pan increasing at the same rate as the reference pan. The computer will plot the difference in heat flow between the sample and reference as a function of temperature, as a DSC thermogram.

![Figure 3.12 Scheme of the DSC Apparatus](image)

A DSC curve of a semi-crystalline polymer during thermal transition is shown in Figure 3.13. From the DSC curve, information such as glass transition temperature, $T_g$, crystallization temperature, $T_c$, melting point, $T_m$ and decomposition temperature, $T_d$. 
of the material can be obtained. Amorphous polymers will not show crystallization or melting peaks.

![DSC thermogram](image)

**Figure 3.13** Schematic DSC thermogram of a semi-crystalline polymer: $T_g =$ glass transition temperature; $T_c =$ crystallization temperature; $T_m =$ melting temperature; $T_d =$ decomposition temperature (Braun et al., 2005)

Glass transition temperature occurs in amorphous and crystalline polymers. It is the temperature where the polymer goes from a hard, glass like state to a rubber like state. Below $T_g$ the material is rigid and hard. Above $T_g$ the material exhibits rubber-like characteristics. DSC measures the change in the heat capacity as the polymer matrix goes from the glass state to the rubber state as the glass transition temperature of the polymer. This is a second order endothermic transition (requires heat to go through the transition) so in the DSC thermogram the transition appears as a step transition, as shown in Figure 3.14.
DSC was performed using TA Instruments DQ200 as shown in Figure 3.15. About 5 mg samples were placed into aluminum cups and sealed. A small hole was done at the top of the cup in order to allow the release of water. An empty cup was used as reference. The experiment consisted of three runs. For each sample, the following thermal cycle was applied: a first scan was made to 40°C to 190°C and cooled to -30°C. The sample was heated again to 205°C as thermal degradation of chitosan was around 240°C. Scanning rate was carried out at 10°C/min under nitrogen atmosphere.
3.6.2 Thermogravimetric Analysis (TGA)

TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. It is principally used to quantify the mass change in a polymer associated with transitions or degradation process. The heart of the thermogravimetric analyzer is the thermobalance. The thermobalance consists of two main components, that is, the furnace and the balance. A sample to be analysed is placed in the furnace while being suspended to one end of the balance arm. The change in sample mass is recorded while the sample is subjected to a controlled temperature programme in a controlled atmosphere. The layout of a typical balance is shown schematically in Figure 3.16 (Stuart, 2002).

![Schematic of a typical thermogravimetric analysis instrument](image)

TGA analysis is widely used to study the thermal stability of polymers. Figure 3.17 shows TGA for chitosan-graft-polyaniline (Ch-g-PANI) and chitosan. TGA indicates that the decomposition of the graft copolymer onsets at 176°C, while decomposition of chitosan onsets 145°C. It indicates that Ch-g-PANI is more thermally stable than chitosan.
Thermogravimetric (TG) analysis was carried out with TA Instrument TGA. All analyses were performed with a 5 mg sample in aluminum pans under a dynamic nitrogen atmosphere between 0 and 1000°C. The experiments were run at a scanning rate of 50°C/min.

3.7 Summary

This chapter describes the experimental details for the preparation of the chitosan electrolyte system. Dielectric studies were carried out to get an insight of the mechanism occurring in the prepared electrolyte system. The prepared electrolyte was characterized by X-ray diffraction and Infrared spectroscopy. Thermal analyses were carried out using DSC and TGA to investigate the behaviour of the prepared samples as a function of temperature.
CHAPTER 4

RESULTS

ELECTRICAL STUDIES

4.1 Introduction

An important property of any electrolyte is its electrical conductivity. In this work, impedance spectroscopy was used to investigate the electrical properties of the prepared films. From the impedance measured in the frequency and temperature range that has been set; the Nyquist plots corresponding to the frequency range and temperature studied are plotted. From these plots the bulk resistance is obtained from which conductivity can be calculated. From impedance results, the dielectric constant and loss, electrical modulus and relaxation time can be determined.

4.2 Impedance studies of chitosan-LiCH₃COO-EC/PC

4.2.1 DC conductivity studies

The conductivity of chitosan-40wt. % LiCH₃COO-30 wt. % - EC/PC (EC: PC=1 w/w) as a function of temperature from 20°C to 90°C at 10°C intervals has been obtained. The complex impedance plots at various temperatures are presented in Figures 4.1 to 4.6.
Chapter 4

Electrical Studies

Figure 4.1 Complex impedance plot of CLA system at 25°C

Figure 4.2 Complex impedance plot of CLA system at 30°C
Figure 4.3 Complex impedance plot of CLA system at $40^\circ$C

Figure 4.4 Complex impedance plot of CLA system at $50^\circ$C
Figure 4.5 Complex impedance plot of CLA system at 60°C

Figure 4.6 Complex impedance plot of CLA system at 70°C
The intercept of the semicircle at the real axis yields the bulk resistance, $R_b$, of the electrolyte. DC conductivity was calculated using

$$\sigma = \frac{t}{R_b A}$$  \hspace{1cm} (4.1)$$

where $t$ is the thickness of the film (cm) and $A$ is the film electrode contact area (cm$^2$).

At lower temperatures the impedance plot reveals a semicircle in the high frequency region and a slanted spike at low frequencies. The semicircle is due to the bulk effect of the electrolyte and can be represented by a resistor and capacitor in parallel combination. The resistor refers to the migration of ions through the polymer matrix and the capacitor represents the polarized immobile polymer chains in the alternating electric field (Nithya et al., 2011). The low frequency spike is related to the effect of electrode polarization. The inclination of the spike is due to formation of double layer (EDL) capacitances by build up of free charges at the interface between the electrolyte and the electrodes (Bhide and Hariharan, 2007; Pradhan et al., 2008; Sengwa et al., 2008).

It is noted that the size of the semicircle portion in high frequency region decreases as the temperature increases. In Figure 4.6, the impedance plot mainly consists of a steeply rising spike indicating conduction is mainly due to lithium ions. It can be deduced that $R_b$ values are strongly influenced by temperature. At higher temperatures the dissociation of salts would be improved and hence more free lithium ions.

Figure 4.7 shows the plot of log conductivity versus 1000/T for CLA system and the conductivity values at different temperatures is tabulated in Table 4.1.
Regression value, $R^2 = 0.99$ is close to unity for the graph in Figure 4.7, suggesting that all the points lie on a straight line. From the graph, it is understood that the conductivity of this electrolyte system follows Arrhenius rule.

$$\sigma = \sigma_0 \exp \left[ \frac{-E_a}{kT} \right] \quad (4.2)$$

where $\sigma_0$ is the pre-exponential factor, $E_a$ is activation energy, $k$ is Boltzmann constant and $T$ is absolute temperature. Activation energy, $E_A$ calculated from the slope of the log $\sigma$ vs. $10^3/T$ graph is found to be 0.82 eV. The pre-exponential factor ($\sigma_0$) has been estimated from the graph as $2.79 \times 10^7$ Scm$^{-1}$. It can also be seen in Table 4.1 that as temperature increases the conductivity value also increases.
Table 4.1 Conductivity for CLA system at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Conductivity, $\sigma_{dc}$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>$4.39 \times 10^{-7}$</td>
</tr>
<tr>
<td>298</td>
<td>$6.18 \times 10^{-7}$</td>
</tr>
<tr>
<td>303</td>
<td>$7.53 \times 10^{-7}$</td>
</tr>
<tr>
<td>308</td>
<td>$9.84 \times 10^{-7}$</td>
</tr>
<tr>
<td>313</td>
<td>$1.53 \times 10^{-6}$</td>
</tr>
<tr>
<td>318</td>
<td>$3.38 \times 10^{-6}$</td>
</tr>
<tr>
<td>323</td>
<td>$4.83 \times 10^{-6}$</td>
</tr>
<tr>
<td>328</td>
<td>$6.22 \times 10^{-6}$</td>
</tr>
<tr>
<td>333</td>
<td>$8.24 \times 10^{-6}$</td>
</tr>
<tr>
<td>338</td>
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</tr>
<tr>
<td>343</td>
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</tr>
<tr>
<td>348</td>
<td>$3.75 \times 10^{-5}$</td>
</tr>
<tr>
<td>353</td>
<td>$5.24 \times 10^{-5}$</td>
</tr>
<tr>
<td>358</td>
<td>$1.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>363</td>
<td>$1.69 \times 10^{-4}$</td>
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<tr>
<td>368</td>
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</tr>
<tr>
<td>373</td>
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</tr>
<tr>
<td>383</td>
<td>$5.50 \times 10^{-4}$</td>
</tr>
<tr>
<td>388</td>
<td>$7.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>393</td>
<td>$8.87 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

At higher temperatures, thermal movement of polymer chain segments increases and the increased vibration between the cation and anion of the salt leads to greater cation-anion distance that weakens the coulombic force between them. This can lead to dissociation of salts, thus enhancing conductivity. Since the conductivity–temperature data obeys Arrhenius relationship, the nature of cation transport is quite similar to that
occurring in ionic crystals, where ions jump into neighbouring vacant sites and hence increases ionic conductivity to a higher value (Ramesh and Arof, 2001).

The increase in the ionic conductivity is quite similar to that reported by Yahya and Arof (2003) and Yahya et al., (2004). In these works, conductivity has been measured from 300 K up to 363 K for chitosan-LiCH₃COO system, chitosan-LiCH₃COO system plasticised with palmitic acid and chitosan-LiCH₃COO system plasticised with oxalic acid. In this work, conductivity was measured until 393K. This shows that chitosan-based electrolytes can show stability at even higher temperatures when the plasticizers (EC/PC 1:1) are used.

### 4.2.2 Dielectric relaxation studies

The study of dielectric constant and dielectric loss factor, as a function of temperature and frequency is one of the most convenient and sensitive methods of studying the polymer structure (Khare and Jain, 2000; Akram et al., 2005; Pathania and Singh, 2009; Yadav et al., 2010). These properties are related to structural considerations such as polarity and molecular flexibility of polymer. It can be understood that the changes in dielectric properties with frequency may be due to presence of the polar functional groups and ions in the prepared electrolyte system (Yadav et al., 2010). In addition, information regarding the conductive behaviour of materials can be acquired from dielectric behaviour (Ramesh et al., 2002). Dielectric loss is a direct measure of energy dissipated and generally comprises the contribution from the ionic transport as well as from the polarization of a charge or a dipole (Stephan et al., 2000; Malathi et al., 2010; Nithya et al., 2011). The dielectric response is generally described by the complex permittivity, \( \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) \), where real \( \varepsilon_r(\omega) \) and imaginary \( \varepsilon_i(\omega) \)
components are the storage and loss of energy in each cycle of applied field (Dutta et al., 2002). Using equations (3.5) and (3.6) dielectric constant and dielectric loss have been calculated. Figures 4.8 and 4.9 illustrate the variation of dielectric constant and dielectric loss as a function of frequency at selected temperatures. From the figures no relaxation peaks can be observed in the frequency range employed for this study. Both dielectric constant and dielectric loss increase with temperature and increase rapidly at low frequencies. The observed dispersion in dielectric constant at low frequency is due to electrode polarisation and charge accumulation at the electrode-electrolyte interface whereas the dispersion observed in dielectric loss is due to free charge motion within the material.

The dielectric constant value is greater than dielectric loss value at frequency of 50Hz, suggesting greater amount of ions accumulate at the electrode-electrolyte surface rather than flow through the polymer. From the graphs (Figure 4.8 – 4.9), it can be observed that the dielectric values appear almost constant at high frequency. However, when the higher frequency region is replotted as shown in Figures 4.10 and 4.11, they show gradual decrease with temperature compared to lower frequencies. In Figure 4.11 the dipolar relaxation is observed at ~158 000Hz. These relaxations are attributed to dipole relaxation and ionic relaxation, usually observed in the frequency range $10^2$- $10^{10}$ Hz. The dipole relaxation is more prominent at higher temperatures.
Figure 4.8 Frequency dependence of dielectric constant, $\varepsilon_r$, for CLA system

Figure 4.9 Frequency dependence of dielectric loss, $\varepsilon_i$, for CLA system
The behaviour of the dielectric constant with temperature at different frequencies is shown in Figure 4.12. It was observed that the dielectric constant increases with increase in temperature. The dielectric behaviour with temperature can be explained as follows: at low temperatures the charge carriers in the samples cannot in most cases
orient themselves in the direction of applied field. Therefore, the ions weakly contribute to polarization and dielectric value. At higher temperatures, the charge carriers have sufficient thermal energy to be able to orient themselves to the external applied field. This in turn enhances polarization and hence increases dielectric values. This suggests that conductivity in CLA system is temperature dependent as mentioned earlier and is in agreement with Arrhenius plot shown in Figure 4.7. It was also observed in Figure 4.12 there is a sudden jump in log \( \varepsilon_r \) value at 333 K. This could be attributed to structural changes occurring at the molecular level. Ethylene carbonate can solidify at room temperature. Its melting point is about 35 °C. The melting of this plasticizer may contribute to the enhancement in log \( \varepsilon_r \) value at 333 K by allowing the charge carriers to orient themselves more readily in the less viscous phase.

![Figure 4.12 Temperature dependence of dielectric constant, \( \varepsilon_r \) at various frequencies for CLA system](image)

Figure 4.12 Temperature dependence of dielectric constant, \( \varepsilon_r \) at various frequencies for CLA system
4.2.3 **Dielectric modulus studies**

An alternative approach to study the electrical response of dielectric materials is to use complex electric modulus, which highlights bulk dielectric behaviour and suppresses the effects of electrode polarisation (Shastry and Rao, 1991; Subban and Arof, 2003). Figures 4.13 and 4.14 show the frequency dependence of real ($M_r$) and imaginary ($M_i$) parts of electric modulus for CLA system. The real $M_r$ and imaginary $M_i$ parts of modulus formalism increase towards high frequencies. The presence of relaxation peaks in the modulus formalism implies that the polymer electrolyte is an ionic conductor. The peak formation at high frequencies is attributed to the bulk effect. From Figure 4.13, the presence of relaxation peaks are observed at 298K, 303K, 313K and 323K. The height of peak decreases with increasing temperature. The decrease in heights of peaks with increase in temperature, suggests a plurality of relaxation times (Mishra *et al.*, 1998). For higher temperatures the relaxation peaks are expected to appear beyond the selected frequency range.

