

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Polymer electrolytes have gained much interest due to their potential applications such as lithium rechargeable batteries and fuel cell [Scrosati (1993), Gray (1997)]. Polymer electrolytes are flexible and possess the ability to transform into desired shapes. Moreover, the flexible polymers can accommodate the shape changes during charge-discharge cycle. The development of polymeric systems with high ionic conductivity is one of the main objectives in polymer research, due to their potential application in electronics such as solid state rechargeable lithium batteries, electrochromic windows, etc [Scrosati (1993), Gray (1991)]. Over the last three to four decades, solid polymer electrolytes (SPEs) have attracted great interest in the field of electrochemical devices ever since Fenton and co-workers discovered ionic conduction in polymer in 1973 [Fenton et al., 1973]. In 1978, Armand and co-workers reported that the solid polymer electrolyte can be of potential use in batteries because it can contribute to improve safety in lithium secondary batteries as compared to their liquid counterparts [Armand et al., 1978]. The disadvantage of polymer electrolytes is that they exhibit lower ionic conductivities than liquid electrolytes [Xu, 2004; Agrawal and Pandey, 2004; Silva et al., 2004; Li et al., 2008].

Electrolytes employed in electrochemical devices generally have two basic tasks, namely to effectively conduct ions and to separate the electrodes in order to avoid short circuit. Ideally, a polymer electrolyte should possess both the conductivity of a liquid and mechanical stability of a solid. Poly(ethylene oxide) (PEO) is the most studied

polymer host for polymer electrolytes [Gauthier et al., 1989, Silva et al., 2006 a, b]. However, PEO- based polymer electrolytes exhibit low conductivity values around 10^{-7} to 10^{-6}Scm^{-1} at ambient temperature [Gray, 1991]. PEO can also crystallize easily and thus hinders its practical use.

Peter V. Wright, a polymer chemist, first showed in 1975 that poly-ethylene oxide (PEO) can act as a host for sodium and potassium salts, thus producing a solid electrical conductor polymer/salt complex (Wright, 1975). Armand et al., (1978) suggested that lithium salt could be dissolved in a solvating polymer matrix through direct interaction of the cation and electron pairs and the complex formed (as a result of the favourable competition between the solvation energy and the lattice energy of the salt) becomes a good conductor at 60° to 80° C. However, understanding the formation of a salt complex and the nature of the charge transport mechanism is more complicated. They required bridging the two communities of polymer and solid-state chemistry, traditionally concerned with inorganic compounds and crystal structures. The intrinsic phenomenon of a solid material exhibiting liquid-like conductivity without motion of the solvent itself was fascinating from theoretical point of view and the applications to electrochemical devices sounded very promising in a time of emerging concerns with energy and pollution. A polymer electrolyte can be easily manufactured into shapes not available to liquid containing systems, and it is safer than liquid electrolytes.

2.2 Polymer electrolyte

A polymer electrolyte is an ion conducting membrane as well as separator with moderate to high ionic conductivity at ambient temperature. There are different types of polymer electrolyte systems, which include solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) etc. SPEs consist of ionic salts dissolved into coordinating polymer hosts, that is PEO, PVC, PMMA etc. While GPEs and CPEs involves the incorporation of an additive in the form of an organic solvent and a filler, respectively in order to improve the characteristics that is ionic conductivity or mechanical stability in the case of GPEs. Compared with liquid electrolyte used in most present commercial rechargeable Li^+ batteries, polymer electrolyte offers the ability to fabricate flexible, lightweight devices that exhibits high specific energy density with long lifetime and wider operational temperature towards electronic miniaturization.

The development of new solid electrolyte material is creating opportunities for new types of electrical power generation and storage systems. These devices include batteries [Ali et al., 2006], fuel cells [Srivinasan,1989] and super capacitors [Lewandowski,2001]. These devices are of tremendous practise in view of our energy and environmental needs. Electrochemical energy production is under serious consideration as an alternative energy sources as it is sustainable as well as more user and environmental friendly [Ahmad, 2009].

