

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The ionic conductor is one of the main components in electrochemical devices such as batteries [Ng and Mohamad, 2008], sensors [Arias–Pardilla *et al.*, 2011], supercapacitors [Lewandowski *et al.*, 2001], fuel cells [Srivinasan *et al.*, 1989] and electrochromic devices [Pawlicka *et al.*, 2004]. 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 polymer electrolytes 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]. Other advantages of polymer electrolytes over liquid electrolytes include resistance to combustion, robustness under extreme conditions, good electrode–electrolyte contact and ability to be fabricated into more compact devices of various shapes due to the flexibility of the polymeric materials [Gray, 1991]. The main 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 the 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} S cm⁻¹ at ambient temperature [Gray, 1991]. PEO can also crystallize easily and thus hinders its practical use.

The drawbacks of PEO prompt researchers to use other polymers such as poly(methyl methacrylate) (PMMA) [Deepa *et al.*, 2004], poly(vinyl chloride) (PVC) [Vickraman *et al.*, 2010], poly(vinylidene fluoride) (PVdF) [Wang *et al.*, 2009], poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [Miao *et al.*, 2008] and poly(vinyl alcohol) (PVA) [Bhargav *et al.*, 2010]. In recent years, biopolymers such as chitosan [Buraidah and Arof, 2006], starch [Mattos *et al.*, 2007] and natural rubber [Idris *et al.*, 2001; Kumutha *et al.*, 2005; Ali *et al.*, 2008] have also been employed in the preparation of polymer electrolytes due to their environmental friendliness, non-toxicity, availability, low cost and biodegradability nature.

2.2 Polymer electrolytes

A polymer electrolyte is an ion-conducting membrane as well as separator with moderate to high ionic conductivity at ambient temperature. There are many types of polymer electrolyte systems, which include solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and composite polymer electrolytes (CPEs). SPEs consist of ionic salts dissolved into coordinating polymer hosts, i.e. PEO, PVC, PMMA, etc while GPEs and CPEs involve the incorporation of an additive in the form of an organic solvent and a filler, respectively, in order to improve the characteristics i.e. 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, light-weight devices that exhibit 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 supercapacitors [Lewandowki, 2001]. These devices are of tremendous practical interest 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, 2008].

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} 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:

- 1) Possess atoms with lone pair electrons,
- 2) Possess high chemical, thermal and electrochemical stabilities,
- 3) Possess high mechanical strength, and
- 4) 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 group(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). Other examples of solvating groups include the oxygen (O) atom i.e. in $-C-O-C-$, the nitrogen (N) atom in NH_2 group and fluorine (F) atom in CF_2 group 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 amorphousness 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 the polymer [Sanchez, 1992].

2.2.1 Natural rubber (NR)

Natural rubber is a biopolymer that is chemically known as 1, 4-*cis*-polyisoprene. In Malaysia, its natural rubber latex source is from the rubber tree (*Hevea brasiliensis*). The purified form of natural rubber is the chemical monomer “isoprene” ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$) shown in Figure 2.1, which can also be produced synthetically.

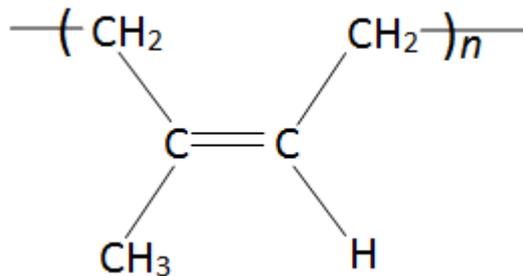


Figure 2.1 Chemical structure of 1,4-*cis*-polyisoprene

Distinctive characteristics that make NR a suitable candidate in polymer electrolyte systems include [Famiza *et al.*, 2006; Idris *et al.*, 2001]:

- 1) low glass transition temperature (T_g),
- 2) soft elastomer characteristics at room temperature,
- 3) good elasticity,
- 4) good adhesion to provide excellent contact with electrodes of devices,
- 5) low in cost, and
- 6) environmental friendly.

