UNIVERSITI TEKNOLOGI MARA

STRUCTURAL AND ELECTRICAL PROPERTIES OF HEXANOYL CHITOSAN-BASED POLYMER ELECTROLYTE

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Candidate's Declaration

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as reference work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

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ABSTRACT

The insolubility of chitosan in a wide range of organic solvents has limited its practical application especially in electrochemical systems. In order to improve its solubility, acyl modification of chitosan was carried out in the present study. Films of hexanoyl chitosan-based polymer electrolyte were prepared by solution casting technique. Lithium perchlorate ($LiClO_4$) was used as the doping salt while titanium oxide (TiO_2) was used as the inorganic filler. In the present study, the plasticized hexanoyl chitosan-based polymer electrolyte was prepared by employing dimethyl carbonate (DMC) as the plasticizing solvent. The X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and impedance spectroscopy (IS) were used to characterize the prepared samples. With addition of 30 wt.% $LiClO_4$, the conductivity of hexanoyl chitosan-based polymer electrolyte was enhanced from 2.37 x 10^{-13} to 1.85 x 10^{-5} S cm^{-1}. For composite polymer electrolyte system, the highest ionic conductivity was achieved at 3.06 x 10^{-4} S cm^{-1} with incorporation of 6 wt.% TiO_2. The highest ionic conductivity value of 4.09 x 10^{-4} S cm^{-1} was obtained with addition of 15 wt.% DMC to hexanoyl chitosan-$LiClO_4$-TiO_2 electrolyte system. The conductivity increased is due to the increase in the number of free ions and their mobility while the decrease in conductivity is attributed to the ion association which decreases the number of charge carriers available for ionic conduction. Conductivity of hexanoyl chitosan-based polymer electrolytes was also studied as a function of temperature ranging from 283 to 333 K. the conductivity is found to increase with increasing temperature. The regression values, R^2 are in the range of 0.97 to 0.99 indicating that all points stretch out in an almost straight line and therefore implying that the conductivity is thermally assisted and can be described by Arrhenius law. Ac conductivity and scaling behaviour of hexanoyl chitosan-based polymer electrolytes were studied at different temperatures. The Jonsher's universal power law was used to discuss the ac conductivity behaviour of the samples. The temperature dependence of the power law exponent *s* for the salted hexanoyl chitosan follows the Overlapping Large Polaron Tunneling (OLPT) model while the conduction mechanism for composited hexanoyl chitosan-based polymer electrolyte systems are interpreted based on the Correlated Barrier Hopping (CBH) model.

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CHAPTER 1

INTRODUCTION

1.1 Background

Solid polymer electrolytes (SPEs) are an important class of conducting solid-state ionic materials having significant potential in a variety of electrochemical devices, especially in secondary (rechargeable) lithium polymer batteries due to their advantages such as high ionic conductivity, high energy density, leak-proof, easy processability and light weight characteristic (Baskaran et al., 2004).

To date, various polymers such as poly(methyl methacrylate) (PMMA) (Ali et al., 2007), polyethylene oxide (PEO) (Wang et al., 2008) and poly(vinyl chloride) (PVC) (Rajendran et al., 2007) have been studied. Among the polymeric materials reported, PEO-based polymer electrolytes are the most commonly studied system due to their easy formation of complex with lithium salts and stable chemical properties (Lin et al., 2005). Although PEO-based electrolytes possess good mechanical properties, they are generally poor conductors ($\sigma \approx 10^{-8}$ S cm^{-1}) at room temperature which limits their practical applications (Gray, 1997).

In the effort to find alternative polymer with good mechanical and electrical properties to act as the host in polymer electrolyte system, chitosan, a biodegradable polymer was studied (Yahya and Arof, 2002). The nitrogen and oxygen atoms in the structure of chitosan act as the electron donors and interact with the doping salts (Khiar et al., 2005). In previous studies, chitosan was dissolved in dilute acetic acid.