

Chitosan–lithium triflate electrolyte in secondary lithium cells

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Abstract

Films prepared from high molecular weight chitosan are shown to exhibit the highest electrical conductivity of $2.14 \times 10^{-7} \text{ S cm}^{-1}$. The electrical conductivity is further enhanced to $1.03 \times 10^{-5} \text{ S cm}^{-1}$ when ethylene carbonate (EC) is used as a plasticizer. X-ray diffraction (XRD) shows that EC disrupts the crystalline nature of chitosan acetate. Infrared (IR) spectroscopy reveals a shift in the amide band from 1590 to 1575 cm^{-1} on addition of LiCF_3SO_3 . A film with a (chitosan + 0.4 g EC) to LiCF_3SO_3 ratio of 80:20 gives the highest electrical conductivity of $3.0 \times 10^{-4} \text{ S cm}^{-1}$. This film is used as an electrolyte for the fabrication of chitosan-based secondary cells, viz., $\text{Li/chitosan-EC-LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$. The characteristics of the cells are presented in this paper. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chitosan; Ethylene carbonate; Conductivity; Secondary cells

1. Introduction

It is known [1,2] that films prepared from polymers of different molecular weights give different values of electrical conductivity. This can be attributed to a difference in the number of available sites for complexation that is due to the difference in chain length. The ionic conductivity of these polymers can be increased by adding certain metal salts and can be further enhanced by the addition of plasticizers, e.g., propylene carbonate (PC), ethylene carbonate (EC), or polyethylene glycol (PEG) [3–5]. Polyethylene oxide (PEO) is the most popular polymer host for electrolytes because of its exceptional ability to solvate ionic salts [6]. Many studies of PEO-based electrolytes and electrochemical cells have been reported in the literature. Other polymers, such as polypropylene oxide (PPO), polyethylene imine (PEI) and polyvinyl chloride (PVC), have also been studied. Chitosan is another polymer which has been shown to be a promising solid electrolyte for solid-state cells [7–11]. Complexation between the Li^+ ion and the nitrogen heteroatom has been demonstrated in earlier work by the authors [12].

In this study, chitosan acetate (AC) films are prepared from high, medium and low molecular weight chitosan powder to determine which molecular weight group of chitosan will give a film with the highest electrical conductivity when formed by the solution-cast technique. Having determined the appropriate chitosan to use, an attempt is made to enhance the electrical conductivity of the chitosan acetate film by adding ethylene carbonate (EC) as a plasticizer. When the optimum content of the plasticizer is known, LiCF_3SO_3 is then used as the doping salt and is added in different amounts to 1% (v/v) acetic acid solutions which contain fixed amounts of chitosan and EC.

Before the film with the highest electrical conductivity is used to fabricate solid-state cells, all samples are characterized by X-ray diffraction (XRD) to examine the effect of the dissolution of salt on the nature of the polymer and to determine the occurrence of complexation. Characterization by Fourier transform infrared spectroscopy (FTIR) is also performed to provide further confirmation of the occurrence of complexation between the salt and the polymer. The electrical conductivity of the films is measured using the technique of impedance spectroscopy. The transference number for the film with the highest electrical conductivity is measured to determine which species of ions acts as the major conductor. The preparation and characterization of batteries which use this film are also reported.

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2. Experimental

2.1. Sample preparation

All samples were prepared by means of the solution–cast technique. In each case, 1 g of chitosan (Fluka) was dissolved in 100 ml, 1% (v/v) acetic acid solution. Ethylene carbonate (EC) and lithium triflate (LiCF_3SO_3) were added in appropriate amounts. The solutions were prepared and the films were allowed to form at room temperature.

2.2. Sample characterization

2.2.1. X-ray diffraction (XRD)

Many researchers have used XRD to determine whether a material is amorphous or crystalline [13,14]. Some workers [15,16] have been successful in proving the occurrence of complexation between the salt and the polymer host. In the case of PEO–AgSCN [17], however, XRD has been unable to detect the existence of a new phase.