However, NR being an insulator exhibits rather low conductivity at ambient temperature. Hence, researchers have modified NR in order to enable it to be a polymer host for ionic conduction without jeopardizing its mechanical strength. The use of modified NR through chemical modification in polymer electrolyte systems has received much attention. NR can be modified by bonding rearrangement, grafting or by attachment of new functional groups onto the NR chain [Blackley, 1997; Ceresa, 1973]. NR can be grafted with various monomers such as acrylonitrile (AN), methyl methacrylate (MMA), stearyl methacrylate (SMA), divinylbenzene (DVB) and styrene [Hashim *et al.*, 2002]. Among all, MMA and styrene are the most suitable monomers for grafting with NR [Hashim *et al.*, 2002; Arayapranee *et al.*, 2003]. Man *et al.* (2008) studied NR grafted with styrene and MMA using fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Dafader *et al.* (2006) investigated the mechanical properties of NR grafted with different types of acrylic monomers including ethylacrylate (EA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA). Besides NR, other synthetic elastomers that have been employed as polymer hosts for ionic conduction are listed in Table 2.1.

Table 2.1: Examples of modified NR-based polymer electrolytes obtained from literature

Polymer electrolyte	σ (S cm ⁻¹)	References
NBR–SBR–LiClO ₄ – γBL–DME	7.2×10^{-4} at 298 K	Matsumoto, 1995
ENR–LiTFSI	10^{-6} at 323 K	Klinklai <i>et al.</i> , 2004
ENR–LiClO ₄	10^{-9} at 323 K	Klinklai <i>et al.</i> , 2004
PEO–ENR50– LiCF ₃ SO ₃ (56:24:20) (w/w)	1.4×10^{-4} at 298 K	Noor <i>et al.</i> , 2010
NBR–EImTFSI	$\sim 10^{-5}$ at 323 K	Marwanta <i>et al.</i> , 2005
ENR–PMMA–LiCF ₃ SO ₃ (30:10:60) (w/w)	5.1×10^{-5} at 298 K	Latif <i>et al.</i> , 2006

Table 2.1, continued

ENR–LiCF ₃ SO ₃ –PC (58.5:31.5:10) (w/w)	4.9×10^{-4} at 298 K	Mohamed <i>et al.</i> , 2008
ENR–LiCF ₃ SO ₃ –EC (52:28:20) (w/w)	2.4×10^{-4} at 298 K	Mohamed <i>et al.</i> , 2008
NR–PEO–LiBs	$\sim 10^{-6}$ at 323 K	Yoshizawa <i>et al.</i> , 2000

Where;

EImTFSI = *N*-ethylimidazolium bis(trifluoromethanesulfonyl) imide

LiBs = lithium benzenesulfonate

LiCF₃SO₃ = lithium trifluoromethane sulfonate

LiClO₄ = lithium perchlorate

LiTFSI = lithium bis(trifluoromethanesulfonyl) imide

NBR = poly(acrylonitrile-*co*-butadiene) rubber

PEO = poly(ethylene oxide)

PC = propylene carbonate

SBR = poly(styrene-*co*-butadiene) rubber

Figure 2.2 shows the chemical structure of 50 % epoxidised NR (ENR50). Modified NRs have shown ionic conductivity comparable to glassy or crystalline polymers [Idris *et al.*, 2001].

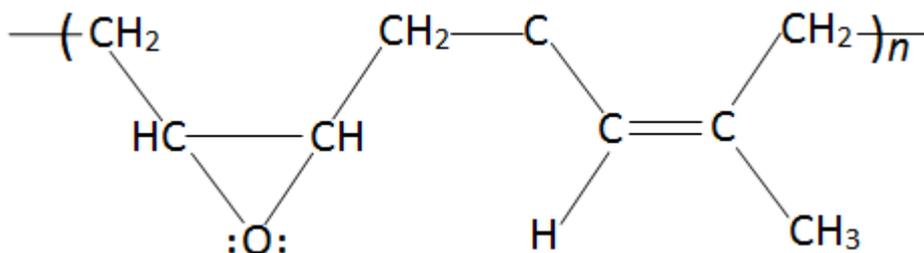


Figure 2.2 Chemical structure of 50 % epoxidised NR (ENR50)

ENR-based polymer electrolytes are difficult to handle due to lower mechanical strength as compared to the graft modified NR which are more free-standing, elastic and flexible [Lu *et al.*, 2001; Glasse *et al.*, 2002].

