Polymer batteries fabricated from lithium complexed acetylated chitosan

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Abstract

It is found that 0.8 g lithium nitrate added to a solution of 1 g chitosan dissolved in 100 ml 1% acetic acid produces a film, via the solution cast technique, with a maximum electrical conductivity of the order of 10^{-4} S cm^{-1}. This film is amorphous. For battery fabrication, metal powder and hydrogen storage material are used for the anode, and a metallic oxide (MnO_2) for the cathode material. The anode contains a mixture of zinc and zinc sulfate in the ratio of 3:1. Batteries with configurations $Zn + ZnSO_4 \cdot 7H_2O/LiCAC/I_2 + C$ and $Zn + ZnSO_4 \cdot 7H_2O/ LiCAC/MnO_2 + C$ (LiCAC = lithium complexed acetylated chitosan) provide open-circuit voltages of 1.113 and 0.765 V, respectively. The discharge characteristics of the batteries are presented. Unfortunately, only short lifetimes and small discharge currents can be obtained. This is possibly due to incompatibility between the electrode materials and the electrolytes.

Keywords: Chitosan; Lithium; Polymer electrolytes

1. Introduction

Chitosan is a biopolymer that may be considered as a binary heteropolysaccharide that contains residues of (1-4) linked 2-acetamide-2-deoxy-β-D-glucopyranose (GlcNac, **A**) and 2-amino-2-deoxy-β-D-glucopyranose (GlcN, **D**) [1]. It is a unique polysaccharide and attracts much attention in many fields such as manufacturing and medicine [2]. In its actual state, a chitosan film has a very low electrical conductivity. Although the structure of chitosan monomer has three hydrogens, they are strongly bonded to the structure and cannot be mobilized under the action of an electric field to make it a proton conductor. We are of the opinion that if chitosan is dissolved in acetic acid and the resulting solution is cast into a thin film, then the H^+ or H_3O^+ and CH_3COO^- ions in the 'acetylated chitosan' film will be dispersed in the immobilized chitosan solvent and these ions can be mobilized under the influence of an electric field. If H^+ or H_3O^+ ions are more mobile than the CH_3COO^- ions the film becomes a proton conductor. Further, if the electrical conductivity of this film increases, then it should be possible to produce a more ionically conducting film by dissolving chitosan in acetic acid solutions of increasing concentration since more H^+ (or H_3O^+) will be contributed by the acetic acid.

The above hypotheses can be tested by impedance spectroscopy. It is expected that the acetylated chitosan films produced by dissolving chitosan in acetic acid solutions of low concentration should exhibit higher bulk resistances in the 'Cole–Cole plot' than AC films produced by dissolving chitosan in acetic acid solutions of higher concentration. The plot of electrical conductivity versus acetic acid concentration should show a maximum of the type observed with plots of electrical conductivity versus doping concentration for other solid electrolytes, including polymer electrolytes. In this paper, a study is carried out on a chitosan biopolymer that was supplied by the Chitin and Chitosan Laboratory, National University of Malaysia. The results show that chitosan can be made an ionic conductor by dissolution in acetic acid and that the conductivity can be improved by adding monovalent ions to the acetic acid–chitosan solution. It is also possible to use this material for the fabrication of solid-state polymer batteries.

2. Experimental

2.1. Material preparation

1 g of chitosan was dissolved in different 100 ml 1% acetic acid solutions. To these, x g of lithium nitrate ($0 \leqslant x \leqslant 1.0$ g) was added in steps of 0.2 g. The solutions were cast into separate Petri dishes and left to dry by evaporation.

Table 1
Battery systems under investigation [a]

Battery	Configuration
Cell 1	$Zn + ZnSO_4 \cdot 7H_2O/LiCAC/I_2 + C$
Cell 2	$Zn + ZnSO_4 \cdot 7H_2O/LiCAC/MnO_2 + C$
Cell 3	$Zn + ZnSO_4 \cdot 7H_2O/salt-free\ AC/MnO_2 + C$
Cell 4	$Zn + ZnSO_4 \cdot 7H_2O/salt-free\ AC/I_2 + C$

