Conductivity Studies on Chitosan/PEO Blends with LiTFSI Salt

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Abstract. Chitosan/PEO-LiTFSI films have been prepared by the solution cast technique. The highest conductivity at room temperature was 1.4×10^{-6} Scm^{-1} and the activation energy was 0.47 eV for chitosan/PEO blends containing 30 wt.% LiTFSI salts. The conductivity of the samples is dependent on the number of mobile ions.

1. Introduction

Chitin and chitosan have gained a lot of commercial interest due to their excellent properties including biocompatibility, biodegradability, and ability to form films and to chelate metal ions [1]. Chitosan is a fiber-like substance derived from chitin, a co-polymer of β-(1,4)-N-acetyl-D-glucosamine unit. Modification of chitosan through blending with other polymers [2,3] and cross-linking [4,5] are both convenient in improving its mechanical strength and increasing the conductivity by suppressing the crystallization of the polymer chain. Quite a number of publications has investigated the structure and properties of chitosan/PEO films [6-8]. It has been reported that chitosan/PEO films exhibit good mechanical properties because of the specific inter-molecular interactions between chitosan and PEO in the blends.

This paper deals with the ionic conductivity of chitosan/PEO blends with low lattice energy and bulk anions of lithium trifluoromethanesulfonimide $(LiN(CF_3SO_2)_2)$ or LiTFSI salts. The density of mobile ions, diffusion coefficient and mobility have been calculated to understand the transport properties of these samples.

2. Experimental Description

Chitosan with medium viscosity obtained from FLUKA and polyethylene oxide (PEO) (MW = 300,000 $gmol^{-1}$) obtained from Aldrich was used as received. Chitosan/PEO (50:50 w/w) solutions were prepared by dissolving chitosan and PEO in dilute acetic acid. The solution was stirred overnight at room temperature until complete dissolution was achieved. In the present study, 5 wt.% to 35 wt.% of LiTFSI salts were added to the chitosan/PEO solution. The solutions were then stirred again and then cast into several petri dishes and left to dry at room temperature for films to form. The films were then transferred into a desiccator for continuous drying before any further experiment.

Impedance spectroscopy was performed using a HIOKI 3522-01 LCR Hi-Tester interfaced to a computer with frequency range of 50 Hz to 1 MHz to study the ionic conductivity of the samples. The onductivity was also studied in the temperature range between 298 and 358 K. The film was sandwiched between two blocking stainless steel electrodes of a conductivity cell. The ionic conductivity of the sample was calculated from

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

where A is the area of the film-electrode contact, t is the thickness of the film and R_b is the bulk resistance of the film in ohms obtained from the complex impedance measurements.

3. Results and Discussions

Figure 1 depicts the variation of ionic conductivity at room temperature, σ_{RT}, and the activation energy, E_a, with the amount of salt added during the preparation. The film with the highest electrical conductivity has the lowest activation energy due to the free volume in the
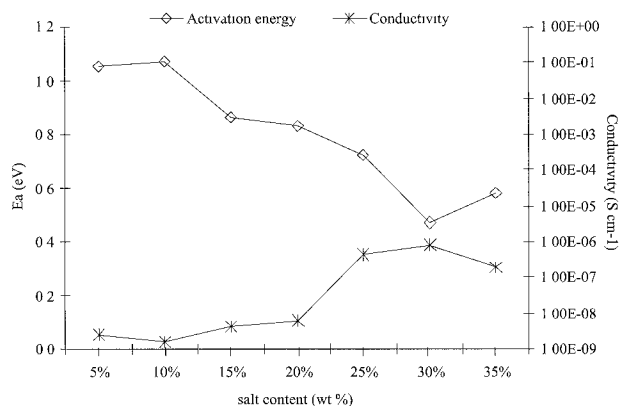
Fig. 1. Variation of the conductivity and activation energy as a function of salt content.

polymer electrolyte system upon increasing temperature [9]. The room temperature electrical conductivity of the highest conducting sample was 1.4×10^{-6} Scm^{-1} for chitosan/PEO blends containing 30 wt.% LiTFSI. The increase in conductivity with salt concentration could be attributed to the increase in the number of mobile ions and vice versa as a result of their involvement in interchain reactions [10].

