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Conductivity and X-ray photoelectron studies on lithium acetate doped chitosan films

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Abstract

Chitosan, ethylene carbonate (EC) and lithium acetate (LiOAc) were mixed in the desired proportions and dissolved in 100 ml of 1% acetic acid solutions. The solutions were then poured into various petri dishes and left to form films at room temperature. Complexation was confirmed by X-ray photoelectron spectroscopy (XPS). The lithium signal can be deconvoluted into three gaussian component peaks. One of the peaks at ~55 eV is attributed to Li–N interaction. The nitrogen signal can be deconvoluted into two gaussian component peaks. The peak at ~403.1 eV is attributed to N–Li interaction. The electrical conductivity of all samples was calculated using the bulk resistance value obtained from the complex impedance plot in the frequency range between 1 kHz and 1 MHz. The highest electrical conductivity obtained for the film containing LiOAc is 7.6×10^{-6} S cm^{-1} at room temperature. The plot of conductivity, σ versus dopant content indicates that σ increases with increasing dopant content up to a dopant amount of 0.8 g LiOAc. The plot of ln σT versus $10^3/T$ for each lithium acetate sample between 298 and 363 K shows beys Arrhenius behavior indicating that the conductivity occurs by way of some thermally assisted mechanism. The chitosan based samples may have potential use in replacing the liquid components of electrochromic devices.

Keywords: Ionic conductivity; Polymer electrolyte; Lithium acetate; Chitosan

1. Introduction

Polymers are being used increasingly as solid media for substituting the liquid component of electrochemical devices such as sensors, displays, supercapacitors, electrochromic windows and rechargeable batteries. In particular, there has been considerable interest regarding the use of polymer gel electrolytes in solid polymer batteries (Glasse, Idris, Latham, Linford, & Schlindwein, 2000). These systems have exhibited higher ionic conductivities compared with conventional solid polymer electrolytes (Yavaroy, Wang, & Wunder, 1999; Kim, Oh, & Choi, 1999).

Among the many polymer electrolytes, polyethylene oxide (PEO) has been widely studied. The majority of the salt doped polymer electrolyte systems have an ionic conductivity of about 10^{-5} S cm^{-1} at room temperature. The variation of room temperature conductivity with salt concentration usually shows a maximum conductivity. According to Mellander and Albinsson (1996), conductivity variation in polymers is attributed to ion association and dissociation. When the salt concentration is very high, the mean interionic distance can be so close that the cations coordinating with the electron donating atom of the polymer may form transient cross-links, thus forming a rigid structure. Under these circumstances the anions can also form connections between the cation cross-links.

Plasticizing with ethylene carbonate (EC) and propylene carbonate (PC) significantly increases the ionic conductivity in the range 10^{-4} S cm^{-1} at room temperature (Glasse et al., 2000). Conductivity enhancement due to ion dissociation in plasticized chitosan polymer-based electrolytes has recently been reported in this journal (Osman, Ibrahim, & Arof, 1998).

Chitosan has aroused a lot of interest in view of its applications in the industrial and biomedical sectors (Wan, Creber, Pepley, & Bui, 2003). Chitosan can also be developed into specialized functional polymers due to the presence of free amino and hydroxyl groups. Films or

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membranes are easily obtained from chitosan. The chitosan membrane is also the first natural polymer chelating membrane. Chitosan and chitosan acetate films do not possess any pores. They are homogeneous and have high mechanical strength (Muzzarelli, 1973). Chitosan can also be readily converted into fibers, coatings and beads thereby increasing its variety of applications. A mechanism for ionic conduction has been suggested and a future application in alkaline polymer electrolytes fuel cells has been predicted by Wan et al. (2003).

In this work, chitosan was doped with lithium acetate dihydrate (LiOAc). In order to check for complexation, XPS was carried out. The binding energy between the lithium cation of the salt and the nitrogen atom of the free amino group is sought for. Since at high salt concentrations, these cations form transient crosslinks and under these circumstances the anions can also form connections between cation crosslinks, therefore the binding energy of the lithium cation in these crosslinks will differ from the binding energy of the lithium cation with the electron donating atom in the polymer and also between the lithium cation and anion of the salt. XPS can be used to prove these cross linkage by determining the binding energies. Conductivity temperature studies will also be carried out and the modulus formalism will be calculated and plotted to show whether the samples are ionic conductors.

