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XRD and Surface Morphology Studies on Chitosan-Based Film Electrolytes

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Abstract: Chitosan was used as the host polymer with lithium acetate (LiOAc) as the doping salt and Palmitic Acid (PA) and Oleic Acid (OA) as plasticizers. The highest conductivity value was obtained for film containing salt 55 wt. % CA and 45 wt. % LiOAc. At this composition, the surface of the film shows clusters of needle or dendrite-like structures. The x-ray diffractogram shows peaks at $2\theta = 16^\circ, 21^\circ, 26^\circ$ and 31° attributed to the salt. The peaks are small and relatively broad in comparison to sample with equal amounts of polymer and salt. The surface of the film shows that the salt has recrystallized out of the film. This could reduce the number of mobile lithium ions in the film and thus lower the conductivity of this sample. Both films formed from solution containing 1.0 g chitosan +0.20 g oleic acid and containing 1.0 g chitosan +0.40 g oleic acid have a porous surface. Such films could be suitable as a separator for lithium ion cells. This surface morphology is different from those films obtained from a solution containing 1.0 g chitosan +0.40 g ethylene carbonate. The highest conducting OA plasticized film contains 50 wt. % CA, 40 wt. % LiOAc and 10 wt. % OA. The surface looks soft and spongy with tunnel-like structures.

Key words: Chitosan, lithium acetate, palmitic acid, oleic acid, XRD, surface morphology

INTRODUCTION

Polymer electrolytes have potential applications in electronic devices such as secondary lithium batteries (Stephan and Nahm., 2006; Park *et al.*, 2006), light emitting cells (Wenzl *et al.*, 2005; Wang *et al.*, 2003), glass tinting layer for smart windows (Kraft *et al.*, 2006), chemical sensors (Sakthivel and Weppner, 2006; He *et al.*, 2006) and capacitors (Yang *et al.*, 2005; Hashmi *et al.*, 2004). The advantages of these Solid Polymer Electrolytes (SPE) are due to their desirable characteristics that show good compatibility with electrodes; no leakage, low self-discharge in batteries, elasticity and easy to process (Stephan and Nahm., 2006; Masuda *et al.*, 2006). One of the problems in fabricating polymer batteries is that once the salt is incorporated in the polymer, the adhesive property of the electrolyte to the electrode material is significantly reduced. However, upon comparing chitosan acetate films and salted chitosan acetate films with plasticizers such as Ethylene Carbonate (EC), it is thought that the use of suitable plasticizers may help to improve such adhesive property.

Chitosan itself is a hydrophilic polymer, which absorbs water at ambient temperature. It is claimed that the cationic nature of chitosan makes it particularly suitable for impounding fatty acids (Lee *et al.*, 2005; Pichavant *et al.*, 2005). Thus, hydrophilicity is reduced. The formation of hydrophobic aggregates may be due

to sorption capacities of chitosan towards some free fatty acids which were ranked in the following order (Ahmad *et al.*, 1995); stearic acid >oleic acid>palmitic acid >linoleic acid >myristic acid. It has also been proven by Ahmad *et al.* (1995) that fatty acids absorbed by chitosan may be due to a weak hydrogen bond or by physical interaction since the IR spectrum and TGA thermogram of chitosan is very similar to that of chitosan after treated with fatty acids. This phenomenon will be more advantageous in reducing the water present in chitosan-based polymer electrolyte. Therefore the addition of fatty acid such as palmitic acid and oleic acid in the chitosan-electrolyte may be useful for the good performance of chitosan-based lithium ion polymer cells.

In the effort to obtain a polymer electrolyte with the optimum electrical conductivity at room temperature, the salt and plasticizer contents need to be optimized. Conductivity studies are sometimes correlated with x-ray diffraction studies in an attempt to explain the variation of conductivity with salt concentration. In the present study, x-ray diffraction and surface morphology studies were carried out in order to understand better the variation of conductivity with salt concentration in the presence of plasticizers content for salted-polymer samples.