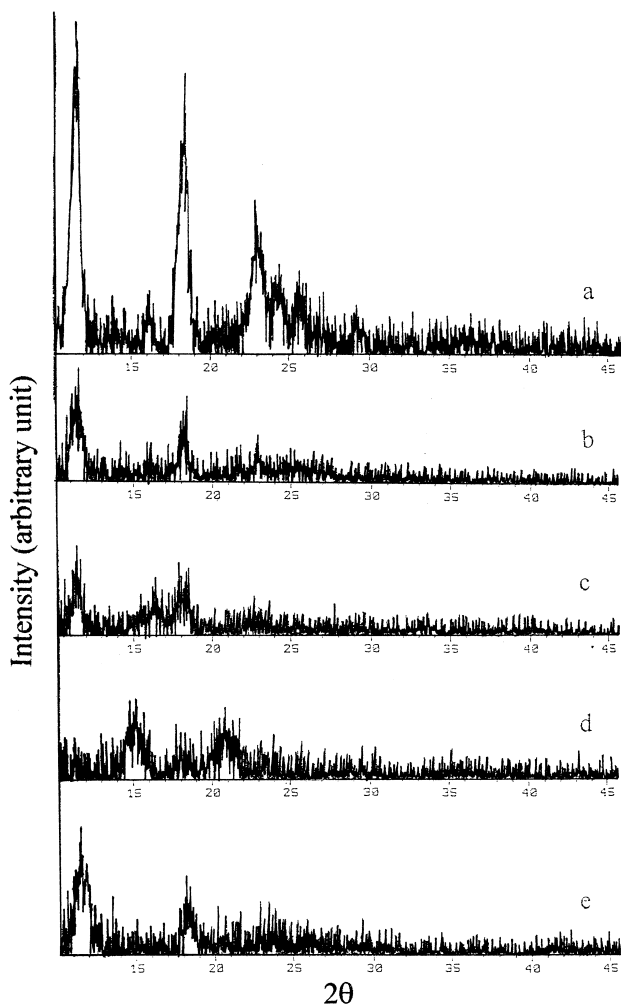


Fig. 1. X-ray diffraction diffractograms of (a) AC pure, (b) AC+0.2 g EC, (c) AC+0.3 g EC, (d) AC+0.4 g EC, (e) AC+0.5 g EC.

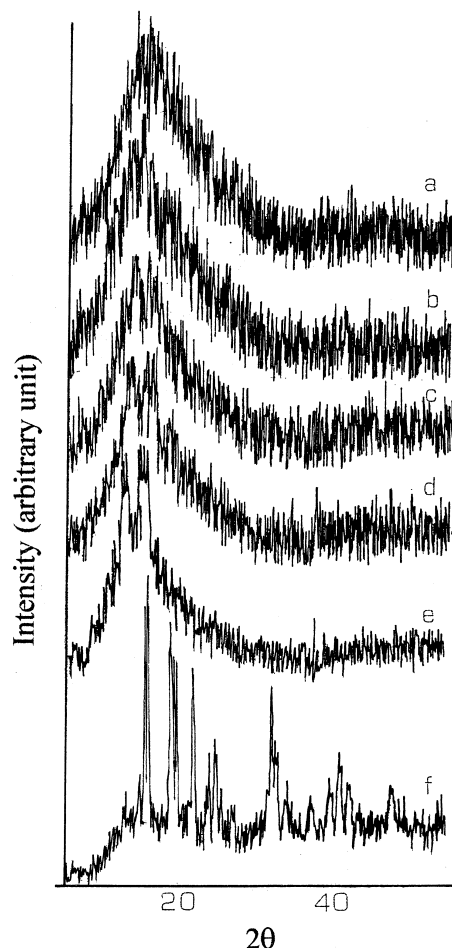


Fig. 2. X-ray diffraction diffractograms of AC film containing (a) 5 (b) 10 (c) 15 (d) 20 and (e) 25 wt.% of LiCF_3SO_3 , and (f) pure LiCF_3SO_3 .

In this work, XRD was used to determine the nature of the materials such that some insight would be gained into other properties of the material, in particular the electrical conductivity. XRD was carried out using a Siemens D-5000 XRD system. The films were fixed to clean microscope slides and then placed in the sample chamber. The samples were scanned with a beam of monochromatic, $\text{Cu } K_\alpha$ X-radiation of wavelength $\lambda = 1.5418 \text{ \AA}$ between a 2θ angle of 10° to 60° . To ensure that the noise level does not obliterate any peak which could demonstrate the sample to be crystalline, the films were irradiated every 0.02° for 1.0 s.