In spite of this overwhelming advantage, the application of SPEs in electrochemical devices have not yet penetrated the market commercially with complete success due to their limitations such as low ionic conductivity especially at ambient temperature and high interfacial resistance of the electrolytes. In recent years, however, the level of ionic conductivity values are limited at $10^{-4} \text{ S cm}^{-1}$ at room temperature, despite innovations

in the design to produce flexible polymers and the use of salts containing asymmetric anions capable of suppressing crystallinity. Such levels of ionic conductivity are insufficient for many electrochemical applications [Chiu et al., 2007]. To overcome these problems, many research efforts have been focused to improve the properties of polymer electrolytes in order to meet the requirements of the devices mentioned.

Some basic properties for a polymeric material to be selected for the preparation of a solid electrolyte [Gray, 1991; Alamgir and Abraham, 1994; Song et al., 2000] include:

- Possess atoms with lone pair electrons.
- Possess high chemical, thermal and electrochemical stabilities.
- Possess high mechanical strength.
- Compatible with electrode materials in the fabrication of devices.

In order to produce polymer electrolyte complexes, it is necessary for polymer hosts to have strong coordination with cations from the salts. The polymer host must contain solvating groups(s) or atom(s) that have unused electrons also known as lone pair electrons. The unused electrons can form a dative bond with the cations of the incorporating salt. A common example of solvating group is the ether oxygen present in poly(ethylene oxide), PEO. Others include the oxygen atom in $-C-O-C$, the nitrogen atom in NH_2 and S_8 atom that are able to form complexes with ionic salts [Gray, 1991].

Conductivity and mechanical strength are among the important properties of polymer electrolytes. Various techniques such as blending of polymers [Rajendran et al., 2002], modification of polymers [Tan and Arof, 2006], incorporation of plasticizer(s) [Zhang and Fang, 2000] and filler [Majid et al., 2005] have been employed by researchers to improve the properties of polymer electrolytes.

It is well known that ionic conduction in polymer electrolytes occurs only in the amorphous phase of the polymer electrolyte [Berthier et al., 1983]. So, it is expected that polymers with larger degree of amorphous nature will exhibit higher ionic conduction in the electrolytes. Therefore, polymers with lower T_g are preferable to provide good flexibility of the polymer chains to produce faster ion transport. This is because ionic transport in polymer electrolytes is closely related to the local structural relaxations, which is characterized by the glass transition of polymer [Sanchez, 1992].

Polyethylene Oxide (PEO)-based complexes are the first solvent-free polymer electrolytes to have reported (Armand, 1987). PEO complexed with lithium salt have been widely investigated. The main reason to choose PEO as the host polymer is because PEO form more stable complexes and possess higher ionic conductivity than any other group of solvating polymers without the addition of organic solvent (Dias et al., 2000). Table 2.1 lists some examples of PEO-based polymer electrolytes. PEO electrolytes are just one of the many types of dry solid polymer electrolytes because it easily dissolves many types of salts and thus dissociating them to produce charge carriers (Laik et al., 1998). In Table 2.1 represents some examples of PEO-based electrolytes.

Table 2.1: Some examples of PEO-based electrolytes

System	Ionic Conductivity (S cm ⁻¹)	Reference
PEO-LiPF ₆	~ 10 ⁻⁵	Suriani Ibrahim et al., 2012
PEO – KHCO ₃	~ 10 ⁻⁷	Vijaya Kumar et al., 2010
PEO – LiClO ₄	~ 10 ⁻⁵	Wang et al., 2005
PEO – AgCF ₃ SO ₃	~ 10 ⁻⁵	Dinesh Kumar Kanchan et al., 2011
PEO,LiI/I ₂ TiO ₂	~ 10 ⁻⁶	Y. Wang, 2009
PEO – NH ₄ PF ₆	~ 10 ⁻⁵	Jitender Paul Sharma et al., 2011
PEO-LiCF ₃ SO ₃	~ 10 ⁻⁵	Ramesh et al., 2007

Where;

