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Chitosan-based electrolyte for secondary lithium cells

A. K. AROF, Z. OSMAN
Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia
N. M. MORNI
Institut Tun Hussein Onn, Batu Pahat, Johor Darul Takzim, Malaysia
N. KAMARULZAMAN
Faculty of Science, University Technology MARA, 40500 Shah Alam, Selangor, Malaysia
Z. A. IBRAHIM, M. R. MUHAMAD
Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

The system chitosan : ethylene carbonate : $LiCF_3SO_3$ was prepared by the solution cast technique.To verify that the conductivity of the material is due to the salt, the electrical conductivity at room temperature of the chitosan acetate film and that of the chitosan acetate films containing different amounts of ethylene carbonate added to it were measured. The order of magnitude of the electrical conductivity was 10^{-10} S cm^{-1}. Films containing fixed content of chitosan and plasticizer but different amounts of salt were then prepared in the same manner and the highest electrical conductivity obtained was 1.3×10^{-5} S cm^{-1} at room temperature. These results indicate that the conductivity is due to the salt. Conductivity-temperature studies show that the $\ln \sigma T$ versus $10^3/T$ graphs obey Arrhenius rule implying that the conductivity occurs by way of some thermally assisted mechanism. Polarization current measurement shows that the lithium ion transference number is ∼0.09. A $LiMn_2O_4$/chitosan-$LiCF_3SO_3$/C cell was fabricated which cycled between 1.5 to 2.5 V with fading capacity. This could be the result of LiF formation due to interaction between the salt and the fluorine in the binding agent.

1. Introduction

Chitosan is a biopolymer that can be derived from chitin or obtained from the cell walls of living things such as *Phycomyces blakesleeanus*. It has an amine group (NH_2) and the nitrogen atoms have lone pair electrons that can behave as potential sites for the complexation of MX uni-univalent metal salt to the polymer. Hence, with the presence of such heteroatoms in its structure, chitosan should be able to solvate inorganic salts such as $LiCF_3SO_3$ and exhibit the properties adherent to polymer electrolytes. The interaction between the lithium cation and the nitrogen atom has been shown by Arof *et al.* [1] by x-ray photoelectron spectroscopy. Therefore, such chitosan-salt complexes can be potential electrolyte materials for battery fabrication. Chitosan-based primary cells have been fabricated [2–4] and Ag/chitosan-$AgNO_3$/I_2 cells have shown reasonably good performance [5]. Secondary cells with configuration Li/chitosan-$LiCF_3SO_3$/V_2O_5 have shown very small output current [6].

In this work, chitosan was dissolved in 1% acetic acid solution to form a chitosan acetate (CA) film. Films of CA : $LiCF_3SO_3$, CA : ethylene carbonate (EC) and CA : EC : $LiCF_3SO_3$ were also prepared. The electrical conductivity of each film was measured by impedance spectroscopy in order to gauge the degree of electronic conductivity which might be one of the reasons for the low current output in the chitosan-based secondary cells [6]. Transference number measurement was also performed to measure the transference number of the lithium ion and a $LiMn_2O_4$/C cell was fabricated using a chitosan: EC : $LiCF_3SO_3$ film exhibiting a conductivity of the order 10^{-5} S cm^{-1}.

2. Experimental

2.1. Material preparation

Films of chitosan-salt complexes were prepared by the solution cast technique. The chitosan powder of average relative molecular weight 6×10^5 (FLUKA) was used in this work. Several sets of solutions were prepared to form (a) a chitosan acetate (CA) film, (b) a CA-$LiCF_3SO_3$ film, (c) CA-ethylene carbonate (EC) films with different amounts of EC in each film and (d) CA-$LiCF_3SO_3$-EC films with a fixed amount of salt but different amounts of EC in each film. After complete dissolution of chitosan, salt and plasticizer have taken place, the solutions were cast into different petri dishes and left to form the film at room temperature. The films were then dried in a dessicator prior to further experimentation.

2.2. Electrical conductivity measurement

The electrical conductivity, σ was calculated using the equation

$$\sigma = \frac{t}{R_B A}$$

where t is the thickness of the film and A is the film-electrode contact area. R_B is the bulk impedance that can be obtained from the complex impedance plot. The impedance was obtained by ac impedance using the HIOKI 3531Z Hi Tester that was interfaced to a computer. The electrical conductivity was also measured at different temperatures.

2.3. X-ray diffraction (XRD)

XRD was carried out to study the nature of the samples and to study the effect of plasticizer and salt on the nature of the chitosan acetate film. The XRD was performed using a Siemens D-5000 X-ray Diffractometer system.