X-ray Diffraction (XRD) analyses were carried out to determine the occurrence of complexation and whether the material is amorphous or crystalline (Sivakumar *et al.*, 2006). To substantiate these results, Scanning Electron

Microscopy (SEM) was performed. SEM is one of the most versatile and widely used tools for the study of surface morphology. In this research, SEM was employed in the study of the morphology of the surface of the chitosan acetate films and compared to the surface morphology of films containing the LiOAc doping salt and oleic acid plasticizer. The surface morphology will be correlated with results from X-ray diffraction to shed some light on the variation of conductivity with salt and plasticizer content. From SEM, samples with soft surface and low degree of roughness, can be determined easily. Such samples can be useful as an electrolyte in an all solid-state battery.

MATERIALS AND METHODS

Sample preparation: 1.0 g of chitosan powder (Aldrich) was mixed with 0.10 to 1.0 g of LiOAc (Aldrich) and dissolved separately in different sets of chitosan acetate (CA) solution in 100 mL of 1.0% acetic acid solution. The solutions were then poured into different plastic petri dishes and left to dry at room temperature (27°C) for film formation. To the highest chitosan-salt conducting sample, this solution composition was used to prepare a plasticized chitosan-salt film by adding different amounts of PA and OA from 0.10 to 0.50 g. Three samples containing chitosan acetate and CA+PA and CA+OA, all without the inorganic salt were also prepared to act as controls. The preparation of these samples were carried out at Solid State Ionics and Devices (SSID) Research Lab, Universiti Teknologi MARA (UiTM).

X-ray diffraction (XRD): In this work, X-ray diffraction were carried out using a Shimadzu XD-5 Diffractometer which employs Cu-K α x-radiation of wavelength $\lambda = 1.5418 \text{ \AA}$ between a 2θ angle of 15° to 70° . X-ray diffraction was carried out to determine the nature of the materials whether a material is amorphous or crystalline.

Scanning Electron Microscopy (SEM): The SEM provides useful analysis of surface structures and morphology. The nature and the morphology of a polymer electrolyte film surface is an important property for a polymer electrolyte. SEM was carried out using the Phillips 515 scanning electron microscope at the Physics Department, University of Malaya. Scanning electron microscopy was performed in order to understand further the results obtained from other techniques such as XRD. XRD may show peaks that can be attributed to the salt, plasticizer or polymer. SEM on the other hand, shows how these crystalline structures look like.

RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of pure chitosan acetate (CA). The surface is smooth and homogenous except for some crystalline structures. These crystalline structures contribute to the peaks in the XRD pattern of CA. The XRD pattern of CA is shown in Fig. 2 with peaks