LiPF₆ = Lithium Hexafluorophosphate

KHCO₃ = Potassium bicarbonate

LiClO₄ = lithium perchlorate

AgCF₃SO₃ = Silver triflate

TiO₂ = Titanium dioxide

NH₄PF₆ = Ammonium hexa fluorophosphates

LiCF₃SO₃ = Lithium triflate

When a salt is dissolved in a polymer matrix, the ionic conductivity of the complex increases as a result of addition of charge carriers. However as the salt concentration is increased above a certain concentration, the conductivity reaches a maximum and then falls. According to Gray (1991), this is a result of introducing an increasing number of transient cross-links in the system, thus reducing the chain mobility. The decrease in

conductivity has been ascribed to the formation of immobile aggregated species at high salt concentrations. High salt concentration can also induce the complex to become crystalline leading to a decrease in conductivity. Conductivity-salt concentration relationship has also been studied and explained [Albinsson et al., 1993]. A polymer consists of a crystalline and an amorphous phase but conduction is thought to occur only in the amorphous phase of the polymer. The polymer dynamics are significantly affected by the reduction in the amount of crystalline materials (Gray, 1991). Andreev and Bruce (2000) have focused on the structure of crystalline polymer-salt complexes. They have shown that if a given composition of PEO-LiCF₃SO₃, the structure is maintained on moving from crystalline to the amorphous phase, then in the crystalline and amorphous phases, the cations will remain within tunnels defined by PEO chain. This suggests that the cation transport occurs, preferably along the tunnel. If this is the case, ion conduction cannot occur in a simple amorphous polymer, but instead if the chains are organized in a more aligned way, transport along and between chains will be facilitated (Fig 2.2). By combining this with sufficient local chain mobility, particularly involving dynamic modes propagating along the axis of the chains, level of ionic conductivity can be increased higher than for the less organized amorphous solids.