![Figure 4.13 Frequency dependence of real part of electrical modulus, $M_r$ at various temperatures for CLA system](image-url)

---

**Figure 4.13 Frequency dependence of real part of electrical modulus, $M_r$ at various temperatures for CLA system**
At low frequencies, $M_r$ and $M_i$ values decrease with increasing temperature for the CLA system as depicted in Figures 4.15 and 4.16. At higher temperatures, the decrease was less noticeable. These changes may be due to the induced dipoles encounter difficulties to follow the alternation of the electric field and thus the resulting relaxation process occurs in the low frequency region and at high temperatures (Patsidis and Psarras, 2008).

Figure 4.14 Frequency dependence of imaginary part of electrical modulus, $M_i$ at various temperatures for CLA system

Figure 4.15 Real part of electrical modulus, $M_r$ at low frequencies for CLA system
4.2.4 Dielectric loss tangent behaviour

Figure 4.17 displays the variation of dielectric loss tangent, $\tan \delta$, with frequency at different temperatures for CLA system. From the plots, it is clear that $\tan \delta$ value increases with frequency at different temperatures, passes through a maximum value and thereafter decreases. The presence of loss peak suggests a dielectric relaxation process.

Figure 4.16 Imaginary of electrical modulus, $M_i$ at low frequencies for CLA system

Figure 4.17 Variation of loss tangent with frequency for CLA system
The peaks present in the above graph show a strong correlation between conduction mechanism and dielectric behaviour in the prepared sample. In this case, the peak is expected when the hopping frequency of the lithium ions is approximately equal to that of external applied field. In this case

$$\omega \tau = 1$$  \hspace{1cm} (4.3)

where $\tau$ is the relaxation time of the hopping process, $\omega$ is the angular frequency of the external field.

$$\omega = 2\pi f_{\text{max}}$$ \hspace{1cm} (4.4)

$$\tau = \frac{1}{\omega}$$ \hspace{1cm} (4.5)

The $\tau$ values were calculated using equation 4.5 and tabulated (Table 4.2). Figure 4.18 shows the relationship between the relaxation time and temperature. This follows Arrhenius rule. The activation energy for relaxation, $E_R$ has been estimated as 0.86 eV. This value is almost equal to the activation energy $E_a = 0.82$ eV which is obtained from DC conductivity studies.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Relaxation time, $\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$5.03 \times 10^{-5}$</td>
</tr>
<tr>
<td>303</td>
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</tr>
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<tr>
<td>323</td>
<td>$7.11 \times 10^{-6}$</td>
</tr>
<tr>
<td>333</td>
<td>$2.52 \times 10^{-6}$</td>
</tr>
<tr>
<td>343</td>
<td>$5.03 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
It is also known that relaxation time \( \tau \) is proportional to jumping probability per unit time, \( P \), according to the relation

\[
\tau = \frac{1}{2P}
\]

(4.6)

The shift of peak (figure 4.17) towards high frequency with increasing temperature indicates that the jumping probability per unit time (\( P \)) increases with increasing temperature (Reddy and Reddy, 1991; Abo et al., 2004). The reciprocal of jump probability per unit time (\( P \)) is a residence time for an ion that moves by that specific type of jump. The figure 4.19 shows that \( P \) increases with increasing temperature. At higher temperatures, the ions have lower residence time. It is observed that there is a sudden increase in \( P \) after 333 K may due to the plasticizer (EC) becomes liquid as mentioned earlier.
Figure 4.19 Variation of $P$ with temperature for CLA system

Figure 4.20 shows the normalized plot of $\tan \delta / (\tan \delta)_{\text{max}}$ vs $\log f/f_{\text{max}}$ for the same sample at various temperatures.

Figure 4.20 Normalised plot of loss tangent for CLA system at selected temperatures
It can be seen that the peaks in Figure 4.20 are not symmetrical. These non-
symmetrical curves indicate that there is more than one relaxation time for the lithium
ions. This implies that dielectric relaxation deviates from the classical exponential
Debye behaviour (Winie and Arof, 2004).

4.3 Impedance studies of chitosan-LiCF\textsubscript{3}SO\textsubscript{3}-EC/PC

The objective of this study is to investigate the electrical properties of chitosan-EC/PC
system polymer electrolyte by incorporating a different lithium salt. Lithium triflate
(LiCF\textsubscript{3}SO\textsubscript{3}) is the chosen salt, as it is well known that it has low lattice energy (Kim
and Kim, 1999; Ramesh and Wong, 2009) and is highly soluble in organic solvents.

4.3.1 DC conductivity studies

In order to understand the mechanism of charge transport of chitosan- LiCF\textsubscript{3}SO\textsubscript{3}-
EC/PC system, temperature dependence studies on ionic conductivities were carried
out over a wide range of temperature. The complex impedance plot at various
temperatures is presented in Figures 4.21 to 4.27. As temperature increases, the
enhancement of conductivity is seen from the reduction of the diameter of the
semicircular arc which is the direct measurement of bulk resistance. At high
temperatures greater than 70°C it is observed that the high frequency semicircular
portion is absent. This reveals the absence of capacitive (Baskaran et al., 2006; Vieira
et al., 2007) and only diffusion of lithium ions occurs.
Figure 4.21 Complex impedance plot of CLT system at 25°C

Figure 4.22 Complex impedance plot of CLT system at 30°C
Figure 4.23 Complex impedance plot of CLT system at 40°C

Figure 4.24 Complex impedance plot of CLT system at 50°C
Figure 4.25 Complex impedance plot of CLT system at 60°C

Figure 4.26 Complex impedance plot of CLT system at 70°C
Figure 4.27 Complex impedance plot of CLT system at 80°C

Figure 4.28 shows the variation of conductivity with temperature for chitosan polymer electrolyte system containing lithium triflate salt.

Figure 4.28 Temperature dependence of conductivity plot for CLT system
The value of conductivity for different temperatures is shown in Table 4.3. Within temperature range investigated, the variation of log $\sigma$ with $1000/T$ is linear with regression value in the range of 0.99. This indicates that the conductivity of this polymer electrolyte system is thermally assisted and can be described by Arrhenius law. The activation energy for the CLT system is 0.31 eV. The trend observed is similar to conductivity versus temperature for CLA system but the lithium ions has a lower energy barrier to overcome than in CLT system. The pre-exponential factor ($\sigma_0$) calculated from Figure 4.28 is 0.15 S cm$^{-1}$.

### Table 4.3 Conductivity versus temperature for CLT system

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Conductivity, $\sigma_{dc}$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>$4.44 \times 10^{-6}$</td>
</tr>
<tr>
<td>298</td>
<td>$5.01 \times 10^{-6}$</td>
</tr>
<tr>
<td>303</td>
<td>$6.00 \times 10^{-6}$</td>
</tr>
<tr>
<td>308</td>
<td>$7.07 \times 10^{-3}$</td>
</tr>
<tr>
<td>313</td>
<td>$8.94 \times 10^{-3}$</td>
</tr>
<tr>
<td>318</td>
<td>$1.11 \times 10^{-3}$</td>
</tr>
<tr>
<td>323</td>
<td>$1.39 \times 10^{-3}$</td>
</tr>
<tr>
<td>328</td>
<td>$1.82 \times 10^{-3}$</td>
</tr>
<tr>
<td>333</td>
<td>$2.28 \times 10^{-3}$</td>
</tr>
<tr>
<td>338</td>
<td>$2.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>343</td>
<td>$2.83 \times 10^{-3}$</td>
</tr>
<tr>
<td>348</td>
<td>$3.00 \times 10^{-3}$</td>
</tr>
<tr>
<td>353</td>
<td>$3.28 \times 10^{-3}$</td>
</tr>
<tr>
<td>358</td>
<td>$3.89 \times 10^{-3}$</td>
</tr>
<tr>
<td>363</td>
<td>$4.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>368</td>
<td>$4.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>373</td>
<td>$4.99 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
4.3.2 Dielectric relaxation studies

The variation of dielectric constant ($\varepsilon_r$) and dielectric loss ($\varepsilon_i$) as function of frequency for chitosan-LiCF$_3$SO$_3$-EC/PC polymer electrolyte (CLT system) are shown in Figure 4.29 and 4.30 respectively. The dielectric values are higher at room temperature for CLT system than CLA system. LiCF$_3$SO$_3$ salt has lower lattice energy than LiCH$_3$COO salt, as the ionic radius of CF$_3$SO$_3^-$ (3Å) (Narayanan et al., 2009) is greater than CH$_3$COO$^-$ (1.27Å) (Murthy and Lakshminarayana, 1989). Lattice energy determines the strength of an ionic bond as it is inversely proportional to the sum of ionic radii. LiCF$_3$SO$_3$ salt will dissociate more readily than LiCH$_3$COO salt and hence greater number of free Li$^+$. This could be correlated with our room temperature DC conductivity value of CLT system is higher than that of CLA system.

Figure 4.29 illustrates that dielectric loss exhibits strong temperature dependence. The increase of dielectric loss was explained by Stevels (1957) who divided the relaxation phenomenon into three parts; conduction losses, dipole losses and vibrational losses (Afifi et al., 2001). Conduction losses is proportional to ($\sigma/\omega$) and hence conduction losses rises with increase in temperature due to greater flow of charge, which in turn causes the value of dielectric loss to increase. From the graphs it is observed that the $\varepsilon_r$ and $\varepsilon_i$ values are higher at high temperature which may be related to the increase in free lithium ions in the electrolyte. This phenomenon would have enhanced the increase in the conductivity with temperature.
Figure 4.29 Frequency dependence of dielectric constant, $\varepsilon_r$, for CLT system

Figure 4.30 Frequency dependence of dielectric loss, $\varepsilon_i$, for CLT system

The dielectric values for higher frequency range have been replotted (Figures 4.31 and 4.32). In Figure 4.32, the dielectric relaxation is observed at $\sim 110000\text{Hz}$. 
Figure 4.31 Dielectric constant, $\varepsilon_r$ at high frequency for CLT system

Figure 4.32 Dielectric loss, $\varepsilon_i$ at high frequency for CLT system
Table 4.4 lists values of the dielectric constant and the dielectric loss at different temperatures at frequency 50 Hz for the chitosan-LiCF$_3$SO$_3$-EC/PC system and chitosan-LiCH$_3$COO-EC/PC system.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Dielectric constant ($\varepsilon_r$)</th>
<th>Dielectric loss ($\varepsilon_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chitosan-LiCH$_3$COO-EC/PC (f=50Hz)</td>
<td>Chitosan-LiCF$_3$SO$_3$-EC/PC (f=50Hz)</td>
</tr>
<tr>
<td>298</td>
<td>3677</td>
<td>57755</td>
</tr>
<tr>
<td>303</td>
<td>4095</td>
<td>68760</td>
</tr>
<tr>
<td>313</td>
<td>7675</td>
<td>94409</td>
</tr>
<tr>
<td>323</td>
<td>13810</td>
<td>116538</td>
</tr>
<tr>
<td>333</td>
<td>25483</td>
<td>189402</td>
</tr>
<tr>
<td>343</td>
<td>96667</td>
<td>218189</td>
</tr>
<tr>
<td>353</td>
<td>175009</td>
<td>259408</td>
</tr>
<tr>
<td>363</td>
<td>307815</td>
<td>343904</td>
</tr>
<tr>
<td>373</td>
<td>482193</td>
<td>389536</td>
</tr>
</tbody>
</table>

Both dielectric constant and dielectric loss increase sharply with temperature at low frequencies for CLA and CLT system. At temperature below 353K at 50Hz both dielectric constant and dielectric loss is greater for CLA system than CLT system. However, the reverse is true for higher temperature. At higher temperature the larger triflate ion may hinder the lithium ion pathway due to greater movement of the ions. This can be explained by the values of CLT and CLA systems at 373 K, the
conductivity value is $4.99 \times 10^{-5}$ Scm$^{-1}$ and $3.12 \times 10^{-4}$ Scm$^{-1}$ respectively. This may be due the lithium ions in the CLT system may have to use longer pathway and hence the lower conductivity.

The effect of temperature on dielectric constant as a function of frequency is shown in Figure 4.33.

![Graph showing temperature dependence of dielectric constant, $\varepsilon_r$, at various frequencies for CLT system](image)

**Figure 4.33 Temperature dependence of dielectric constant, $\varepsilon_r$, at various frequencies for CLT system**

It is clear from the graph that the value of dielectric constant increases with temperature. Othman *et al.* (2007) and Prajapati *et al.* (2010) have observed a similar trend for their polymer electrolyte systems. The increase in the dielectric constant with temperature may be due the increase in the salt dissociation and hence the free charges built up at the interface between electrolyte and electrode. Similar trend has also been observed for the CLA system. It is noted that there is a sudden increase in the dielectric constant value at the same temperature (333 K) as the CLA system. This may be again due to the melting of EC plasticizer.
4.3.3 Dielectric modulus studies

Figure 4.34 and Figure 4.35 illustrate the variations of the electric modulus formalism for CLT system. The value of both real and imaginary parts of electrical modulus decreases with increasing temperature. The maxima of these values shift towards higher frequency with increasing temperature. This may be due to the intensity of dielectric relaxation is activated thermally in the hopping of charge carriers (Prabakar et al., 2003). This may be further explained by the increase in mobility of lithium ions at higher temperatures and therefore causing the relaxation times to decrease and consequently the dispersion peaks shift to high frequency. A similar trend was observed for the system containing lithium acetate salt (CLA system).

![Figure 4.34 Frequency dependence of real part of electrical modulus, $M_r$, at various temperatures for CLT system](image-url)
In the low frequency regime as shown figures 4.36 and 4.37, the values of both electrical moduli also decrease with increasing temperature.
4.3.4 Dielectric loss tangent behaviour

Figure 4.38 shows the variation of loss tangent, \( \tan \delta \) versus log f of chitosan-Li\(_2\)SO\(_4\)-EC/PC system at different temperatures. The behaviour of the loss tangent is typical in that it increases with frequency, reaches a maximum value and thereafter decreases. The maximum of \( \tan \delta \), \( (\tan \delta_{\text{max}}) \) shift towards higher frequencies with temperature and at the same time, the height of \( (\tan \delta_{\text{max}}) \) is also found to increase with temperature. The increase in the height of \( (\tan \delta_{\text{max}}) \) with temperature could be attributed to the decrease in resistivity of the sample (Prabakar et al., 2003).
Figure 4.38 Variation of loss tangent with frequency for CLT system

Figure 4.39 and table 4.5 shows that the frequency for relaxation peaks increases with temperature and hence relaxation time decreases with increase in temperature. The decrease in relaxation time with increasing temperature is due to faster movement of lithium ions that synchronizes with the direction of applied field and increased motion of charge carriers in the polymer matrix. The activation energy of relaxation, $E_R$ is 0.36 eV.