2. Experimental

2.1. Sample preparation

In this work, chitosan was obtained from FLUKA and was used as received. The molecular weight was 600,000 g/mol. Two sets of samples were prepared. In the first set, different amounts of lithium acetate dihydrate, $LiC_2H_3O_2·2H_2O$ (LiOAc) were added to different beakers containing 1.0 g chitosan that has been dissolved in 100 ml of 1% acetic acid solution. The mixtures were stirred with a magnetic stirrer for several hours at room temperature. In the second set, different amounts of $LiC_2H_3O_2·2H_2O$ were added to different beakers containing 1.0 g chitosan, 0.40 g EC that have been dissolved in 100 ml of 1% acetic acid solution. A chitosan–acetic acid solution and chitosan–EC–acetic acid solution were also prepared to act as controls. The solutions were then poured into different plastic petri dishes and left to dry in air at room temperature for the films to form. The films were then transferred into a desiccator for continuous drying before being used in further experiments. This is to ensure that the films were completely dried prior to subsequent experimentation.

2.2. X-ray photoelectron spectroscopy

The XPS studies in this work were carried out using a Kratos XSAMHS surface analysis spectrometer with a Mg Kα X-ray source (1523.6 eV). The spectrum was taken at an operating current of 10 mA and an operating voltage of 14 kV. The spectrometer was calibrated using a clean Ag plate and the Ag $3d_{5/2}$ line was set at 368.25 eV. The C 1s binding energy at 284.5 eV was used as a second reference. The solid polymer sample was mounted onto a standard stub holder using double-sided adhesive tape. The survey scan was recorded in the energy range between 10 and 1100 eV. The pass energy and step size energy was 160 and 1 eV step^{-1}, respectively. Sweep time was set at 300 s per sweep. For the narrow scan, smaller pass energy 20 eV with lower step size, 0.1 eV step^{-1} was utilized. The sweep time was 59.898 s per sweep. Narrow scans were obtained for the C 1s, O 1s, N 1s, and Li 1s signals. The sample analysis chamber was kept at $\approx 5.0 \times 10^{-9}$ Torr or less during the scans. The vision software provided by Kratos deconvoluted all core-level spectra into gaussian component peaks. Charging effects were corrected for using the C 1s binding energy at 284.5 eV. For XPS work samples in to which 0.2, 0.5 and 0.8 g of LiOAc has been added were used.

2.3. Impedance spectroscopy

The impedance was measured with a HIOKI 3531-01 LCR Hi-Tester that has been interfaced to a computer. This bridge has been set to measure the impedance and phase angle from 1 kHz to 1 MHz. The software controlling the measurements also calculates the real and imaginary impedance. A plot of negative imaginary impedance versus real impedance on a graph with horizontal and vertical axes having the same scales will give a semicircle if the sample exhibits Debye characteristics. From the complex impedance plot, the bulk resistance, R_b can be obtained and the electrical conductivity, σ of the sample can be calculated from the equation

$$\sigma = \frac{t}{R_b A} \tag{1}$$

A micrometer screw gauge was used to measure the thickness, t of the polymer films and the diameter of the films was measured with a vernier caliper to calculate the area, A. The thickness of the films ranges from 0.06 to 0.15 mm. The conductivity measurement for each sample was also carried out from room temperature, 298 up to 363 K. The real and imaginary parts of the modulus formalism were calculated from the equations below

$$M' = -\omega C_c Z'' \tag{2}$$

$$M'' = j\omega C_c Z' \tag{3}$$

where Z' is the magnitude of the real impedance, Z'' is the magnitude of the imaginary impedance, $\omega = 2\pi f$, f being the signal frequency (which is changed until the frequency range is completed) and $C_c = \varepsilon_o A/t$ and ε_o is the permittivity of free space.