2.2.2 Poly(methyl methacrylate) (PMMA)

PMMA is a transparent polymeric material that possesses many attractive properties such as light-weight, high chemical resistance, resistance to weather corrosion and good insulating properties. It is amorphous in nature and has T_g of 120 °C. The chemical structure of PMMA is illustrated in Figure 2.3.

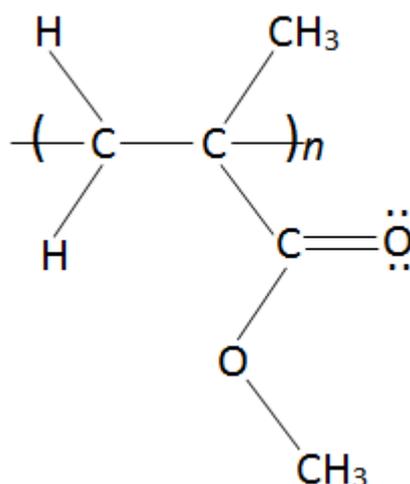


Figure 2.3 Chemical structure of PMMA

PMMA has a polar functional group in its monomer with high affinity for lithium ions and plasticizing organic solvent which make it a potential candidate for polymer electrolyte material. The carbonyl group (C=O) of PMMA provides oxygen atom which is expected to form coordinate bond with the lithium ions from the incorporated salt. Iijima *et al.* (1985) first reported the use of PMMA as polymer host to form polymer electrolytes. To date, PMMA based electrolyte has received much attention and has been tested in electrochemical devices [Bohnke *et al.*, 1993; Appetecchi *et al.*, 1995]. To add to its advantage, PMMA has also been previously reported to have a low reactivity towards lithium metal electrodes [Bohnke *et al.*, 1992].

The most critical drawback of PMMA system is poor mechanical property [Rho *et al.*, 1997]. Blending the polymer with another polymer can reduce problems associated with poor mechanical properties. Rho *et al.* (1997) has proven the blend concept in PVC/PMMA electrolyte system. The mechanical strength of PMMA is increased as the content of PVC is increased. However, the conductivity of the system is decreased due to poor adhesion that leads to the increase of interfacial resistance.

Some of PMMA based electrolytes in its single and blended forms are summarized in Table 2.2.

Table 2.2: Examples of PMMA-based polymer electrolytes obtained from literature

Electrolyte Composition	σ at 298 K (S cm ⁻¹)	Reference
PMMA–LiClO ₄ –PC	5×10^{-3} to 5×10^{-5}	Bohnke <i>et al.</i> , 1993
PMMA–PVdF–LiClO ₄ – DMP (7.5:17.5:8:67)	4.2×10^{-3} at 303 K	Rajendran <i>et al.</i> , 2002
PVA–PMMA–LiBF ₄ –EC (15:10:8:67) (w/w)	1.29×10^{-3} at 302 K	Rajendran <i>et al.</i> , 2004
PVAc–PMMA–LiClO ₄ (56:24:20) (w/w)	1.76×10^{-3} at 303 K	Baskaran <i>et al.</i> , 2006
PMMA–LiTFSI (85:15)	3.65×10^{-5}	Ramesh and Ang, 2010
PMMA–Li ₂ B ₄ O ₇ –EC (42:18:40)	1.29×10^{-5}	Ramesh <i>et al.</i> , 2011b

Where;

BmImTFSI = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide)

EC = ethylene carbonate

Li₂B₄O₇ = lithium tetraborate

LiBF₄ = lithium tetrafluoroborate

LiClO₄ = lithium perchlorate

LiTFSI = lithium bis(trifluoromethanesulfonylimide)

PC = propylene carbonate

PVA = poly(vinyl alcohol)

PVAc = poly(vinyl acetate)

PVdF = poly(vinylidene fluoride)

2.2.3 Natural rubber (NR) grafted with poly(methyl methacrylate) (PMMA)

Owing to several benefits of both PMMA and NR, various chemical modifications have been attempted to modify their properties and extend their usage.

