CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will start with an introduction to PE, some examples of high performance PE systems and PEs based on eco-friendly materials. The selection criteria of materials and classification of PEs are presented in Section 2.3 and 2.4. Section 2.5 gives some examples of PEs based on ammonium salts. The characteristics of PCL and a review of the PCL-based PEs are covered in the last section.

Fossil fuel has been the major contributor of energy to support human daily activities such as cooking, heating, air-conditioning and transportation. The high dependence on fossil fuel has resulted in expensive oil price. The high oil price of USD 135 per barrel recorded on 11 July 2008 [Sornette *et al.*, 2009] is an evidence. Furthermore, world population is expected to exceed 7.5 billion by 2020 and the respective energy use is projected to be approximately 12 Gtoe per year (1 Gtoe = 4.19×10^{19} J) [Chefurka, 2007]. New emerging economies and changes in life style, especially in the Asian region are responsible for the increase in energy demand.

All these factors create thirst for alternative energy. It also directly boosted research and development of renewable energies such as solar energy, wind power, tidal or ocean energy, geothermal and biomass [Serrano *et al.*, 2009]. This, in turn, created demand for good electrical energy storage (EES) systems [Baker *et al.*, 1999]. Among different types of EES technologies such as flywheel, pneumatic storage and pumped storage that store energy mechanically, batteries, supercapacitors and fuel cells are examples that can convert energy electrochemically and are highly demanded by portable devices [Kondoh *et al.*, 2000; Chalk & Miller, 2006].

Electrolyte is an indispensable component in all electrochemical devices. The basic function of an electrolyte is to serve as the medium for the charge transfer to occur, in which the charges are in the form of ions between a pair of electrodes. There are basically two types of electrolyte, the liquid (aqueous) type and solid (nonaqueous) type. Electrolyte often decides the rate of energy transfer by controlling the rate of ion flow within the electrochemical device.

A good electrolyte should be a good ionic conductor to ease the ion transport and a good electronic insulator to keep a minimum of self-discharge. It should also possess wide electrochemical window to avoid electrolyte degradation within the working potentials range of both electrodes. Another requirement is the high electrochemical stability, meaning inert to cell separators, electrode materials and cell packaging materials. Finally, a practical electrolyte should also be strong against electrical, mechanical or thermal abuses.

Liquid electrolyte suffers many problems in practical applications. Firstly, it suffers the irreversible process of surface layer formation (SEI) on both electrodes. This will cause quantitative loss of the active material, resulting in permanent capacity loss [Matsumura, *et al.*, 1995]. The nature of liquid phase also imposes temperature limits to the operation of the cells. At lower temperature limit, it suffers from high cell impedance problem [Ding, *et al.*, 2000] while high temperature may produce hazardous gas due to the degradation of SEI [Blyr, *et al.*, 1998]. This narrow temperature window restricts the applications in military, space and vehicle traction. The highly flammable electrolyte with low flash point may also cause thermal runaway or fire explosion [Gray, 1997].

2.2 Polymer Electrolytes

PE is a polymer membrane incorporated with appropriate salt to achieve high ionic conductivity. Back in the 20th century, synthetic polymers were mainly used as structural materials or as electric insulators. However, in 1973, Fenton, Parker and Wright, polymer chemists from Sheffield, UK first discovered ionic conductivity in a PEO host added with sodium or potassium salt. Then, Armand *et al.* (1978) contemplated the potential application of polymer electrolytes in solid-state batteries.

PE is the central component of a solid state EES device. The uniqueness of PE compared to liquid or inorganic solid electrolyte is that polymer matrix is responsible for the solvation of ions and the ion position sites are flexible to move along with polymer segments. Many efforts have been spent over the past few decades to improve the room temperature (RT) conductivity through plasticization [Wu *et al.*, 2011], polymer blending [Baskaran *et al.*, 2006] and addition of fillers [Aravindan *et al.*, 2007].

PE has many advantages over the liquid electrolyte. Since it is in solid phase, PE has minimum leakage problem and provide better safety because the flammable organic solvents are absent. PE is mechanically stable and plays the role of both an electrolyte and separator. It is flexible thus could accommodate the volume changes of electrodes that occur during the charge-discharge cycles of the electrochemical devices. In addition, PE can be rolled or folded into various shapes and desired designs. It can be made into ultrathin film which is light in weight and low in resistance. Therefore, PE can offer high energy and power density.