Table 4.5 Temperature versus relaxation time for CLT system

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Relaxation time, $\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$3.99 \times 10^{-6}$</td>
</tr>
<tr>
<td>303</td>
<td>$2.25 \times 10^{-6}$</td>
</tr>
<tr>
<td>313</td>
<td>$1.79 \times 10^{-6}$</td>
</tr>
<tr>
<td>323</td>
<td>$1.42 \times 10^{-6}$</td>
</tr>
<tr>
<td>333</td>
<td>$1.13 \times 10^{-7}$</td>
</tr>
<tr>
<td>343</td>
<td>$3.99 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
The figure 4.40 shows that P increases with increasing temperature. At higher temperatures, the ions have lower residence time since inverse of P values is related to residence time of ions. It is observed that there is sudden increase in P after 333 K.
Figure 4.41 represents the normalized plot of \( \tan \delta / (\tan \delta)_{\text{max}} \) at different temperatures.

![Figure 4.41 Normalised plot of loss tangent for CLT system at selected temperatures](image)

The normalized plot of \( \tan \delta / (\tan \delta)_{\text{max}} \) against \( f/f_{\text{max}} \) for different temperatures is given in figure 4.41. The \( \tan \delta \) represents the value of loss tangent at any frequency and \( (\tan \delta)_{\text{max}} \) represents the value of loss tangent at the corresponding \( f_{\text{max}} \). It can be seen that maxima peaks are not symmetrical at around the maximum frequency as shown in Figure 4.41 suggesting that a distribution of relaxation time for the relaxation process (Agrawal et al., 2009). This shows the dielectric relaxation process deviates from the classical Debye behaviour.
4.4 Impedance studies of chitosan-LiCF$_3$SO$_3$-EC/PC-SiO$_2$

One of the most promising ways to improve the morphological and electrochemical properties of polymer electrolytes is by addition of ceramic fillers (Croce et al., 1998; Itoh et al., 2003; Stephan and Nahm, 2006). Materials consisting of polymer electrolyte and ceramic fillers are identified as composite polymer electrolytes. The addition of ceramic fillers is known to enhance the conductivity of polymer hosts, mechanical properties and their interfacial properties in contact with the lithium electrode. Increase in ionic conductivity can be explained by increase of amorphousness of the polymer (Ramesh and Yi, 2009; Agrawal and Mahipal, 2011).

4.4.1 DC conductivity studies

In order to investigate the effect of fumed silica on the ionic conductivities, the ionic conductivities of the chitosan-LiCF$_3$SO$_3$-EC/PC system was determined as a function of nanosized fumed silica content.

Figures 4.42 to 4.46 show the impedance plot chitosan-LiCF$_3$SO$_3$-EC/PC system with different wt% of silica at room temperature. In the impedance response behaviour, the disappearance of the high frequency semicircular portion in the complex impedance plot on addition of filler to CLTS1, CLTS 3 and CLTS 4 led to the conclusion that current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction (Jacob et al., 1997; Rajendran et al., 2003). The intercept on the real axis gives the electrolyte bulk resistance.
Figure 4.42 Complex impedance plot of CLTS1 at 25°C

Figure 4.43 Complex impedance plot of CLTS2 at 25°C
Figure 4.44 Complex impedance plot of CLTS3 at 25°C

Figure 4.45 Complex impedance plot of CLTS4 at 25°C
The ionic conductivity value of chitosan- LiCF₃SO₃-EC/PC: x SiO₂ complexes at various amounts of silica are tabulated in Table 4.6.

**Table 4.6 Average conductivity value of chitosan-40wt.%LiCF₃SO₃-30wt.%EC/PC: x SiO₂ complexes at room temperature**

<table>
<thead>
<tr>
<th>Percentage x SiO₂</th>
<th>Average Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>5.01 × 10⁻⁶</td>
</tr>
<tr>
<td>0.5%</td>
<td>1.14 × 10⁻⁵</td>
</tr>
<tr>
<td>1.0%</td>
<td>5.69 × 10⁻⁶</td>
</tr>
<tr>
<td>1.5%</td>
<td>2.63 × 10⁻⁵</td>
</tr>
<tr>
<td>2.0%</td>
<td>5.41 × 10⁻⁵</td>
</tr>
<tr>
<td>2.5%</td>
<td>9.23 × 10⁻⁶</td>
</tr>
</tbody>
</table>
Figure 4.47 shows the effect of inclusion of nanosized fumed silica in chitosan-LiCF$_3$SO$_3$-EC/PC system at room temperature.

![Graph showing conductivity vs silica composition](image)

**Figure 4.47 Conductivity of chitosan- 40wt.%LiCF$_3$SO$_3$-30wt.%EC/PC: x SiO$_2$ system at room temperature**

From the plot it can be seen that the addition of nanosized fumed silica causes the change in conductivity of CLT system. The addition of nanosized fumed silica above 1 wt. % increases the conductivity and reaches a maximum at 2.0 wt. % silica. The conductivity of the highest conducting sample is calculated to be $5.41 \times 10^{-5}$ S cm$^{-1}$ at room temperature. There is reduction in conductivity observed when 2.5 wt. % fumed silica has been added. This reduction in ionic conductivity was attributed due to the displacing and impeding effect of the non-conducting material (Best et al., 1999).

The enhancement in ionic conductivity with the addition of ceramic fillers can be explained as follows:
i. The silica nano particles can be well mixed with the electrolyte system and the formability of the film could be enhanced. This can be attributed to the higher volume fraction of the amorphous phase surrounding near the fillers (Aravindan and Vickraman 2007).

ii. Inorganic fillers cause changes in the microstructure and morphology of polymer electrolyte. The surface group on silica may interact with cations and anions and provide additional sites creating favourable high conducting pathways in the vicinity of grains for the migration of ions. These interactions would be able to provide transient sites for the hopping ions, thereby providing additional conductivity pathways for ionic migration (Pitawala et al., 2007).

The decrease in conductivity after the optimum concentration of silica content can be explained as follows:

i. At high filler concentrations, the grains get so close to each other that the blocking effect dominates and the conductivity starts to drop (Dissanayake et al., 2003).

ii. High concentrations of the ceramic filler, leads to well-defined crystallite regions (Rajendran and Uma, 2000; Uma et al., 2004). The filler grains act as nucleation centres. Since ionic conduction takes place primarily through the amorphous phase of the polymer, hence high crystallinity lowers conductivity.
The temperature dependence of electrical conductivity \( \log \sigma \) versus \( 1000/T \) for different compositions is shown in Figure 4.48. The plot reveals that the conductivity varies linearly as the temperature increases similar to electrolyte systems studied earlier in the absence of inert fillers. The regression values are close to unity, indicating that the temperature-dependent ionic conductivity for all silica composition content obeys Arrhenius rule. This implies the nature of \( \text{Li}^+ \) transport is quite similar to that in ionic crystals, where ions jump into neighbouring vacant sites and thus increase the ionic conductivity to a higher value. The activation energy decreases with increase in conductivity.

![Figure 4.48 Temperature dependence of conductivity plot for chitosan-40 wt. % LiCF$_3$SO$_2$-30 wt. % EC/PC: x SiO$_2$ system](image)

Figure 4.49 shows activation energy does not increase linearly with silica content. The activation energy of the higher conducting electrolyte using 2.0 wt \% SiO$_2$ has been found to be 0.27 eV. It can be concluded that the system with 2.0 wt \% silica composition required the least minimum energy to overcome the energy barrier for lithium ion transfer as it has the highest ionic conductivity.
4.4.2 Dielectric relaxation studies

The dielectric relaxation behaviour of the polymer electrolyte brings about important insights into the ionic transport phenomenon (Hema et al., 2008). Figure 4.50 and 4.51 represent the frequency dependence of $\varepsilon_r$ and $\varepsilon_i$, respectively for chitosan-LiCF$_3$SO$_3$-EC/PC-2% SiO$_2$ at different temperatures. According to the Maxwell-Wagner model and Koop’s’ phenomenological theory, the dielectric material with a heterogeneous structure can be imagined as a structure consisting of well conducting grains separated by poorly conducting grain boundaries (Koops, 1951; Abo El Ata et al., 2004; George et al., 2006). The low frequency dispersion region is attributed to the contribution of charge accumulation at the electrode-electrolyte interface (Howell et al., 1974; Baskaran et al., 2004) and further confirming its non-Debye dependence. From the figures, it is clear that the values of dielectric constant and dielectric loss are higher than the CLT system.
Figures 4.52 and 4.53 show the variation of dielectric constant and dielectric loss for CLTS4 system at high frequencies. These values decrease with temperature even at higher frequencies as observed for CLT system. The dipolar relaxation for CLTS4 occurs at ~63100 Hz.
Figure 4.52 Dielectric constant, $\varepsilon_r$ at high frequency for CLTS4 system

Figure 4.53 Dielectric loss, $\varepsilon_i$ at high frequency for CLTS4 system

Figure 4.54 shows the variation of dielectric constant with temperature. It is observed that the dielectric permittivity increases slowly with temperature up to 333K as observed for CLA and CLT systems. For higher frequencies, variation in $\varepsilon$ is nominal
since the dipoles are not free to orient at a higher frequency and hence the orientation polarization will be less at higher frequencies (George et al., 2006). Furthermore, at very high temperatures the chaotic thermal oscillations of molecules are intensified. Thus the total increase in polarization will be less with the rise in temperature at higher frequencies (George et al., 2006).

![Figure 4.54 Temperature dependence of dielectric constant, $\varepsilon_r$, at various frequencies for CLTS4 system](image)

**4.4.3 Dielectric modulus studies**

Figures 4.55 and 4.56 depict the frequency dependence of $M_r$ and $M_i$, respectively, for CLTS4 system at different temperatures. Both plots show an increase at the high frequency end but the relaxation peaks are not observed due to frequencies exceeding the range permitted by instrument used in the present study. As the temperature increases, the possible peak maxima shifts to higher frequencies which indicate that the conductivity of the charge carrier has been thermally activated (Ramya et al.,
2008). Also, it is found that at low frequencies region as shown Figures 4.57 and 4.58, the modulus values decrease gradually with increasing temperature.

**Figure 4.55** Frequency dependence of real part of electrical modulus, $M_r$, at various temperatures for CLTS4 system

**Figure 4.56** Frequency dependence of real part of electrical modulus, $M_i$, at various temperatures for CLTS4 system
Figure 4.57 Real part of electrical modulus, $M_r$ at low frequencies for CLTS4 system

Figure 4.58 Imaginary part of electrical modulus, $M_i$ at low frequencies for CLTS4 system
4.4.4 Dielectric loss tangent behaviour

Figure 4.59 shows the variation of tan δ as a function of frequency for chitosan-LiCF$_3$SO$_3$-EC/PC-2%SiO$_2$ system at different temperatures. As the temperature increases the relaxation peak shifts to higher frequencies indicating that the charge carrier is thermally activated (Ramya et al., 2008).

![Figure 4.59 Variation of loss tangent with frequency for CLTS4 system](image)

The variation of relaxation time with temperature is presented in Figure 4.60 and Table 6.7. The temperature dependence of relaxation time appears to be thermally activated and can be described by Arrhenius law. Activation energy for relaxation, $E_R$ is 0.28 eV.
Table 4.7 Temperature versus relaxation time for CLTS4 system

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Relaxation time, ( \tau ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>( 8.61 \times 10^{-7} )</td>
</tr>
<tr>
<td>303</td>
<td>( 6.78 \times 10^{-7} )</td>
</tr>
<tr>
<td>313</td>
<td>( 6.12 \times 10^{-7} )</td>
</tr>
<tr>
<td>323</td>
<td>( 4.14 \times 10^{-7} )</td>
</tr>
<tr>
<td>333</td>
<td>( 1.66 \times 10^{-7} )</td>
</tr>
</tbody>
</table>

Figure 4.61 shows the variation of jumping probability per time (P) with temperature. A sudden increase in the P values has been observed in polymer electrolyte system even with the addition of nano fillers.
Figure 4.61 Variation of $P$ with temperature for CLTS4 system

The normalized plot of $\tan \delta / (\tan \delta_{\text{max}})$ against $f/f_{\text{max}}$ for the highest conducting sample at selected temperatures is given in Figure 4.62. The figure shows that all the data collapsing almost into one single master curve and this implies that the relaxation mechanism is independent of temperature (Mariyappan and Govindaraj, 2004).

Figure 4.62 Normalised plot of loss tangent for CLTS4 system at selected temperatures
4.5 Rice and Roth Model

The transport mechanism for lithium ion conduction is more complex in a composite polymer electrolyte system. Not only does one need to be concerned about the transport mechanisms in pure polymer and ceramic components, but also the chemical and physical interaction between the phases and the resulting structure, such as morphology and phase boundaries (Kumar and Scanlon, 2000). An expression for conductivity, $\sigma$, is expressed by equation 4.7

$$ \sigma = \mu ne z $$ (4.7)

Where

- $n$ = number of ions per cubic centimetre,
- $e$ = electronic charge,
- $\mu$ = mobility of ions
- $z$ = valence on ion

According to Majid and Arof (2005), the conductivity pattern can be interpreted by transport parameters such as concentration of free ions, diffusion coefficients and mobility of ions which can be calculated using the value of number density $n$, and that can be obtained from Rice and Roth equation (2.7).

