Transport Studies on Filler-doped Chitosan Based Polymer Electrolyte

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Abstract. The room temperature conductivity of the chitosan complex containing 40 wt.% of salt increased from 6.02×10^{-6} Scm^{-1} to 2.10×10^{-5} Scm^{-1} after the addition of 1.0 wt.% aluminosilicate. Conductivity of the electrolyte is contributed from the charge carrier density and ionic mobility. The Rice and Roth model was applied in calculating the mobility, μ and density of ions, n. The number density of ions, n, increases with temperature, while mobility, μ decreases with increasing temperature. This work also suggests that the filler did not change the conduction mechanism of the charge carrier in chitosan-salt-filler complexes but helped to increase the conductivity value of the materials.

1. Introduction

Conducting polymer composites have attracted the attention of materials researchers. The addition of filler such as SiO_2 [1], and Al_2O_3 [2-3] to polymer-salt complexes has been reported to help improve the mechanical stability of the sample and also increase the conductivity. Chitosan is a deacetylated form of chitin; chitosan is more useful for biomedical applications and dehydrations of aqueous solutions than chitin, since it has both hydroxyl and amino groups that can be easily modified [4]. We have previously report a transport studies on chitosan acetate complexed with NH_4NO_3 using the Rice and Roth model [5-6] in order to investigate the effect of salt to this polymer.

In the present work, to the Chitosan-NH_4NO_3 complex composition that exhibits the highest room temperature conductivity aluminosilicate was added. The effects of such fillers on the conduction mechanism of the charge carriers were investigated.

2. Experimental Method

2.1. Film Preparation. 1 gram of chitosan was dissolved in 100 ml 1 % acetic acid and was continuously stirred at room temperature for several hours. The solution was then added with 40 wt.% ammonium nitrate salt. The homogenous solution then was cast into several plastic Petri dishes to get the salted chitosan films. Several sets of salted chitosan solution were prepared. Aluminosilicate filler in the concentration range from 0.3 to 3 wt.% was added to each set of solution. The solutions were then cast and left to dry to form chitosan-salt-filler films. Listed in Table 1 are the prepared samples.

2.2. Conductivity Measurements. The dried films were cut into a suitable size and mounted on the conductivity holder with stainless steel electrodes of diameter 1 cm under spring pressure. The conductivity measurement of all samples was measured using the HIOKI 3531-01 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz and also at temperatures of 298 K-373 K. The electrical conductivity was then calculated using the equation:

Table 1. Chitosan acetate complexed with 40 wt.% NH_4NO_3 with various filler content.

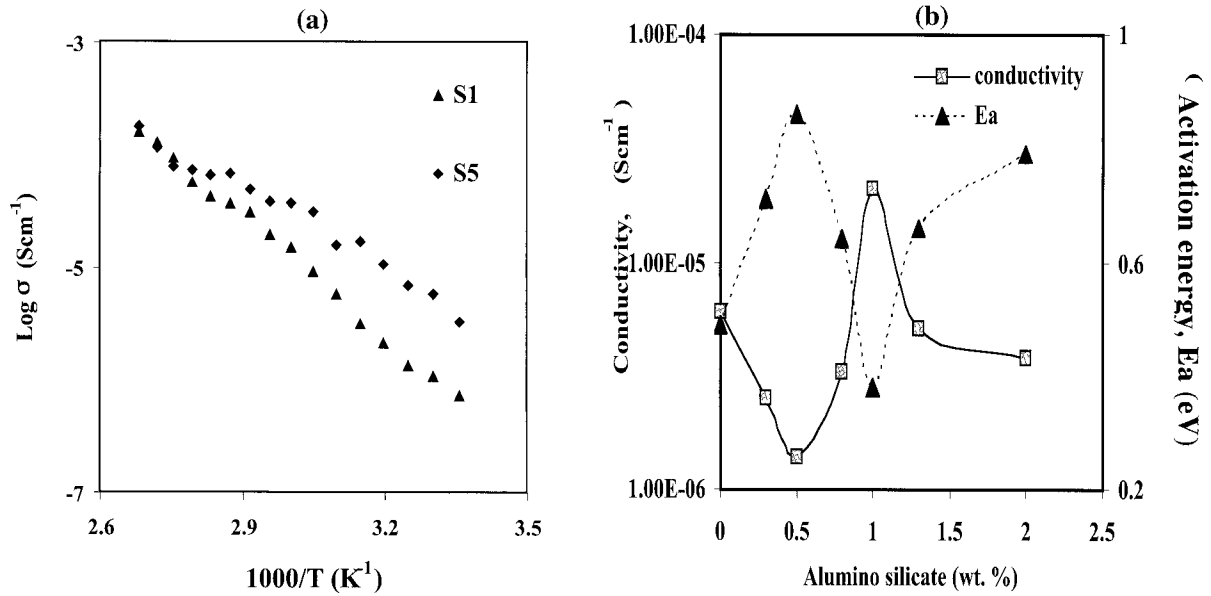| Designation	Al_2SiO_5 Content (wt.%)
S1	0
S2	0.3
S3	0.5
S4	0.8
S5	1.0
S6	1.3
S7	2.0

Fig. 1. (a) Temperature dependence conductivity versus temperature Conductivity and (b) Activation energy versus filler content.

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

Here t is thickness of the sample, A is the surface area of contact and R_B is the bulk resistance of the sample.