The grafting of PMMA to NR has combined their properties in a synergistic way. Grafted polymers have been reported to have improved properties [Ali *et al.*, 2008; Ahmad *et al.*, 2011; Idris *et al.*, 2000; Kumutha *et al.*, 2005] such as:

- 1) The ability to improve the mechanical properties of GPEs,
- 2) Increased adhesion to the electrodes,
- 3) Increased solvent intake,
- 4) Increased solubility,
- 5) Enhanced conductivity,
- 6) Improved the formation of flat, thin and flexible films,
- 7) Low T_g , and
- 8) Soft elastomer characteristics at room temperature.

The grafted-copolymer consisting natural rubber and methyl methacrylate has gained attention as polymer matrix due to its polar characteristics [Alias, 2005]. PMMA-grafted NR such as 49 % PMMA-grafted NR (MG49) [Alias *et al.*, 2005; Kamisan *et al.*, 2009; Su'ait *et al.*, 2009; Low *et al.*, 2010a; Low *et al.*, 2010b] and 30 % PMMA-grafted NR (MG30) [Kumutha *et al.*, 2005; Kumutha *et al.*, 2006; Ali *et al.*, 2006; Ali *et al.*, 2008] has been employed as polymer hosts to produce polymer electrolytes.

Nowadays, the commercial trade name of the grafted copolymer of natural rubber with PMMA is called Heveaplus MG with 30 % PMMA (MG30) and with 49 % PMMA (MG49). MG30 and MG49 can be used for the preparation of various polyelectrolyte complexes due to the existence of oxygen atoms at the carbonyl (C=O) and C–O–C groups contributed from PMMA monomers that have lone pair electrons.

Table 2.3 lists MG30 and MG49–based polymer electrolyte systems that have been reported by other researchers. Figure 2.4 depicts the chemical structure of MG30 used in the present work.

Table 2.3: Examples of MG30 and MG49–based polymer electrolyte systems obtained from literature

Electrolyte composition	σ at 298 K (S cm ⁻¹)	Reference
MG49–LiCF ₃ SO ₃	4.0×10^{-6} to 3.7×10^{-5}	Idris <i>et al.</i> , 2001
MG49–LiCF ₃ SO ₃ –(EC:PC)	6.0×10^{-5} to 4.3×10^{-4}	Idris <i>et al.</i> , 2001
MG49–LiCF ₃ SO ₃ –PC	4.8×10^{-7} to 1.84×10^{-6}	Alias <i>et al.</i> , 2005
MG30–LiCF ₃ SO ₃ (65:35) (w/w)	8.4×10^{-4}	Ali <i>et al.</i> , 2006
MG30–LiCF ₃ SO ₃ –PC (26:14:60) (w/w)	3.1×10^{-3}	Ali <i>et al.</i> , 2008
MG49–NH ₄ CF ₃ SO ₃ –PC	3.3×10^{-2}	Kamisan <i>et al.</i> , 2009
MG49–LiBF ₄ (80:20) (w/w)	2.3×10^{-7}	Su'ait <i>et al.</i> , 2009
MG49–LiClO ₄ (85:15) (w/w)	4.0×10^{-8}	Su'ait <i>et al.</i> , 2009
MG49–LiClO ₄ –TiO ₂ –EC	1.1×10^{-3}	Low <i>et al.</i> , 2010a
MG49–LiBF ₄ –TiO ₂	1.4×10^{-5}	Low <i>et al.</i> , 2010b

Where;

Al₂SiO₅ = aluminum silicate

EC = ethylene carbonate

LiBF₄ = lithium tetrafluoroborate

LiClO₄ = lithium perchlorate

NH₄CF₃SO₃ = ammonium trifluoromethane sulfonate

PC = propylene carbonate

TiO₂ = titanium dioxide

Lithium bis(trifluoromethanesulfonimide) also known as lithium imide, has greater charge delocalization as compared to the triflate salt, therefore could promote a higher degree of dissociation [Webber *et al.* 1991]. Higher ionic conductivities in polymer electrolytes employing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were reported owing to its low lattice energy as compared to LiCF_3SO_3 . The chemical structures of lithium triflate and lithium imide are shown in Figure 2.5 (a) and (b) respectively.