2.2.2. Infrared spectroscopy (IR)

Infrared spectroscopy was employed to verify the occurrence of complexation. Complexation is known to occur between chitosan and an inorganic salt if there is a shift in the infrared band of $\text{O}=\text{C}-\text{NHR}$ from 1650 to 1620 cm^{-1} , a shift in the band of $-\text{NH}_2$ from 1590 to 1575 cm^{-1} , and a shift in the band of $-\text{NH}_3^+$ from 1560 to 1510 cm^{-1} . These shifts imply that not only $-\text{NH}_2$ or NH_3^+ groups but also *N*-acetyl-amino groups remaining in the chitosan

macromolecule have considerable interaction with the metal ions or the metal salts themselves [18]. The metal ions will introduce modifications which depend on the nature of the metal ion, its concentration, and also on its counter-anion.

Infrared spectroscopy was performed by means of a MAGNA-IR550 Spectrometer-Series II in the wavenumber region 4000 to 400 cm^{-1} . The films, reasonably transparent and ~ 0.02 mm in thickness, were cut into suitable sizes and placed in the specimen holder of the spectrophotometer. A beam of infrared radiation penetrated the samples. The beam was split by KBr and detected by a DTGS KBr detector. To get a good impression, the samples were scanned 100 times with an aperture of 100.

2.2.3. Impedance spectroscopy

Conductivity measurements of the samples were carried out using the technique of impedance spectroscopy. The impedance was measured with a HIOKI 3531-01 LCR Hi-Tester that was interfaced to a computer. The bridge was set to measure the impedance and phase angle from 50 Hz to 5 MHz. The software controlling the measurement also calculated the real and imaginary impedance. A graph of negative imaginary impedance vs. real impedance on a graph with horizontal and vertical axes having the same scale was plotted from which the bulk impedance of the sample could be determined and the electrical conductivity of the material calculated.

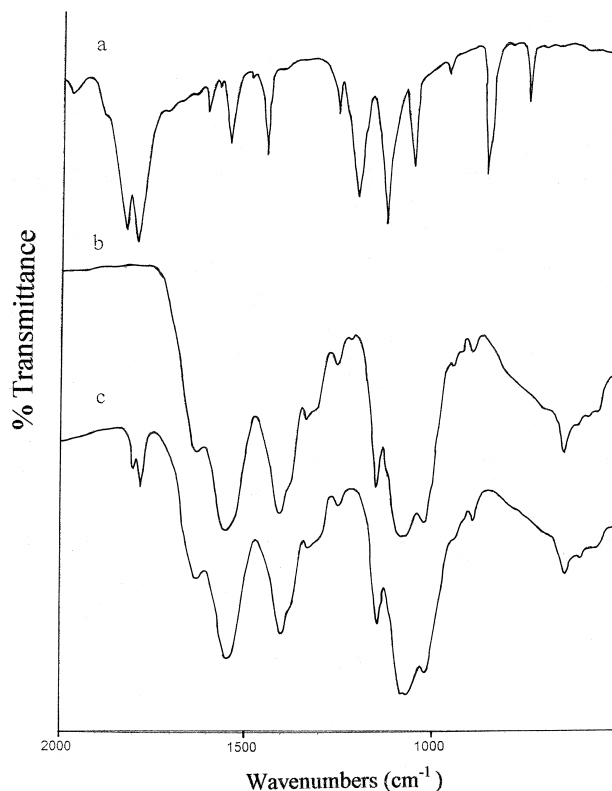


Fig. 3. FTIR spectra of: (a) EC; (b) pure chitosan acetate; (c) AC + 0.4 g EC.