3. Results and discussion

By deconvoluting the Li 1s and the N 1s core level spectra into their gaussian component peaks; the binding energy of the N–Li interaction can be determined. Fig. 1(a)–(c) shows the deconvoluted Li 1s core level spectrum for the samples that has been added with 0.2, 0.5 and 0.8 g LiOAc and Fig. 2(a)–(c) show the deconvoluted N 1s core level spectra.

Following Arof, Morni, and Yarmo (1998), the binding energy of ~55 eV is attributed to Li–N interaction in accordance with the binding energy of Li 1s electron in LiN_3 or (LiNN*N), where the asterisk indicates the N to which the Li has interacted (Chastin, 1992). To be exact

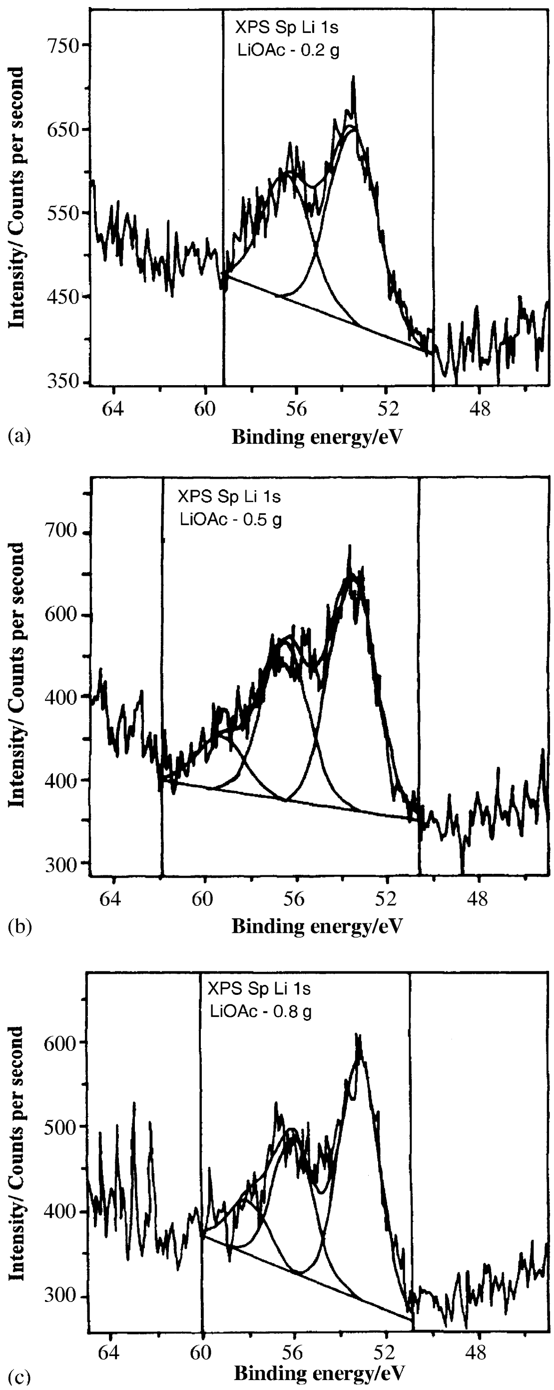

Fig. 1. XPS narrow scan for Li 1s signal obtained from sample containing (a) 0.2, (b) 0.5, (c) 0.8 g LiOAc. These are the original spectra that have not been corrected for charging effect.