Table 2.4: Examples of lithium salts used in polymer electrolytes

Type of lithium salt	Structural formula	Reference
Lithium trifluoromethane sulfonate (LiTf)	LiCF_3SO_3	Ahmad <i>et al.</i> , 2006
Lithium bis(trifluoromethanesulfonimide) (LiTFSI)	$\text{LiN}(\text{CF}_3\text{SO}_2)_2$	Pehlivan <i>et al.</i> , 2010
Lithium bisperfluoroethanesulfonimide (LiBETI)	$\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$	Ahmad <i>et al.</i> , 2008
Lithium tetrafluoroborate	LiBF_4	Vieira and Pawlicka, 2010
Lithium hexafluorophosphate	LiPF_6	Ren <i>et al.</i> , 2009
Lithium perchlorate	LiClO_4	Saikia and Kumar, 2004
Lithium hexafluoroarsenate	LiAsF_6	Bushkova <i>et al.</i> , 2008
Lithium sulfate	Li_2SO_4	Ramesh <i>et al.</i> , 2008
Lithium iodide	LiI	Freitas <i>et al.</i> , 2008



Figure 2.5 Chemical structures of (a) lithium triflate and (b) lithium imide

Some researchers have incorporated more than a single inorganic salt into polymer host in order to achieve high conductivities. This is because studies of mixed-salt system containing mixed cations [Moryossef *et al.*, 1985; Yang and Farrington, 1993] or mixed anions [Henderson *et al.*, 2000; Ramesh and Arof, 2000; Deepa *et al.*, 2002b] have been found to exhibit better ionic conductivity as compared to single-salt system. For example, Moryoussef and co-workers (1985) reported higher ionic conductivity value of PEO–CaBr₂–CaI₂ (30:1:1) as compared to PEO incorporated with only either CaBr₂ or CaI₂ salt. Improved ionic conductivity values were also observed for PEO-based on ZnBr₂ mixed with LiBr electrolytes [Yang and Farrington, 1993] and PEO containing both Zn(CF₃SO₃)₂ and Cu(CF₃SO₃)₂ salts with same composition [Giua *et al.*, 1996]. Table 2.5 lists some examples of mixed-salt polymer electrolyte systems.

Table 2.5: Examples of mixed-salt polymer electrolyte systems obtained from literature

Composition	σ (S cm ⁻¹)	Reference
PMMA–LiClO ₄ –LiCF ₃ SO ₃ – γ BL	10 ⁻³	Deepa <i>et al.</i> , 2002b
PEO–LiClO ₄ –LiCF ₃ SO ₃	10 ⁻⁷ to 10 ⁻⁶	Henderson <i>et al.</i> , 2000
PVC–LiCF ₃ SO ₃ –LiBF ₄ (50:15:35) (w/w)	5.2 × 10 ⁻³	Ramesh and Arof, 2000

Where;

PVC = poly(vinyl chloride)

LiBF₄ = lithium tetrafluoroborate

LiClO₄ = lithium perchlorate

LiCF₃SO₃ = lithium trifluoromethane sulfonate

γ BL = γ -butyrolactone

2.4 Plasticizer

Solid polymer electrolytes usually exhibit low room temperature ionic conductivity. Hence, in order to obtain enhanced room temperature conductivity, an alternative approach is preferred by adding additives such as low molecular weight

plasticizer(s). In salt–plasticizer–polymer hybrid system, the plasticizer is retained in the electrolytes and helps in the dissociation of salt and provides a medium for conduction. The plasticized polymer electrolytes are also known as gel polymer electrolytes (GPEs). Examples of non–aqueous plasticizers used in polymer electrolyte systems are ethylene carbonate (EC), propylene carbonate (PC), *N, N*–dimethyl formamide (DMF), dimethyl carbonate (DMC), diethyl carbonate (DEC), γ –butyrolactone (γ BL) and poly(ethylene glycol) (PEG).