Pitawala *et al.*, (2008) had prepared PEO-based PE with lithium triflate ($LiCF_3SO_3$) as salt, dispersed with aluminum oxide (Al_2O_3) ceramic filler and plasticized with a propylene carbonate (PC) and ethylene carbonate (EC) mixture. The poor mechanical properties as a result of the incorporation of PC and EC have been compensated by incorporating ceramic fillers to the plasticized system. The highest room temperature conductivity obtained was 1.2×10^{-4} S cm^{-1} with 15 wt.% filler and 50 wt.% plasticizer (75 wt.% EC + 25 wt.% PC).

PAN-based gel type PE was investigated by Appetecchi *et al.* (1998). 20 wt.% lithium perchlorate ($LiClO_4$) was added as salt with EC and diethyl carbonate (DEC) as plasticizers showing a high room temperature conductivity of $\sim 10^{-3}$ S cm^{-1}. Similar PAN-$LiClO_4$ PE was also reported by Kuo *et al.* (2013) with PC as plasticizer achieving an optimum conductivity of 4.16×10^{-3} S cm^{-1} at 90 °C.

According to Reiter *et al.*, (2005), PMMA-based gel PE with PC as plasticizer and added with various perchlorate salts of different cations (Li, Na, Mg, Ca, Zn, Cd) showed promising conductivity in the order of 10^{-4} S cm^{-1} at room temperature. The PE membrane also demonstrated high optical transparency (> 90 % in the visible spectrum) and this property is very stable, lasting for a few months. PMMA was also blended with PVDF by Zhou *et al.* (2013) to obtain an electrospun gel PE. $LiClO_4$, EC, PC and TiO_2

were added to achieve 3.9×10^{-3} S cm^{-1} room temperature conductivity with electrochemical stability up to 5.1 V versus Li^+/Li.

The ionic conductivity studies of a blend of PVC/PEO as a host polymer and $LiCF_3SO_3$ as salt have also been conducted [Ramesh *et al.*, 2013]. The ionic conductivity obtained was low for battery application. Thus, a mixture of EC and dibuthyl phthalate (DBP) as plasticizers and silica (SiO_2) as the nanocomposite filler were added to achieve the highest conductivity of 3.32×10^{-4} S cm^{-1}.

On the other hand, there are several projects aiming at exploring eco-friendly materials as polymer host to reduce environmental loads. Such materials include the natural biodegradable polymers eg. cellulose, starch and chitosan and synthetic biodegradable polymers eg. PVA and PCL. Pawlicka *et al.*, (2004) had obtained a conductivity value of 2.08×10^{-5} S cm^{-1} at 40 °C for PE system based on cellulose grafted with poly(ethylene oxide) diisocyanate (DPEO) and $LiClO_4$ as salt. The researchers had used this biomaterial to fabricate solid-state electrochromic device with a configuration of WO_3/PE /CeO_2–TiO_2.

Solid PE based on starch [Lopes *et al.*, 2003] was reported to achieve a maximum conductivity value of 5.05×10^{-5} S cm^{-1} at 30 °C. This PE system contained $LiClO_4$ as salt (with salt concentration [O]/[Li] = 6) and 30 % of glycerol as plasticizer. From the NMR measurements, the position of the ^7Li relaxation rate maxima had been shifted from T_{max} = 350 K of the unplasticized system to 323 K of the plasticized system, suggesting that the Li^+ possessed a relatively higher mobility due to the addition of glycerol.

The possibility of using chitosan as polymer host was demonstrated [Majid and Arof, 2005]. Chitosan acetate-ammonium nitrate (NH_4NO_3) films have achieved the highest conductivity of 2.5×10^{-5} S cm^{-1} at room temperature with 45 wt.% salt. The FTIR result showed that complexation had occurred by exhibiting shifts in amine and carbonyl bands from 1553 to 1520 cm^{-1} and 1636 to 1617 cm^{-1}. Wan and co-workers (2006) had also prepared chitosan-based films by adding KOH for ionic functionality. Their result showed that the PE was feasible for alkaline fuel cell applications but the power density obtained were still low.

Hema *et al.*, (2009) examined the proton conducting PE based on PVA and NH_4X (X = Cl, Br, I) in which they found that the samples had amorphous nature from XRD analysis. The higher ionic conductivity (2.5×10^{-3} S cm^{-1}) of PVA added with NH_4I than PVA added with NH_4Br (5.7×10^{-4} S cm^{-1}) and NH_4Cl (1.0×10^{-5} S cm^{-1}) was attributed to the large anionic size and lower lattice energy of NH_4I (in comparision to NH_4Br and NH_4Cl). The ionic conductivity versus temperature plot for all the PVA: NH_4X displayed an Arrhenius behavior.