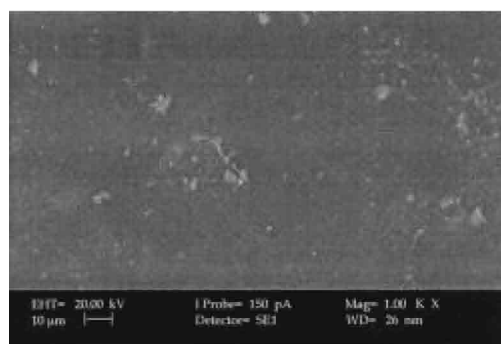


Fig. 1: SEM micrograph of chitosan acetate (CA) film

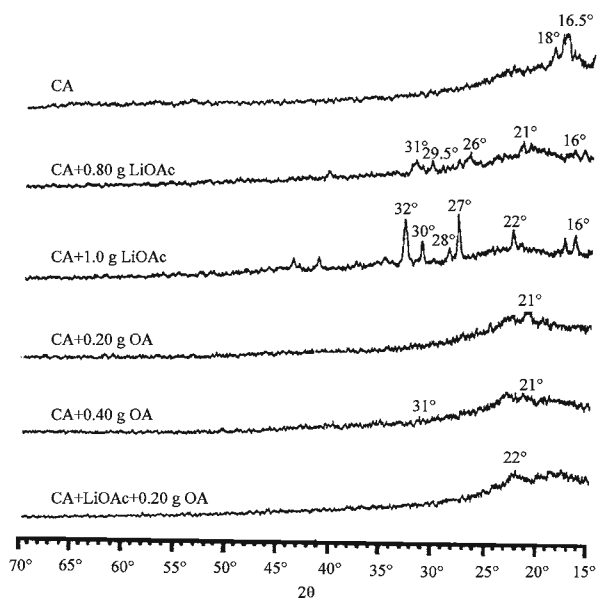


Fig. 2: X-ray diffraction patterns of chitosan films

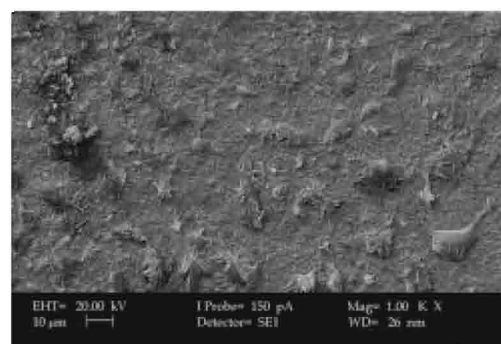


Fig. 3: SEM micrograph of CA+0.80 g LiOAc

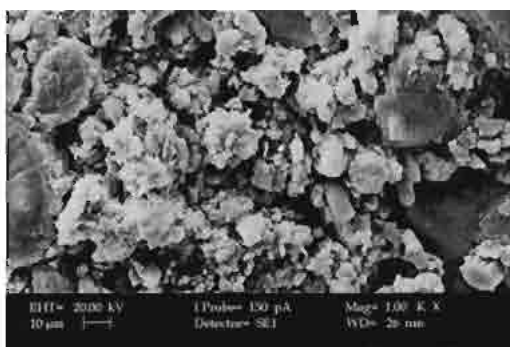


Fig. 4: SEM micrograph of CA+1.00 g LiOAc

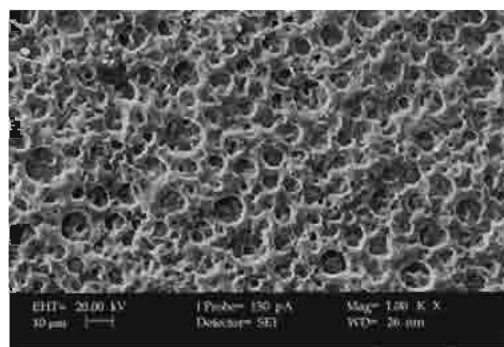


Fig. 6: SEM micrograph of CA+0.40 g OA

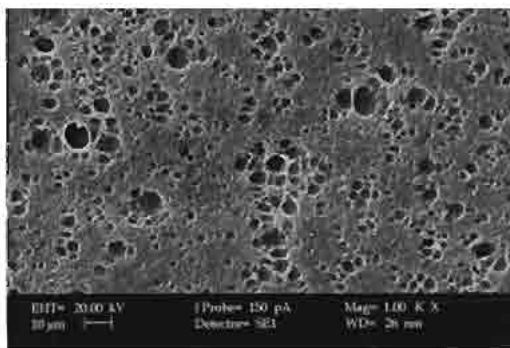


Fig. 5: SEM micrograph of CA+0.20 g OA

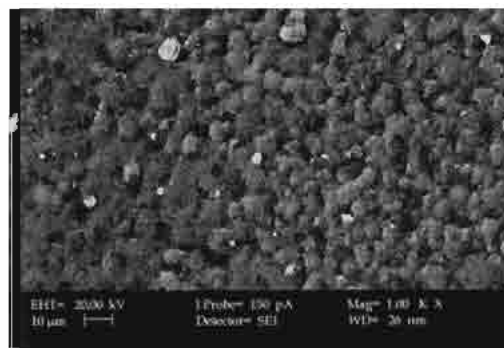


Fig. 7: SEM micrograph of CA+LiOAc+0.20 g OA

at $2\theta = 16.5^\circ$ and 18° . Ritthidej *et al.* (2002) have also reported peaks in the XRD pattern of chitosan-acetic acid salts in the 2θ angle range between 16° and 20° .

