Conductivity study on plasticized solid bio-electrolytes CMC-NH_4Br and application in solid-state proton batteries

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Abstract

This paper present the development of plasticized solid bio-electrolytes (PSBs) which has been accomplished by incorporating various composition of plasticizer namely ethylene carbonate (EC) with carboxy methylcellulose doped NH_4Br via solution casting method. The plasticized polymer–salt ionic conduction of PSBs has been analyzed by electrical impedance spectroscopy. Plasticization using EC in PSBs system assists the enhancement of NH_4Br dissociation and therefore increases the protonation process in the system. The highest ionic conductivity obtained for CMC–NH_4Br containing with 25 wt. % NH_4Br was achieved at 1.12 x 10^{-4} Scm^{-1} and improved to 3.31 x 10^{-3} Scm^{-1} when EC was added in PSBs system. The ionic conductivity-temperature for PSBs system was found to obey the Arrhenius relationships where the ionic conductivity increases with temperature. The solid-state proton batteries were assembled with the formation of Zn + $ZnSO_4.7H_2O$ || highest conducting PSBs system || MnO_2 and achieve with a maximum open circuit voltage (OCV) of 1.48 V at room temperature and showed good in rechargeablity performance with more than 10 cycles.

Keywords: bio-electrolytes; ionic conductivity; solid-state proton batteries; discharge capacity.

1.0 INTRODUCTION

Solid electrolytes based on polymer materials have received great attentions in electrochemical devices application due to their advantages such as good contact electrode-electrolyte and ease to produce [1]. In comparison to synthetic polymer, polymer natural based have been reported to be highly potential and suitable for development in polymer electrolytes system and this due the low cost material, bio-degradable and easy to handle [2, 3]. Amongst those types of biopolymer, carboxymethyl cellulose (CMC), a natural anionic polysaccharide which is widely used in many industrial and research sectors [4-6].

Generally, solid polymer electrolytes (SPEs) based polymer-salt complexes are normally insufficient for the application in electrochemical device due to low in ionic conductivity [7]. In order to develop polymer electrolytes with high conductivity, several approaches had been conducted such as polymer blending, copolymerization and addition of ceramic filler or plasticization in polymer-salt complexes. Plasticization is most common technique use by researchers in order to improve the conductivity of an electrolyte. Plasticizer such as ethylene carbonate, poly carbonate, dibutyl phthalate, dimethylformamide and poly ethylene was added into polymer-salt complexes has been reported for improvement in the mechanical stability of the sample hence enhance the ionic conductivity [8-10]. Plasticizer play a role by assists the dissolution and dissociation of salt, hence increases transport properties of polymer electrolytes [11]. Moreover, the introducing of plasticizer in polymer-salts complexes can increase the amorphous content and lower the value of glass transition temperature (*Tg*) [12]. Previously, we have reported on CMC doped NH_4Br system and have found that CMC incorporated with 25 wt. % NH_4Br achieved the optimum conductivity value of 1.12 × 10^{-4} S cm^{-1} [13]. In this work, CMC doped 25 wt. % NH_4Br and plasticized with various amounts of ethylene carbonate (EC) is presented. The highest conducting sample in this work is applied in the fabrication of solid-state proton batteries.

2.0 METHODOLOGY

2.1 Preparation of plasticized solid bio-electrolytes

In this work, a series of PSBs films were prepared using solution casting technique contain with CMC (Acros Organics Co., D.S. 0.7, with average molecular weight is 90000) doped 25 wt. % NH_4Br (due to the highest ionic conductivity from the previous work) [13] and addition of ethylene carbonate, EC (Sigma Aldrich Co.) in different amount (wt%). 2 g of CMC was dissolved in distilled water. Then, the CMC solution was added with 25 wt. % NH_4Br and the mixture was stirred