For application in electrochemical devices, a PE must satisfy some requirements [Koksbang *et al.*, 1994; Gray, 1997].

a) Conductivity – the PE must possess high ionic conductivity in the range from 10^{-4} to 10^{-2} S cm^{-1} at room temperature for high current flow.
b) Electrochemical stability – the PE should possess wide electrochemical stability window. This voltage range sets the operating voltage limit to prevent any damages to PE.

c) Mechanical stability – the PE must be mechanically stable to run charge-discharge cycles to ensure safety and durability.

d) Thermal stability – the PE should be thermally stable when in contact with electrode materials. Poor thermal stability means the polymer membrane may decompose easily and then cause damages on electrodes.

e) Compatibility – the PE must be compatible chemically and also electrochemically with electrode materials.

f) Availability – the raw materials must be in abundance and inexpensive.

2.3 Selection Criteria of Materials

The polymer host must contain polar groups which can act as electron donors (i.e. atoms that possess lone pair electrons) in order to form a dative bond with the cation of the incorporating salt. It should possess low glass transition temperature, T_g such that the operating temperature is always higher than T_g where the liquid-like amorphous phase will facilitate ionic transport with its local segmental motion, yielding good conductivity characteristics. The mechanical stability of the polymer is important to reduce the film thickness and lower the ohmic drop in the PE to avoid short circuit. The polymer should also form film easily with large chemical and electrochemical window stabilities. Some selected polymers and their properties are shown in the Table 2.1.

Table 2.1
Properties of some polymers

Polymer	Glass Transition Temperature (°C)	Dielectric Constant	Polar Group
poly(ethylene oxide) (PEO)	-64	5	O
poly(vinylidene fluoride) (PVdF)	-40	7.72	F
Poly(vinyl alcohol) (PVA)	85	1.9	O
poly(vinyl chloride) (PVC)	81	3.4	Cl
poly(methymethacrylate) (PMMA)	105	2.6	O
Poly(ethylene imine) (PEI)	215	n.a.	N
poly(ε-caprolactone) (PCL)	-60	2.9	O

Keynote: n.a. = not available

The solvent used should ideally possess high dielectric constant, ε to ensure dissociation of salt, low viscosity which results in higher mobility, low melting point and high boiling point. There are generally two types of solvent, polar and non-polar solvent. The polar solvent dissolve polar compounds while the non-polar solvent dissolve non-polar compounds. Properties of some solvents are listed in Table 2.2.

Table 2.2
Properties of some common solvents

Polymer	Density (g/mL)	Viscosity at 20 °C	Melting point (°C)	Boiling Point (°C)
Acetic acid	1.049	1.22 mPas	16.5	118.1
Acetone	0.793	0.31 cP	-94.9	56.5
Dimethylformamide	0.944	0.92 cP	-61.0	153.0
Methanol	0.792	0.59 mPas	-97.0	64.7
Tetrahydrofuran	0.889	0.48 cP	-108.4	66.0
Toluene	0.867	0.59 cP	-93.0	110.6
Water	1.000	0.001 Pas	0	100.0

The selected salt should have weak ion-ion bonding and with low lattice energy in order to be easily dissociated. Lattice energy is the energy required to completely separate one mole of a solid ionic compound into free cations and anions. This incorporating salt should preferably have large anion radius so that the anion is less mobile. This can boost the cation mobility. High cation mobility is important for devices. Lattice energy can be calculated using several methods such as Born-Haber Cycle (based on thermochemical calculations), Born-Lande equation (derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term), Born-Mayer equation (similar as Born-Lande equation with an improved repulsion term) and Kapustinskii equation (based on Goldschmidt ionic radii for cation and thermochemical radii for polyatomic anion). Table 2.3 displays the lattice energy of some salts determined from the Kapustinskii equation.

Table 2.3
Lattice energy of some salts based on Kapustinskii equation

Salts	Lattice energy (kJ mol^{-1})
NH_4CH_3COO	703.1
NH_4SCN	661.1
NH_4NO_3	648.9
NH_4BF_4	587.7
NH_4ClO_4	576.6
NH_4BrO_3	645.4
$LiCF_3SO_3$	730.3
$LiNO_3$	831.7
$LiClO_4$	717.5
$LiBF_4$	734.7
$LiCH_3COO$	921.4

2.4 Classification of Polymer Electrolytes

PE can be classified into the following categories:

(i) Solid polymer electrolytes
(ii) Plasticized polymer electrolytes
(iii) Composite polymer electrolytes