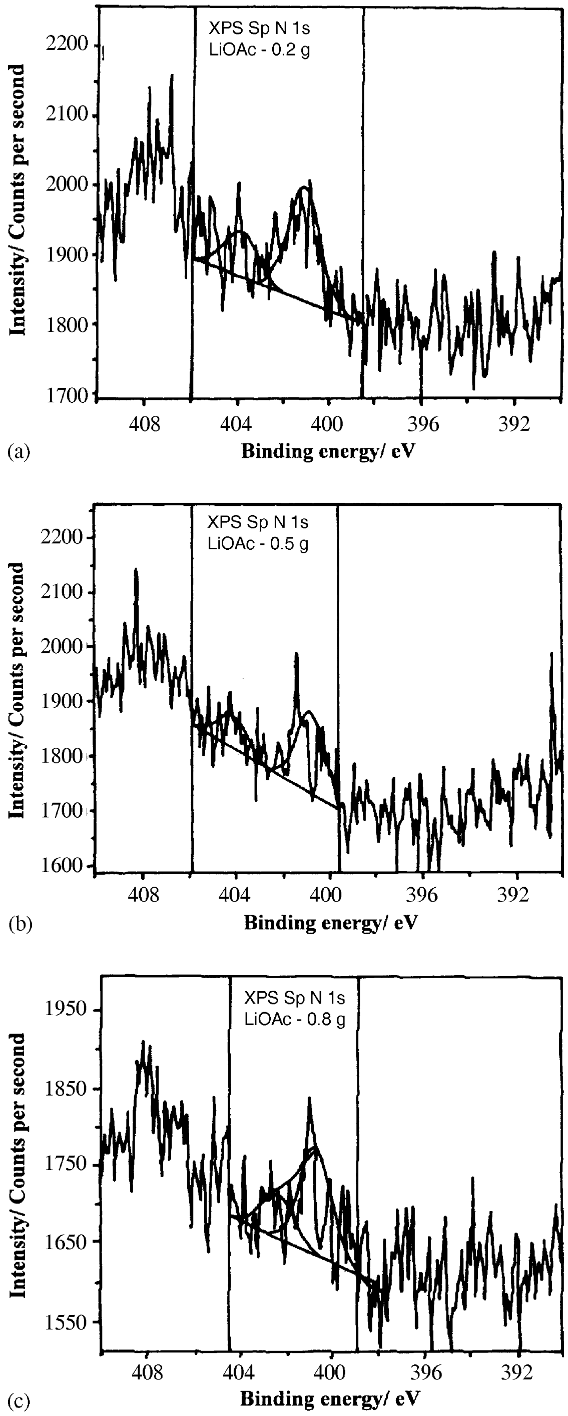

Fig. 2. XPS narrow scan for N 1s signal obtained from sample containing (a) 0.2, (b) 0.5, (c) 0.8 g LiOAc. These are the original spectra that have not been corrected for charging effect.

the value of binding energy is 55.2 eV. Hence our results are confirming that the salt has complexed with the polymer because in all of our samples, Li–N 1s electron binding energy is 55.3, 55.5 and 55.2 eV after charging correction has been made. This clarifies complexation between lithium and nitrogen. The binding energy at ~52 eV is attributable to LiOAc. The appearance of the gaussian component with binding energy between 57 and 59 eV could be attributed to lithium ions that have formed transient crosslinks (Mellander & Albinsson, 1996). The variation in binding energy could be attributed to the degree of crosslinking. The gaussian component peak at binding energy 403.1 eV is also indicative of N–Li interaction. Our results are also close to that of this reference being 402.8 and 403.2 eV (Chastin, 1992). H–N interaction implying the formation of chitosan–acetic acid salt is represented by the gaussian component peak at ~400 eV which is approximately the binding energy of N 1s electron in materials such as $HN(CH_2COOH)_3$ (400.7 eV) and H_3NCH_2COO (400.6 eV, Chastin, 1992).

The conductivity of the undoped and plasticized undoped chitosan films is of the same order of magnitude. These results are in agreement with that of Osman, Ibrahim, and Arof (2001) and also with Wan et al. (2003). With addition of the same amount of salt to the undoped and plasticized undoped films the conductivity increases. The increase in the ionic conductivity with salt is higher in the plasticized system. This shows that the plasticizer has increased the number of mobile cations by weakening the coulombic force between the anion and cation of the salt and thereby resulting in the dissociation of the salt. The conductivity graph can be divided into two regions. The increase in conductivity in Region 1 is attributed to ion dissociation and that in Region 2 can be attributed to ion association and to increase in crystallinity of the samples (Yahya, Muhamad, & Arof, 1998). The highest electrical conductivity obtained for the LiOAc doped plasticized chitosan polymer is 7.6×10^{-6} S cm^{-1} and that of the unplasticized sample is 2.2×10^{-7} S cm^{-1} (Fig. 3).