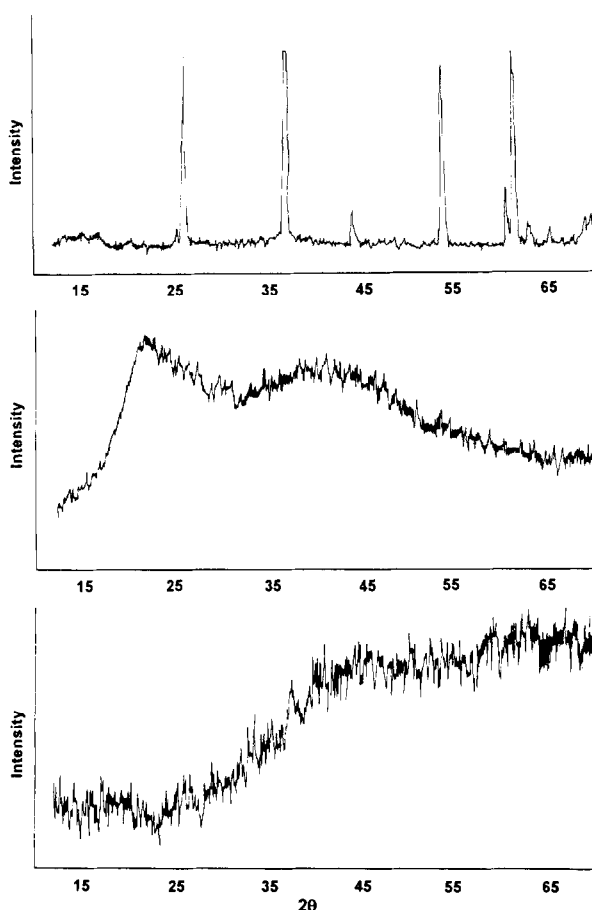[a] AC = acetylated chitosan; CAC = complexed acetylated chitosan.

Fig. 1. XRD patterns of (a) $LiNO_3$, (b) acetylated chitosan film, and (c) lithium complexed acetylated chitosan film.

2.2. Material characterization

2.2.1. Electrical conductivity

Electrical conductivity measurements were performed with a HIOKI 3520-01 LCR Hi Tester that was interfaced to a microcomputer. The frequency range was 40 to 100 kHz. The samples, or films, were placed between two discs in a die and then subjected to a pressure of 2500 kPa. The inner surface of the die was insulated. External connections to the bridge were achieved through connecting leads. The measurements were carried out at room temperature.

2.2.2. X-ray diffraction

X-ray diffraction (XRD) analysis of the films was performed with a compact diffractometer (Model PW1840). X-radiation of wavelength 154.2 pm was used.

2.3. Battery fabrication

Batteries were fabricated both from the film that gave the highest electrical conductivity, and from the salt-free film to provide a benchmark. 0.3 g of zinc powder and 0.1 g of $ZnSO_4 \cdot 7H_2O$ were mixed with carbon cement. The mixture was painted on one side of the film to form the anode of the battery, while a mixture of carbon cement and 0.5 g of active material (either iodine or MnO_2) was painted on the other side as the cathode. Table 1 shows the battery systems that were fabricated.

2.4. Battery characterization

The open-circuit voltage was measured with a Keithley multimeter. To study the discharge characteristics, each battery was connected to an ammeter and a rheostat in series. A voltmeter was connected across the battery to monitor the voltage under a constant-current load of ~5 mA.

3. Results

Fig. 1 gives the XRD patterns for: (a) lithium nitrate; (b) salt-free acetylated chitosan film, and (c) lithium nitrate complexed acetylated chitosan film. Fig. 2 shows the Cole–Cole plot for the highest conducting film, i.e., with 0.8 g $LiNO_3$ added to the acetic acid–chitosan solution. The bulk impedance is estimated to be ~28 Ω. The electrical conductivity is given by:

