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## Effect of ZnS Dispersoid in Structural and Electrical Properties of Plasticized CA-NH<sub>4</sub>I

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### Abstract

Plasticized solid polymer electrolytes composed of cellulose acetate (CA) host polymer, ammonium iodide (NH<sub>4</sub>I) salt, propylene carbonate (PC) plasticizer were prepared by solution cast technique. The highest room temperature ionic conductivity ( $1.17 \times 10^{-4} \text{ S cm}^{-1}$ ) was achieved for sample with composition of CA: 25 wt. % NH<sub>4</sub>I: 40 wt. % PC. The addition of zinc sulfide (ZnS) dispersoid ceramic filler to the highest conductivity of plasticized CA-NH<sub>4</sub>I system enhanced the ionic conductivity up to  $6.24 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy confirmed the complexation between polymer and salt. The disruption of the crystalline peaks of ZnS and NH<sub>4</sub>I on the X-ray diffraction (XRD) pattern of CA-NH<sub>4</sub>I, plasticized CA-NH<sub>4</sub>I and composited CA-NH<sub>4</sub>I-PC established the complexation between polymer and salt were takes place and reduce the crystallinity of the samples and hence increasing in ionic conductivity. The transference number suggested that the charge transport is predominantly due to ions.

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### 1. Introduction

Solid polymer electrolytes (SPEs) have attracted widespread attention in recent years due to possibility of device applications [1, 2]. SPEs are lightweight, show good thin film forming ability, processing ease, flexibility and elasticity [3]. However its major drawbacks are low ionic conductivity at room temperature and poor electrode-electrolyte contact. Many attempts have been adopted to encounter these issues viz

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blends [4-6], plasticization [7-9] and dispersal of ceramic fillers [10-12]. The incorporation of plasticizers into SPEs has contributed in enhancement of ion pair dissociation into free ions, leading to high ionic conductivity [7, 13]. The interaction between polymer chain and plasticizer will speed up the viscoelastic response of the polymer and increase the ionic mobility in the electrolyte hence enhance ions transport in electrolytes which results in high ionic conductivity [14-15]. This paper focuses on developing composite polymer electrolytes in the presence of propylene carbonate (PC) as the plasticizer and zinc sulfide (ZnS) as the ceramic filler which anticipated to possess high ionic conductivity while maintaining the ability to stand freely in the thin film form.

## 2. Experimental

Cellulose acetate (CA), ammonium iodide ( $\text{NH}_4\text{I}$ ) and acetone solvent were purchased from Sigma-Aldrich. The salted CA-based SPEs were prepared by doping various weight percentages of  $\text{NH}_4\text{I}$ . Each composition was stirred using magnetic stirrer for 24 hours at room temperature until homogenous solution obtained. The solution was then poured into a glass Petri-dish and left to dry at room temperature (303 K) until a thin film formed. The steps were repeated for preparing plasticized and composited CA- $\text{NH}_4\text{I}$  samples. The different weight percentages of PC and ZnS were added into the highest conducting polymer-salt and plasticized polymer-salt solutions, respectively. In order to prepare well dispersed samples, CA- $\text{NH}_4\text{I}$ -PC and ZnS solutions were stirred separately using the magnetic stirrer and sonochemical disperser, respectively. Both solutions were then mixed together and stirred again using sonochemical disperser until viscous-homogenous solution appeared. The composited solution was then poured into Petri-dish and dried in room temperature for 24 hours to form a thin film. The films were kept in desiccator to eliminate the trace of water before being characterized. Several methods were employed to characterize the physical and electrical properties of the prepared samples including impedance spectroscopy, ATR-FTIR spectroscopy, X-Ray diffraction, UV-Visible and transference number.