2.4.1 Solid Polymer Electrolytes

Dry solid PEs are formed using polar high molecular weight polymer to solvate ionic salts and to support the mechanical matrix forming thin membranes. Research on solid PEs started with PEO-lithium complexes [Wright, 1975; Dias *et al.*, 2000]. The oxygen atoms in the structure of PEO form polar groups which can act as electron donors to coordinate with cation of lithium salts. However, solid PEs have low conductivity (~ 10^{-8} S cm^{-1}) at room temperature and possess high degree of crystallinity. As a result, researchers have been developing strategies to improve the ionic conductivity. One alternative is to use other types of polymer with high electron donating power such as PAN, PVDF and PVA to enhance the ionic conductivity. Other methods include reducing the effective polymer chain length using co-polymerization [Park and Lee, 2005], cross-linked polymer networks [Watanabe and Nishimoto, 1995], and comb formation [Ding, 1997]. This will reduce the chain interactions (such as Van der Waals attractions and entanglements) leading to a decrease in viscosity, glass transition temperature and an increase of the polymer chain mobility [De Gennes, 1979].

2.4.2 Plasticized Polymer Electrolytes

The plasticized PEs are formed by adding small amount of low molecular weight polar solvent with high dielectric constant [Murata *et al.*, 2000] to a PE to enhance the conductivity. It was first introduced by Feuillade and Perche (1975). It has been widely reported that ionic transport is confined only in amorphous phase rather than in the crystalline phase. The addition of plasticizer has been shown to increase the amorphousness of the PE and lowering the T_g, both of which resulting in enhancing the conductivity. T_g is the temperature at which the polymer changes from the glassy state (hard and rigid) to soft rubbery state(flexible and rubber-like). Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are among the most commonly used plasticizers and their properties are listed in Table 2.4.

Table 2.4
Physical Properties of some plasticizers

Plasticizer	Dielectric constant	Melting Point (°C)	Boiling Point (°C)	Viscosity at 25 °C (mPa s)
Ethylene carbonate	89.8	36.4	248	1.90 (40 °C)
propylene carbonate	64.9	-48.8	242	2.53
dimethyl carbonate	3.1	4.6	91	0.59 (20 °C)
diethyl carbonate	2.8	-74.3	126	0.75
ethyl methyl carbonate	2.96	-53	110	0.65
γ-Butyrolactone	39.0	-43.3	204	n.a.
N,N-Dimethyl formamide	36.7	-61	153	0.80 cP
Poly(ethylene glycol) 200	20	n.a.	n.a.	50 cP

Keynote: n.a. = not available

2.4.3 Composite Polymer Electrolytes

Electrochemically inert particulate fillers are introduced into the PE system to obtain composite PEs. Weston and Steele [1987] were the first to introduce fillers into polymer system to improve the mechanical strength of the polymer matrix. They discovered that the conductivity was also enhanced. The presence of fillers is reported to disrupt the formation of crystalline phase matrix leading to an enhancement of amorphous phase. Addition of fillers can also add more conducting pathways for the carriers through the interfacial interaction between the filler grain surface and polymer. This creates additional ion hopping sites (immobilised coordination sphere) leading to higher ion mobility. Consequently, the conductivity is enhanced. Ceramic oxides such as SiO_2, TiO_2, Al_2O_3, ZrO_2, MgO, $LiAlO_2$ and SnO_2 are used to prepare composite PEs.

2.5 Polymer Electrolytes Based on Ammonium Salts

The development of proton conducting PEs started with the perfluorinated sulfonic membranes in the 1960s [Bozkurt and Meyer, 2001] by incorporating strong inorganic acids (H_3PO_4, H_2SO_4 and HCl). Active research was initiated by Du-Pont patent, 1972 on Nafion in connection with the Gemini fuel cell program and by Potier's group that used oxanium perchlorate in 1973. Proton conductors have attracted researchers' interest because hydrogen is projected as one of the non-conventional energy source in the 21st century. Thus, a proton conducting PE could be used in hydrogen producing electrolysers. H^+ ions are very small and can be applied in intercalation-based devices. The surface reactivity of proton conductor is often sufficient to develop it as gas sensors.