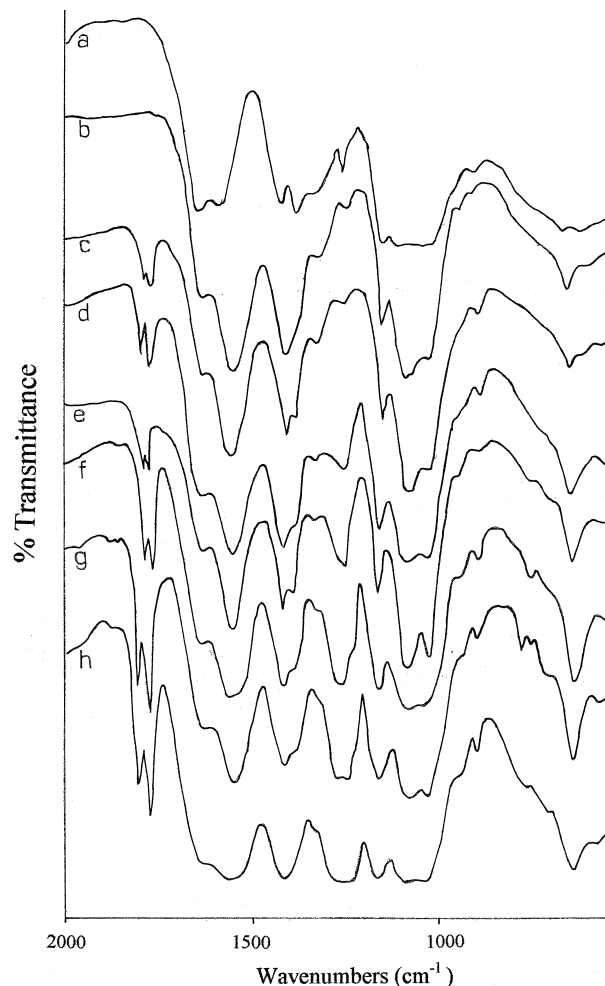


Fig. 4. FTIR spectra of: (a) pure chitosan; (b) pure chitosan acetate (AC); (c) AC + 0.4 g EC; (d) AC' + 5 wt.% LiCF_3SO_3 ; (e) AC' + 10 wt.% LiCF_3SO_3 ; (f) AC' + 15 wt.% LiCF_3SO_3 ; (g) AC' + 20 wt.% LiCF_3SO_3 ; (h) AC' + 25 wt.% LiCF_3SO_3 . Note: AC' = AC + 0.4 g EC.

2.2.4. Ionic transference number measurement

The ionic transference number was measured by a polarization technique with a voltage of ~ 1.5 V applied to the sample, which was connected in series to an ammeter and a switch. When the switch was set to 'ON', a current flowed through the circuit. According to Linford [19], electron conduction can be neglected in polymer electrolytes. Thus, at the beginning of polarization, the total current, i_T , flowing in a polymer can be assumed to consist of cationic and anionic currents, i.e., $i_T = i_+ + i_-$, where i_+ is current due to cations and i_- is current due to anions. The ions will travel to the electrode connected to the terminal which has an opposite charge to that of their own. The polymer film was sandwiched between two blocking electrodes. A back emf was produced and polarization occurred. Hence, the polarization current in the circuit decreased and its value was taken every 15 s until a constant current attributable to cations was obtained. An-

ionic current is impeded by concentration polarization. Thus at saturation of polarization current, the cationic transference number t_+ is given by:

$$t_+ = \frac{i_{+\infty}}{i_T} \quad (1)$$

where $i_{+\infty}$ is the cationic current at saturation.

2.3. Solid-state electrochemical cell fabrication

The polymer–plasticizer–salt complex film with the highest electrical conductivity was used as the electrolyte in the fabrication of the chitosan-based polymer secondary electrochemical cells. Vanadium pentoxide (V_2O_5) was chosen as the cathode material since it is able to deliver a reasonably high voltage and high discharge capacity [20,21]. Lithium metal was used as the anode. The composite cathode was prepared by mixing 67 wt.% V_2O_5 , 0.5 wt.% PVC, as a binding agent and 32.5 wt.% electrolyte solution. A 5-ml portion of acetone was added to the mixture and stirred with a magnetic stirrer to form a homogeneous mixture. After the acetone had evaporated and the composite electrode had dried thoroughly, the mixture was subjected to grinding. The powdered composite cathode was distributed on a copper mesh current-collector and pressed under a pressure of 20,000 kPa. The cell was assembled into a casing with the electrolyte sandwiched between the lithium anode and the composite cathode under argon atmosphere in a glove box.