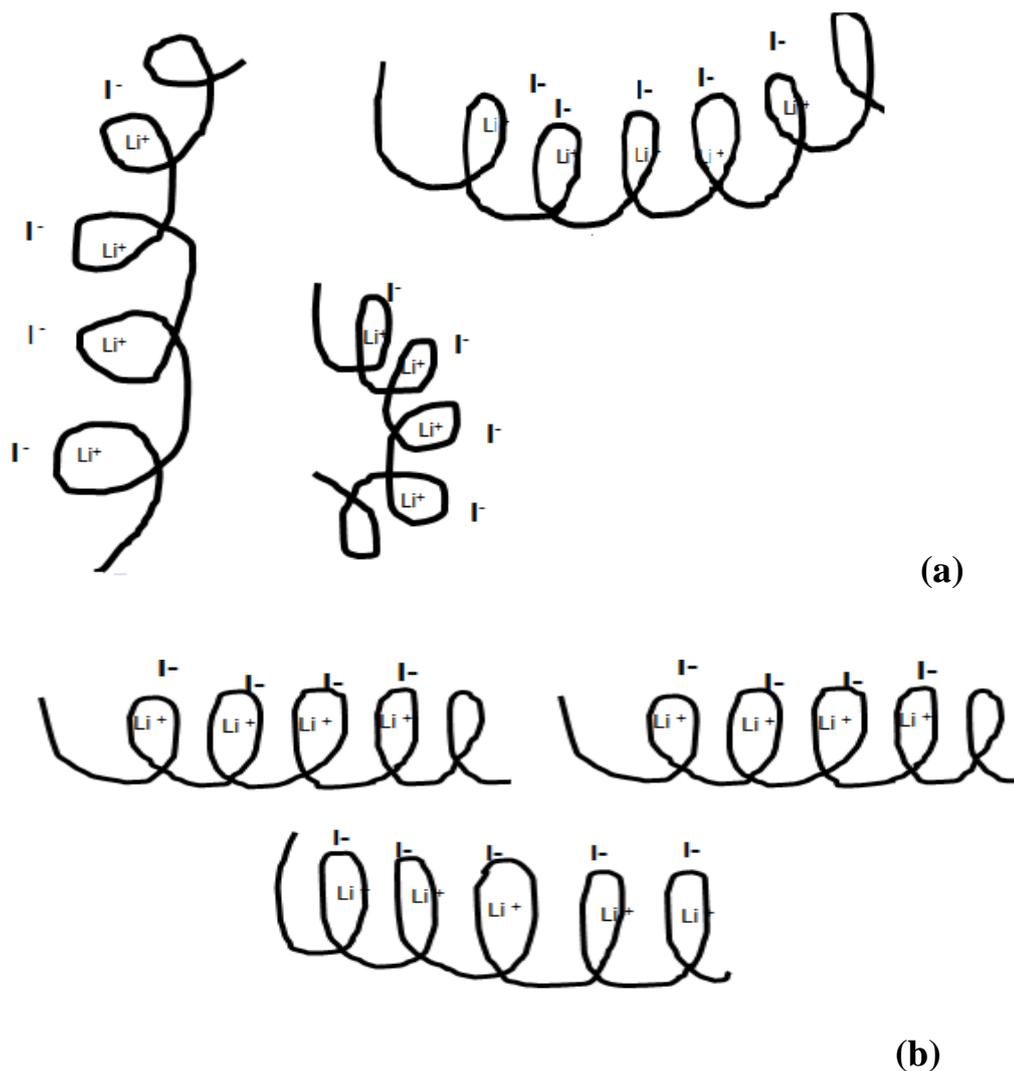


Figure 2.2: Disorganized (a) and organized (b) models of an amorphous polymer electrolyte (Andreev and Bruce, 2000)

Another type of dry solid system that has been established is the polyelectrolyte. In the polymer electrolytes both the anions and cations are mobile. By contrast, the polyelectrolyte comprises of charge groups covalently attached to the polymer backbone. This results in the free cations having long range ionic mobility (Dias et al., 2000).

Highly charged ionic polymers have the potential to interact with water to form polyelectrolyte. The extent of interaction will depend on the density of charged groups

in the polymeric chains and also on the nature of the counter ion. The conductivity of these polymers in the dry state is in the order of 10^{-15} to 10^{-12} S cm⁻¹, as the polar moieties tend to segregate into stable, immobile clusters. The ionic conductivity is a function of water content. Unlike the polyether systems, polyelectrolyte may be thought of a classical conductor in which ion transport is through the aqueous medium in which the polymer is dispersed (Gray, 1987).

2.3 Use of Li⁺ cation

Many researchers have reported polymer electrolytes based on inorganic salts containing various types of cation, for example lithium, Li⁺ [Deepa et al., 2002], ammonium, NH₄⁺ [Shuhaimi et al, 2010], magnesium, Mg²⁺ [Pandey et al., 2009; Ramesh et al., 2010], Zinc, Zn²⁺ [Ye and Xu, 2007], silver, Ag⁺ [Kim et al, 2003] etc. The reason behind why lithium based salts are commonly used in polymer electrolytes is due to lithium being the lightest of all metals in the periodic table, and will provide a wide electropositive potential window when used as an anode in lithium ion electrolytes. Hence, very high energy density lithium ion batteries can be produced. In fact, it has been reported that Li⁺ions batteries have surpassed other battery systems such as Pb-acid, Ni-Cd and Ni-MH [Takeshita, 2000]. Table 2.2 records the types of lithium salts commonly used in polymer electrolytes.

In most electrolyte systems based on polymer–salt complexes, the salt is not completely dissociated which results from a relatively high salt concentration and low dielectric constant of the polymer solvent. If the salt is not fully dissociated, there exists a series of equilibria and some associated species as ion-pairs, triplets and higher aggregates are formed. All of them can be mobile in the electrolyte and affect the gross charge transport. In lithium batteries, the electrodes are active only towards one of the

ion constituents (Li^+) and blocking the others. So, one can assume that the mobile cations are the only electrode active species.

Table 2.2: Examples of lithium salts used in polymer electrolytes

Type of lithium salt	Structural formula	Reference
Lithium Iodide	LiI	Freitas et al., 2008
Lithium perchlorate	LiClO_4	Saikia and Kumar, 2004
Lithium sulphate	Li_2SO_4	Ramesh et al., 2008
Lithium tetrafluoroborate	LiBF_4	Vieira and Pawlicka, 2010
Lithium hexafluorophosphate	LiPF_6	Ren et al., 2009
Lithium trifluoromethane sulfonate (LiTf)	LiCF_3SO_3	Ahmad et al., 2006

2.4 Polymer Composites

Polymer electrolytes which involve dispersion of micro/nano sized filler particles into the host polymers are known as polymer composites. Composites are an important class of materials. They comprise two or more phases mixed in predetermined proportions to obtain superior performance as compared to any of the pure, single-phase, solid components. However, the application of composites as electrical conductors, both electronic and ionic, is in its infancy (Kumar and Fellner, 2003). Weston and Steele (1982) first demonstrated the idea of incorporating electrochemically inert particulate fillers into polymer matrixes as a means to increase mechanical stability of the polymer.

Incorporating composites in polymer electrolytes helps to increase conductivity, has been mainly attributed to the decrease in the level of polymer crystallinity in presence of the fillers (Dias et al., 2000).