Proton conducting PEs can also be developed using ammonium salts such as NH_4SCN, NH_4NO_3, NH_4CH_3COO, NH_4F, NH_4ClO_4, $NH_4CF_3SO_3$, NH_4I and $(NH_4)_2SO_4$. Some examples of ammonium based PEs and their conductivity are tabulated in Table 2.5

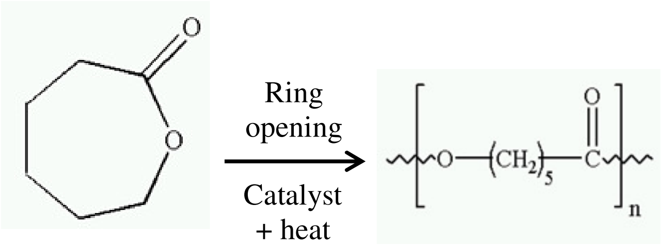
Table 2.5
Conductivities of some ammonium-based PEs

Salts	Polymer	σ (S cm^{-1}) at r.t.	References
NH_4SCN	PVP	1.7×10^{-4}	[Ramya *et al.*, 2007]
NH_4NO_3	Chitosan:PVA (40:60)	2.1×10^{-5}	[Kadir *et al.*, 2010]
NH_4CH_3COO	PVA	5.6×10^{-6}	[Hirankumar *et al.*, 2005]
NH_4F	PEO	1.1×10^{-6}	[Kumar and Sekhon, 2002]
NH_4ClO_4	PESc	2.2×10^{-7}	[Srivastava and Chandra, 1992]
$NH_4CF_3SO_3$	Chitosan	1.0×10^{-6}	[Khiar *et al.*, 2006]
NH_4I	Chitosan	3.7×10^{-7}	[Buraidah *et al.*, 2009]
$(NH_4)_2SO_4$	PEO	2.7×10^{-6}	[Ali *et al.*, 1998]

2.6 Polycaprolactone

2.6.1 Introduction

PCL is a synthetic thermoplastic polymer that is derived from renewable natural sources. Biological systems such as plant and animal tissue can produce PCL biotechnologically. They can also be synthesized chemically by ring opening the cyclic internal ester and polymerized to become aliphatic polyester, as shown in Fig. 2.1.



ε-caprolactone Poly(ε-caprolactone)

Fig. 2.1 Ring opening of poly(ε-caprolactone)

The chemical formula for the ε-caprolactone as a monomer is $C_6H_{10}O_2$. There are also other types of monomer that having the same chemical formula such as γ-caprolactone and δ-caprolactone. This PCL biopolymer is often non-toxic and fully biodegradable in aqueous medium and when in contact with microorganisms such as bacteria, fungi and algae [Goldberg, 1995]. Thus, PCL can firstly reduce environmental impact from industrial waste and protects the soil by enhancing soil carbon level.

Woodruff and Hutmacher (2010) has made a good review on PCL describing why the research interest on PCL increases drastically in the 21st century after being forgotten for the last two decades. PCL has superior rheological and viscoelastic properties over many other resorbable polymers making it easy to be manufactured into a large range of implants and devices. It is non-toxic as approved by Food and Drug Administration (FDA) with tailorable degradation kinetics. This means PCL can be manipulated physically, chemically and biologically to suit various specific anatomical applications.

PCL has good oil, water and chlorine resistance, excellent level of biocompatibility and bio-resorbability [Coombes *et al.*, 2004; Amass *et al.*, 1998], thus making it widely applied in biomedical fields. PCL has been endorsed by FDA for applications in human body such as sutures and fibres for wound dressings, capsules for drug delivery [Lanza *et al.*, 1998], scaffolds for tissue repair and tissue engineering, root canal filling for oral surgery, interpositional spacer in osteoarthritis, patch for torn tendon replacement, and long term implantable biomaterials [Wang *et al.*, 2005; Ikada *et al.*, 2000]. It is used as additive in resin to improve the impact resistance property which is applicable in surface coating, adhesives, fabrics and synthetic leather. Biodegradable packaging plastics also make use of PCL as one of the raw materials for environmental benefits. Calandrelli *et al.*, (2000) has made a good review on the preparation and characterization of composites based on PCL for in-vivo application.

The dielectric behaviour of PCL is classified as type A2-polymers according to Urakawa [Urakawa *et al.*, 1994] as shown in Fig. 2.2. This is because the electric dipole of PCL carries two components, which are normal and parallel to the main polymer chain. Therefore, the end-to-end dipole vector is not parallel to the backbone but might be configuration dependent. It can be applied as a candidate polymer host for ionic conduction because it contains the ester oxygen that can coordinate cations. The parallel bond dipole moment, m_P and perpendicular bond dipole moment, m_S in the ester group were estimated to be 0.64 D and 1.60 D, respectively, by Baysal and Stockmayer (1994).

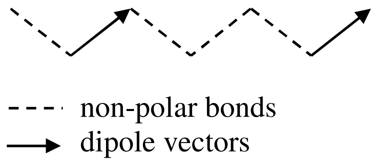


Fig. 2.2 Schematic representation of type A2 chains.

