CHAPTER 1

INTRODUCTION TO THE PRESENT WORK

1.1 Background

Fighting the global warming and the search for renewable green energy are now the efforts being made to prolong human civilization [Reeve *et al.*, 2011]. Physics has laid the foundations for inventions to make human life more comfortable. Solid state devices would be the future global green energy converters if they can be successfully commercialized [Singh *et al.*, 2008]. Much attention has been focused on the developments of electric vehicles, fuel cells and portable power sources largely due to the growing interest in finding substitutions for petroleum–based products. Among the many electrochemical device options, lithium ion batteries constitute an important component in the growth and development of energy storage devices [Lindley, 2010; Kang and Ceder, 2009]. The development of new solid electrolyte materials is creating opportunities for new types of electrical power generation and storage systems. The development alternative energy technologies require the search of suitable materials that can also play the role of an electrolyte.

Although in current commercial electrochemical devices, liquid electrolytes are being used, they are not without problems. The use of liquid electrolytes tends to make some devices bulky and heavy, thus lowering the specific energy and specific power densities of these devices. Devices must be handled with care for any damage may allow the liquid electrolyte to leak out. The liquid electrolyte may consist of volatile solvents making their storage difficult and their use unfriendly to the environment.

These problems have led to the development of solid electrolytes in particular polymer electrolytes in the solid state. The first report on solid electrolytes was by Wright in the seventies and later on Armand showed the technological importance of such materials. Solid polymer electrolytes are also not without problems. Their room temperature ionic conductivity is still low. This, among other factors led to the study on solid polymer electrolytes using natural rubber grafted with poly(methyl methacrylate). The objectives of this work are given in the next section.

1.2 Objectives of the present work

1) To expand knowledge on the electrical conductivity of solid polymer electrolytes based on natural rubber (NR) that has been grafted with poly(methyl methacrylate) that is designated as MG30. The salts that will be incorporated are lithium triflate (which has been used by other researchers) and added with PEG200 (which is tried for the first time in this work for MG30–based electrolytes). A double–salt (lithium triflate and lithium imide) system will also be tried for the first time with the said polymer.
2) To expand knowledge on vibrational spectroscopy aspects of MG30 based polymer electrolytes using fourier transform infrared spectroscopy.
3) To understand conductivity variation from X–ray diffraction and morphology studies.

With these objectives in mind, the scope of the thesis has been set and explained in the following section.

1.3 Scope of the present thesis

Solid polymer electrolytes (SPEs) based on natural rubber (NR) grafted with 30 wt.% poly(methyl methacrylate) (PMMA) or MG30 have been studied. Grafted polymer has been employed by many researchers worldwide in order to obtain better electrolyte conductivity with good mechanical properties [Suksawad *et al.*, 2011; Walkowiak *et al.,* 2011; Liu *et al.,* 2011]. However, there are few publications on natural rubber (NR) grafted with poly(methyl methacrylate) (PMMA) [Idris *et al.*, 2001; Kumutha *et al.,* 2005; Ali *et al.,* 2008] and also few reports on the application of NR–based electrolytes in electrochemical devices [Ali *et al.,* 2006, Kamisan *et al.*, 2009]. Therefore, a general introduction, literature review on different components of Li–based polymer electrolytes such as salts, solvent, polymers and types and kinds of different polymer electrolytes i.e. solid and gel polymer electrolytes will be discussed in Chapter Two.

Chapter Three in this thesis will not only outline the experiments carried out to prepare samples, but will also cover the techniques involved to study the characteristics of the samples. All the polymer electrolyte samples in this work have been prepared using the solution cast method. MG30 i.e. natural rubber grafted with 30 wt. % PMMA polymer will be incorporated with $LiCF_3SO_3$ before poly(ethylene glycol) 200 (PEG200) is added as plasticizer to the highest conducting sample in the polymer–salt system. The effect of double salt, namely $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ as the incorporating salt is also investigated.

Chapter Four describes X–ray diffraction (XRD) and scanning electron microscopy (SEM) studies that have been carried out to examine the effect of adding

$LiCF_3SO_3$, $LiN(CF_3SO_2)_2$ and PEG200 in different concentrations to MG30–based polymer electrolytes. The nature of the samples whether crystalline, amorphous or both will be determined. This work demonstrates that amorphousness and surface morphology of polymer electrolytes can also shed some indication towards the decrement and increment of the conductivity.

Interactions between polymer–single salt, polymer–double salt and polymer–salt–plasticizer have been verified using fourier transform infrared (FTIR) spectroscopy and are presented in Chapter Five. FTIR studies have been performed to verify the occurrence of complexation between the lithium ion and the polymer. These are necessary as these interactions can affect the ionic conductivity and conductivity mechanism of the ions.

Chapter Six deals with electrochemical impedance spectroscopy (EIS) to study the electrical properties of polymer electrolytes. Conductivity behavior at various temperatures of the samples can be determined from the impedance studies. Conductivity is an important parameter for all electrolytes. From literature, the conductivity obtained is of the order of 10^{-4} S cm^{-1}. Other admittance responses such as complex permittivity and complex electrical modulus will be analyzed from impedance data in order to obtain a deeper understanding on the conducting behavior of the samples. The activation energy and conduction mechanism of the electrolytes will also be determined.

All results presented in this thesis will be discussed in Chapter Seven and Chapter Eight concludes the thesis with some suggestions for future work.