## 3. Results and discussion

The plasticized conducting polymer solid electrolyte obtained with the composition of CA: 25 wt. %  $\text{NH}_4\text{I}$ : 40 wt. % PC was improved the ionic conductivity up to  $1.17 \times 10^{-4} \text{ S cm}^{-1}$  compare to unplasticized sample (CA: 25 wt. %  $\text{NH}_4\text{I}$ ) only demonstrated the highest ionic conductivity around  $8.42 \times 10^{-8} \text{ S cm}^{-1}$  at room temperature. The presence of plasticizer favored the ionic mobility by dissociating of undissociating salt into ions lead to increase more free mobile ions and hence increasing the conductivity [9]. As would be expected that the plasticizers have great influenced on the physical and electrical properties of polymer electrolytes and the ability of plasticizers to penetrate into polymer chains and increase polymer chain flexibility results improved the ionic conductivity. However, the mechanical properties of the samples will decrease at high plasticizer content. To encounter this problem, ZnS dispersoid was introduced into the plasticized electrolyte system. ZnS dispersoid plays a role as filler and will increase mechanical properties and improved the electrode-electrolyte contact, which enhances the conductivity ( $6.24 \times 10^{-4} \text{ S cm}^{-1}$ ).

Fig. 1 represents the dielectric constant,  $\epsilon_r$  of pure CA, CA- $\text{NH}_4\text{I}$ , plasticized CA- $\text{NH}_4\text{I}$  and composited CA- $\text{NH}_4\text{I}$ . As shown in Fig. 1, composited CA- $\text{NH}_4\text{I}$  exhibits the highest dielectric constant value. The addition of ZnS dispersoid increased the dielectric constant, which should lead to conductivity enhancement since the increase in dielectric constant will increase the number of dissociated ions. The real electric modulus,  $M_r$  of CA-based systems is illustrated in Fig. 2. The real electric modulus is seen to approach zero at lower frequencies suggesting the presence of an appreciable electrode that make negligible contribution to real electric modulus value.

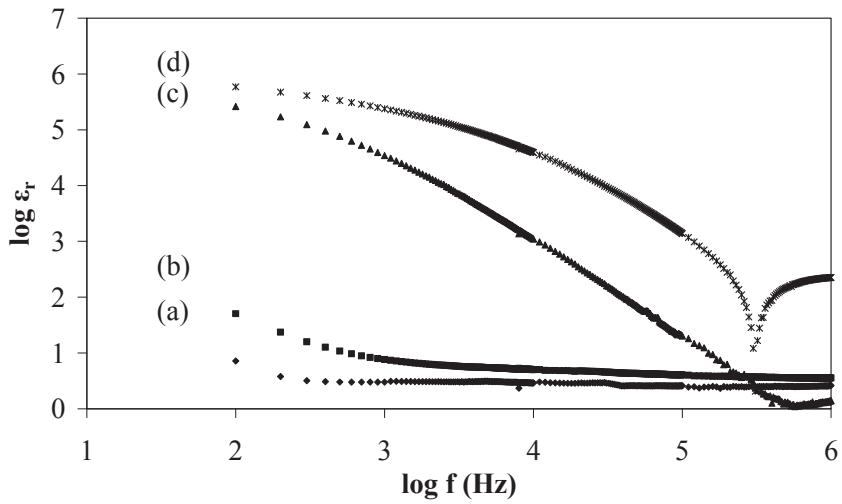


Fig. 1. Dielectric constant versus frequency for (a) pure CA, (b) CA-NH<sub>4</sub>I, (c) plasticized CA-NH<sub>4</sub>I and (d) composited CA-NH<sub>4</sub>I