2.6.2 Characteristics of PCL

2.6.2.1 Structure

The monomer has 5 carbon atoms in the parent hydrocarbon chain with methylene bonds that give the prefix of the monomer epsilon. Fig. 2.3 shows the chemical structure of PCL. Two oxygen atoms in the ester functional group each bear lone pair electrons that could form dative bonds with a cation.

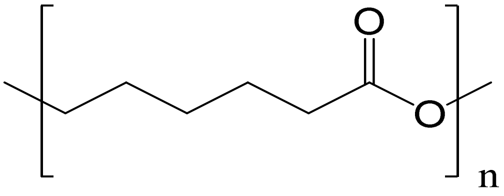


Fig. 2.3 Chemical structure of poly(ε-caprolactone)

2.6.2.2 Solubility

PCL has a semi-crystalline structure that limits its solubility in many solvents which are able to dissolve other amorphous polyester structures. It is soluble in anisole, chloroform, methylene chloride, acetyl chloride, tetrahydrofuran, pyridine, 2,2,2-trifluoroethanol, trifluoroacetic acid and 1,2-dichloroethane. The experimental estimation of the solubility parameters was done by swelling tests using Hansen theory [Bordes *et al.*, 2009]. Other solvents include dichloromethane, carbon tetrachloride, benzene, toluene, cyclohexanone and 2-nitropropane [Woodruff and Hutmacher, 2010].

2.6.2.3 Glass transition Temperature

PCL also possesses low glass transition temperature, T_g (-60 °C) similar to polyethylene oxide (PEO) [Fonseca *et. al.*, 2007]. T_g characterizes the local segmental motion of the polymer that facilitates the ionic transport mechanism. It also determines the mechanical strength and processibility of a polymer material.

2.6.3 PCL-based Polymer Electrolytes

PCL can be a candidate polymer host for ionic conduction because it contains a Lewis base (ester oxygen) that can coordinate cations [Stoeva *et al.*, 2003]. The low glass transition temperature of PCL enables the polymer chain to exhibit segmental motion at room temperature. This enables the ions to easily move from one complexation site to another. A number of lithium salts such as lithium perchlorate ($LiClO_4$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), lithium tetrafluoroborate ($LiBF_4$) and other types of salt such as magnesium trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$), europium trifluoromethanesulfonate ($Eu(CF_3SO_3)_3$) and potassium trifluoromethanesulphonate (KCF_3SO_3) have been added to PCL in smart window and battery applications as shown in Table 2.6.

Chiu and co-workers (2004) have investigated the miscibility behavior, ionic conductivity and interaction mechanism of $LiClO_4$/PEO/PCL ternary blend by using solid-state Li-NMR spectroscopy, DSC, FTIR and ac impedance measurements. They have shown that the individual three binary blends are fully miscible. However, the