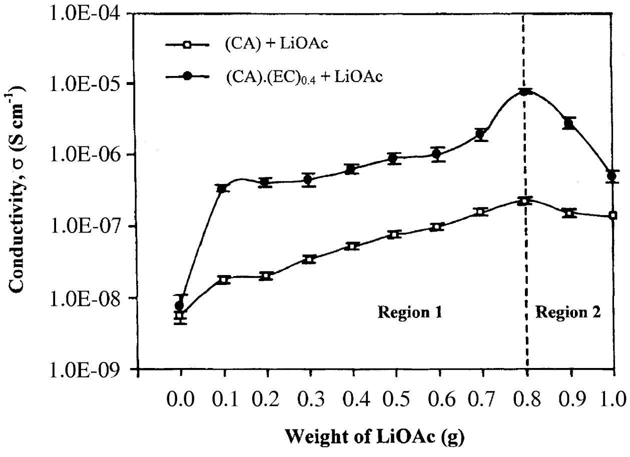

Fig. 3. Conductivity versus amount of dopant added for LiOAc films.

Fig. 4 depicts the plot of $\ln(\sigma T)$ versus $10^3/T$ for samples containing 0.1–1.0 g LiOAc in 1.0 g chitosan + 0.4 g EC dissolved in 100 ml 1% acetic acid solution. In order to determine whether the points for each sample lies on a straight line the regression value, r^2 was calculated. The r^2 value lies in the range from 0.988 to 0.998. This indicates that the relationship between $\ln(\sigma T)$ and $10^3/T$ is almost linear and therefore the conductivity and temperature relationship obey Arrhenius rule

$$\sigma(T) = (\sigma_o/T)\exp\{-E_A/k_T\} \qquad (4)$$

Here σ_o is the pre-exponential factor, E_A is the activation energy, k is Boltzmann constant and T is absolute temperature. As temperature increases, the vibration of the NH_2 groups that has formed a bond with the cation of the salt becomes more rigorous, and the transfer of ions could occur at a faster rate leading to an increase in conductivity. In other words the conductivity mechanism is thermally assisted. For the sake of comparison, in the EC plasticized $LiCF_3SO_3$ salted PEO polymer (Bandara, Dissanayake, & Mellander, 2000), the room temperature conductivity is 1.4×10^{-6} S cm^{-1} which is comparable to the conductivity of our system, 7.6×10^{-6} S cm^{-1}. The highest room temperature α-alumina added EC plasticized $LiCF_3SO_3$ salted PEO film reported by the same authors is 3.1×10^{-5} S cm^{-1}. At 108 °C the conductivity for the α-alumina added sample is 2.6×10^{-3} S cm^{-1}. This is comparable to the conductivity of the highest conducting plasticized sample in the present work which is 2.7×10^{-3} S cm^{-1}. Hence, if the conventional polymer systems have potential application in the development of

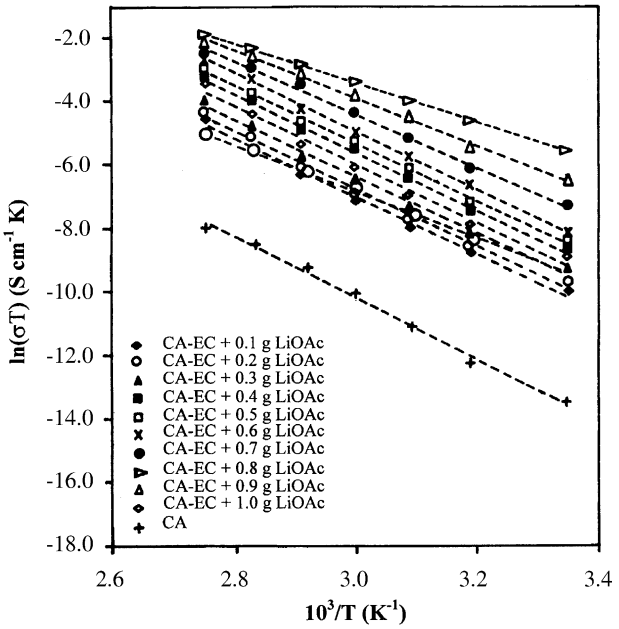

Fig. 4. The Arrhenius plot for different weights of dopant of LiOAc in acetylated chitosan (AC) + 0.4 g EC.