Figure 2 depicts the plot of log σ versus $10^3/T$ for the highest conducting sample from which the activation energy was evaluated using Arrhenius' equation

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where σ_o is the pre-exponential factor, E_a is the activation energy, T is the absolute temperature and k is Boltzmann's constant. The increase in conductivity with
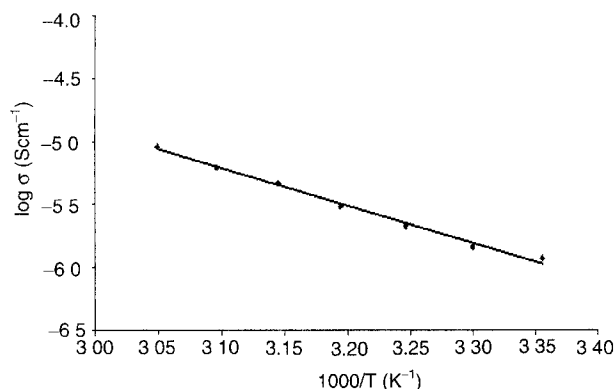

Fig. 2. Temperature dependence of the ionic conductivity for the 30 wt.% LiTFSI in chitosan/PEO blends.
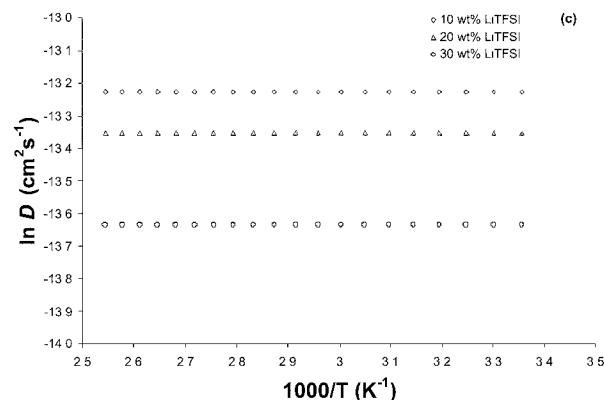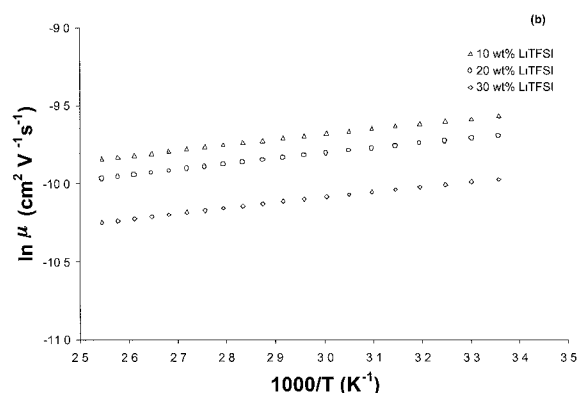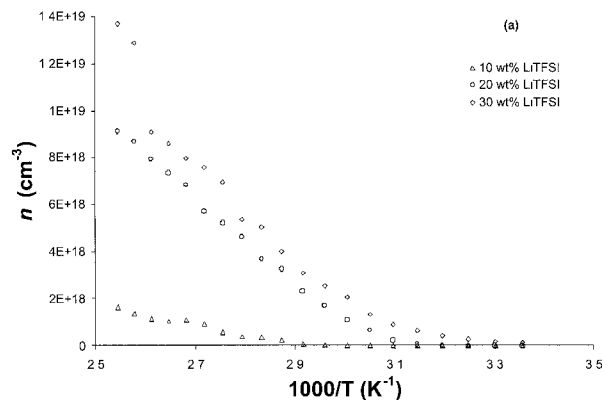

Fig. 3. (a) Plot of density of mobile ions, n versus 1000/T (b) plot of ln mobility, μ, versus 1000/T and (c) plot of ln diffusion coefficient, D, versus 1000/T.

temperature is quite similar to that occurring in ionic crystal where ions jump into a neighboring vacant site [11].

The number density of mobile ions (n), mobility (μ) and diffusion coefficient (D) for samples containing 10, 20 and 30 wt.% LiTFSI salt are shown in Fig. 3(a-c). It is observed that as the temperature increases, the values

for n and D increase and the values for μ decrease. From the Rice and Roth model [12], the ionic conductivity, σ is given by

$$\sigma = \left[\frac{2(Ze)^2}{3kTM}\right] nE\tau \ \exp\left(\frac{-E_a}{kT}\right) \qquad (3)$$

with the assumption that after receiving energy E, the ionic carrier will be excited from a localized state to another state with velocity v. The velocity is given by

$$v = \sqrt{\frac{2E_a}{M}} \qquad (4)$$

where M is the mass of the ion and the mean free path, l is given by $l = v\tau$. The mean free path is the distance between two chitosan monomers and was taken as $\sim 10^{-9}$ m [13]. Knowing the value of n, the values of μ and D can be calculated using the formula

$$\mu = \frac{\sigma}{nq} \qquad (5)$$

$$D = \frac{kT\sigma}{ne^2} \qquad (6)$$

The mobility values obtained in this work are comparable with the values reported by Gorecki et al. [14].

4.   Conclusion

Chitosan/PEO blends were prepared using the solution cast technique. The highest conductivity obtained at room temperature was 1.4×10^{-6} Scm^{-1} and the activation energy was 0.47 eV for chitosan/PEO blends containing 30 wt.% of LiTFSI salt. From the calculation using the Rice and Roth model, the conductivity was found to be dependent on the number of mobile ions.

5.   References

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