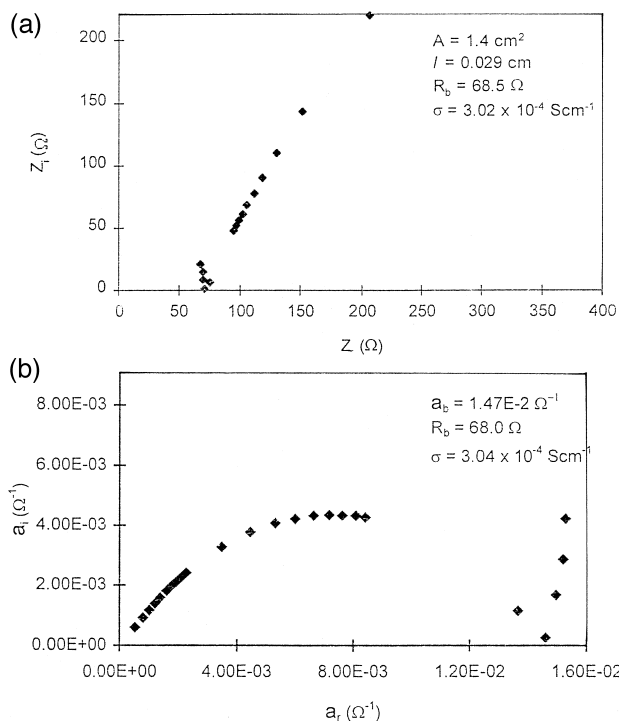


Fig. 5. (a) Complex impedance plot for 20 wt.% $LiCF_3SO_3$ in (AC+0.4 g EC). (b) Complex admittance plot for 20 wt.% $LiCF_3SO_3$ in (AC+0.4 g EC).

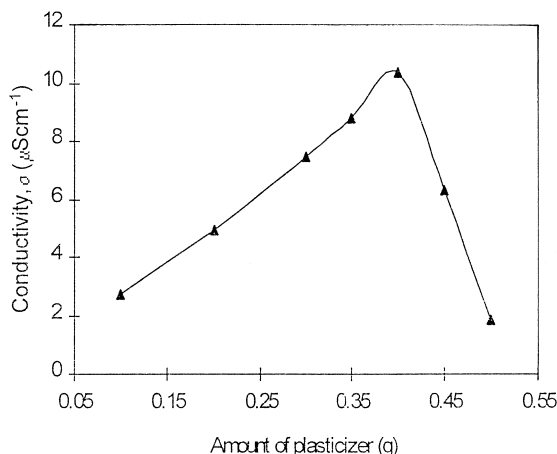


Fig. 6. Variation of conductivity with the amount of plasticizer (EC) in the sample.

2.4. Charge–discharge characteristics

The charge–discharge characteristics were studied using a BAS LG50 computer-controlled galvanostat. The cell $Li/AC-EC-LiCF_3SO_3/V_2O_5$ was charged with a constant current of 100 nA and discharged at 10 nA.

3. Results

Figs. 1 and 2 show the XRD patterns of some of the samples prepared. The data in Fig. 1a show that the AC sample is partly crystalline with peaks at 2θ angles of 11.5° , 17° and 23° and partly amorphous; this is typical of polymers. Upon addition of EC, the sample becomes more amorphous, i.e., the plasticizer disrupts the crystalline

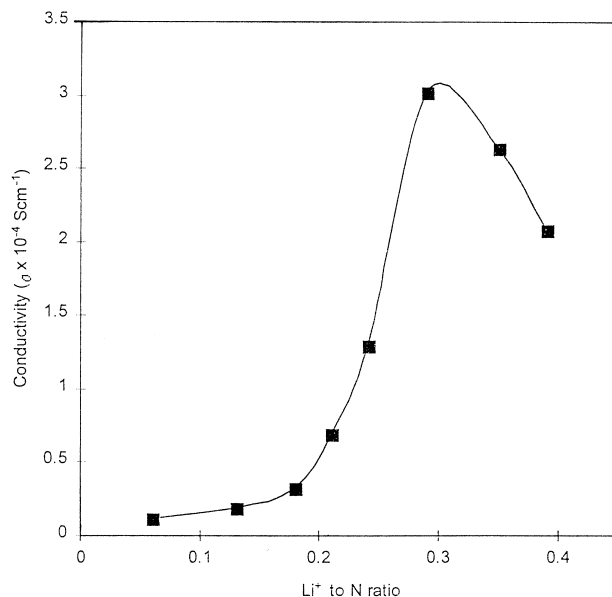


Fig. 7. Variation of conductivity with wt.% $LiCF_3SO_3$ in the sample.

