

Electrical Properties of Plasticized Chitosan-Lithium Imide with Oleic Acid-Based Polymer Electrolytes for Lithium Rechargeable Batteries

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Abstract. Solid polymer electrolytes (SPEs) were prepared and their electrochemical characteristics were characterized. The composition of SPEs containing chitosan, lithium trifluoromethane sulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) and oleic acid (OA) was optimized employing ac impedance measurements at various temperatures. The electrical conductivity of the SPEs with OA shows the highest value and the presence of OA does not change the structure of the polymer.

1. Introduction

The importance of ionic motion in solvent free polymeric matrices has only been recognized during the past decade [1,2]. The electrochemical properties of such polymers are limited by the solvent and the conductivity occurs via interconnected structures of solvent and ions. In polymer electrolytes, the polymer acts as solvent for a salt which will be partially dissociated in the matrix, leading to ionic conductivity. The polymers contain polar groups that can act as electron donors. These electrons will form a dative bond with the ions of the incorporating salt. The polymer is said to solvate the salt if there is direct interaction between the lone pair electron of the heteroatom such as oxygen or nitrogen in the polymer and cation of the salt. In chitosan, the nitrogen atom in the amine functional group and the oxygen atom in the hydroxyl functional group each bear a lone pair electron [3,4]. The cation of the inorganic salt will form a dative bond with the oxygen or nitrogen and hence a chitosan-salt complex is formed. Hence, to establish chitosan as an ionic conducting polymer it is necessary to show that complexation occurs between the heteroatom in chitosan and the cation of the salts. The addition of plasticizers into the polymer will increase the value of electrical conductivity. This is due to the ability of the plasticizer to

disrupt the crystalline phase in the polymer so as to become more amorphous and the presence of the plasticizer also acts as a lubricant in the polymer electrolytes [5]. In the present study, oleic acid (OA) is used as plasticizer with the presence of lithium salt in chitosan acetate (CA).

2. Experimental Description

Chitosan powder used in the present investigation was obtained from Sitiawan, Perak, Malaysia. All samples were prepared by the solution cast technique. Chitosan with 1×10^{-6} gmol⁻¹ of molecular weight was used. A stock solution of composition 1.0 g chitosan in 100 ml 1% acetic acid was prepared. The inorganic salt, recrystallized lithium trifluoromethane sulfonimide $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or lithium imide was taken in different stoichiometric ratios and dissolved in the stock solution. The mixtures were continuously stirred with a magnetic stirrer for several hours at room temperature to ensure complete dissolution of the salt. The solutions were then cast into different plastic Petri dishes and allowed to dry at room temperature. The films were formed after about several weeks. The resulting films were then kept dry in a desiccator for further experiments. To enhance the conductivity, the sample with the highest electrical con-

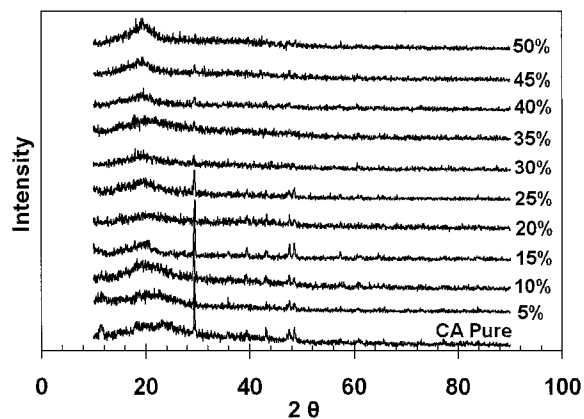


Fig. 1. X-ray diffraction patterns of CA pure and CA with different wt.% of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

ductivity was added with different ratio of oleic acid as a plasticizer. The above method was repeated to prepare the plasticized films. All samples were characterized by several techniques in order to determine the characteristics of the chitosan-based electrolytes. These techniques include X-ray diffraction, infrared spectroscopy and impedance spectroscopy.

3. Results and Discussion

Figure 1 shows the XRD patterns of the sample prepared. It can be observed that the pure chitosan acetate sample is partially crystalline with high intensity peak at 2θ angle 29.45° , 43.2° , 47.4° and 48.55° , and partially amorphous. On addition of salt, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ the peaks attributed to chitosan acetate in the range $20^\circ \leq 2\theta \leq 50^\circ$ gradually disappear and at above 35 wt.% of salt addition the peak completely fade away. The film seems to be completely

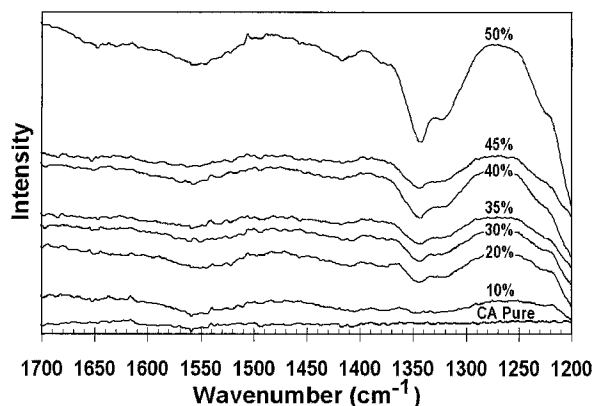


Fig. 2. The FTIR spectra of pure chitosan and different wt.% of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in chitosan acetate films.

