CHAPTER 1

INTRODUCTION TO THE THESIS

1.1   Background

Technology advancement and the rise in the demand for sophisticated electronic gadgets such as tablet computers, smart phones, laptops, etc; electric vehicles have driven research in energy storage and devices such as batteries, solar cells and electrochromic windows. Since the discovery of ion–conducting polymers based on poly(ethylene oxide) (PEO) by Fenton and co–workers (1973), research on polymer electrolytes (PEs) has been attracting huge interest due to their potential as ionic conductors in energy devices. It is no doubt that solid–state polymer electrolytes are seen as the alternative to replace the conventional liquid electrolytes as they can overcome the limitations of the latter.

Liquid electrolytes (LEs) contain solvents which are volatile and flammable. Even though LEs offer high conductivity, they exhibit limitations in terms of safety due to their physical characteristics. For example, LEs are prone to leakage from sealant and can ignite or even explode when exposed to the environment [Wang et al., 2012]. Unlike liquid electrolytes, polymers do not vaporize and they decompose at higher temperatures. Hence, the incorporation of polymer to form solid–based electrolyte system can reduce the degradation of the electrolyte at high temperatures. The advantages of solid polymer electrolytes (SPEs) over their liquid counterparts have prompted research efforts to improve its physical setbacks. SPEs make it possible for electrolytes to be made into thin, lightweight and leakage–free ionic conductors. Their

physical attributes also enables them to be used as separators in applications such as rechargeable batteries, which save costs.

To date, a number of polymers have been utilized as polymer hosts in polymer electrolytes such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride–co–hexafluoropropylene) (PVdF–HFP), etc. Table 1.1 lists some examples of polymer electrolytes and their ionic conductivities. It could be observed that the polymer electrolyte systems incorporated with additives such as ethylene carbonate (EC) and propylene carbonate (PC) could achieve higher ionic conductivities in the order of 10^{-3} S cm^{-1} as compared to the ones without ($\approx 10^{-7}$ to 10^{-5} S cm^{-1}). Mixing polymers to form a polymer blend (for example, PVdF/PMMA) is also one method to improve the characteristics of the polymer electrolytes.

Table 1.1 Several polymer electrolyte systems and their conductivities

Polymer electrolyte system	Ionic conductivity at ambient (S cm^{-1})	Reference
PVdF/PMMA (3:7) – 1 M LiPF$_6$ – (EC/DMC) (1:1)	1.21×10^{-3}	Idris et al. (2012)
PVdF – 1 M LiClO$_4$ – (PC/DEC) (1:1) – MMT	2.30×10^{-3}	Deka and Kumar (2011)
PVP – LiClO$_4$	$\approx 5.00 \times 10^{-5}$	Rodriguez et al. (2013)
PAN – LiClO$_4$	4.80×10^{-6}	Chen et al. (2011)
PVA – Mg(Ac)$_2$	1.34×10^{-7}	Polu and Kumar (2013)

EC = ethylene carbonate
DEC = diethyl carbonate
DMC = dimethyl carbonate
MMT = modified montmorillonite
Mg(Ac)$_2$ = magnesium acetate
LiClO$_4$ = lithium perchlorate
LiPF$_6$ = lithium hexafluorophosphate
PAN = polyacrylonitrile
PC = propylene carbonate
PMMA = poly(methyl methacrylate)
PVdF = poly(vinylidene fluoride)
PVA = poly(vinyl alcohol)
PVP = polyvinylpyrrolidone

To the knowledge of the author, poly(ethyl methacrylate) (PEMA)/poly(vinylidene fluoride–co–hexafluoropropylene) (PVdF–HF) blend polymer electrolytes have not yet been reported by other researchers. Hence, this thesis focuses on the preparation and characterizations of PEMA/PVdF–HFP blend based polymer electrolytes to understand their vibrational, conductivity structural and thermal behaviours.

1.2   Objectives of the present work

From this investigation, the author hopes to shed some light on understanding the conduction mechanism in such electrolytes.

- To prepare and optimize the polymer blend–salt composition in PEMA/PVdF–HFP–LiTf system in terms of conductivity by electrochemical impedance spectroscopy (EIS) at room temperature.

- To improve the ionic conductivity of the optimized PEMA/PVdF–HFP–LiTf composition with the addition of carbonate–based plasticizers i.e. ethylene carbonate (EC) and propylene carbonate (PC), and imidazolium–based ionic liquids i.e. 1–butyl–3–methylimidazolium iodide (BMII) and 1–butyl–3–methylimidazolium triflate (BMITf). Four polymer blend electrolyte systems will be prepared:

    1. PEMA/PVdF–HFP–LiTf–EC

    2. PEMA/PVdF–HFP–LiTf–PC

    3. PEMA/PVdF–HFP–LiTf–BMII

    4. PEMA/PVdF–HFP–LiTf–BMITf

- To study the molecular interactions i.e. complexations that occur in each system by fourier transform infrared (FTIR) spectroscopy.

- To determine the thermal stabilility of all PEMA/PVdF–HFP blend systems using thermogravimetric analysis (TGA).

1.3   Thesis organization

This thesis contains eight chapters including this introductory chapter. Chapter 2 is an overview of polymer electrolytes based on PEMA, PVdF–HFP, LiTf, EC, PC, BMITf and BMII. Chapter 3 describes the materials, preparation methods of the various polymer electrolyte systems and the characterization techniques used. Chapter 4 shows the results obtained from FTIR studies that investigate the interaction between the components of each system. Chapter 5 presents ionic conductivity results determined from impedance studies obtained from EIS. Chapter 6 displays the thermal stabilities of polymer electrolytes obtained from TGA results. Chapter 7 discusses the results obtained and correlates them to ionic conductivity. Lastly, Chapter 8 concludes the thesis with some suggestions for future work.