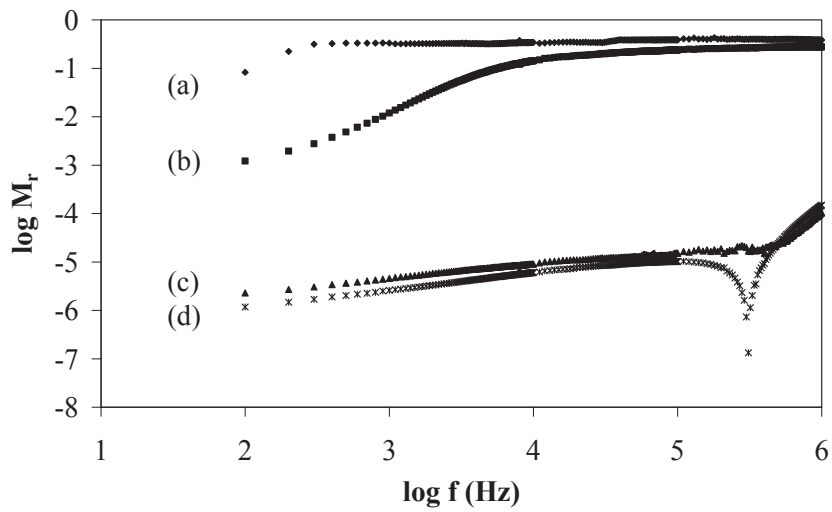


Fig. 2. Real electric modulus versus frequency for (a) pure CA, (b) CA-NH<sub>4</sub>I, (c) plasticized CA-NH<sub>4</sub>I and (d) composited CA-NH<sub>4</sub>I

The ATR-FTIR spectra of different CA-based systems in region 2000-600  $\text{cm}^{-1}$  is shown in Fig. 3. It is noticeable that there are three new peaks appear due to addition of PC (Fig. 3(e)). The peaks appear at 1795, 783 and 718  $\text{cm}^{-1}$  is similar to the pure PC indicating that the PC did not interact with salt in the polymer-salt complexes. The C-O-C stretching peak at 1041  $\text{cm}^{-1}$  and CH symmetrical bending mode at 1373  $\text{cm}^{-1}$  of CA have shifted towards higher wavenumbers and increased in intensity. This indicates that the complexation has occurred between polymer and salt. It can also be observed that the peaks remain at the same position in composited CA-NH<sub>4</sub>I system (Fig. 3 (g)) indicating that there is no interaction between ZnS dispersoid and other components in polymer electrolytes.

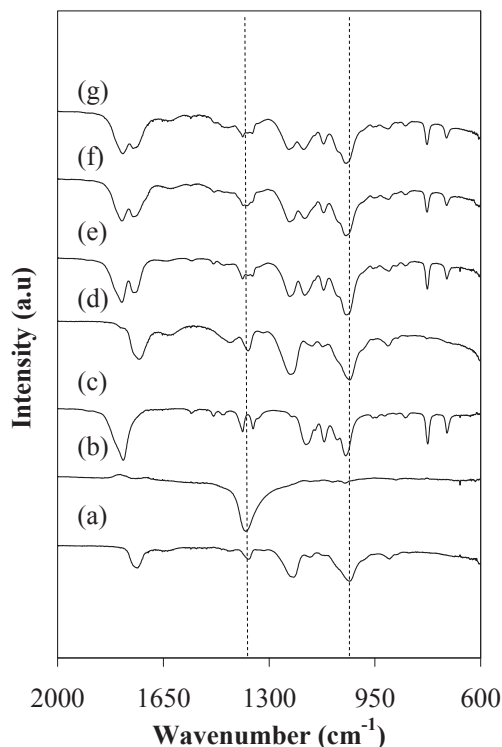


Fig. 3. The ATR-FTIR spectra of (a) pure CA, (b) pure NH<sub>4</sub>I, (c) pure PC, (d) CA-25 wt. % NH<sub>4</sub>I, (e) CA-40 wt. % PC, (f) CA-25 wt. % NH<sub>4</sub>I-40 wt. % PC and (g) CA-25 wt. % NH<sub>4</sub>I-40 wt. % PC-3 wt. % ZnS

The XRD patterns of the highest conductivity of electrolyte for unplasticized, plasticized and composited CA systems are shown in Fig. 4. The diffractogram of pure CA exhibits the halo crystalline nature seems to reduce by the addition of NH<sub>4</sub>I. The crystallinity of the CA-NH<sub>4</sub>I film seems to decrease by the introduction of ZnS and hence improve the ionic conductivity. This result is in agreement with conductivity studies where composited system posses highest conductivity.