The basic idea of the Rice and Roth model is that in an ionic conductor there is energy gap $E$ above which conducting ions of mass $m$ can be thermally excited from localized ionic states to free ion-like states in which the ion propagates throughout the solid with velocity, $v$. Such an excited free ion-like state has a finite life time, $\tau$. The velocity is can be found using equation (2.5) and mean the ‘mean free path’ or distance from one complexed site to another,$l$ be calculated using equation (2.6).
The distance between two adjacent chitosan monomers is $10^{-9}$ m (Okuyama et al., 2000) and hence $\tau$ can be calculated. From the temperature-dependence conductivity behaviour all the filler electrolyte system studied obeys Arrhenius rule. Therefore the activation energy can be obtained from the slope of the graph and hence the number density of the mobile ions, $n$, can be calculated. The calculated value $n$ is then used to calculate the ionic mobility, $\mu$. Figures 4.63 and 4.64 shows the transport parameter for chitosan-LiCF$_3$SO$_3$-EC/PC system with varying concentration of SiO$_2$ fillers. From the graph, it can be observed that the mobility is temperature dependent. The calculated mobility value for filler added system lies between $10^{-13}$ to $10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$. From the plots it is clear that conductivity on addition of fillers is controlled mainly by mobility of ions.

![Figure 4.63](image-url)  
*Figure 4.63 Transport parameter of number of ion for CLTS systems at various temperatures*
4.6 Transference Number

The transference number corresponding to ionic ($t_i$) transport has been evaluated in chitosan polymer electrolyte systems electrolyte system using Wagner’s polarization technique. In this technique, the sample is sandwiched between two stainless steel blocking electrodes and a fixed voltage is applied, and the current is monitored as a function of time until it saturates. The plot of polarized current for the CLT system is shown in Figure 4.65.

Figure 4.64 Transport parameter of mobility for CLTS systems at various temperatures
The ionic transference numbers for the electrolyte systems were calculated using the following equation (Selvasekarapandian et al., 2005)

$$t_i = \frac{I_{ionic}}{I_0} \quad (4.10)$$

The values of the calculated transference numbers are listed in Table 4.8.

**Table 4.8 Cationic transference numbers**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ionic Transference Number</th>
<th>Electronic Transference Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLA</td>
<td>0.90</td>
<td>0.10</td>
</tr>
<tr>
<td>CLT</td>
<td>0.91</td>
<td>0.09</td>
</tr>
<tr>
<td>CLTS4</td>
<td>0.96</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Chapter 4  
Electrical Studies

The high ionic transference numbers suggest that the charge transport in chitosan based polymer electrolytes films is predominantly due to ions.

4.7 Summary

The conductivity–temperature studies indicate chitosan polymer electrolyte systems show Arrhenius behaviour. The ionic conductivity of chitosan electrolyte system is dependent on the type of anion present in the salt. The system with lithium triflate salt showed higher room temperature conductivity than with lithium acetate salt which is $6.18 \times 10^{-7} \text{ S cm}^{-1}$ and $5.01 \times 10^{-6} \text{ S cm}^{-1}$ respectively. The addition of filler, 2 wt. % SiO$_2$ can enhance the ionic conductivity of the plasticized chitosan-LiCF$_3$SO$_3$ salt system to $5.41 \times 10^{-5} \text{ S cm}^{-1}$. Studies on dielectric behaviour of chitosan systems show strong dependence on frequency and temperature. The dielectric constant values of 50Hz for CLTS4 > CLT > CLA. A similar trend was observed for room temperature conductivity, where $\sigma$ of CLTS4 > CLT > CLA at room temperature. From the Rice and Roth model studies for CLTS systems, it can be understood that conductivity mainly depends on the mobility of lithium ions.
5.1. Introduction

Information pertaining to ion-polymer interaction, ion-pairing and ion solvation can be obtained from FTIR studies, as these factors influence conductivity (Deepa et al., 2002). Muzzarelli (1977) reported, when chitosan chelates with a metal salt, the carbonyl, O=C-NHR, amine, NH₂ and ammonium, NH₃⁺ bands will shift from 1650, 1590 and 1560 cm⁻¹ to towards the lower wavenumbers. FTIR is an important tool to study the molecular structures and interactions.

The aim of the present study is to investigate the interactions present in chitosan-LiCF₃SO₂-EC/PC and chitosan-LiCF₃SO₂-EC/PC-x%SiO₂ polymer electrolyte systems with the hope to gain some insight on the ion conductivity mechanism of the electrolyte systems.

5.2. The Infrared Spectra of Chitosan and Chitosan Acetate (CA)

Figure 5.1 and Figure 5.2 depicts the spectrum of pure chitosan and chitosan acetate in the region 700 to 1900 cm⁻¹.
Figure 5.1 FTIR spectrum of pure chitosan

Figure 5.2 FTIR spectrum of chitosan acetate
The characteristic vibrational bands for pure chitosan and chitosan acetate have been reported by other researchers and are tabulated in Table 5.1.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide I (O=C-NHR band)</td>
<td>1635-1665</td>
<td>Singh and Ray, 1997; Kweon, 2001; Prashanth, 2002; Jang and Nah, 2003; Cardenas and Miranda, 2004; Nie et al., 2005, Salleh et al., 2009</td>
</tr>
<tr>
<td>Amide II (NH₂ band)</td>
<td>1583-1604</td>
<td>Kweon 2001, Prashanth 2002; Cardenas and Miranda, 2004; Nie et al., 2005, Salleh et al., 2009</td>
</tr>
<tr>
<td>CH₂ bending</td>
<td>1425-1434</td>
<td>Prashanth, 2002; Cardenas and Miranda, 2004; Salleh et al., 2009</td>
</tr>
<tr>
<td>CH₃ symmetrical deformation mode</td>
<td>1375-1381</td>
<td>Qu et al., 2000; Prashanth, 2002; Zia, 2005</td>
</tr>
<tr>
<td>Amide III</td>
<td>1314- 325</td>
<td>Peniche et al., 1999; Qu et al., 2000; Baran, 2008, Salleh et al., 2009</td>
</tr>
<tr>
<td>CH₂ wagging (ω (CH₂))</td>
<td>1307</td>
<td>Singh and Ray, 1997</td>
</tr>
<tr>
<td>C-O-C asymmetric stretching (νas(C-O-C))</td>
<td>1151-1158</td>
<td>Peniche et al., 1999; Kweon 2001; Cardenas and Miranda, 2004; Salleh et al., 2009</td>
</tr>
<tr>
<td>C-O stretching (ν (C-O))</td>
<td>1032-1082</td>
<td>Peniche et al., 1999; Kweon, 2001, Salleh et al., 2009</td>
</tr>
<tr>
<td>Saccharide structure</td>
<td>896-1153</td>
<td>Qu et al., 2000</td>
</tr>
</tbody>
</table>
In Figure 5.1 the pure chitosan spectrum consists of O=C-NHR at 1652 cm$^{-1}$, NH$_2$ at 1575 cm$^{-1}$, CH$_2$ bending ($\delta$(CH$_2$)) mode at 1418 cm$^{-1}$, CH$_3$ symmetrical deformation mode at 1376 cm$^{-1}$, O=C-NH$_2$ at 1317 cm$^{-1}$, C-O-C asymmetrical stretching ($\nu_{as}$(C-O-C)) at 1150 cm$^{-1}$, C-O stretching ($\nu$(C-O)) at 1035 cm$^{-1}$ and 1062 cm$^{-1}$. The band due to saccharide was observed at 895 cm$^{-1}$. These values are in agreement with the tabulated assignments listed in Table 5.1.

Chitosan acetate (CA) film was prepared by dissolving chitosan in 1% acetic acid solution. Figure 5.2 shows the carbonyl band has shifted from 1652 cm$^{-1}$ to 1647 cm$^{-1}$ and the amine band from 1575 cm$^{-1}$ to 1559 cm$^{-1}$. The pure chitosan acetate spectrum indicates dative covalent bonding may have occurred between some of the hydrogen ions in the acetic acid and the nitrogen atom of the chitosan polymer. Carbonyl absorption peak at higher than 1700 cm$^{-1}$ due to acetic acid was not observed. This behaviour is in good agreement with Ritthidej et al. (2002) who reported carboxylic acids are not present in chitosan acetate film.

5.3. The Infrared Spectra of Chitosan Acetate (CA)-LiCF$_3$SO$_3$

Figure 5.3 presents the structure of lithium triflate salt. It has been used as a dopant in conducting polymer as it is soluble in organic and aqueous solvents (Alia et al., 1997). The spectrum of trifluoromethanesulfonate ion shows clear distinction between free triflate ions, cation-anion pairs and highly associated species (Bishop et al., 1996; Osman and Arof, 2003; Kumar et al., 2005).
Figure 5.3 Structure of lithium triflate salt

Cation-anion association occurs at the SO$_3$ end of the anion; thus, the symmetric and asymmetric SO$_3$ stretching modes (shown in Figure 5.4) are highly sensitive to changes in the co-ordination state of the anion i.e. co-ordination of triflate ion with cation (Bishop et al., 1996).

Figure 5.4 Symmetric and asymmetric SO$_3$ stretching modes of LiCF$_3$SO$_3$

It has been well established that CF$_3$ symmetric deformation $\delta$(CF$_3$) mode reflects ionic, association of the triflate anion at the SO$_3$ end through redistribution of charge (as shown in Figure 5.5) accompanying the formation of ionic pairs and aggregates (Rhodes and Frech,1999; Rhodes and Frech, 2000; Kumar et al., 2005). These regions provide useful information pertaining to the types of aggregation and strengths of ionic interactions which may occur between salt and polymer.
The FTIR spectrum of pure LiCF$_3$SO$_3$ is shown in Figure 5.6 in the region of 750 cm$^{-1}$ to 1350 cm$^{-1}$ while Table 5.2 summarizes the vibrational modes and wavenumbers exhibited by lithium triflate.

The intense band appearing at 1036 cm$^{-1}$ is assigned to symmetric SO$_3$ stretching, $\nu_s$(SO$_3$). This band is due to the presence of free triflate (CF$_3$SO$_3^-$) ions. The ion pairs (LiCF$_3$SO$_3$, Li(CF$_3$SO$_3$)$_2^-$ and Li((CF$_3$SO$_3$)$_3^2^-$) band appears at 1267 cm$^{-1}$ due to asymmetric SO$_3$ stretching mode, $\nu_{as}$(SO$_3$). It can also be observed from the
spectrum, that symmetric CF<sub>3</sub> stretching mode, \( \nu_s(CF_3) \) at 1227 cm<sup>-1</sup>, antisymmetric CF<sub>3</sub> stretching mode, \( \nu_{as}(CF_3) \) at 1192 cm<sup>-1</sup> and symmetric deformation of CF<sub>3</sub>, \( \delta_s \) (CF<sub>3</sub>) at 772 cm<sup>-1</sup>.

Table 5.2: Vibrational modes with corresponding wavenumbers for lithium triflate

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavenumbers</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric CF&lt;sub&gt;3&lt;/sub&gt; stretching mode, ( \nu_s(CF_3) )</td>
<td>1224-1227</td>
<td>de Zea Bermudez et al., 1999; Deepa et al., 2002; Winie and Arof, 2006b</td>
</tr>
<tr>
<td>Antisymmetric SO&lt;sub&gt;3&lt;/sub&gt; stretching mode, ( \nu_{as}(SO_3) )</td>
<td>1260-1290</td>
<td>Laik et al., 1998; de Zea Bermudez et al., 1999; Deepa et al., 2002; Winie and Arof, 2006b; Ramesh et al., 2007</td>
</tr>
<tr>
<td>Antisymmetric stretching CF&lt;sub&gt;3&lt;/sub&gt; stretching mode, ( \nu_{as}(CF_3) )</td>
<td>1188-1157</td>
<td>de Zea Bermudez et al., 1999; Winie and Arof, 2006b</td>
</tr>
<tr>
<td>Symmetric SO&lt;sub&gt;3&lt;/sub&gt; stretching mode, ( \nu_s(SO_3) )</td>
<td>1033-1044</td>
<td>de Zea Bermudez et al., 1999; Deepa et al., 2002; Winie and Arof, 2006; Ramesh et al., 2007</td>
</tr>
<tr>
<td>Symmetric CF&lt;sub&gt;3&lt;/sub&gt; deformation mode, ( \delta_s(CF_3) )</td>
<td>757-776</td>
<td>Deepa et al., 2002; Winie and Arof, 2006b</td>
</tr>
</tbody>
</table>

The peak observed at 764 cm<sup>-1</sup> is due to symmetric deformation for CF<sub>3</sub>. The saccharide structure peaks were observed at 897 cm<sup>-1</sup> and 948 cm<sup>-1</sup>. Vibrational peaks observed in Figure 5.7 are in agreement with reported results (Laik et al., 1998; Winie and Arof, 2006b; Ramesh et al., 2007).
Figure 5.7 Infrared spectrum of chitosan acetate- lithium triflate in the region 700 to 1000 cm\(^{-1}\)

Figure 5.8 shows the chitosan acetate-lithium triflate spectrum in the region 1000 to 1300 cm\(^{-1}\). The C-O stretch at 1027 cm\(^{-1}\) in CA appears to be shifted to 1029 cm\(^{-1}\) in the chitosan acetate-lithium triflate spectrum. The presence of the free ions in these complexes could be deduced from the existence of the \(\nu_s(SO_3)\) and \(\nu_s(CF_3)\) peaks at 1029 and 1228 cm\(^{-1}\) which has shifted from 1036 and 1227 cm\(^{-1}\), respectively (Winie and Arof, 2006b). The peak at 1192 cm\(^{-1}\) attributed to the antisymmetric stretching mode of CF\(_3\), \(\nu_{as}(CF_3)\) of the salt and the peak at 1151 cm\(^{-1}\) due to C-O-C asymmetric stretching of chitosan have merged to form a broad band at 1177 cm\(^{-1}\) with addition of LiCF\(_3\)SO\(_3\).
Figure 5.8 Infrared spectra of (a) lithium triflate (b) chitosan acetate and (c) chitosan acetate-lithium triflate in the region between 1000 to 1300 cm\(^{-1}\).

Apart from that, the \(\nu_{\text{as}}(\text{SO}_3)\) peak at 1267 cm\(^{-1}\) and another prominent peak of LiCF\(_3\)SO\(_3\) at 1291 cm\(^{-1}\) is observed to overlap and form a broad band that peaks at 1251 cm\(^{-1}\). This shows that chitosan and LiCF\(_3\)SO\(_3\) have interacted.