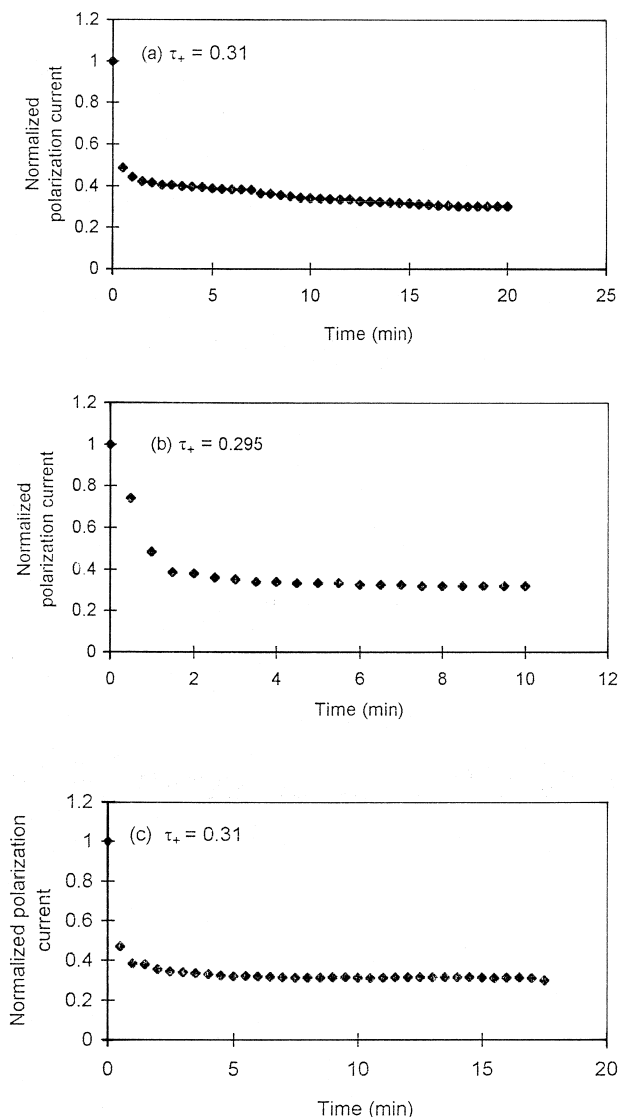


Fig. 8. Normalized current vs. time using different nonblocking electrodes: (a) silver conducting cement; (b) silver powder; (c) carbon conducting cement.

nature of the chitosan acetate film. The amorphous nature of the samples increases with increasing amounts of EC from 0.2 g to 0.4 g, as shown in Fig. 1b to d. When 0.5 g EC was added, however, the sample starts to become crystalline again, Fig. 1e. The sample containing 0.4 g EC is the most amorphous sample.

Fig. 2a to e present the diffractograms of samples which have been doped with LiCF_3SO_3 . The X-ray diffractogram of LiCF_3SO_3 shows peaks at $2\theta = 16^\circ$ and $2\theta = 19^\circ$ (Fig. 2f). If the diffractogram in Fig. 2e can be considered to contain crystalline peaks at $2\theta = 14^\circ$ and 17° , respectively, that can be attributed to LiCF_3SO_3 , then upon comparing Fig. 2e and f, the LiCF_3SO_3 peaks at 2θ angles of 16° and 19° have shifted to lower angles and this provides some evidence that complexation has occurred between the salt and the polymer.