Table 2.6 Conductivities and applications of PCL-based PEs

Salts	σ (S cm^{-1})	Applications	References
$LiClO_4$	6.3 x 10^{-7} at r.t.	Electrical, DSC, FTIR, solid NMR studies PEO-PCL + 25 % $LiClO_4$	[Chiu *et al.*, 2004]
$LiClO_4$	~6 x 10^{-7} at r.t.	Electrical, DSC, FTIR studies MPEG-PCL + 25 % $LiClO_4$	[Chiu *et al.*, 2005]
$LiClO_4$	1.2 x 10^{-6} at r.t	Electrical, DSC, CV studies PCL + 10 % $LiClO_4$	[Fonseca *et al.*, 2006a]
		Lithium Batteries $LiNiCoO_2$ | PCL + 10 % $LiClO_4$ | Li	[Fonseca *et al.*, 2006b]
$LiClO_4$, $LiCF_3SO_3$, $LiBF_4$	2.26 x 10^{-4} at r.t 4 x 10^{-5} at r.t 1.5 x 10^{-7} at r.t	Electrical, DSC, CV studies PCL + 10% PC + 12 % $LiClO_4$ PCL + 10% PC + 12 % $LiCF_3SO_3$ PCL + 10% PC + 12 % $LiBF_4$	[Fonseca *et al.*, 2007]
$LiClO_4$	n.a.	FTIR studies PCL + $LiClO_4$	[Wu *et al.*, 2007]
$LiClO_4$	~2 x 10^{-6} at 30 °C.	Electrical, DSC, FTIR studies PCL + $LiClO_4$	[Lin *et al.*, 2011]
$LiCF_3SO_3$	4 x 10^{-6} at 35 °C	Electrical, DSC, TGA, NMR, XRD studies PCL-siloxane + $LiCF_3SO_3$	[Nunes *et al.*, 2006]
		FTIR, SEM studies PCL-siloxane + $LiCF_3SO_3$	[Nunes *et al.*, 2008]
$LiCF_3SO_3$	4.99 x 10^{-4} at r.t.	Electrical, SEM, XRD studies PCL + 30% EC + 15% $LiCF_3SO_3$	[Ng *et al.*, 2011]
$Mg(CF_3SO_3)_2$	8 x 10^{-9} at 35 °C	Electrical, DSC, TGA studies PCL-siloxane + $Mg(CF3SO_3)_2$	[Teixeira *et al.*, 2010]
KCF_3SO_3	1 x 10^{-7} at 35 °C	Electrical, DSC, TGA, SEM, XRD, FTIR studies PCL-siloxane + KCF_3SO_3 Electrochromic window Glass|IZO|WO_3|PCL-siloxane + KCF_3SO_3|IZO|glass	[Fernandes *et al.*, 2011a]
$LiCF_3SO_3$, $Eu(CF_3SO_3)_3$	3 x 10^{-6} at 35 °C	Electrical, FTIR, CV studies PCL-siloxane + $LiCF_3SO_3$ + $Eu(CF_3SO_3)_3$ Electrochromic window Glass|IZO|WO_3|PCL-siloxane + $LiCF_3SO_3$ + $Eu(CF_3SO_3)_3$|IZO|glass	[Fernandes *et al.*, 2011b]
$LiClO_4$	9.58 x 10^{-6} at 25 °C	Electrical, DSC, TGA, CV studies PCL-siloxane + $LiClO_4$ Electrochromic window Glass|IZO|WO_3|PCL-siloxane + $LiClO_4$ |In_2O_3:ZnO|glass	[Rodrigues et al., 2012]

Keynote: n.a. = not available

ternary blend phase diagram displayed a closed immiscibility loop due to the complicated interactions between $LiClO_4$, PEO and PCL. PCL was found to suppress the degree of crystallinity of PEO and lead to higher ionic conductivity. Li^+ cation was observed to prefer coordinating with the oxygen atom of carbonyl group of PEO rather than with PCL. The preference was explained due to the ability of PEO to donate its electron is higher than that of PCL. They achieved a maximum room temperature ionic conductivity value of 6.3×10^{-7} S cm^{-1} at the composition of 25/60/15 ($LiClO_4$:PEO:PCL). This group of researchers later [Chiu *et al.*, 2005] substituted PEO to methoxypoly(ethylene glycol) (MPEG) forming MPEG-PCL diblock copolymer. Again, the enhancement in conductivity was mainly attributed to the reduction of crystallinity of MPEG upon addition of PCL. FTIR analysis showed that the relative intensity of PCL's complexed carbonyl stretching band increases with increasing $LiClO_4$ content and lengthening PCL block. They also obtained a room temperature conductivity value of around 6×10^{-7} S cm^{-1} by adding 25 wt.% of lithium salt into MPEG-PCL blend.

The electrochemical stability and potential for rechargeable lithium battery application of PCL-based electrolyte were first reported by Fonseca *et al.* (2006a; 2006b). 10% $LiClO_4$ was added to PCL matrix to achieve the highest conductivity of 1.2×10^{-6} S cm^{-1} at room temperature. A high electrochemical stability window of 5 V was reported. This makes the application in low environmental impact battery promising. The biodegradation was found to occur after 110 days. The researchers have prepared $LiNiCoO_2$ film by sol-gel synthesis and applied as the cathode. The Li | PCL+10% $LiClO_4$ | $LiNiCoO_2$ battery demonstrated a specific charge/discharge capacity of 182 $mAhg^{-1}$ (first cycle) and 120 $mAhg^{-1}$ (after 50 cycles). The Li^+ chemical diffusion coefficients obtained by impedance spectroscopy was high due to the porous high surface area electrode. Fonseca *et al.*, (2007) later explored the possibility of using PC as plasticizer in PCL-Li salt compolexes. Three types of Li salts were used ($LiClO_4$, $LiCF_3SO_3$, $LiBF_4$). In DSC studies, addition of PC was observed to reduce the crystalline phase of the gel polymer electrolyte while T_g increased with increasing Li salts. The complex 78 % PCL + 10% PC + 12 % $LiClO_4$ exhibited the highest conductivity (2.26×10^{-4} S cm^{-1} at room temperature) among the three Li salts. Their results also showed that the temperature dependence conductivity obeyed VTF model with a pseudoactivation energy in the range of 10^{-2} eV.