Figure 5.9 shows the chitosan acetate-lithium triflate spectrum in the region 1300 to 1800 cm\(^{-1}\). The band at 1322 cm\(^{-1}\) due to CH\(_2\) wagging disappears on addition of salt into the films. Peaks due to CH\(_3\) symmetrical deformation mode and CH\(_2\) bending vibration have shifted from 1378 cm\(^{-1}\) and 1409 cm\(^{-1}\) to 1381 and 1419 cm\(^{-1}\) respectively on addition of salt. The relative intensity of the band at 1381 cm\(^{-1}\) decreases whereas the relative intensity of band at 1419 cm\(^{-1}\) increases. The shifts and changes in intensity of these bands further confirm interaction between the salt and the polymer. There was a shift in the wavenumbers of the peaks observed for NH\(_2\) and O=\text{C}-\text{NHR} bands of chitosan at 1557 cm\(^{-1}\) and 1645 cm\(^{-1}\) respectively on addition of...
salt into the films. This implies that complexation has occurred by the formation of a
dative covalent bond between the lithium cation from the salt with the lone pair of
electrons at the nitrogen atom of the O=C-NHR and NH$_2$ bands as illustrated in Figure
5.10

![Infrared spectrum of (a) chitosan acetate and (b) chitosan acetate-lithium triflate in the region between 1300 to 1800 cm$^{-1}$]

Figure 5.9 Infrared spectrum of (a) chitosan acetate and (b) chitosan acetate-lithium triflate in the region between 1300 to 1800 cm$^{-1}$

![Dative covalent bonding between the lithium cations and nitrogen atoms in chitosan]

Figure 5.10 Dative covalent bonding between the lithium cations and nitrogen atoms in chitosan
Table 5.3 compares the interaction between chitosan polymer and lithium triflate with work done by other researchers. It is noticed that the peaks in the present study are in good agreement with the findings by Osman and Arof, 2003. The small difference in wavenumber with the present work and those observed by Winie and Arof (2006b) is probably due to the amine group being substituted by hexanoyl group.

Table 5.3 Comparison of vibrational modes with corresponding wavenumbers for chitosan-lithium triflate

<table>
<thead>
<tr>
<th></th>
<th>Chitosan-LiCF$_3$SO$_3$ (in present study)</th>
<th>Chitosan-LiCF$_3$SO$_3$ (Osman and Arof, 2003)</th>
<th>Hexanoyl chitosan-LiCF$_3$SO$_3$ (Winie and Arof, 2006b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_s$(CF$_3$)</td>
<td>764 cm$^{-1}$</td>
<td>761 cm$^{-1}$</td>
<td>772 cm$^{-1}$</td>
</tr>
<tr>
<td>NH$_2$ band</td>
<td>1560 cm$^{-1}$</td>
<td>1560 cm$^{-1}$</td>
<td>Not applicable</td>
</tr>
<tr>
<td>O=C-NHR</td>
<td>1646 cm$^{-1}$</td>
<td>1648 cm$^{-1}$</td>
<td>1635 cm$^{-1}$</td>
</tr>
</tbody>
</table>

5.4. The Infrared Spectra of EC and PC with LiCF$_3$SO$_3$

Plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) are known to enhance conductivity at ambient temperatures of polymers incorporated with inorganic lithium salts (Yang et al., 1995; Kim and Oh, 2000; Kim and Smotkin, 2002; Glasse et al., 2002; Leo et al., 2002; Chiang et al., 2003; Yue et al., 2003; Meneghetti et al., 2004; Idris et al., 2007). The choice of choosing ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers is due to their higher dielectric constant when compared with other plasticizers and are highly compatible with most polymers (Doucey et al., 1999; Jacob and Arof, 2000; Rajendran and Sivakumar, 2008). Hence, plasticization has been recognized as one of the effective and efficient routes available for the reduction of crystallinity and subsequent enhancement of the amorphous nature.
of composite polymer electrolytes and for arriving at a high ionic conductivity in such systems (Suthanthiraraj et al., 2009). Ethylene carbonate and propylene carbonate has been used as plasticizers in this system. The chemical structure of EC and PC are shown in Figure 5.11 and Figure 5.12.

In order to examine the differences in the interaction EC and PC with salt, FTIR spectra was carried out on pure EC, pure PC, EC-LiCF$_3$SO$_3$, PC-LiCF$_3$SO$_3$ and EC/PC-LiCF$_3$SO$_3$. The vibrational modes and wavenumbers of EC and PC are listed in Tables 5.4 and 5.5 respectively.
Table 5.4 Vibrational modes and wavenumbers exhibited by EC

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O stretching</td>
<td>1773-1798 and 1803-1865</td>
<td>Wang et al., 1996; Huang 1996; Osman et al., 2005; Rajendran and Sivakumar, 2008; Aravindan and Vickraman, 2009</td>
</tr>
<tr>
<td>CH(_2) bending</td>
<td>1480</td>
<td>Aravindan and Vickraman, 2009</td>
</tr>
<tr>
<td>CH(_2) wagging</td>
<td>1394 and 1420</td>
<td>Wang et al., 1996; Aravindan and Vickraman, 2009</td>
</tr>
<tr>
<td>Skeletal stretching</td>
<td>970-1180</td>
<td>Angell, C.L., 1956; Osman and Arof, 2003</td>
</tr>
<tr>
<td>Ring breathing</td>
<td>890 -897 and 1067</td>
<td>Wang et al., 1996; Kim and Oh, 2000; Kumutha et al., 2005</td>
</tr>
<tr>
<td>C=O bending</td>
<td>717-720</td>
<td>Starkey and Frech, 1997; Kumutha et al., 2005; Aravindan and Vickraman, 2009</td>
</tr>
</tbody>
</table>
Table 5.5 Vibrational modes and wavenumbers exhibited by PC

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O stretching, νs (C=O)</td>
<td>1784-1800</td>
<td>Doucey <em>et al.</em>, 1999; Rajendran <em>et al.</em>, 2001; Starkey and Frech, 1997; Deepa <em>et al.</em>, 2002; Deepa <em>et al.</em>, 2004; Alias <em>et al.</em>, 2005</td>
</tr>
<tr>
<td>δ(CH) ring structure</td>
<td>1557</td>
<td>Deepa <em>et al.</em>, 2002</td>
</tr>
<tr>
<td>δCH (CH₂)</td>
<td>1483</td>
<td>Doucey <em>et al.</em>, 1999</td>
</tr>
<tr>
<td>δCH (CH₃)</td>
<td>1453</td>
<td>Doucey <em>et al.</em>, 1999</td>
</tr>
<tr>
<td>δOCH₂</td>
<td>1390</td>
<td>Doucey <em>et al.</em>, 1999</td>
</tr>
<tr>
<td>δCH₃</td>
<td>1354-1358</td>
<td>Doucey <em>et al.</em>, 1999; Frech and Chintapalli, 1996; Alias <em>et al.</em>, 2005</td>
</tr>
<tr>
<td>ν(C-O)</td>
<td>1150-1155</td>
<td>Doucey <em>et al.</em>, 1999</td>
</tr>
<tr>
<td>Ring breathing mode</td>
<td>777-985</td>
<td>Deepa <em>et al.</em>, 2002; Alias <em>et al.</em>, 2005</td>
</tr>
<tr>
<td>Symmetric ring deformation</td>
<td>712-715</td>
<td>Doucey <em>et al.</em>, 1999; Starkey and Frech, 1997; Deepa <em>et al.</em>, 2002; Alias <em>et al.</em>, 2005</td>
</tr>
</tbody>
</table>

The FTIR spectrum of ethylene carbonate is shown in Figure 5.13. Figure 5.13 shows the vibrational bands of ethylene carbonate in the region between 650 cm⁻¹ and 1900 cm⁻¹.
cm\(^{-1}\). The bands observed at 714 and 769 cm\(^{-1}\) are due to the C=O bending and ring breathing band, respectively. Bands at 1487 cm\(^{-1}\) and 1391 cm\(^{-1}\) are assigned to CH\(_2\) bending and wagging mode respectively. The peaks at 971, 1059 and 1136 cm\(^{-1}\) can be assigned to skeletal stretching. According to Huang et al. (1996) and Osman and Arof (2003), EC has a pair of intense peaks observed at 1798 cm\(^{-1}\) and 1773 cm\(^{-1}\) and 1774 cm\(^{-1}\) and 1803 cm\(^{-1}\) respectively. In the present work these peaks due to the C=O stretching vibration modes are observed at 1789 and 1770cm\(^{-1}\).

![FTIR spectrum of pure EC in 650-1900 cm\(^{-1}\) region](image)

Figure 5.13 FTIR spectrum of pure EC in 650-1900 cm\(^{-1}\) region

In the EC spectrum (Figure 5.13), the splitting of the peaks at 1770 and 1800 cm\(^{-1}\) is attributed to Fermi resonance of the C=O stretching mode with an overtone of the ring breathing mode and the existence of short-range ordering of the molecular orientation that originated from the dipole–dipole coupling of two EC molecules (Huang et al., 1996; Rajendran and Sivakumar, 2008) which is illustrated in Figure 5.14.
The FTIR spectrum of pure PC is represented in the region of 650 -1900 cm\(^{-1}\) and is displayed in Figure 5.15. The characteristic vibrational frequencies for pure PC and its corresponding assignments from previous studies are given in Table 5.5. Results of the present spectroscopic studies on PC are comparable with the results given in table.

A very strong and a broad band appears at 1781 cm\(^{-1}\) which is attributed to C=O stretching mode. This high carbonyl frequency in PC is undoubtedly related to the ring strain in five membered ring structures (Deepa et al., 2002). Two strong peaks at 1388 cm\(^{-1}\) and 1353 cm\(^{-1}\) are ascribable to CH stretching and bending vibrations of CH\(_2\) groups. Peaks at 1174, 1148, 1117, 1074 and 1048 cm\(^{-1}\) are assigned to the C-O stretching mode in PC (Doucey et al., 1999). In the region below 1000 cm\(^{-1}\), infrared bands of PC molecules appear as a pair of peaks at 956 and 945 cm\(^{-1}\) and other peaks are also seen at 918 and 849 cm\(^{-1}\) (Deepa et al., 2002). These bands correspond to ring stretching and breathing modes of PC. The PC spectrum also shows sharp intense peaks at 775 and 711 cm\(^{-1}\) due to ring deformation and breathing modes respectively.
Figure 5.15 FTIR spectrum of pure PC in 650-1900 cm⁻¹ region

Figure 5.16 shows the infrared spectra for pure EC and the mixture of EC-LiCF₃SO₃ of mole ratio 1:1 in the C=O bending region. The C=O bending band in pure EC at 714 cm⁻¹ has shifted to higher wavenumbers and broadened with the addition of LiCF₃SO₃. A new peak is observed at 728 cm⁻¹. The shift to higher wavenumber can be assigned to interaction between lithium ion and EC, Li⁺←O=C. These results are in agreement with earlier studies done by Chintapalli and Frech (1996). Shift in band was also noted in the ring breathing band of EC at 892 cm⁻¹. On addition of salt, the ring breathing band of EC shifts to 904 cm⁻¹.
Figure 5.16 FTIR spectra of pure EC and EC-LiCF$_3$SO$_3$ in 700-910 cm$^{-1}$ region

Figure 5.17 depicts the spectrum in the region between 1560 cm$^{-1}$ and 1950 cm$^{-1}$ where C=O stretching can be observed. The pair of peaks due to C=O stretching at 1789 and 1770 cm$^{-1}$ in the spectrum of EC has shifted to 1766 and 1805 cm$^{-1}$ with changes in bandwidth and relative intensity. The shift in the carbonyl group peak of EC indicates there is interaction between lithium salt and EC molecule which is probably due to the lone pair electrons on the oxygen atom of carbonyl group being able to form dative covalent bond with lithium ions.

Figure 5.17 FTIR spectra of pure EC and EC-LiCF$_3$SO$_3$ in 1560-1950 cm$^{-1}$ region
Figure 5.18 shows spectrum in the region between 980 to 650 cm$^{-1}$ for pure PC and PC-LiCF$_3$SO$_3$. The C=O bending mode experiences an upward shift by 10 cm$^{-1}$ upon incorporation of lithium triflate i.e. from 711 to 722 cm$^{-1}$. The higher frequency component has been assigned to the interaction between lithium triflate and PC (Chintapalli and Frech, 1996). A second intense peak of PC observed due to ring deformation mode is observed at 775 cm$^{-1}$. In Figure 5.6, a band at 772 cm$^{-1}$, was assigned to the $\delta$(CF$_3$) mode of LiCF$_3$SO$_3$. In the spectrum of LiCF$_3$SO$_3$-PC three bands are observed at 783 cm$^{-1}$, 765 cm$^{-1}$ and 741 cm$^{-1}$. This is due to the presence of ‘free’ ion, ion pair and aggregate due to different interactions between Li$^+$ and CF$_3$SO$_3^-$ in the presence of solvent (Chintapalli and Frech, 1996). Peaks due to breathing mode are observed at 850, 921 and 959 cm$^{-1}$ for the LiCF$_3$SO$_3$-PC spectrum. The pair of peaks observed in PC at 945 and 956 appears as a single peak in the presence LiCF$_3$SO$_3$, further reconfirming interaction between lithium ions and PC. This is in agreement with Starkey and Frech (1997) where it is reported that lithium ions most likely coordinates with the three oxygen atoms present in PC.

Figure 5.18 FTIR spectra of pure PC and PC-LiCF$_3$SO$_3$ in 650-980cm$^{-1}$ region
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The C=O stretching band, Figure 5.15 observed at 1781 cm\(^{-1}\) in pure PC has shifted to 1770 cm\(^{-1}\) in the PC-LiCF\(_3\)SO\(_3\) spectrum (Figure 5.19) further reconfirming interaction between salt and PC.