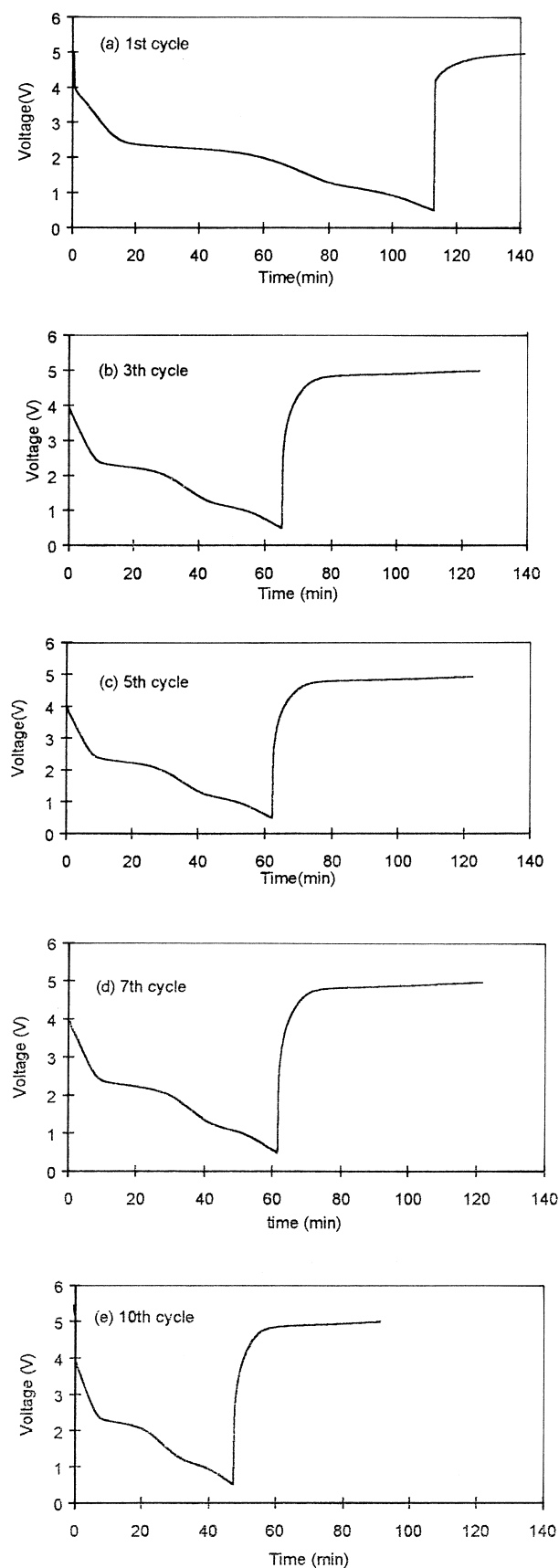


Fig. 9. Discharge-charge characteristics of $\text{Li}/(\text{AC} + \text{EC}) + \text{LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$ cell.

Fig. 3 shows the IR spectrum of (a) EC, (b) chitosan acetate (AC), and (c) chitosan acetate with EC added (AC + 0.4 g EC). It is obvious that the spectrum for AC is almost similar to that of the plasticized AC and this implies that EC acts as a lubricant in the same manner as AgI in silver phosphate glasses [22]. The position of the amide bands at 1590 cm^{-1} is very little affected by the introduction of the plasticizer. In other words, EC and AC do not interact with each other. The bands at 1800 and 1700 cm^{-1} are due to C=O vibrations in the carbonate group of EC [23].

Fig. 4a shows the IR spectrum of pure chitosan (without acetate). The spectrum is quite similar to that given by Muzzarelli [18]. The acetate component was removed by soaking the material in sodium hydroxide solution. From Fig. 4b to h, it can be observed that the amide band at 1590 cm^{-1} has shifted to lower wavenumbers at 1575 cm^{-1} . This indicates that some complexation has occurred either between the salt and the nitrogen atom of the amide group or between the acetic acid and the nitrogen atom. As more salt is added to the solution in preparation, however, the shift increases further towards lower wavenumbers and overlaps with the $-\text{NH}_3^+$ band at 1560 cm^{-1} .