2.4. Transference number measurement

According to Linford [7], in polymers the electronic conduction can be considered to be negligible. Hence the polarization current can be considered to be made up of cationic and anionic currents. At saturation, the current is due to cations. The anionic current has been impeded by concentration polarization. Hence the cationic transference, τ_+, number can be calculated from the equation

$$\tau_+ = \frac{I_\infty}{I_0}$$

Here, I_0 is the initial current comprising contributions from cations and anions. I_∞ is the current at saturation and equals the cationic current.

2.5. Electrochemical cell fabrication and characterization

$LiMn_2O_4$ was mixed with activated carbon and polyvinyledene fluoride (PVDF) in the weight ratio 80 : 10 : 10. The ingredients were dissolved in n-methyl pyrolidinone (NMP) and the slurry was bladed onto an Al mesh. Natural graphite and petroleum coke was blended and the blend was mixed with PVDF in the weight ratio 90 : 10 and dissolved in NMP. The slurry was bladed onto a Cu mesh. When the electrodes have dried, a chitosan electrolyte film was sandwiched between the electrodes and placed inside a casing for characterization. In the assembled state the cell exhibits a voltage of a few hundred milivolts.

3. Results and discussion

In order to verify that the material has negligible electronic conduction, the electrical conductivity of the chitosan films with and without EC but definitely without salt were measured. Fig. 1 shows the room temperature electrical conductivity of these samples. The conductance exhibited by these samples could be due to unavoidable contaminants.

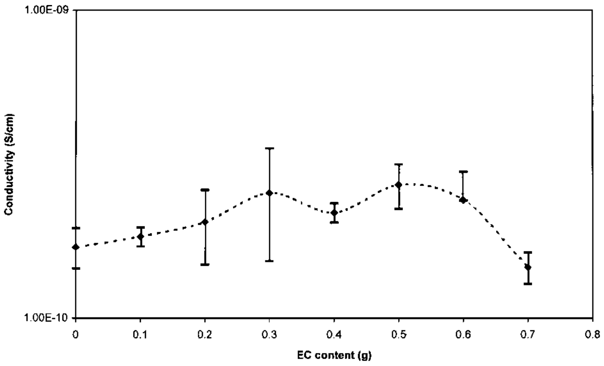

Figure 1 Room temperature electrical conductivity for the films CA and CA containing EC. There is no $LiCF_3SO_3$ added to these samples.

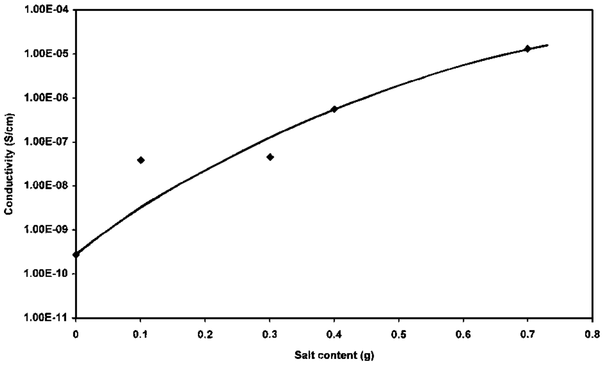

Figure 2 Room temperature electrical conductivity for films of fixed CA and EC content but containing different amounts of salt.

When $LiCF_3SO_3$ was added, the conductivity increases by almost five orders of magnitude, Fig. 2. In this paper, the conductivity is reported for samples containing up to 0.7 g $LiCF_3SO_3$. The conductivity obtained for the sample containing 1 g chitosan, 0.5 g EC and 0.7 g $LiCF_3SO_3$ (equivalent to 32 wt% salt) is 1.3×10^{-5} S cm^{-1} at room temperature. This is the lower limit for a material to be considered a superionic conductor. From Figs 1 and 2, it can be deduced that the conductivity is due to the salt and not to the plasticizer or electrons. Thus this material is suitable for use as an electrolyte in solid polymer batteries.

Fig. 3 represents the conductivity versus temperature studies. It is observed that the $\ln \sigma T$ versus $10^3/T$ graph is almost a straight line with a regression value of almost unity. The glass transition value, T_g for chitosan was reported as 203°C [8]. Thus it is possible that the T_g value for the samples studied is still above the temperature range investigated that the graphs do not show any deviation from linearity. Hence, the lithium ion conduction in the material could be attributed to some thermally assisted mechanisms. From the graphs presented in Fig. 3, the activation energy as calculated from the Arrhenius equation ranges between 0.3 to 0.7 eV.