![Figure 5.19 FTIR spectra of pure PC and PC-LiCF\(_3\)SO\(_3\) in 1620-1990 cm\(^{-1}\) region](image)

5.5. The Infrared Spectra of EC-PC systems

In order to determine the existence of interactions between the two plasticizers, the spectrum of a mixture of EC and PC in mole ratio of 1:1 is analyzed. The FTIR spectra of EC and PC are included in Figure 5.20 for comparison purpose. It has been mentioned earlier that the pair of peaks observed at 1770 and 1789 cm\(^{-1}\) in EC and the strong intense peak at 1781 cm\(^{-1}\) in PC is due to C=O stretching mode. A pair of peaks at 1771 and 1788 cm\(^{-1}\) is observed in the EC-PC spectrum and it is noticed that the relative intensity of both the peaks are less intense than that observed for pure EC. It can be proposed that these two peaks of EC-PC arise from a splitting of the nondegenerate C=O stretch fundamental of a single molecule (EC or PC) into two components (Ostrovskii et al., 1998; Meneghetti et al., 2004).
This implies there is interaction between EC and PC. Since the main changes in the spectrum of the complex were observed in the C=O group of the PC molecules, it will be reasonable to suggest that EC molecule with strong polarity interacts with the PC molecules by way of the C=O group of the PC molecules. However, the interactions between the EC-PC may not be strong as EC-EC due to the carbonyl group being less polar in PC molecule.

**5.6. The Infrared Spectra of chitosan-EC/PC systems**

Figure 5.21 represents the spectra of pure CA, CA-EC, CA-PC and CA-EC/PC in the region 650 to 1650 cm$^{-1}$. In this region, the bands due to the saccharide structure at 896 cm$^{-1}$, the C-O stretching bands at 1027 and 1065 cm$^{-1}$, the C-O-C asymmetric stretch at 1151 cm$^{-1}$, CH$_2$ wagging band at 1322 cm$^{-1}$, the CH$_3$ symmetrical stretching band at 1378 cm$^{-1}$, the CH$_2$ bending band at 1409 cm$^{-1}$, the NH$_2$ band at 1559 cm$^{-1}$ and O=C-NHR band at 1647 cm$^{-1}$ are observed. No noticeable changes in peaks are noticed on addition of plasticizers of EC, PC or EC/PC. This shows the CA-double plasticizer system exists as mixed phase with no interaction between the polymer and plasticizer.
Figure 5.21 FTIR spectra of CA, CA-EC, CA-PC and CA-EC-PC in 650-1650 cm$^{-1}$ region

5.7. The infrared spectra for CA-LiCF$_3$SO-EC/PC

The FTIR spectra of EC/PC plasticized chitosan LiCF$_3$SO$_3$ were analysed only in the $\delta$(CF$_3$) and $\nu$(SO$_3$) region as shown in Figure 5.22. The increase in intensity in both regions on addition of plasticizers implies the increase in the number of free ions from
the salt (Osman and Arof, 2003; Winie and Arof, 2006b). From these observations it can be established that plasticizers help in dissociation of salt.

Figure 5.22 (i) The FTIR spectra of (a) of CA-LiTf and (b) CA-LiTf -EC/PC in the region of δ(CF₃) (ii) The FTIR spectra of (a) of CA-LiTf and (b) CA-LiTf -EC/PC in the ν₃(SO₃) region

5.8. The Infrared Spectra of CA-LiCF₃SO₃-EC/PC- x%SiO₂ systems

Fumed silica (SiO₂) has been used as filler in the present work. Figure 5.23 shows the infrared spectrum of pure SiO₂ in the region of 650 to 1850 cm⁻¹. A prominent band at 1100 cm⁻¹ is observed due to Si-O band (Ramesh et al., 2007) and weak SiO₂ stretching peak is observed at 810 cm⁻¹(Niu et al., 2007). Figure 5.24 shows structure of silica.
The FTIR spectra of CA-LiCF$_3$SO$_3$-EC/PC-x% SiO$_2$ system in the region between 900 and 1450 cm$^{-1}$ is shown in Figure 5.25. The addition of fumed silica does not show its characteristic bands in the spectra possibly because the size is so small that it just disrupts the initial order in the polymer matrix (Ahmad et al., 2006). The peak intensity at 1182 cm$^{-1}$ due to CF$_3$ symmetric stretching changes upon addition of filler. This shows there is possible interaction between salt and filler as shown Figure 5.26.
Figure 5.25 FTIR spectra of (a) CA-LiCF$_3$SO$_3$-EC/PC (CA') (b) CA'-0.5% SiO$_2$ (c) CA'-1.0% SiO$_2$ (d) CA'-1.5% SiO$_2$ (e) CA'-2.0% SiO$_2$ and (f) CA'-2.5% SiO$_2$ in the region of 900-1450 cm$^{-1}$

![FTIR spectra](image)

Figure 5.26 Possible interaction between Li ion and fumed silica

![Interaction diagram](image)
Ion association occurs at the SO₃ end of the anion, thus the symmetric SO₃ stretching modes will be highly sensitive to changes in the coordination state of the anion. The deconvolution of symmetric SO₃ stretching was used to investigate the effect of filler concentration on ion association in the polymer electrolyte. Band fitting of the SO₃ regions will provide information pertaining to free ions, ion pairs and ion aggregates. The curve-fitted infrared spectrum of the same for CLTS4 is presented in Figure 5.27.

![Deconvoluted profile of triflate band associated with SO₃ stretching mode for CLTS4 system](image)

**Figure 5.27 Deconvoluted profile of triflate band associated with SO₃ stretching mode for CLTS4 system**

According to literature (Huang and Frech, 1994; Rhodes and Frech, 1999) the bands at 1027 cm⁻¹, 1037 cm⁻¹ and 1061 cm⁻¹ can be assigned to free ions, ion pairs and ion aggregates respectively. This shows that conductivity of the composite electrolyte systems may be influenced by the presence of these ions.

The fractions of free ions, ion pairs and ion aggregates present in the sample were calculated using the following formula (Sharma and Thakur, 2010; Shukla and Thakur, 2010) below:
Chapter 5

**FTIR**

\[
\text{Fraction of free ions} = \frac{\text{Area of free ions}}{\text{Total peak Area}} \quad (5.1)
\]

\[
\text{Fraction of ion pairs} = \frac{\text{Area of ion pair}}{\text{Total peak Area}} \quad (5.2)
\]

\[
\text{Fraction of ion aggregates} = \frac{\text{Area of ion aggregates}}{\text{Total peak Area}} \quad (5.3)
\]

Figure 5.29 shows variation pattern for free ions, ion pairs and ion aggregates as a function of filler concentration. The free ion peak area gives a direct measure of the free mobile ions available for conduction (Shukla and Thakur, 2010). The film with 2 wt% filler has the highest value of free lithium cations and hence highest ionic conductivity.

**Figure 5.29** Free ions, ion pairs and ion aggregates as a function of filler concentration
5.9. Summary

FTIR studies show ion polymer interaction occurs between chitosan and lithium triflate salt due to formation of chitosan salt complex. Interaction between plasticizer and salt occurs at the C=O bond and C-O bond of the ring structure. Ion-solvation was observed for both plasticizers, EC and PC with lithium triflate salt. Dipole-dipole interactions occur between EC and PC molecules. Studies on polymer-plasticizer spectra suggest there is no polymer–solvent interaction. From the FTIR studies of the addition of nano SiO$_2$ filler confirms the availability of ‘free’ ion, ion pair and aggregate in the electrolyte. Maximum number of free lithium ions has been observed for the electrolyte containing 2 wt.% silica which also has the highest ionic conductivity.
CHAPTER 6

RESULTS

XRD STUDIES

6.1 Introduction

X-ray diffraction (XRD) studies can provide information on the nature of a material whether amorphous or crystalline which are characterized by the presence of peaks (Rajendran et al., 2008). Studies have shown that ionic conduction mainly occurs in the amorphous region (Awadhia and Agrawal, 2007; Bhargav et al., 2007; Agrawal and Mahipal, 2011). In this chapter the X-ray diffraction patterns of chitosan will be studied upon the addition of salt, plasticizer and filler.

6.2 X-Ray diffraction of chitosan-LiCF$_3$SO$_3$ and chitosan-LiCH$_3$COO

Figure 6.1 depicts the XRD pattern of the salt free chitosan film. The film exhibits two broad band at 2θ=22.4° and 17.2° indicating chitosan film is partially crystalline. The shape of the diffractogram is quite similar to that reported by Ritthidej et al. (2002), Yahya et al. (2006), Bangyekan et al. (2006) and Aziz et al. (2010b). The characteristic chitosan peak at 2θ=22.4° is comparable with that reported by Twu et al. 2005 and Pawlicka et al. (2008) for chitosan powder.
The X-ray diffraction patterns of lithium acetate, LiCH$_3$COO (LiAc) and lithium triflate, LiCF$_3$SO$_3$ (LiTr) salts are shown in Figures 6.2 and 6.3 respectively. The data shows that LiCH$_3$COO is obviously a crystalline phase with peaks at 2θ angles of 16.3°, 21.1°, 26.0°, 27.0° and 30.9°. High intensity peaks are observed at 2θ angles of 16.4°, 16.7°, 19.9° 20.5°, 22.6° and 22.8° for LiCF$_3$SO$_3$ salt. These values have good agreement with the JCP number 2:00-014-0840 for LiAc and 2:01-081-0813 for LiTr.

Figure 6.1 XRD spectrum of chitosan film

Figure 6.2 XRD spectrum of pure lithium acetate
The XRD spectra for the salted chitosan polymer are shown in Figure 6.4.

It is observed that the two peaks in the diffractogram of pure chitosan disappear and a broad halo is observed for LiCH$_3$COO-doped chitosan and also in the LiCF$_3$SO$_3$-
doped chitosan. The presence of a broad halo peak at $2\theta=22.4^\circ$ on addition of salt reveals the amorphous nature of the complexed system (Achari et al., 2007; Ramya et al., 2008; Hema et al., 2008). This may be explained as follows. Chitosan forms hydrogen bonds between hydroxyl groups and amino groups in chitosan film (Uragami et al., 1994). Introduction of additional substituents into polysaccharide structures would disrupt the crystalline structure of chitosan, especially by the loss of the hydrogen bonding (Sankararamakrishnan and Sanghi, 2006). Peaks corresponding to LiCH$_3$COO and LiCF$_3$SO$_3$ are not observed in the electrolyte leading to the conclusion that both salts have dissolved in the polymer matrix and does not remain as a separate phase (Rajendran et al., 2001). The absence of peaks in the XRD due to addition of salts indicates complexation must have occurred between lithium ions from the salt and the free amine and hydroxyl groups present in chitosan.

Compared with the LiCH$_3$COO-doped chitosan, the intensity of the peak at $2\theta=22.4^\circ$ for LiCF$_3$SO$_3$-doped chitosan is less intense and broader. The degree of crystallinity of samples was quantitatively estimated following the method of (Nara and Komiya, 1983; Shujun et al., 2005).

The equation of the degree of crystallinity is as follows:

$$X_c = \frac{A_c}{A_c + A_a}$$

Where: $X_c =$ refers to the degree of crystallinity  
$A_c =$ refers to the crystallized area on the X-ray diffractogram  
$A_a =$ refers to the amorphous area on the X-ray diffractogram
Table 6.1 Degree of crystallinity of chitosan-LiCH₃COO and chitosan-LiCF₃SO₃ films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-40%wt.LiCH₃COO</td>
<td>12.6</td>
</tr>
<tr>
<td>Chitosan-40%wt.LiCF₃SO₃</td>
<td>6.3</td>
</tr>
</tbody>
</table>

These results show that LiCF₃SO₃-doped chitosan is more amorphous than LiCH₃COO-doped chitosan, as the larger triflate ion causes greater disruption of hydrogen bonds present in the chitosan polymer.

6.3 X-Ray diffraction of chitosan-LiCF₃SO₃-EC/PC

Figure 6.5 shows the X-ray diffraction spectrum of plasticized chitosan-LiCF₃SO₃.

![XRD spectrum](image)

Figure 6.5 XRD spectra of chitosan-LiCF₃SO₃-EC/PC

Table 6.2: Degree of crystallinity for chitosan-LiCF₃SO₃-EC/PC film

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-LiCF₃SO₃-EC/PC</td>
<td>2.4</td>
</tr>
</tbody>
</table>
It is apparent from Table 6.2 that the addition of a third component, EC/PC into chitosan-LiCF<sub>3</sub>SO<sub>3</sub> complex decreases the crystallinity. Many studies (Benedict et al., 1998; Periasamy et al., 1999; Leo et al., 2002; Ragavendran et al., 2004; Rajendran et al., 2004; Suthanthiraraj et al., 2009) have shown that addition of plasticizers increases the amorphousness of salt-doped polymers. According to Pawlicka et al. (2008) the presence of plasticizer, can cause the distancing of the polymer chains and hence change the crystalline structure.

6.4 X-Ray diffraction of chitosan-LiCF<sub>3</sub>SO<sub>3</sub>-EC/PC-SiO<sub>2</sub>

Despite the intense scientific research in the area of nanocomposite polymer there is still a limited understanding about the conduction mechanism to explain the conductivity enhancement in these polymer electrolyte systems.

Kumar et al. (2007) showed the addition of nano-size MgO to PMMA–LiClO<sub>4</sub>–EC & DEC electrolyte system caused an enhancement in conductivity. The addition of nano-sized MgO particles in the gel polymer electrolyte caused the peak present in the XRD pattern for PMMA–LiClO<sub>4</sub>–EC & DEC to decrease in intensity and an increase of broadness of area under the peak upon. They suggested that the dependence of ionic conductivity with MgO content was due to improvement in the amorphosity and viscosity.

However, Subban and Arof (2003a) did not obtain similar results on addition of filler to the polymer-salt system. They obtained optimum conductivity with 5% SiO<sub>2</sub>. Upon addition of 2 % SiO<sub>2</sub> fillers to PVC-LiCF<sub>3</sub>SO<sub>3</sub> the XRD pattern showed the peak
becoming broader. When 5 % SiO$_2$ was added, the peak becomes narrower, indicating increasing crystallinity. The conductivity enhancement on addition of fillers could not be assigned to the amorphous region of the polymer since the crystalline region increased as more SiO$_2$ is added (Subban and Arof, 2003a).

Fumed silica is an amorphous, non-porous form of silicon dioxide, and is electrochemically inert (Raghavan et al., 1998; Fan et al., 1998). The XRD pattern of fumed silica is shown in Figure 6.6. The diffraction pattern confirms amorphous nature of fumed silica as there were no peaks observed.