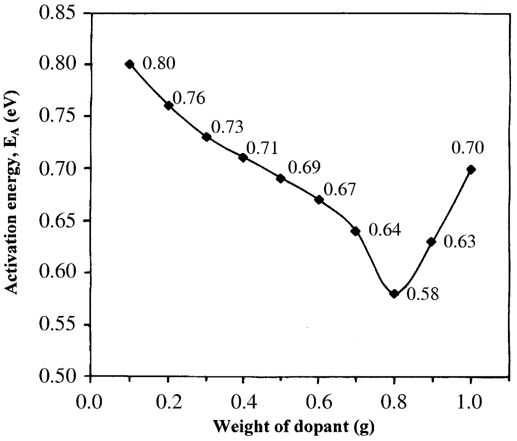

Fig. 5. Activation energy dependence on LiOAc content.

electrochemical devices, it may also be true for the system investigated in the present work.

Fig. 5 depicts the variation of E_A with the amount of lithium salt added during preparation. The film exhibiting the highest electrical conductivity has the lowest activation energy. This is because the amorphous nature of the chitosan polymer electrolyte facilitates the fast Li-ion motion in the polymer network and it further provides a higher free volume in the polymer electrolyte system upon increasing the temperature (Micheal, Jacob, Prabaharan, & Radhakrishna, 1997).

Fig. 6 depicts the imaginary part, $M''(\omega)$ of the modulus formalism with respect to frequency. It can be observed that the peak of the plots shifts towards the low frequency region as the conductivity of the sample decreases. The peak represents the conductivity relaxation peak for the distribution of relaxation times of the free charge (Mishra, Baskaran, Ramakrishna, & Rao, 1998). The peak shifts to higher frequency as the conductivity increases indicating that the relaxation time decreases as conductivity increases. The existence of such peaks may be indicative that the samples are ionic conductors (Mellander & Albinsson, 1996).

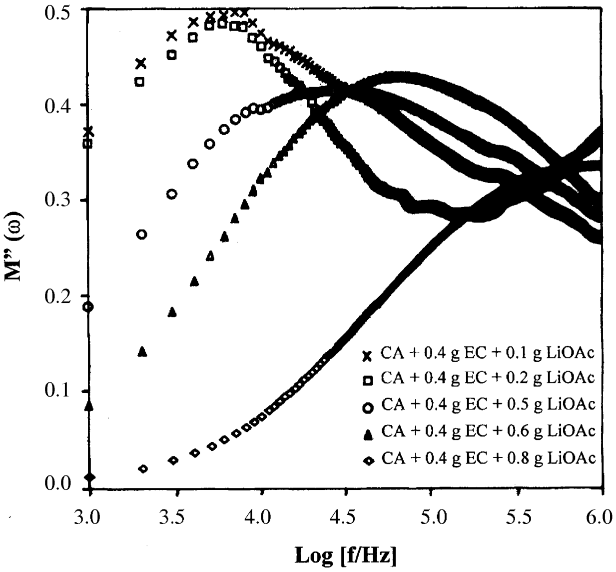

Fig. 6. Imaginary part of modulus formalism versus frequency at different LiOAc salt concentration.

4. Conclusion

XPS confirms complexation between the polymer and salt. The peak of the Li 1s binding energy at ~55.2 eV in the lithium signal and the peak at binding energy of 403.1 eV in the nitrogen signal are conclusive evidence for the N–Li complexation. XPS studies also show the possible formation of transient crosslinks. Ion association and dissociation controls the conductivity of the system under investigation. Conductivity–temperature studies for chitosan–LiOAc–EC complexes indicate that the conductivity increases with temperature. The plot of ln(σT) versus $10^3/T$ obeys Arrhenius rule. The work has also shown that the chitosan biopolymer can be a potential candidate to replace the liquid components in electrochromic devices.

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