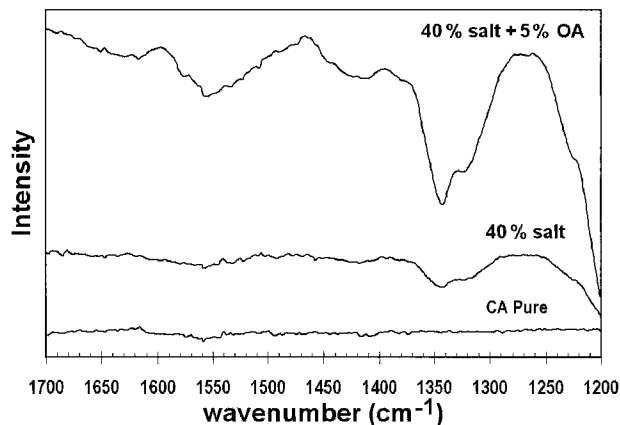


Fig. 3. The FTIR spectra of pure chitosan, $\text{CA-LiN}(\text{CF}_3\text{SO}_2)_2$ (40 wt.%) and $\text{CA-LiN}(\text{CF}_3\text{SO}_2)_2$ (40 wt.%) + OA (5 wt.%).

amorphous upon addition of 40 wt.% $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salt.

Figure 2 shows the FTIR spectra of some of the samples prepared and the spectrum of pure chitosan is quite similar to that given by Muzzarelli [6]. There are two main peaks observed i.e. at wavenumbers 1660 cm^{-1} and 1555 cm^{-1} which are due to vibrations of $\text{O}=\text{C}-\text{NHR}$ and NH^{3+} respectively. These peaks are observed to have shifted to lower wavenumbers due to the formation of the chitosan acetate where the hydrogen of the acetic acid has formed a dative bond with the nitrogen of the chitosan functional group. The shifting of these peaks particularly depends on the types of cation interacting with chitosan acetate, the type of counter anion and the salt concentration [4]. The position of this band is shifted to lower wavenumbers indicating that some complexation has occurred between the salt and the nitrogen atom or between the acetic acid and the nitrogen atom of the chitosan functional group. However, when more salt is added to the solution, the shift increases further towards lower wavenumbers. This implies that complexation does occur between the salt and polymer. Therefore, chitosan acetate can be considered as a successful host polymer for the dissolution of the lithium imide salt. Figure 3 depicts that the spectra of plasticized chitosan acetate is almost similar to that of the pure chitosan acetate film. This implies that oleic acid does not react with the host polymer and acts as a lubricant.

Impedance studies show that the highest conductivity value is obtained when 40 wt.% lithium imide was added into 1.0 g CA sample. Figure 4 shows the conductivity plot of the samples and it appears to go through a maximum value at 40 wt.% salt and dramatically de-

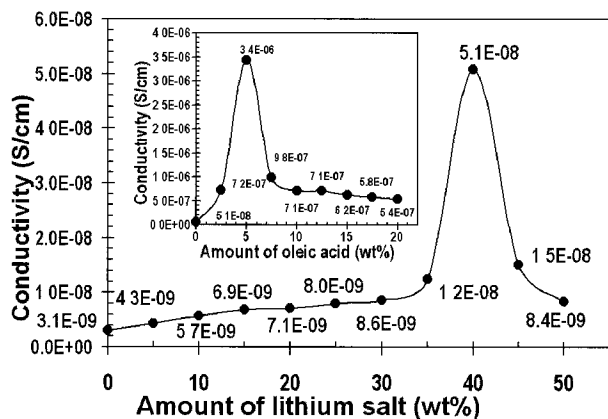


Fig. 4. Conductivity versus amount of salt in CA-LiN(CF₃SO₂)₂ films and the conductivity versus amount of oleic acid in [CA-LiN(CF₃SO₂)₂ - OA] films (insert).