Wu and Chang (2007) examined the interaction behavior between Li^+ ion and carbonyl functional groups of PCL using FTIR analysis within various $LiClO_4$ concentrations. FTIR spectrum ranging from 1800 to 1650 cm^{-1} was used to calculate quantitatively the absorptivity coefficient of ‘‘free/Li^+ bonded C=O”. The oxygen atom of C=O interacted strongly with Li^+ ion. The electrical studies and DSC analysis was later reported by other researchers [Lin *et al.*, 2011]. The maximum conductivity at 30 °C of PCL-$LiClO_4$ complexes was 2×10^{-6} S cm^{-1} occurred at a composition of PCL/$LiClO_4$ (80/20). From DSC studies, strong increase of T_g was observed suggesting that the PCL-$LiClO_4$ binary blend was miscible and an interaction occurs between $LiClO_4$ and the amorphous region of PCL.

A complete characterization (electrical, DSC, TGA, NMR, XRD, CV, FTIR and SEM studies) of PCL-siloxane + $LiCF_3SO_3$ was analysed by Nunes *et al.* (2006, 2008). Their results revealed that short PCL chains were covalently bonded through urethane linkages to the siliceous network. A maximum conductivity value of 4×10^{-6} S cm^{-1} at 35 °C was obtained by this biohybrid matrix. An encouraging wide electrochemical window between 1 and 6 V versus Li^+ showed that the biohybrid composition was worth pursuing. The XRD patterns and the DSC thermograms indicated that the materials were completely amorphous. TGA analysis demonstrated that thermal decomposition only occurred at temperatures higher than 300 °C. $LiCF_3SO_3$ appeared to de-stabilise the hybrid structure in a non-oxidising atmosphere. The cation coordination of this non-porous and homogeneous film was accompanied by hydrogen-bonded aggregates formation. Li^+ ions interacted with the urethane and ester carbonyl oxygen atoms. The relative concentration of "free" anions and coordinated anions such as weakly coordinated anions, $Li^+CF_3SO_3^-$ ion pairs, $[Li(CF_3SO_3)_2]^-$ triplets, aggregates I ($[Li_2(CF_3SO_3)]^+$) and aggregates II ($[Li_3(CF_3SO_3)]^{2+}$) explained the variation of the room temperature ionic conductivity. SEM micrographs showed that the lithium salt was homogeneously dispersed within the hybrid framework.

Ng *et al.* (2011) have prepared plasticized PCL-EC-$LiCF_3SO_3$ and characterized the electrolyte using electrical, SEM and XRD studies. The highest conductivity achieved was 4.99×10^{-4} S cm^{-1} at room temperature with composition 55 % PCL+30 % EC+15 % $LiCF_3SO_3$. The addition of plasticizer improved the ionic mobility and salt dissociation rate.

Polymer electrolytes based on PCL-siloxane hybrid matrix containing different types of triflate salts have been studied by a group of researchers [Teixeira *et al.*, 2010; Fernandes *et al.*, 2011a and Fernandes *et al.*, 2011b]. Triflate salts such as $LiCF_3SO_3$, $Mg(CF_3SO_3)_2$, $Eu(CF_3SO_3)_3$ and KCF_3SO_3 were incorporated. $LiCF_3SO_3$ showed the highest conductivity of 3×10^{-6} S cm^{-1} at 35 °C. The cations of the salt were observed to bond to the oxygen atoms of the carbonyl groups of the PCL and urethane groups. $LiClO_4$ was later [Rodrigues *et al.*, 2012] added to the same hybrid matrix achieving a conductivity as high as 9.58×10^{-6} S cm^{-1} at 25 °C. The same group of researchers also assembled the prototype solid state electrochromic window (ECW) using the PCL-siloxane based system as dual-function electrolyte/adhesive component. Configuration such as Glass|IZO|WO_3|PCL-siloxane polymer electrolyte |In_2O_3:ZnO|glass was used in the smart window application and exhibited fast switching time, good open circuit memory. The ECW displays an average transmittance in the visible region of 55 % (in the colored state) and 76 % (in the bleached state). They found that this ECW using solid state electrolyte has a lot of advantages over the conventional liquid electrolytes such as cycle lifetime, durability and optical performance.

2.7 Summary

Although this review is not completely exhaustive, to the author's knowledge, there are no reports on incorporating any type of ammonium salts to PCL matrix to form a PCL-ammonium salt polymer electrolyte. The experiments in this work are described in the next chapter.