The effect of a plasticizer depends on the nature of the plasticizer such as the dielectric constant, ϵ and viscosity, η . A good plasticizer should possess high ϵ and low η [Pradhan *et al.*, 2009]. The former property is an important parameter, where a high value ensures better dissociation of the salt which subsequently results in an increase in the number of free mobile charge carriers [Rajendran *et al.*, 2010]. In addition, the plasticizer should have low η value which increases ionic mobility and enables the ions to diffuse easily in the polymer electrolyte and hence improves conductivity. Addition of plasticizers causes decoupling of ionic motion from that of the polymer chain and increases ionic mobility by lowering the viscosity of ionic environment [Rajendran *et al.*, 2010].

In accordance with the basic requirements for electrolyte, solvent should meet the following minimal criteria:

- (1) It should have a high dielectric constant (ϵ),
- (2) It should be fluid (low viscosity, η), so that ion transport can occur easily,
- (3) It should remain inert to all cell components,
- (4) It should remain liquid in a wide temperature range,
- (5) It should be safe, nontoxic, and economical,

- (6) It should have compatibility with both the polymer host and the salt,
- (7) It should have low melting point, and
- (8) It should have high boiling point.

Table 2.6 tabulates the types of plasticizers commonly used in polymer electrolytes and their properties. Plasticizers which have been incorporated into PMMA-grafted NR are PC [Idris *et al.*, 2001; Alias *et al.*, 2005; Ali *et al.*, 2006; Ali *et al.*, 2008] and EC [Ali *et al.*, 2006; Kumutha *et al.*, 2005; Kumutha and Alias, 2006; Low *et al.*, 2010a]. Alias and co-workers [Alias *et al.*, 2005] improved the ionic conductivity of MG49–LiCF₃SO₃ film from $1.8 \times 10^{-7} \text{ S cm}^{-1}$ up to three orders of magnitude at $1.8 \times 10^{-4} \text{ S cm}^{-1}$ with the addition of 45 wt.% PC. Other researchers such as Ali and co-workers (2006) also obtained higher ionic conductivities after plasticizing MG30–LiCF₃SO₃ films with EC and PC. On another hand, Idris and co-workers (2001) reported a highest conductivity value of $4.3 \times 10^{-4} \text{ Scm}^{-1}$ on MG49–LiCF₃SO₃–(EC+PC) composition.

Table 2.6: Examples of plasticizers and its physical properties

Plasticizer	Melting point (°C)	Boiling point (°C)	Density (g cm ⁻³)	Dielectric constant, ϵ	Viscosity, η (cP)
Ethylene carbonate (EC)	36.4	248	1.32	89.78 at 313 K	1.90
Diethyl carbonate (DEC)	-43.0	126	0.98	2.82	0.748
Dimethyl carbonate (DMC)	2.4	90	1.06	3.12	0.584
<i>N,N</i> -dimethyl formamide (DMF)	-61	153	0.94	36.1	0.80

Propylene carbonate (PC)	-55.0	240	1.19	64.4	2.53
Poly(ethylene glycol) 200 (PEG200)	-65.0	250	1.13	19.95 at 293 K	50.0*
γ -butyrolactone (GBL)	-43.3	204	1.12	39.1	1.75

*at 298 K

Although carbonate based plasticizers such as EC and PC can produce high ionic conductivity in polymer electrolytes, these solvents are volatile and flammable which pose safety risks when used in applications such as lithium ion batteries. Hence, non-carbonate based plasticizers such as PEG can be used to enhance the ionic conductivity in polymer electrolytes. Abraham and co-workers (1997) proposed the use of low molecular weight PEG as plasticizer and obtained high ionic conductivities without loss of thermal stability. PEG was reported to have properties like PEO [Abraham *et al.*, 1997]

The employment of PEG200 as the plasticizer in this work is due to its low T_g at -74 °C as compared to other PEG of higher molecular weight. For example, PEG 400 and PEG600 exhibit higher T_g value at -62 and -50 °C, respectively. Figure 2.6 illustrates the chemical structure of PEG200.

