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 Al_2O_3, SiO_2, TiO_2 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 α-Al_2O_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_3PO_4 increased from 5.36 x 10^{-5} to 1.12 x 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_2O_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_2TiO_5 [Andrianainarivelo et al., 1997; Coury et al., 1994]. No work reported on the use of Al_2TiO_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_2TiO_5) as a filler material by sol-gel method

(b) prepare CA-NH_4SCN-Al_2TiO_5 composite polymer electrolyte system

(c) study the effect of Al_2TiO_5 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_2TiO_5 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_2TiO_5 filler. The polymer electrolyte will be prepared by the solution cast technique. The conductivity will be optimised using the Al_2TiO_5 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_2TiO_5 is presented in Chapter 4. Impedance spectroscopy results for chitosan-NH_4SCN complexes and chitosan-NH_4SCN-Al_2TiO_5 composites will be described in Chapter 5 in order to determine the effect of Al_2TiO_5 the electrical conductivity of chitosan-NH_4SCN 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.