creases at higher salt concentrations. The increase in electrical conductivity at lower salt concentration implies that the number of available mobile ions was proportionally increasing with doping salt. The presence of mobile ions also will increase the amorphous structure of the polymer and therefore ion migration easily takes place [7]. When more than 40 wt.% of salt concentration has been added, the value of electrical conductivity drastically dropped. This implies that the sample become crystalline again. This phenomenon exists due to the occurrence of non-conducting ion-pair [8]. When more ion pairing exists in the bulk, the lithium ion that has interacted with a nitrogen atom in the chitosan acetate structure will be congested and as a result there is a decrease in ionic migration and hence a reduction in the segmental motion of polymer chains [9]. It can also be explained that the mobility of ions depend on the salt concentration and the nature of organic salt in which interactions with the polymeric chain occur. As such, the result above agrees with the XRD and FTIR studies where the complexation is seen to occur between the salt and the polymer. Due to the complexation, the conductivity of the polymer electrolytes was enhanced. From Fig. 4, it can be inferred that the addition of plasticizer increases the conductivity of the salted polymer to two orders of magnitude when compared to the plasticizer free samples at room temperature. The increase in the ionic conductivity of the sample has been explained before [5]. According to Huang and co-workers [5], polymer electrolytes containing plasticizer is called a mixed phase electrolyte system in which the plasticizer functions as a lubricant and make the ions more mobile within the polymer system. This means that

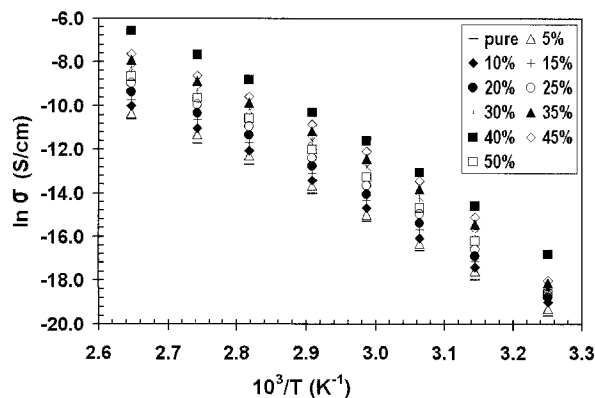


Fig. 5. Arrhenius plot for different wt.% of LiN(CF₃SO₂)₂ in chitosan acetate films.

the components in the system are just mixed together without interacting with each other. However, the addition of more than 5 wt.% of oleic acid causes the electrical conductivity to decrease. This may be attributed to the formation of linkages between the plasticizer itself causing it to recrystallize and resulting in a decrease in ionic conductivity.

Figure 5 shows that the conductivity-temperature dependence is seen to show Arrhenius behavior with a regression value of about unity. It can be implied that the conductivity is thermally assisted. It has been explained that, the conductivity mechanism is quite similar to that occurring in ionic crystals where ions (produced by thermal agitation) jumps into neighboring vacant sites [10]. So the same explanation seems plausible in the case of the present investigation. It can also be seen that the samples do not show any abrupt depletion indicating the fact that these electrolytes exhibit a completely

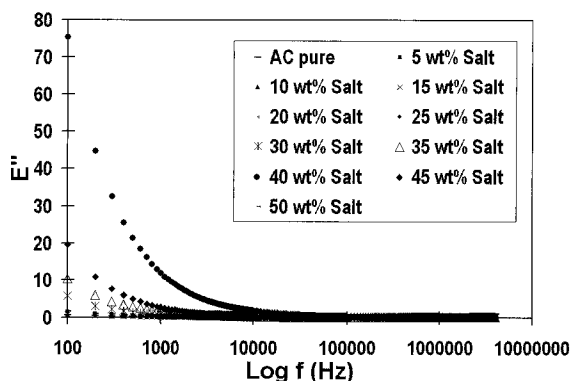


Fig. 6. Dielectric loss versus frequency for different wt.% of LiN(CF₃SO₂)₂ in chitosan acetate films.

amorphous structure and the increase in conductivity with temperature may be linked to the decrease in viscosity hence increasing the chain flexibility [11].

Figure 6 shows that the imaginary part of the dielectric loss increases with decreasing frequency. This is attributed to the space charge effect at low frequency which is due to the accumulation of charges at the electrode-electrolyte interface. As the frequency increases, the electric field changes direction very rapidly so that the charges are prevented from accumulation at the interface for a long time [12]. Hence, at high frequency there are more mobile species in the bulk rather than at the interface. Thus the dielectric loss decreases but the conductivity increases with increasing frequency.

4. Conclusion

The information given by XRD spectroscopy shows that the lithium salt disrupts the crystalline nature of the polymer indicating that complexation has occurred between the salt and polymer. These complexations were confirmed by FTIR spectroscopy and the presence of plasticizers does not change the structure of the host polymer. The conductivity value of pure chitosan acetate was enhanced from $3.1 \times 10^{-9} \text{ Scm}^{-1}$ to $5.1 \times 10^{-8} \text{ Scm}^{-1}$ by addition of 40 wt.% of lithium salt. Upon addition of 5 wt.% of oleic acid as plasticizer, the electrical conductivity value has gained three orders of magnitude compared to the pure sample with a conductivity of $3.4 \times 10^{-6} \text{ Scm}^{-1}$. The conductivity that has been obtained by adding lithium imide and OA the plasticizer to chitosan will make this material potentially interesting for electrochemical devices.

5. Acknowledgement

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6. References

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