The addition of silica to chitosan-LiCF$_3$SO$_3$-EC/PC system causes the peak observed at 22.6° in chitosan-LiCF$_3$SO$_3$-EC/PC to broaden which is illustrated in Figure 6.7. An additional small peak is observed at 19.2° and 9.4°. The system with 2 wt. % SiO$_2$ shows a much broader hump at 22.6° compared to samples with 0.5%, 1.0%, 1.5% and 2.5% SiO$_2$. The crystalline peak for the CLTS4 system has been plotted as given in Figure 6.8. The calculated % crystallinity of CLTS4 was found to be 2.03.
Figure 6.7 XRD spectra of chitosan-LiCF$_3$SO$_3$-EC/PC (a) 0.5% silica (b) 1.0% silica (c) 0 1.5% silica (d) 2.0% silica and (e) 2.5% silica

From Figure 6.9, it can be observed sample with the highest room temperature conductivity i.e. 2.0 wt% silica has the smallest degree of crystallinity.
Figure 6.9 Degree of crystallinity for films with various concentration of silica

6.5 Summary

XRD result shows the chitosan acetate polymer film is partially crystalline. It was found type of salt added to the polymer influences the amorphousness of the film. In the case of the composite chitosan system, the crystalline region was smallest with filler concentration 2.0 wt. % SiO$_2$. 
CHAPTER 7

RESULTS

THERMAL STUDIES

7.1 Introduction

Thermal techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TGA) are important analytical techniques to monitor physical and chemical changes in both natural and synthetic polymers. From DSC curves, the thermal transition of a polymer can be studied i.e. changes that take place when a polymer is heated. TGA measures the changes of sample mass with temperature. In TGA, most weight losses involve loss of a volatile component which provides information about the nature and extent of degradation of a polymeric material.

7.2 Differential Scanning Calorimetry (DSC)

The glass transition temperature of chitosan is still a much debatable subject. The main reason may be that, being a natural polymer, some properties like crystalline, molecular weight and deacetylation degree, can present wide variations according to the source and/or method of extraction and will influence the $T_g$ (Neto et al., 2005). Mishra et al. (2010) observed $T_g$ for chitosan to be around 150°C using differential scanning calorimetry. On the other hand, Sakurai et al. (2000) observed the $T_g$ of chitosan at 203°C, while Kittur et al. (2002) found no evidence for $T_g$. Figure 7.1 shows the DSC curve for pure chitosan acetate film. The $T_g$ value is observed at 198.6°C value which is in close agreement with that reported by Sakurai et al. (2000). At 198.6°C, the chitosan polymer goes from a hard, glass like state to a rubber like state. Above $T_g$ value, the chitosan polymer becomes soft, flexible and rubbery.
Figure 7.1 DSC traces for chitosan acetate film

Figure 7.2 and 7.3 illustrates the $T_g$ value for chitosan salted with lithium acetate and lithium triflate. $T_g$ value for chitosan salted system with lithium acetate was lower than chitosan acetate film. Whereas, there is no significant change in $T_g$ value on addition of lithium triflate salt to chitosan. Generally, $T_g$ increases with addition of salt due to formation of transient cross-linking between polymer chains via coordination between polymer chains and salt. However, at high salt concentrations the decrease in $T_g$ of complexes arises due to electrostatic repulsion between anions and from the decreased interaction between polymer chains and salt owing to the formation of ion pairs and and/or high order ion aggregates (Huh et al., 2004). The $T_g$ value for chitosan salted with lithium acetate was lower than chitosan salted with lithium triflate. Similar behavior has been reported by Cruickshank et al. (1995). Cruickshank et al. (1995) measured the glass transition temperature, $T_g$, and ionic conductivity, $\sigma$, for mixtures of low molecular weight poly(ethylene glycol)s with LiCF$_3$SO$_3$, LiClO$_4$, NaClO$_4$, LiBF$_4$ and NaBF$_4$. They reported that both $T_g$ value and conductivity is dependent on the nature of anion present in salt but not the cation.
Figure 7.2 DSC traces for salted chitosan acetate (chitosan-LiCH₃COO) film

Figure 7.3 DSC traces for salted chitosan acetate (chitosan-LiCF₃SO₃) film

Figure 7.4 and 7.5 present DSC curves for of chitosan-LiCH₃COO system and chitosan-LiCF₃SO₃ system plasticized with EC and PC. The $T_g$ value for plasticized chitosan-LiCH₃COO system is 119.42°C and chitosan-LiCF₃SO₃ system is 197.74°C. A decrease in $T_g$ values was observed for both chitosan salted systems on addition of EC/PC plasticizers. The lower $T_g$ value on addition of the plasticizers suggest lithium
ions coordinating with oxygen atoms present in EC and PC molecules, hence reducing the number of lithium ions able to coordinate with amine groups of chitosan. According to Forsyth et al. (1995) addition of plasticizer reduces $T_g$ and increases mobility of polymer chain.

Figure 7.4 DSC traces for salted and plasticized chitosan acetate (chitosan-$\text{LiCH}_3\text{COO}$-EC/PC) film

Figure 7.5 DSC traces for salted and plasticized chitosan acetate (chitosan-$\text{LiCF}_3\text{SO}_3$-EC/PC) film
Figure 7.6 depicts the DSC thermogram for the composite polymer electrolyte. It can be observed that the $T_g$ for chitosan-LiCF$_3$SO$_3$-EC/PC system on addition of 2 wt.% fumed silica decreases to 166.31°C. This means that the addition of SiO$_2$ causes the $T_g$ to decrease.

The decrease in $T_g$ means that the mobility of polymer segments has increased which means that SiO$_2$ helps to soften the polymer backbone (Subban and Arof, 2003a). This can be further explained by assuming that the nanosized silica filler, due to its large surface area, prevents organized chitosan polymer chains and hence greater degree of disorder.

### 7.3 Thermogravimetric Analysis (TGA)

The thermal properties of the prepared films were examined by TGA. Figure 7.7 shows the weight loss for chitosan acetate film. The first stage ranges between 35 and 235°C and shows of 14.78% loss of mass. This may be attributed to the loss of bound water and acetic acid from the solvent. The second stage of mass loss starts at
235.31°C and continues up to about 400°C during which there was 41% mass loss. The second weight loss is due to the degradation of chitosan. This value agrees well with the results reported by Don et al., 2002 and Huang et al. (2010).

![Figure 7.7 TGA curve for chitosan acetate film](image)

Figure 7.7 TGA curve for chitosan acetate film

The weight-loss curves of the chitosan-salted films, as a function of temperature, are shown in Figure 7.8 and 7.9. The onset temperatures of thermal degradation for chitosan-LiCH₃COO and chitosan-LiCF₃SO₃ were lower than chitosan acetate film. The second decomposition took place at 388.31°C for chitosan-LiCH₃COO film and 420.51°C for chitosan-LiCF₃SO₃ film. The weight loss for second decomposition was 50.00% and 44.81% respectively. The second decomposition can be explained in terms of the salts. Osman (2005) suggested that weight loss for chitosan acetate-lithium triflate film above 400°C was due to decomposition of the lithium triflate salt. Chitosan polymer system with lithium triflate salt shows better thermal stability than lithium acetate salt.
Figure 7.8 TGA curve for salted chitosan acetate (chitosan-LiCH$_3$COO) film

Figure 7.9 DSC traces for salted chitosan acetate (chitosan-LiCF$_3$SO$_3$) film

TGA curves of adding EC/PC to chitosan salted systems are shown in Figure 7.10 and 7.11. For chitosan-LiCH$_3$COO-EC/PC system, first thermal degradation took place at
235.65°C and the second thermal degradation occurs at 388.08°C. Weight loss for first thermal degradation was 16.42% and 44.73% for second thermal degradation. In the case of chitosan-LiCF₃SO₃-EC/PC first thermal degradation takes place at 225.56°C with a weight loss of 11.21% and second thermal degradation at 420.91°C with a weight loss 40.66%. An increase in temperature for onset of thermal degradation is observed on addition of plasticizers EC/PC for chitosan-LiCH₃COO, whereas negligible change is observed for addition of EC/PC to chitosan-LiCF₃SO₃ system. However, the second thermal degradation temperatures remain the same for both systems on adding plasticizers.

Figure 7.10 TGA curve for salted and plasticized chitosan acetate (chitosan-LiCH₃COO-EC/PC) film
TGA curve of chitosan-LiCF$_3$SO$_3$-EC/PC-2% SiO$_2$ is shown in figure 7.12. Three major losses are observed in the TGA curve. The first stage occurs between 50°C to 160°C with a weight loss of approximately 15%. The second stage takes place between 232.78°C and 413.71°C with a weight loss of 28.28% and third stage takes place...
between 413.71°C and 560.00°C with a weight loss of 32.72%. The first stage weight loss is assigned to weight loss of low molecular weight species such as water, EC and PC. The second stage weight loss can be related to the complex dehydration of the saccharide rings, depolymerization, and decomposition of the acetylated and deacetylated units of the polymer (Neto et al., 2005). The first thermal degradation for chitosan-LiCF$_3$SO$_3$-EC/PC-2% SiO$_2$ system was greater than chitosan-LiCF$_3$SO$_3$-EC/PC system, which shows incorporation of silica improves thermal stability of plasticized salted chitosan electrolyte system. As mentioned before, the third stage weight loss is due to decomposition of lithium triflate salt.

7.4 Summary

In this chapter, the thermal properties of chitosan systems were analysed using DSC and TGA. The $T_g$ value for chitosan is similar to the value obtained by Sakurai et al. (2000). Addition of lithium acetate salt to chitosan causes a decrease in $T_g$ value. However, no significant change in $T_g$ was observed when lithium triflate was added. Incorporation of plasticizers EC and PC reduced the $T_g$ of chitosan salted system suggesting the chitosan polymer chains are becoming more flexible. In the composite system, addition of SiO$_2$ filler causes a significant drop of $T_g$ value.

Thermal studies show that chitosan decomposes at 235°C. Introduction of salt decreases the thermal decomposition value of chitosan. A second thermal decomposition was observed due to decomposition of salt. A similar trend was not observed for chitosan-LiCF$_3$SO$_3$ system. Incorporation of 2 wt. % silica improves thermal stability of plasticized salted chitosan (CLT) electrolyte system.
CHAPTER 8

DISCUSSION

Ionic polymer complexes have attracted much interest because of their potential industrial application in solid state electrochemical devices such as lithium batteries electrochemical display devices/smart windows and sensors. Since the discovery of ionic conductivity in the complex of PEO and alkaline salts by Fenton et al. (1973), extensive research has been carried on PEO-complexes. Compared to liquid electrolyte, solid polymer electrolytes (SPEs) have several advantages such as ease of mouldability, elimination of volatile organic liquids, suppression of lithium dendrite formation, free from leakage, mechanical strength and flexibility of design, thereby permitting miniaturization. Unfortunately, ionic conductivity of PEO/alkali metal salt mixture was of the order of only $10^{-7}$ S cm$^{-1}$ at room temperature (Tominaga et al., 2000). Various methods have been employed to enhance conductivity, such as cross-linking of PEO synthesizing comb-type polymers, using new salts having lower dissociation energy and addition of ceramic powder (Tominaga et al., 2000). Alternative polymer systems such as PAN, PVC, PMMA, PVdF have been investigated in an effort to find polymer electrolyte system with room temperature conductivity suitable for utilization in electrochemical devices. Even though these materials exhibit favorable mechanical properties, their conductivities are not high at room temperature (Rajendran et al., 2007).

The choice of polymer electrolyte depends on satisfying the requirements mentioned in chapter two such as high ionic conductivity, good thermal and chemical stability, high mechanical strength and low cost. In this study chitosan was investigated as a
potential candidate for polymer electrolytes. Chitosan has lone pairs of electrons present on nitrogen and oxygen atom which allows for chelation of metal ions. Furthermore, chitosan is a non-toxic, biocompatible, and biodegradable polymer and found abundantly in nature. These polymers also can easily form films. Chitosan has very low electrical conductivity. Many researchers have carried out studies to improve the conductivity by adding different salts and plasticizers (Arof et al., 2001, Pawlicka et al., 2008, Arof et al., 2010).

In this present study, lithium acetate and lithium triflate salts were selected. Lithium triflate is used, as it is nontoxic, highly resistant to oxidation and thermally stable (Ahmad et al., 2006; Ramesh and Liew, 2010). According to Ismail et al. (2009) LiCH$_3$COO is highly soluble in many types of solvent and is cheaper than other lithium salts. Plasticizers are known to enhance the conductivity and dissociation ions of the polymer salt electrolyte system. In this study a mixed solvent of EC and PC were used as plasticizers.

Comparative studies between the two different anions were carried out. It is found that the system with triflate ion shows higher conductivity than the corresponding system with acetate ion.

<table>
<thead>
<tr>
<th>Electrolyte System</th>
<th>Ionic conductivity at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-40 wt.% LiCF$_3$SO$_3$-30wt.% EC/PC</td>
<td>$5.01 \times 10^{-6}$ Scm$^{-1}$</td>
</tr>
<tr>
<td>Chitosan-40 wt.% LiCH$_3$COO-30wt.% EC/PC</td>
<td>$6.18 \times 10^{-7}$ Scm$^{-1}$</td>
</tr>
</tbody>
</table>

From XRD diffractograms the degree of crystallinity calculated for chitosan doped with lithium triflate is 6.3% and for chitosan doped with lithium acetate salts is 12.6%.
Chapter 8  Discussion

The increase in amorphousness is probably due to the large CF₃SO₃⁻ anion that reduces the crystallinity of the complex. It can be suggested the increase in conductivity in CLT system is due to the amorphizing properties of the large CF₃SO₃⁻ ion present in the system. Furthermore, the lattice energy of lithium triflate is lower than lithium acetate. The lattice energy of these salts were calculated using Kapustinskii equation,

\[ U = \frac{1.202 \times 10^5 V Z^+ Z^-}{r^+ + r^-} \left(1 - \frac{34.5}{r^+ + r^-}\right) \]

where

- \( Z^+ \) = number of charge on cation
- \( Z^- \) = number of charge on anion
- \( V \) = number of ions per unit formula
- \( r^+ \) = ionic radii of cation
- \( r^- \) = ionic radii of anion

The calculated lattice energy for lithium acetate is 921.4 kJ mol⁻¹ and for lithium triflate is 730.3 kJ mol⁻¹. This shows lithium triflate salt tends to dissociate more readily than lithium acetate salt as it has lower lattice energy.

