UNIVERSITI TEKNOLOGI MARA

INVESTIGATION OF CELLULOSE ACETATE-AMMONIUM SALT COMPLEXES POLYMER ELECTROLYTES FOR PROTON BATTERY

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Thesis submitted in fulfilment of the requirements for the degree of Master of Science

Faculty of Applied Sciences

December 2009

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Candidate's Declaration

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ABSTRACT

CA-salt complexes and plasticized CA-salt complexes were prepared using solution cast technique. Cellulose acetate (CA) was used as polymer host. ammonium trifluoromethanesulfonate or triflate (NH4CF3SO3) as complex salt, and ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers. Pristine CA has low ionic conductivity (~10⁻¹⁰ S cm⁻¹). Salt was added at different concentration from 5 wt.% to 50 wt.% to form CA-salt complexes films. The complexation and interactions between polymer and salt, polymer and plasticizers, and plasticizers and salt were confirmed using Fourier Transform Infrared Spectroscopy (FTIR). It was found that NH4 group of salt interacted with lone pair C=O of CA chain since there were band shifts at C=O (from 1733 cm⁻¹ to 1724 cm⁻¹) and NH4⁺ group (from 1630 cm⁻¹ to 1620 cm⁻¹). Salt provides CA chain with charge carriers (or mobile ions) and thus increases the conductivity from $\sim 2 \times 10^{-10} \text{ S cm}^{-1}$ to 6.55 x 10⁻⁵ S cm⁻¹ by addition of 50 wt.% salt. Plasticizers further enhanced the ionic conductivity. CA with 35 wt.% salt was chosen to be plasticized with EC and PC. From FTIR studies, EC and PC plasticizers did not show any interaction with CA but did show interaction with salt. EC has enhanced ionic conductivity of CA-salt complexes better than PC and improved the conductivity up to four orders of magnitude (6.36 x 10⁻⁸ S cm⁻¹ to 1.75 x 10⁻⁴ S cm⁻¹) compared to PC by just three orders (from 6.36 x 10⁻⁸ S cm⁻¹ to 9.85 x 10⁻⁵ S cm⁻¹) by addition of 50 wt.% plasticizers. Temperature dependence studies has shown that the conductivity increase with increasing temperature indicates 'thermally assisted hopping' mechanism. Dielectric studies show the B-relaxation or orientation of dipolar acetyl group of CA in following electric field direction. The orientation become faster and time taken to orient become less since relaxation frequency (f_r) increases but relaxation time (τ) decreases as amounts of plasticizers as well as temperature increased. Two cells (Cell A and Cell B) with configuration of Zn || (CA-35 wt.% salt) + 50 wt.% EC || MnO2 and Zn || (CA-35 wt.% salt) + 50 wt.% PC || MnO2 respectively were fabricated and characterized. Cell A and Cell B stabilized the open circuit voltage (OCV) test at ~1.5 V and ~1.4 V respectively. The discharge capacity of both cells were nearly the same.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Before 1950's, most of the batteries used were either Leclanché zinc-carbon primary cell or secondary cell namely lead acid and nickel-iron (Owens et al., 1994). Since the advances in transistor and integrated circuit (IC)-termologies and for different portable electronic devices, the need for compact solid state batteries have been felt. Many new battery systems are now in use while the original batteries are still important because their performance characteristics have greatly improved (Linden., 1994). Conventionally, the electrolyte used in batteries is liquid. However, the availability of solid electrolytes with high ionic conductivity has stimulated the development of solid electrolyte batteries. The solid electrolytes could be polycrystalline, glasses, gel or polymer electrolytes. Polymer electrolytes is a preferred choice because polymers have many advantages like mechanical stability, chemical less reactivity, ability to form into different shapes like films, low cost and etc. The first solid polymer electrolyte was a polymer-salt complex discovered by Wright in 1973. Armand in 1975, was the first to propose that the polymer electrolyte can be used as solid electrolyte in battery application. Thin film solid polymer electrolyte batteries offer the possibility of safe battery design with good high rate capability (Owens et al., 1994).