Figure 3 depicts the surface morphology for the film with the highest conductivity, containing salt which has a composition of 55 wt. % CA and 45 wt. % LiOAc. The details report of the conductivity studies on this polymer electrolyte was reported in this journal (Yahya *et al.*, 2006). The surface of these samples consists of needle-like crystalline structures. The XRD peaks are shown in Fig. 2. Thus the incorporation of salt has made the chitosan acetate surface, rough and uneven. This could explain why the incorporation of salt to a polymer reduces the adhesion to electrode materials.

On further addition of 1.0 g salt, CA + 1.0 g LiOAc, the conductivity dropped. This can be understood on examination of the surface morphology (Fig. 4). The surface of the film is partially covered by some crystalline structures. XRD shows that these crystalline structures are that of the LiOAc salt. This suggests that when equal weight percentage of salt and chitosan was added, ion reassociation (Khar *et al.*, 2006) takes place and crystallizes out at the surface. Thus SEM has provided a proof for ion reassociation. The reassociation and crystallization out at the surface, reduces the number of mobile ions in the material and led to a decrease in conductivity.

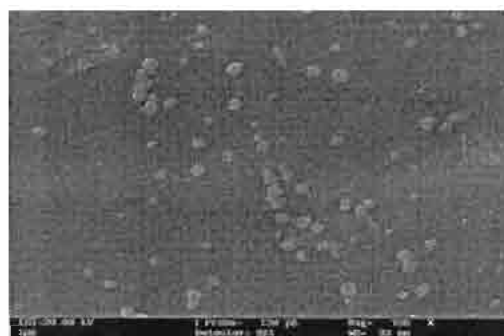


Fig. 8: SEM micrograph of CA+0.40 g EC

On addition of 0.20 g OA to CA (Fig. 5), the surface of the sample appears like a sponge. The peak at 21° in the XRD pattern in Fig. 2 is attributed to OA. The diameter of the voids varies between a few microns to about $10\ \mu\text{m}$. It is possible that the addition of OA to the chitosan-acetic acid-water solution during preparation has reduced the surface tension of the solution and increased the wetting ability of the solution. When the solution is cast to form the film, the water molecules in the solution will spread from all sides of the container. While spreading, the water molecules will push the chitosan and plasticizer molecules to its edges forming a boundary that separates the water molecules and the chitosan-plasticizer phase. After some time, the water molecules stop spreading and regions rich

in water molecules and rich in chitosan and plasticizer are formed. On drying, the water molecules evaporate and the region rich in chitosan and plasticizer forms the surface of the film. The region rich in water molecules will be left as voids that are observed in the micrograph. The voids extend into the bulk of the film.

The XRD pattern for the sample containing 0.40 g OA (Fig. 2) shows peaks at 21° and 31°, which are assigned to OA. In Fig. 6, the surface is more porous and the pores can be seen to extend into the bulk as observed in the micrograph of the former sample. The sample containing 0.40 g OA is more spongy-like. Such porous films could be useful as separators in lithium ion batteries. The separators in lithium ion batteries are porous. The SEM micrograph of the salted sample containing 0.20 g OA is depicted in Fig. 7. The voids as observed in Fig. 5 are also present. Thus the “soft-spongy” like texture could be due to some interactions with the salt since in the absence of salt only voids are observed on the surface of the film, (Fig. 5).

Figure 8 shows the SEM micrograph of CA containing 0.40 g EC. The surface is quite smooth compared to the softer and spongy characteristic of the fatty acid plasticized film. A smooth surface could make the electrolyte/electrode adhesion less strong.

CONCLUSION

Surface morphology studies complemented by XRD can help to shed some light to conductivity-salt variation. It can also provide an alternative proof for ion reassociation that usually takes place in polymers that has been added with a large amount of salt. From microscopy, it may be possible to predict a particular application for the polymer membrane due solely from its morphology.

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