The activation energy also influences conductivity of the electrolyte system. Systems with lower activation energy have higher conductivity. This has been proven in this work, as the activation energy calculated from temperature-conductivity graph for system containing lithium triflate and lithium acetate salt is 0.31 eV and 0.82 eV respectively. Both polymer electrolyte systems obeyed Arrhenius behaviour and showed linear enhancement of ionic conductivity with increasing temperature. This is
expected as the temperature increases the polymer expands to produce more free volume and greater dissociation of ions.

These ions can jump more readily into neighbouring vacant sites. The conductivity trend with increasing temperature is consistent with those observed by other researchers for polymer-salt-plasticized system (Ramesh et al., 2001; Puteh et al., 2005; Hema et al., 2009). At temperature 373 K, the conductivity of CLA system was higher than CLT system. At this temperature, the ions will have greater movement. The larger triflate anions may block the pathway of the lithium ions and lead the lithium ions having to take longer pathway as shown in Figure 8.1 and hence the reduced conductivity.

Calculations using the Rice and Roth model showed that the conductivity in CLA and CLT system is mainly due to mobility of ions. The pre-exponential factors $\sigma_0$ for CLA and CLT systems, were substituted into equation 2.7 and the ratio of number density of ions in CLT system to CLA system was found to be $1.41 \times 10^{-8}$. Using $\sigma=nq\mu$, where $\sigma$ is conductivity, $n$ is the number density of mobile ions (considered constant), $q$ is charge of the mobile species and $\mu$ is mobility, and it was found the ratio of mobile ions was very much greater than number density of mobile ions.
The migration metal ions from the salt in chitosan polymer can be explained by the formation chitosan-metal cation complex. Guibal (2004) has suggested that cation chelation in chitosan can take place at the nitrogen and oxygen atoms in the amine and hydroxyl groups respectively, but more likely to occur at the nitrogen site. The lithium ion can chelate with the amine group on the second carbon of the chair like structure of chitosan. A free lithium ion with sufficient energy may collide with the chelated lithium ion causing ion exchange to take place. The distance between nitrogen atoms in the amine group in one monomer to the next is about 10.4 Å (Okuyama et al., 2000). Therefore, the exiled lithium ion which has gained energy can form a dative bond with an uncomplexed neighbouring nitrogen atom or knock out lithium ion attached to the nitrogen atom and occupy its place (Yahya et al., 2006) similar to a “pendulum like” movement. Since oxygen atom has lone pair of electrons it is possible for the freed lithium ion to also originate from oxygen site and get transferred to another oxygen or nitrogen site.

The FTIR studies can be used to verify the complexation between chitosan and the cation of a salt. Osman and Arof (2003) observed shift in peaks on addition on salt for NH$_2$ and O=C-NHR band of chitosan acetate. In the present study, a slight shift in the amine and carbonyl band was observed for chitosan- lithium triflate FTIR spectrum. The decrease in intensity of amine peak and increase in carbonyl band were agreeable with those observed by Osman and Arof (2003). Hence, it can be concluded that lithium ions can form dative bond with nitrogen atoms of chitosan acetate. It is well known that EC and PC plasticizers in polymer electrolytes can enhance conductivity value. The plasticisers chosen usually have high dielectric constant so to help in dissociation of salt and hence increase the conductivity. From FTIR spectrum Figure 5.22 it is observed the intensity of peak at 770 cm$^{-1}$ attributed to CF$_3$ deformation
mode of salt increases on addition of plasticizers EC and PC. Furthermore, the introduction of the dual plasticizers allows a new pathway for the lithium ions.

A pioneering research work by Weston and Steele (1982) suggested incorporating inert filler (α-alumina) into PEO system significantly improved the mechanical stability of the material at temperatures in excess of 100°C. Capuano et al. (1991) observed that the addition of up to 10 wt% γ-LiAlO₂ in the PEO-based polymer electrolyte increases room temperature conductivity by one order of magnitude. Furthermore, the composite electrolytes exhibited improved mechanical strength and enhanced interfacial stability. The main reason for preparing a composite polymer electrolyte is that the filler provides a solid like support matrix, allowing the amorphous polymer to maintain its liquid-like characteristics in terms of fast ionic mobility at the microscopic level (Khan et al., 1994). The interest in using fumed silica stems from its unique ability to form network structures in a liquid (Khan et al., 1994). In the present study, nano fumed silica (SiO₂) was selected to serve as filler. X-ray diffraction study showed addition of 2 wt. % silica to CLT system caused the peak observed at 22.6° to be broader. The CLTS4 system is more amorphous than the other systems with filler. This increase in amorphosity of the sample may cause an increase in conductivity. The calculated degree of crystallinity was found to be the lowest for the CLTS4 system. Room temperature conductivity was highest with 2 wt. % fumed silica. Ahmad et al. (2006) reported that PMMA gel electrolyte had maximum conductivity at optimum content 2 wt. % fumed silica. The FTIR showed no prominent silica peak present in chitosan-salt-plasticised system. Since fumed silica is small it just disrupts the initial order in the polymer matrix and hence may cause local structural changes (Ahmad et al., 2006). Band fitting of the SO₃ regions was carried to obtain information of free ions, ion pairs and ion aggregates in the composite system.
Chapter 8

The presence of free ions, ion pairs and ion aggregates in the electrolyte systems with filler were found by the appearance of the peaks at 1027 cm\(^{-1}\), 1037 cm\(^{-1}\) and 1061 cm\(^{-1}\) respectively. This shows that conductivity of the composite electrolyte systems may be influenced by the presence of these ions. It is found that the presence free ions are mainly responsible for conductivity for the composite system.

The conductivity-temperature dependence of the all five CLTS systems has followed Arrhenius behaviour. The activation energy for conduction for the highest conducting composite film is 0.27 eV and the lowest conducting composite film is 0.47 eV. The highest conducting sample seems to possess the lowest activation energy and vice-versa. A minimum is observed at 1.0 wt. % silica. This result suggests that the addition of the ceramics filler can take both roles of a promoter for ionic dissociation and a barrier for ionic conduction. The observed initial increase in conductivity may be explained as follows. When SiO\(_2\) is added to the highest conducting sample in the chitosan-salt-plasticiser system, surface-charge layer is formed at the polymer-filler interface which provides a conducting pathway for the lithium ions. However, when the SiO\(_2\) content is further increased to 1 wt. % the conductivity tends to decrease slightly but then increases again as the filler content is increased to 2 wt.%. The decrease in conductivity as the filler content increases to 1 wt. % is attributed to the blocking of some of the existing conducting pathways and the possible conglomeration of the excess SiO\(_2\) filler that reduces the polymer-filler interface and hence reduces the conducting pathways. As filler content is further increased, the filler grains get close enough to each other so that the high conducting regions in the vicinity of the grain surfaces start to get interconnected (Majid et al., 2007). The migration of Li\(^+\) ion can travel along interconnected high conducting pathways giving
rise to the increase in conductivity. Eventually, further increase in filler results in the blocking and the termination of the formation of the conducting pathways.

The Rice and Roth model was used quantitatively to explain the variation in conductivity for the system containing nano fumed silica. The transport parameter, number density of mobile ions does not give significant contribution to the conductivity compared to mobility. These results are in agreement with those observed by Idris et al. (2009) for chitosan – adipic acid system.

The dielectric properties of the polymer electrolyte can be useful to discuss the conductivity of the electrolytes. It can be understood that the highest conducting film has the highest dielectric constant and dielectric loss. This implies that more ions are present at lower frequency for higher conducting material. The dielectric constant value at 50 Hz for CLTS4 > CLT > CLA. The dielectric values at higher frequency for the chitosan based electrolyte system did not approach a constant. The appearance of peaks at high frequencies for dielectric loss spectra for the three mentioned systems is attributed to the relaxation phenomena of polymer (motion of salt free chain segment) (Pradhan et al., 2008). Similar types of observations have been reported in literature (Marzantowicz et al., 2007; Pradhan et al., 2008). The dipole relaxation peaks shifted to lower frequencies in the following order: CLA followed by CLT and finally by CLTS4. This can be attributed to decrease in viscosity of the polymer electrolyte systems. The plots depicting the temperature variation of real (M_r) and imaginary (M_i) part of electrical modulus for all the systems are similar. The maxima of the modulus curves shifts towards higher frequency with increasing temperature. At low frequencies the modulus values did not approach zero. This could be due to high salt content of the prepared electrolyte systems where there are many possible types of
interactions occurring and hence modulus value above zero was observed. Relaxation peaks are observed for the conductivity processes for imaginary part of modulus spectra. This suggests ionic conduction is predominant in the polymer electrolyte systems (Nithya et al., 2011). So the conduction in polymer electrolytes takes place through charge migration of ions between coordinated sites of the polymer. Transference number studies further confirmed that the ionic motion in these electrolyte systems is predominantly due to ionic charge transport. The relaxation times for ionic charge carriers determined from the loss tangent maximum peak and are shown below for the different systems at room temperature.

<table>
<thead>
<tr>
<th>Electrolyte System</th>
<th>Relaxation time at room temperature, τ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan-40wt.% LiCF$_3$SO$_3$-30wt.% EC/PC</td>
<td>5.03 x 10$^{-5}$</td>
</tr>
<tr>
<td>Chitosan-40wt.% LiCH$_3$COO-30wt.% EC/PC</td>
<td>3.99 x 10$^{-6}$</td>
</tr>
<tr>
<td>[Chitosan-40wt.% LiCF$_3$SO$_3$-30wt.% EC/PC]-2%SiO$_2$</td>
<td>8.61 x10$^{-7}$</td>
</tr>
</tbody>
</table>

The system with the presence of composite filler had the shortest relaxation time at room temperature. The normalized plot of tan δ / (tan δ$_{max}$) versus f/ f$_{max}$ shows that all the data collapsing almost into one single master curve for the CLTS4 system. However this was not observed for the CLA and CLT systems. It can be implied that the distribution of relaxation time is independent of temperature for the CLTS4 system. The activation energy, $E_a$ and relaxation activation energy, $E_R$ are reasonable agreement for CLA, CLT and CLTS4 systems. This implies that the lithium ions for all three systems have the same energy barrier as well as relaxation time.
CHAPTER 9

CONCLUSIONS AND SUGGESTIONS

The search for polymer electrolyte system with high ionic conductivity and preferentially environmentally friendly is the main objective for polymer electrolyte research. To achieve this objective, several approaches have been suggested in the literatures, including using new polymer host, salts, plasticizers and ceramic filler. In this study, films of chitosan- LiCH$_3$COO-EC/PC, chitosan-LiCF$_3$SO$_3$-EC/PC and chitosan-LiCF$_3$SO$_3$-EC/PC-SiO$_2$ have been successfully prepared by the solution cast technique.

The ionic conductivity of CLT system at room temperature was $5.01 \times 10^{-6}$ Scm$^{-1}$ and CLA system is $6.18 \times 10^{-7}$ Scm$^{-1}$. This shows the system with triflate anion showed greater conductivity than with acetate anion. This is due to LiCF$_3$SO$_3$ salt has lower lattice energy than lithium acetate salt and hence LiCF$_3$SO$_3$ salt dissociates more readily and thereby providing more conducting ions. The conductivity – temperature dependence for both systems followed Arrhenius rule. It can be inferred that the lithium ion conduction follows hopping mechanism. FTIR results also show that the lithium ions can form complex with polymer host, which would provide the platform for ion hopping.

The effect of fillers was analysed in this study. Addition of 2 wt. % fumed silica to CLT system showed an enhancement in conductivity. The room temperature conductivity for CLTS4 was found to be $5.41 \times 10^{-5}$ Scm$^{-1}$. The calculation of percentage of crystallinity obtained from XRD studies showed CLTS4 system had the
least degree of crystallinity. This could be due to silica fillers preventing the polymer chains being organised and hence greater degree of disorder. The effect of filler can be reflected from FTIR studies. FTIR showed that the CLTS4 had the greatest number of free ions. It can be suggested number of free ions influences conductivity. Calculations based on the Rice and Roth model shows conductivities of the chitosan - LiCF$_3$SO$_3$-EC/PC filler system polymer electrolytes are strongly influenced by the mobility of ions. Furthermore the CLTS4 system has the lowest activation energy. The lower activation energy may provide a pathway for the lithium ions to hope easily from one site to another.

The dielectric formalism and electric modulus of CLA, CLT and CLTS4 systems were found to be highly dependent on temperature and frequency. At 50Hz the dielectric constant value for CLTS4 > CLT > CLA showing there are greater number of lithium ions in CLTS4 system. Dielectric values at high frequency and modulus values at low frequencies did not approach a constant value for chitosan based electrolyte systems. The conductivity increased with temperature for all the systems, which may be due to the ions having greater average kinetic energy and jump probability per unit time. The normalized plot of $\tan \delta / (\tan \delta_{\text{max}})$ against $f/ f_{\text{max}}$ for CLTS4 data collapses into a single master curve, implying that the relaxation mechanism is independent of temperature. The relaxation activation energy, $E_R$ and conductivity activation energy, $E_a$ for CLA, CLT and CLTS4 system were found to be similar further confirming the transport of lithium ions in chitosan-based electrolyte systems occurs via a hopping mechanism. It can be suggested that the lithium ions in these systems has to overcome the same energy barrier while conducting as well as relaxing.
Work should be continued to further enhance the conductivity chitosan-based electrolyte systems. This may be possible by:

(i) Blending the chitosan with other polymers. Blending chitosan with other polymers such as PVA may lower $T_g$ of chitosan and hence increase the polymer mobility.

(ii) Using salts such as lithium imide salts. These salts have large anions with delocalized negative charge.

(iii) Replacing the fumed silica with active ceramic fillers such as Li$_2$N and LiAl$_2$O$_3$ may improve conductivity. This is because active fillers can contribute to lithium ion transport process.

(iv) Using low viscosity ionic liquids instead of as plasticizers. Ionic liquids can reduce crystallinity of the chitosan films without affecting mechanical stability and can act as a source of ionic species.