Fig. 4 gives the cationic transference number of the sample prepared by dissolving 0.7 g salt, 0.5 g EC and 1.0 g chitosan in 100 ml 1% acetic acid solution. The

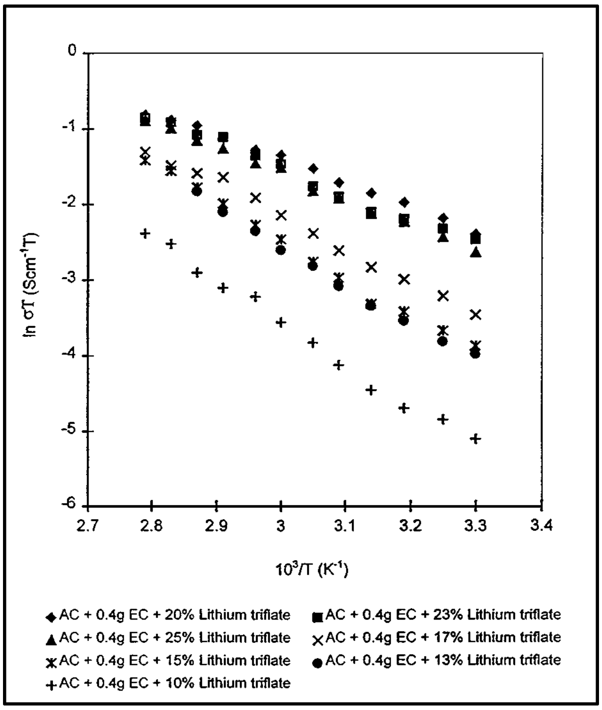

Figure 3 Arrhenius plots. Activation energy value range between 0.3 to 0.7 eV.

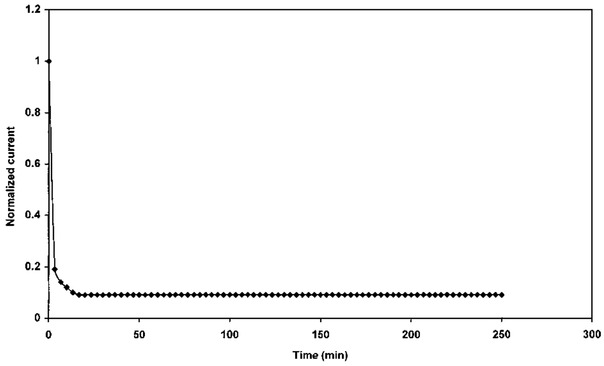

Figure 4 Normalized polarization current for transference number measurements. $\tau_{\mathrm{Li}} \sim 0.09$.

cationic transference number is 0.09. The lithium ion transference number depends on the type of salt and also on the type of polymer. For example, Ramesh and Arof [9] have shown that the lithium ion transference number for a PVC-$LiCF_3SO_3$ complex is 0.3, whereas it has been reported that the lithium ion transference number in a PVC-LiTFSI is between 0.03 to 0.08 [10]. Fig. 5 shows the discharge characteristics of the $LiMn_2O_4$/chitosan-$LiCF_3SO_3$/C cell. From the inset in Fig. 5, it is clear that the capacity of the cell decreases after the first cycling. According to Sandi *et al.* [11], several factors such as the electrolyte mixture and the binder might contribute to the irreversible capacity. The possibility of LiF formation due to the corrosion mechanisms of the binding agent by the lithium salt may lead to this high irreversibility as explained by

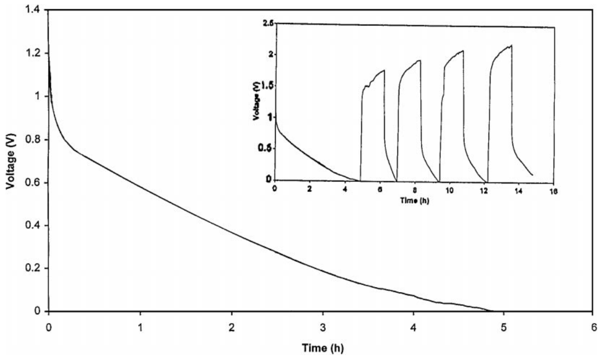

Figure 5 Charge-discharge characteristics of $LiMn_2O_4$/chitosan-$LiCF_3SO_3$/C cell for the first 5 cycles.

some authors [12–14] who have studied the corrosion mechanisms of PTFE by alkali metals amalgams.

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