$$\sigma = \frac{l}{R_B A} \tag{1}$$

where l is the thickness of the film, R_B the bulk impedance obtained from the Cole–Cole plot, and A the area of the film.
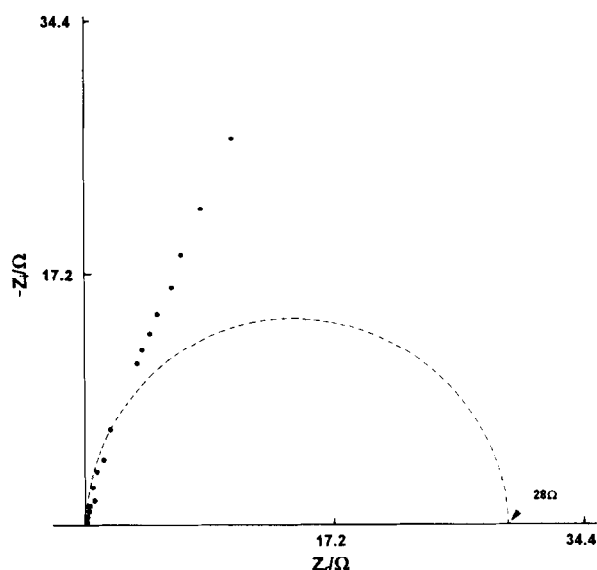

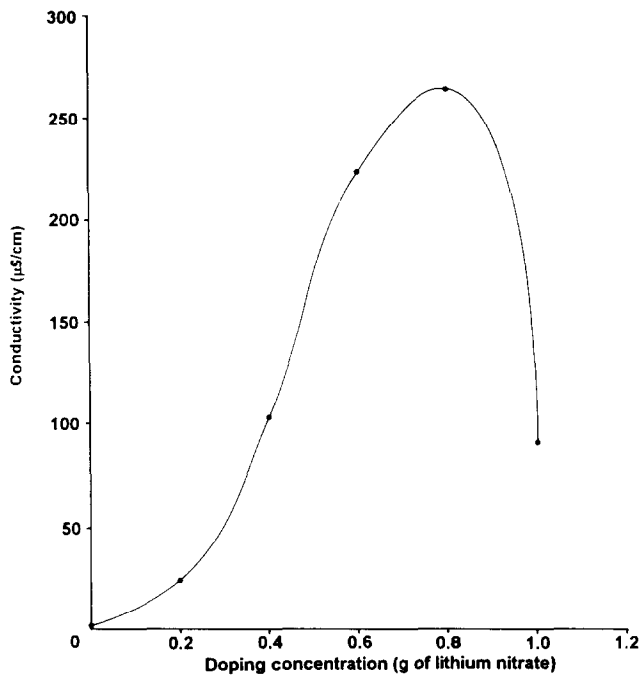Fig. 2. Cole–Cole plot for acetylated chitosan with 0.8 g $LiNO_3$.

Fig. 3. Electrical conductivity vs. LiNO₃ concentration.

Using Eq. (1), the electrical conductivity is found to be 2.7×10^{-4} S cm^{-1} at a room temperature of 30 °C. The variation of electrical conductivity with the amount of lithium nitrate added is given in Fig. 3. It is observed that the electrical conductivity increases by an order of magnitude when 0.2 to 0.8 g of LiNO₃ is added to the salt-free film. From the highest conducting LiCAC film, cells 1 and 2 (Table 1) were fabricated. The open-circuit voltages (OCV) of cells 1 and 2 were 1.113 and 0.765 V, respectively. From the discharge characteristics of the two cells (Fig. 4), the internal resistances of cells 1 and 2 are 2.7 and 25 kΩ, respectively. The internal resistance, r, was calculated as follows:

$$r = \frac{\text{OCV} - \text{voltage at beginning of discharge}}{\text{current drawn}} \tag{2}$$

For the sake of comparison, two other cells (cells 3 and 4) were fabricated with a salt-free film, but with the same configuration as cells 1 and 2. The OCVs were 0.871 and 0.651 V for cells 3 and 4, respectively. The corresponding internal resistances were 104 and 94 kΩ. The discharge times of these batteries are very short.

4. Discussion

The amorphous nature of the films is clear from the XRD patterns, and also from the XRD pattern for other films. The impedance plot implies that the bulk impedance semicircle overlaps with the grain boundary semicircle. The grain boundary contribution to the impedance can be attributed to microvoids in the polymer structure. These have been confirmed through studies of the piezoelectric properties [3]. The conduction of ions could take place via these microvoids.