The plots of transference number for plasticized and composited CA-NH<sub>4</sub>I systems are illustrated in Fig. 5. The value of the ionic transference number ( $t_i$ ) for plasticized system is 0.977, suggesting that the charge transport in this polymer electrolyte film is predominantly due to ions. The incorporation of ZnS dispersoid into the plasticized system, was decreased the value of ionic transport, implying that ZnS

provides a small number of electronic charges but the major contribution to this conductivity is still due to ions ( $t_i = 0.905$ ).

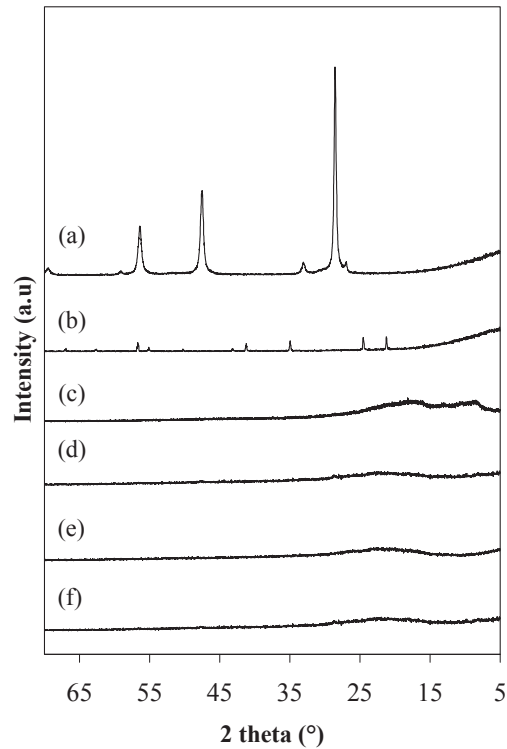


Fig. 4. The XRD pattern of (a) ZnS, (b)  $\text{NH}_4\text{I}$ , (c) CA, (d) CA-25 wt. %  $\text{NH}_4\text{I}$ , (e) CA-25 wt. %  $\text{NH}_4\text{I}$ -40 wt. % PC and (f) CA-25 wt. %  $\text{NH}_4\text{I}$ -40 wt. % PC-3 wt. % ZnS

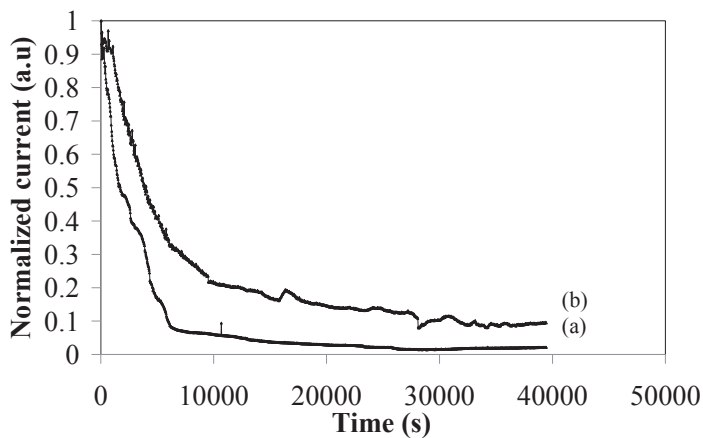


Fig. 5. The plot of polarization current as a function of time for (a) CA-25 wt. %  $\text{NH}_4\text{I}$ -40 wt. % PC and (b) CA-25 wt. %  $\text{NH}_4\text{I}$ -40 wt. % PC-3 wt. % ZnS

#### 4. Conclusion

The room temperature conductivity of the electrolyte was improved by adding ZnS dispersoid into polymer matrix. The ATR-FTIR analysis showed that complexation has occurred between polymer and salt while ZnS dispersoid do not interact with other materials as no significant changes in peaks of composited CA-NH<sub>4</sub>I system. The XRD studies showed that the addition of ZnS reduced the crystallinity of the samples.

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