The impedance and admittance plots of the highest conducting film, i.e., the film of (1 g chitosan + 0.40 g EC) + LiCF_3SO_3 , are shown in Fig. 5. This sample has an electrical conductivity of $3.0 \times 10^{-4}\text{ S cm}^{-1}$. The admittance plot reconfirms the position of the bulk resistance obtained from the impedance plot and which is essential for the calculation of the electrical conductivity. Fig. 6 shows the variation of room temperature conductivity with different amounts of plasticizer in the chitosan films. Fig. 7 presents the variation of conductivity with the amount of LiCF_3SO_3 for a fixed EC content. The conductivity decreases when the salt concentration is more than 20 wt.%. Fig. 8 shows the normalized polarization current vs. time for the highest conducting plasticized chitosan acetate-salt film. The cationic transference number is ≈ 0.3 . The discharging and charging characteristics of the Li/AC + EC + $\text{LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$, as given in Fig. 9, shows that the internal resistance of the cell is very high $\sim 10^8\ \Omega$ whereas the resistance of the electrolyte is less than $100\ \Omega$.

4. Discussion

Ethylene carbonate renders chitosan acetate films amorphous and, therefore, enhances the conductivity of the material. Only one broad hump is observed in almost all the diffractograms of the films formed when different amounts of LiCF_3SO_3 are added to 100 ml of 1 wt.% acetic acid solution containing 1 g chitosan and 0.4 g EC, Fig. 2a to d. When more than 20 wt.% LiCF_3SO_3 is added, however, the sample starts to become crystalline. Peaks are observed at 2θ angles of 14° and 17° . If this can be attributed to the shift in the peaks at $2\theta = 16^\circ$ and 19° ,

then some evidence of complexation between chitosan and the lithium salt has been provided by XRD.

The shifting of the band at 1590 cm^{-1} implies further proof that complexation does occur between the salt and chitosan. Complexation occurs when lithium from the salt interacts with the lone pair electrons of the nitrogen atom from the amide group of the chitosan. X-ray photoelectron spectroscopy has also confirmed Li–N interaction [12]. Since LiCF_3SO_3 is able to dissolve in chitosan, it can be considered to be a polymer host for electrolyte application in solid-state batteries.

From the graph of conductivity vs. EC content, the film containing 0.4 g EC exhibits the highest electrical conductivity. The conductivity in these samples is attributed to the conduction of protons from the acetic acid. Due to thermal agitation, some hydrogen ions (protons) are able to detach themselves from the matrix and thus can hop from one complexation site to another.

The observed increase in conductivity for samples containing different amounts of LiCF_3SO_3 salt and a fixed amount of EC can be explained in terms of the nature of the samples. As more and more salt is added, the conductivity increases due to the sample becoming more amorphous. When 25 wt.% of salt has been added, the sample becomes crystalline again. This can be observed from the peaks at 14° and 17° in the respective diffractogram.

Even when using different nonblocking electrodes such as silver dag, silver powder and carbon dag, the same value of transference number, viz., ≈ 0.30 , was obtained. This means that the major conducting species is the CF_3SO_3^- anion. Other studies have obtained a lithium ion transference number of 0.31 [24], the salt being lithium triflate as in the present study, and 0.20 [25] for LiI. A film with a (AC + 0.4 g EC) to LiCF_3SO_3 ratio of 80:20 gives the highest electrical conductivity of $3.0 \times 10^{-4}\text{ S cm}^{-1}$. This film was used for the fabrication of Li/(chitosan–EC– LiCF_3SO_3)/ V_2O_5 cells.

The internal resistance is found to be constant during each charge–discharge cycle. The resistance is high and is attributable to the interfacial resistance between the electrolyte and electrode [26]. The plateau voltage occurs at 2.25 V. It can be calculated that on the first discharge of the Li/AC + EC + $\text{LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$ cell, the capacity of the cell is 6.6 nAh. After ten cycles, the percentage loss of discharge capacity is 61.5%. This effect may be associated with the growth of lithium microdendrites across the cell [27]. Furthermore during repeated charging of the battery, dendritic lithium forms on the anode and finally grows through the electrolyte and comes into contact with the cathode to create high impedance or a self-short, as reported in Refs. [28,29].

5. Conclusions

The film with a (chitosan + 0.4 g EC) to LiCF_3SO_3 ratio of 80:20 has an electrical conductivity of $3.0 \times$

$10^{-4} \text{ S cm}^{-1}$. This film is applicable as an electrolyte in a secondary solid-state battery. Further work is being carried out to improve the cell lifetime and performance.

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