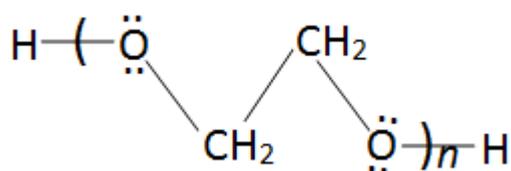


Figure 2.6 Chemical structure of PEG200

As a lower T_g promotes the ionic mobility of ions and reduces the crystallinity of polymer electrolytes [Nishio *et al.*, 2000; Jacob and Arof, 2000], the use of PEG200 is expected to increase the ionic conductivity of polymer electrolytes to a larger extent as compared to other PEG solvents. Subban *et al.* (2005) reported higher ionic conductivity in PVC–LiCF₃SO₃ and LiClO₄ samples containing PEG of lower molecular weights. Besides that, high dielectric constant of PEG200 helps to dissociate the salt or ion aggregates [Pradhan *et al.*, 2009]. Dielectric constant of PEG200 is reported to be 18.4 at 303 K [Awwad *et al.*, 2002; Kinart *et al.*, 2007]. XRD studies carried out by Pradhan *et al.* (2007) on PEO–sodium iodide (NaI)–dodecyl amine modified montmorillonite (DMMT) based polymer electrolytes revealed decrease in crystallite size with addition of PEG200, which indicated increase in amorphousness of the films upon plasticization. SEM result reported by Pradhan *et al.* (2005) which showed change in PEO–NaClO₄–SnO₂ composite polymer electrolyte films from surface roughening, crystalline structure and agglomeration to smoother morphology upon added with PEG200 attributable to reduction in crystallinity of the polymer host. Some PEG–plasticized polymer electrolytes are listed in Table 2.7.

Table 2.7: Examples of polymer electrolytes containing PEG as plasticizer from literature

Composition	σ (S cm ⁻¹)	Reference
MC–NH ₄ NO ₃ –PEG (63.75:21.25:15) (w/w)	1.1×10^{-4} at 298 K	Shuhaimi <i>et al.</i> , 2010
PVC–LiCF ₃ SO ₃ –PEG (55:30:15) (w/w)	1.3×10^{-4} at 298 K	Subban <i>et al.</i> , 2005
PESc–NH ₄ ClO ₄ –PEG (55:30:15) (w/w)	$\sim 10^{-4}$ at 298 K	Srivastava and Chandra, 2000

2.5 Models for Ionic Conduction

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, n , 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) behavior.

2.5.1 Arrhenius behavior

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

Noor *et al.* (2010a and b) have reported that the conductivity–temperature relationship of PEO–ENR50 polymer electrolytes follow Arrhenius equation. This is depicted in Figure 2.7.

