

CHAPTER 1

INTRODUCTION

1.1 Background

The development of electrochemical devices such as battery, fuel cell and supercapacitor has rapidly taken place globally over the last decade [Baskaran *et al.*, 2008; Bhargav *et al.*, 2009]. The huge demands for energy storage systems are mainly due to the increasing popularity of portable devices and electric vehicles. The use of liquid electrolytes in these electrochemical devices is faced with many safety issues such as the production of gas during overcharge or over discharge, flammable electrolyte leakage problem, risky thermal explosion at high operating temperatures and the hazardous materials in the liquid electrolytes [MacCallum and Vincent, 1987; Scrosati, 1993].

An alternative solution is to use the free standing polymer electrolyte (PE) in such devices so that the leakage problem is no longer an issue. PE has many other advantages such as light weight, high compliance in shape, easy to process and allow volume changes during device operation [Agrawal *et al.*, 2011]. It often acts as both electrolyte and separator. PE has been extensively studied over the last few decades for application in an all-solid-state functional device which also includes solar cells, thus contributing to renewable energy development [Baker and Collinson, 1999].

There are many polymeric materials that fulfill the selection criteria as a polymer host in PE systems. Polymers such as poly(ethylene oxide) (PEO) [Cha *et al.*, 2006], poly(vinylidene fluoride) (PVdF) [Magistris *et al.*, 2002], poly(vinyl chloride) (PVC) [Ramesh and Arof, 2001], poly(acrylonitrile) (PAN) [Choi *et al.*, 2005] and poly(methylmethacrylate) (PMMA) [Appetecchi *et al.*, 1995] have been studied in the effort to achieve high room temperature conductivity. For any practical applications, a minimum room temperature conductivity of $\sim 10^{-4}$ S cm⁻¹ and a high cation transference number are needed. Other requirements include the availability of the materials, high electrochemical, mechanical and thermal stabilities.

Another concern of the growing sector of battery and fuel cell is the toxic technological garbage [David, 1995] left behind upon disposal. It will “attack” the environment leading to long term waste management issues. As such, the use of environmental friendly materials comes to the picture to lower environmental impact throughout all phases of the product cycle life. Such materials include biodegradable polymers that can be efficiently degraded in aqueous medium and in contact with microorganisms [Goldberg, 1995]. These polymers will be degraded to water-soluble oligomers that are non-toxic and can be used for energy recovery through quaternary recycling [Sinha *et al.*, 2010]. The oligomers will be burned in incinerator to produce heat in the form of hot steam, then generating electricity through turbine generators. The remaining residual heat from this hot stream can also be channeled to heat residential and industrial buildings. The left-over melt residue would be disposed by landfill.

So far, there is still not much work where poly(ϵ -caprolactone) (PCL) is used as the polymer host in a PE system (PCL-based has ~ 15 publications compared to PEO-

based ~2500 publications from year 2004 to 2013 using Scopus search). PCL is an aliphatic polyester that is non-toxic and fully biodegradable [Calandrelli *et al.*, 2000] with long methylene bonds between the polar ester groups. It is a semicrystalline synthetic thermoplastic that is widely used in biomedical applications [Coombes, *et al.*, 2004]. Due to PCL's excellent level of biocompatibility and bio-resorbability [Amass *et al.*, 1998], it is used as biodegradable packaging materials, compostable sutures and fibres for wound dressings, contraceptive devices, scaffold fabrication for tissue engineering applications, long term implantable biomaterials and microparticles for drug delivery [Lanza *et al.*, 1998; Ikada *et al.*, 2000; Wang *et al.*, 2005]. The preparation and characterization of composites based on PCL for in-vivo application was reviewed by Calandrelli *et al.*, (2000). It is also used in resin for surface coating, adhesives, fabrics and synthetic leather.

In a common polymer electrolyte system, the polymer should possess polar groups in the molecular chain so that it can solvate and coordinate the cation of the salt through Lewis acid-base interaction. The Lewis base will serve as the electron donor while Lewis acid will act as electron acceptor. 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]. PCL has low glass transition temperature, -60 °C (as low as PEO) and this enables the polymer chain to exhibit segmental motion at room temperature. The ions should be able to move easily from one complexation site to another.

1.2 Objectives of the present work

The aims of the present work are as follows:

- (a) To develop polymer electrolyte based on PCL and ammonium thiocyanate (NH_4SCN) by solution cast technique. Ethylene carbonate (EC) will be then added to the highest conducting PCL- NH_4SCN sample to further enhance the conductivity.
- (b) To study the role of ion dissociation on ionic conductivity enhancement in PCL- NH_4SCN and PCL- NH_4SCN -EC systems.
- (c) To analyze the coupling effect of ionic motion and polymer segmental motion in both PCL- NH_4SCN and PCL- NH_4SCN -EC systems.

1.3 Thesis organization

An overview of the classification of PE system and PCL-based PEs are presented in Chapter 2. Chapter 3 outlines the sample preparation and experimental methods undertaken to characterize the PCL-based PE samples through thermal, morphology, structural, vibrational and electrical analyses. In order to investigate the correlation between glass transition temperature, T_g , melting point, T_m and the ionic conductivity of the PEs, Differential Scanning Calorimetry (DSC) studies are carried out and results are presented in Chapter 4.

Chapter 5 covers the results from Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analyses. SEM is carried out to give an insight on the shape, size, texture and/or phase distribution of the solid polymer electrolyte system prepared. XRD

is employed to study the nature of polymer so that the degree of crystallinity of the polymer membrane can be determined. Chapter 6 deals with vibrational studies using FTIR spectroscopy. The interactions between PCL, NH_4SCN and EC will be discussed in this chapter. The SCN^- stretching mode will be deconvoluted to study the ion dissociation/reassociation effect.

Chapter 7 discusses electrical investigation by impedance spectroscopy. The influence of NH_4SCN and EC on the conductivity variation was studied at room temperature. Temperature dependent studies at selected compositions were also carried out. The relevant model has been used to explain the temperature dependent conductivity trend of the samples. The composition and temperature dependence of dielectric behavior of PCL- NH_4SCN and PCL- NH_4SCN -EC systems are analyzed in detail. These dielectric properties include the complex relative permittivity, complex electric modulus, loss tangent and complex conductivity. The outcome of the study should shed some light on the ion transport properties of both systems.

All the characterization studies from Chapter 4 to 7 address the first objective of the work. The deconvolution of SCN^- stretching mode in Chapter 6 and the composition dependence of dielectric studies in Chapter 7 address the role of ion dissociation on ionic conductivity enhancement in the two systems. The coupling effect of ionic motion and polymer segmental motion are also addressed in the temperature dependence of conductivity and complex electric modulus analyses.

The overall results obtained in the present work will be discussed in Chapter 8. The final Chapter 9 will conclude the thesis with some suggestions for future work.