CHAPTER 1

INTRODUCTION

1.1 Introduction

Polymer composite electrolytes have attracted considerable attention due to their improved mechanical stabilities and enhanced ionic conductivities [Liquan 1986, Plocharski et al., 1988, Plocharski et al., 1989, Przyluski et al., 1990]. High technology electronic devices require new high dielectric permittivity materials (known as high-κ materials), with suitable dielectric properties, high mechanical strength and processability [Patsidis et al, 2008]. Materials with suitable dielectric properties can help to enhance the electrical conductivity of a material. Ceramic fillers such as Al₂O₃, SiO₂, TiO₂ are examples of materials that can help to enhance conductivity. On the other hand, there are many contradicting reports [Weston and Steele, 1982; Croce et al., 1989; Panero et al., 1992], where fillers of similar types have shown negligible or reducing effect on the conductivity. It is often ambiguous to compare the reported results since conductivity of polymer electrolytes is dependent on many factors such as salt species, salt concentration, particle size, temperature, thermal history, and preparative methods. To examine the effects of various fillers, one needs to measure various physical properties by carefully maintaining the same experimental condition.

According to Wieczorek et al., (1996), the enhancement of in conductivity can be explained by the Lewis acid-base interaction and the increase in amorphousness of the composite polymer electrolytes. Nanosized fillers are more effective in enhancing
conductivity of the samples due to their high surface area. Besides that, Wieczoreck et al., (1998), who studied filler effects in liquid polyethylene glycols (PEG), showed that the addition of $\alpha$-Al$_2$O$_3$, rich with Lewis acid surface groups, resulted in enhancing conductivities for high salt content electrolytes. Sun et al., (2000) have added further support to the influence of Lewis acid groups through their investigation of BaTiO$_3$ materials, which are ferroelectric and have a significant Lewis acid character. They showed that additions of just 1.5 wt.% of this filler could enhance the conductivity by a factor of 3. The effect of these ferroelectric ceramic particles appeared to be highly dependent on the nature of the salt used in the PEO-based systems, with LiClO$_4$ showing the most dramatic effects.

According to Majid and Arof (2007), conductivity of 59 vol% chitosan-41 vol% H$_3$PO$_4$ increased from $5.36 \times 10^{-3}$ to $1.12 \times 10^{-4}$ S cm$^{-1}$ on addition of 15 wt.% aluminosilicate filler. The ionic conductivity of poly(ethylene oxide) and its complexes has been enhanced by incorporating Al$_2$O$_3$ [Tambelli et al., 2002], TiO$_2$ [Wang et al., 2005] and other fillers such as BaTiO$_3$ [Itoh et al., 2003]. Walls et al., (2000) studied the effect of fumed silica filler in poly(ethylene glycol) dimethyl ether (MW 250 and 500) based polymer electrolyte. They reported that conductivity can be enhanced to as high as $10^{-3}$ S cm$^{-1}$.

Aluminium titanate is another type of ceramic material that maybe used to act as filler material to enhance conductivity of polymer electrolytes. At the time this work was carried out, many papers have discussed only on the method of preparation of aluminium titanate, Al$_2$TiO$_5$ [Andrianainarivelo et al., 1997; Coury et al., 1994]. No work reported on the use of Al$_2$TiO$_5$ as a ceramic filler to enhance conductivity.
1.2 Objectives of the Dissertation

The objectives of this work are to:

(a) prepare aluminium titanate (Al$_2$TiO$_3$) as a filler material by sol-gel method
(b) prepare CA-NH$_4$SCN-Al$_2$TiO$_3$ composite polymer electrolyte system
(c) study the effect of Al$_2$TiO$_3$ on the electrical conductivity of polymer-salt complexes
(d) investigate the effect of filler on the nature of the polymeric material.

1.3 Scope of the Dissertation

The purpose of this work is to study the effect of Al$_2$TiO$_3$ on the electrical and structural behaviour of polymer-salt complexes. To the author’s knowledge no work has been done to study the effect of chitosan conductivity with Al$_2$TiO$_3$ filler. The polymer electrolyte will be prepared by the solution cast technique. The conductivity will be optimised using the Al$_2$TiO$_3$ filler prepared. Aluminium titanate will be prepared using the sol-gel technique. An inexhaustive literature review involving the present status of knowledge about polymer composite electrolytes, in particular, is provided in Chapter 2. The experimental methods and necessary information about the techniques used are discussed in Chapter 3.

X-ray diffraction (XRD) results confirming the material prepared is Al$_2$TiO$_3$ is presented in Chapter 4. Impedance spectroscopy results for chitosan-NH$_4$SCN complexes and chitosan-NH$_4$SCN-Al$_2$TiO$_3$ composites will be described in Chapter 5 in order to determine the effect of Al$_2$TiO$_3$ the electrical conductivity of chitosan-NH$_4$SCN samples. The dielectric constant and electrical modulus will be calculated and analysed.
in order to understand the effects of the filler on the electrical conductivity of the electrolyte material.

Fourier transform infrared (FTIR) spectroscopy was performed to confirm the occurrence of complexation. Since complexation is a criteria of polymer electrolytes FTIR results will be presented in Chapter 6. One of the factors that determine conductivity of polymer electrolyte is the degree of the amorphousness of the material. To determine the degree of amorphousness/crystallinity XRD was carried out. To further understand the conductivity variation scanning electron microscopy (SEM) was also performed. All results on XRD and SEM will be described in Chapter 7. Chapter 8 presents an overall discussion and the study is concluded with some suggestions for further work in Chapter 9.