Since all the films that have been prepared are amorphous, the decrease in electrical conductivity, when 1.0 g of LiNO₃ is added, cannot be attributed to the film becoming crystalline in nature on the addition of more LiNO₃. The variation in electrical conductivity with LiNO₃ concentration probably would best be explained in terms of weak electrolyte theory. The weak electrolyte theory [4] states that the electrical conductivity σ is given by:

$$\sigma = \eta q \mu \tag{3}$$

where η is the number of mobile charge carriers which will be in motion under the action of an electric field, q the electronic charge, and μ the mobility of the ionic species. The mobility of the charge carrier is given by:

$$\mu = \frac{d^2}{\tau V} \tag{4}$$

where d is the distance of traverse, τ the time of flight to traverse a distance d, V the voltage applied which provides an electric field across the distance d. In the preparation of the films, 100 ml of 1% acetic acid solution was used to dissolve 1 g of chitosan. Different amounts of lithium nitrate were added to each solution. Hence, the volume of the host matrix (i.e., the volume of the acetylated chitosan) is the same for all films. As more and more lithium nitrate is added, the host matrix becomes more and more crowded with the dopant ions. Such overcrowding can reduce the number of charge carriers since the weak electrolyte theory assumes constant mobility.

From this investigation, 0.8 g of LiNO₃ is the optimum amount to add to acetylated chitosan in order that the electrical conductivity attains a maximum. The internal resistance of the fabricated batteries is quite high and the current that
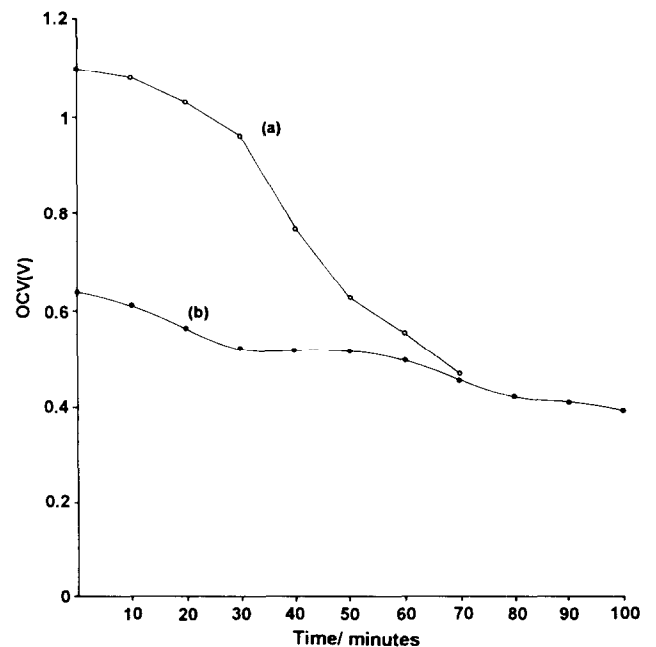

Fig. 4. Discharge characteristic of (a) cell 1, and (b) cell 2.

can be drawn is quite low. For the sake of comparison, a battery prepared from the polymer electrolyte poly(ethylene) (PEO) + NaYF$_4$ [5] and a battery fabricated according to the configuration Na/PEO + NaYF$_4$/I$_2$ + carbon + electrolyte gives an OCV of 2.4 V. Upon discharging under a constant load of 10 MΩ, the voltage dropped to 1.25 V. The current drawn was 3.5 μA. Hence, from Eq. (4), the internal resistance is 328.6 kΩ. This is of the same order of magnitude as in our present study.

Following Ref. [6], the failure of the battery could be due to the formation of (ZnOH$_2$), HI at the electrode–electrolyte interfaces, and/or other low conducting discharge products. In an earlier study [7], the transference number of an AgCAC (silver complexed acetylated chitosan) film obtained via Wagner's polarization technique was reported to be only 0.8. Hence, AgCAC is not a pure ionic conductor. This may also be true of LiCAC. Many polymer electrolytes are known to be mixed conductors, and one of the problems encountered in polymer electrolytes is that one cannot be sure of the main conducting species [8].

5. Conclusions

From the scope of the present investigation, we have been able to show that chitosan can be used as a host matrix for the conduction of ions. Moreover, a lithium complexed acetylated chitosan film can be used to fabricate polymer batteries.

Acknowledgement

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