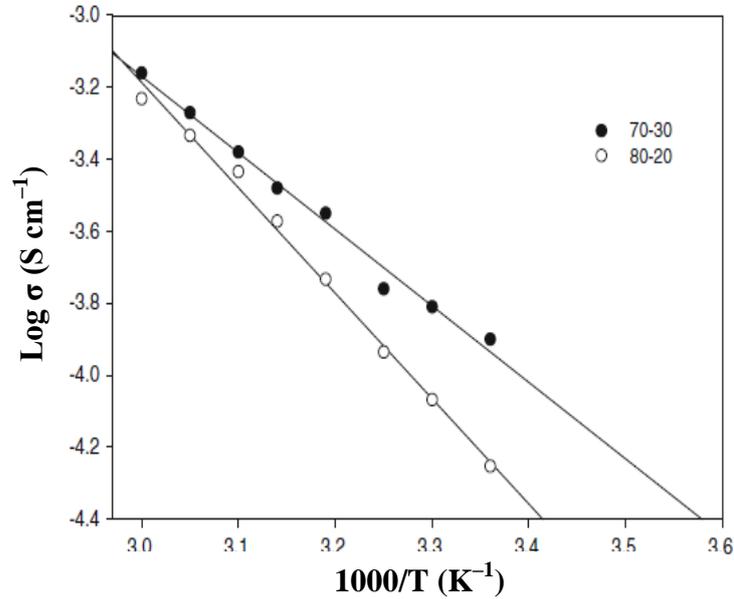


Figure 2.7 Arrhenius plot for the electrolyte with ratio PEO/ENR50 of 70/30 and 80/20 at 20 wt. % LiCF_3SO_3 [Noor *et al.*, 2010a]

2.5.2 Vogel–Tammann–Fulcher (VTF) behavior

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

$$\sigma = \sigma_o T^{-1/2} \exp\left(\frac{-B}{K(T_o - T)}\right) \quad (2.3)$$

where, σ_o is the pre exponential factor, B is the pseudoactivation energy of the ion and T_o is the thermodynamic glass transition or ideal glass transition temperature. E_a can be obtained from the non–linear least–square fit of the data from $\log \sigma$ versus $1000/T - T_o$ plot provided T_o is known. Mohammad *et al.* (2010) showed that ENR–50/PEMA– $\text{NH}_4\text{CF}_3\text{SO}_3$ electrolytes follow the VTF rule conductivity–temperature behavior.

2.5.3 Activation Energy (E_a)

Energy is required to begin for the ion movement, whether obtained from its surrounding or through heat applied. When the ion has gained enough energy to remove from its initial state, it is called a “free ion”. The minimum energy that need by the ion for that purpose is named the activation energy.

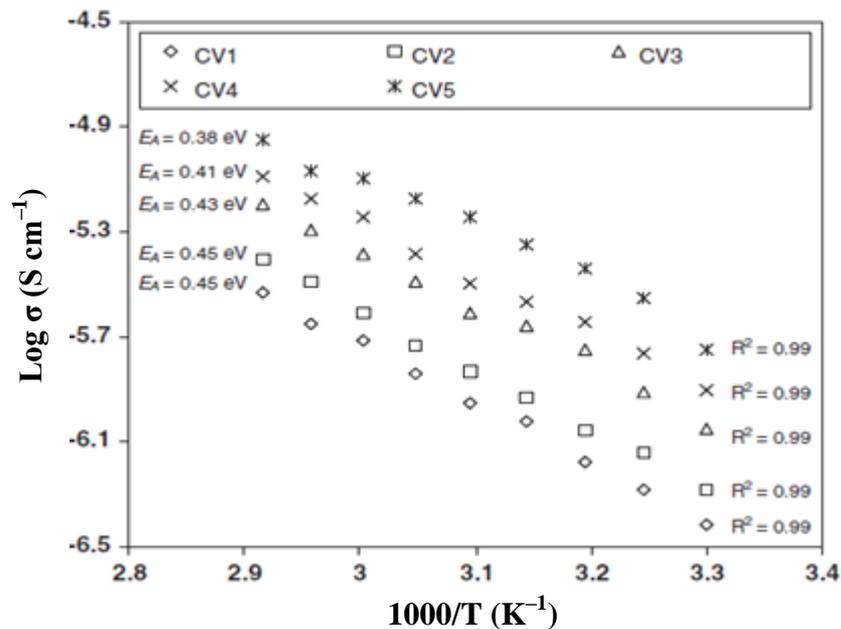


Figure 2.8 Temperature dependent ionic conductivity, E_a and R^2 value for chitosan–NH₄I added with various concentration of PVA [Buraidah and Arof, 2011]

Generally, it can be noticed that value of E_a is decreasing with the increase in conductivity of the samples. This indicates that the ion in a highly conducting sample requires lower energy for migration. The calculation of activation energy can be made by using Arrhenius equation as in Equation (2.2) as shown by Buraidah and Arof (2011). From Figure 2.8, we can observe that the highest conducting sample also possesses the lowest activation energy.

2.6 Summary

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