Composite polymer electrolytes can be prepared in different ways, but all techniques can be placed into two major groups (i) the inorganic component is performed and then mixed with a polymer or (ii) the inorganic component is formed in situ within a polymer electrolyte. The former method can be represented by the incorporation of inorganic fillers (TiO_2 , Al_2O_3 , SiO_2 , etc.) or clay platelets in polymers. The latter method is represented by formation of metal oxides within a polymeric system, thus fresh interfaces between inorganic and polymer components are developed (Bronstein et al., 2005). The new idea of composite by dispersing inert ceramic fillers is an attractive approach to enhance the stabilizing properties by modifying (Pradhan et al., 2005)

- Local structure/ morphology,
- Degree of crystallinity
- Flexibility of polymeric segments,
- Chemical nature of filler particles and
- The nature of the interaction in a heterogeneous polymer-salt-filler system.

The enhancement in mechanical properties is normally explained on the assumption that the filler particles act as a supporting matrix for the conductive polymer electrolyte so as to retain an overall solid structure, even at elevated temperatures. The chemical (acidic/ alkaline/ amphoteric) nature of the filler particles also plays a major role in governing the nature of interaction in a heterogeneous composite system. Some examples are listed in Table 2.3.

Table 2.3: Examples of polymer composites electrolytes

Electrolyte composition	Conductivity (Scm ⁻¹)	Reference
PEO-LiClO ₄ -SiO ₂	~ 10 ⁻⁴	Mengzhong Cui et al., 2005
PEO – LiClO ₄ - Al ₂ O ₃	~10 ⁻⁴	Xinping Qiu et al., 2005
PEO-LiF-AlCl ₃ -Calix4	~10 ⁻⁵	Kalita et, al., 2009
PEO-I ⁻ -Calix4	~10 ⁻⁵	Kalita et al., 2007
PEO-Al ₂ O ₃ -calix6pyrrole	~10 ⁻⁵	Golodnitsky et. al., 2007
PEO- LiClO ₄ - TiO ₂	~10 ⁻⁵	Croce et al., 2000
(PEO) ₉ -LiCF ₃ SO ₃ -Al ₂ O ₃	~10 ⁻³	Dissanayake et al., 2003
PEO ₂₅ -NH ₄ ClO ₄ -SnO ₂ - PEG	~10 ⁻⁵	Pradhan et al., 2005

Where;

SiO₂ = **Silicon dioxide**

Al₂O₃ = **Aluminium Oxide**

AlCl₃ = **Aluminium chloride**

PEG = **Poly(ethylene glycol)**

To improve the transport properties, the overall conductivity and lithium transference number anion receptors (supramolecular compounds) calix arenes, which interact with anions by several hydrogen bonds to the PEO-based electrolytes resulted in the improvement of their conducting properties. A calixarene is a macrocycle or cyclic oligomer based on a hydroxyalkylation product of a phenol and an aldehyde. The word calixarene is derived from calix because this type of molecule resembles a vase and

from the word arene that refers to the aromatic building block. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions. Both cations and anions are mobile in polymer electrolytes, with cationic transference numbers nearly always below 0.5. According to Golodnitsky et al., 2007, who studied the effect of calix (6) pyrrole on the electrochemical properties of PEO-LiN (CF₃SO₂)₂ (LiTFSI) complexes, the anionic mobility reduces limiting current density and forms an undesirable salt concentration gradient across the polymer electrolyte. Subsequently, this leads to a voltage drop during constant current operation, which in turn, affects the high power capability of the battery. Also of the importance is the fact that the mobile anions involved in unwanted electrode reactions and reduced the active area of the electrode. Blazejczk et al.,2004 achieved a lithium –ion transport number equal to 1 with an appreciable conductivity and suggested that an anion-trapping mechanism was induced by calixarene additive. Blazejczyk et al.,2005 suggested use of less complex anion-binding receptors or more open conformation besides immobilization of anions and cations by interaction with their counterparts.

2.5 ION CONDUCTION MODELS IN POLYMER ELECTROLYTES

According to Austin Suthanthiraraj et al. (2010), information on salt-polymer interaction is very much dependent on ionic conductivity, salt concentration, temperature, type of salt etc.

Ionic conductivity of electrolyte depends on the charge, q , carrier concentration, and carrier mobility, μ , as follows;

$$\sigma = n \times q \times \mu \quad (2.1)$$

Here n , q and μ are the number density, charge and mobility of charge carriers respectively. Polymer electrolytes usually exhibit two dominant conduction mechanisms [Ratner et al., 2000] that can be determined from temperature dependent conductivity studies. They exhibit either Arrhenius or Vogel-Tamann-Fulcher (VTF) behaviour.

- Vogel-Tamman Fulcher (VTF) behaviour throughout the available thermal range.
- Arrhenius behaviour for low temperatures and VTF behaviour at higher temperature.
- Arrhenius behaviour throughout, but with two different activation energies, high E_a closer to T_g and a smaller E_a at higher temperatures.
- VTF behaviour for temperatures slightly greater than T_g , but Arrhenius behaviour for higher temperatures.
- Behaviour which is very unlike either Arrhenius or VTF at all temperatures.

The VTF rule describes the ionic transport mode which is promoted by the polymeric chain movement. The VTF equation is given as:

$$\sigma = \sigma_0 T^{\frac{1}{2}} \exp \frac{-B}{K(T_0-T)} \quad (2.2)$$

Where, σ_0 is the pre exponential factor, B is the pseudoactivation energy of the ion and T_0 is the thermodynamic glass transition or ideal glass transition temperature.

In the form of plot of $\log \sigma$ versus $1/T$ where σ denotes the conductivity and T is the absolute temperature, the Arrhenius behaviour can be determined. The plot shows that the electrolyte system obeys Arrhenius rule if the correlation factor for all the samples above 0.90 [Noor et al., 2010]. The Arrhenius can be represented as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{K_b T}\right) \quad (2.2)$$

Where σ_0 is a pre-exponential factor, E_a is the activation energy, T is the temperature in Kelvin, and K_b is the Boltzmann constant.

Kalita et al., (2008) have reported that the conductivity-temperature relationship of PEO-LiTfSI-Calix6P polymer electrolytes follow Arrhenius equation. This is depicted in Figure 2.3

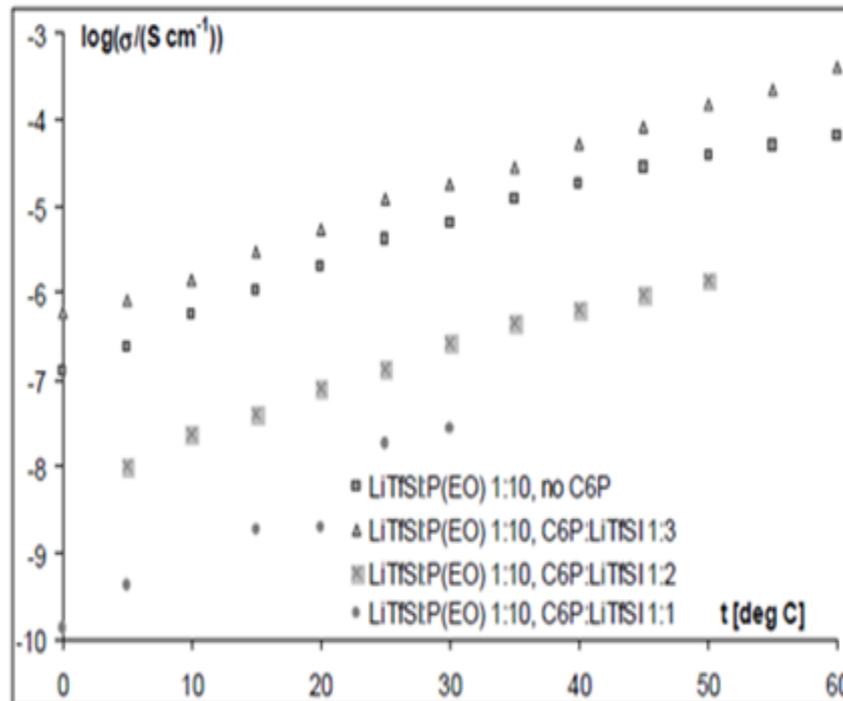


Figure 2.3: Thermal dependency of conductivity for PEO-LiTfSI-Calix6P systems

2.6 Summary

From this chapter, some overview on the knowledge on polymer electrolytes has been presented. This overview has been shown in order to relate with the work carried out in this present research.