3. Results and Discussion

Figure 1(a) shows the temperature dependence of conductivity for sample S1 and S5 as representative examples

at various temperatures for this system. It can be noted that the conductivity increases as temperature increases showing that the conductivity is thermally assisted. This also implies that the conductive environment of H^+ in the sample is liquid like and remains unchanged in the investigated temperature regions [7]. The activation energy can be calculated from the slope of the plot and illustrated in Fig. 1(b). The highest conducting film shows the lowest activation energy.
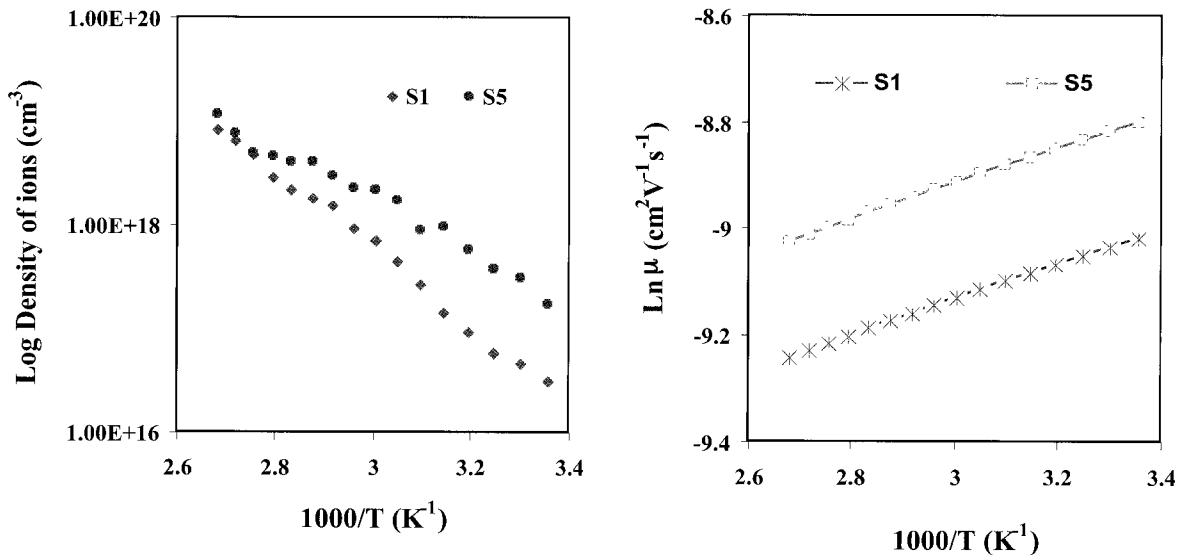

Fig. 2. (a) Number density of ions and (b) Mobility of ions versus temperature.
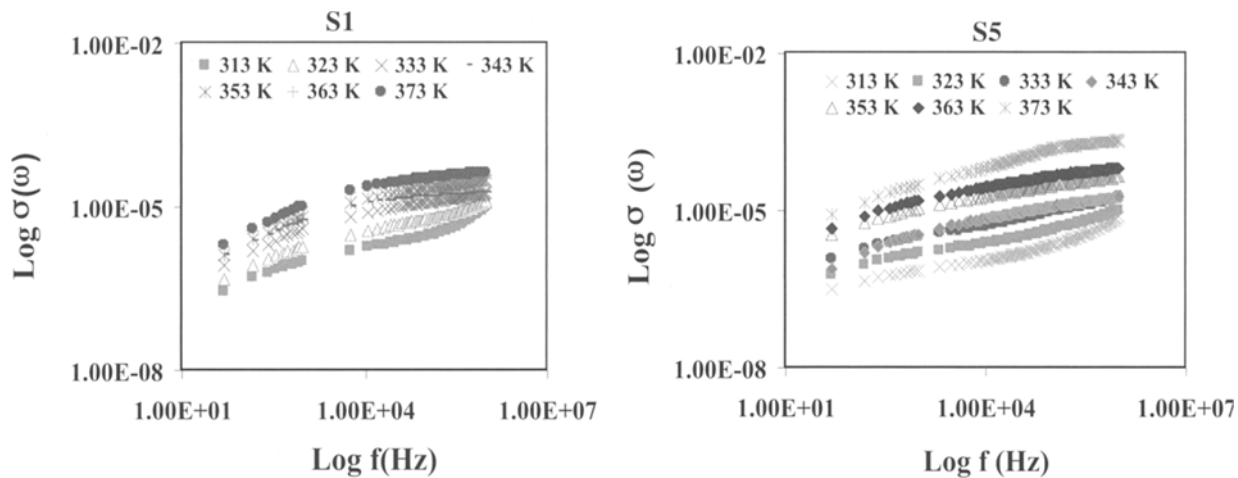
Fig. 3. Variation ac conductivity versus frequency for S1 and S5 at selected temperatures.

Presented in Fig. 2(a) is the number density of ions and (b) is mobility of ions, n at various temperatures. This parameter, n is calculated using following this equation:

$$n = \frac{\sigma k TM}{2(Z_e)^2 E\tau \exp(E/kT)}$$

while the ionic mobility can be expressed as:

$$\mu = \frac{\sigma}{\eta q}$$

Here k is Boltzman constant, T is temperature, M is mass of charge carrier, Z is number of charge carrier, e is elementary charge, E is activation energy and τ is relaxation time. The number density of ions, n for S5 is calculated to be higher than S1 where from Fig. 1(a) the conductivity of this sample is also higher than S1. This implies that when the sample was exposed to heat, more ions were created suggesting that the filler has helped the salt to dissociate more ions which contribute to the increase in conductivity. However, the tendency of ions to be more mobile decreases because the increase of mobile ions has blocked the pathway of ions as can be seen in Fig. 2(b). Agrawal et al. [8] reported that the increase of n
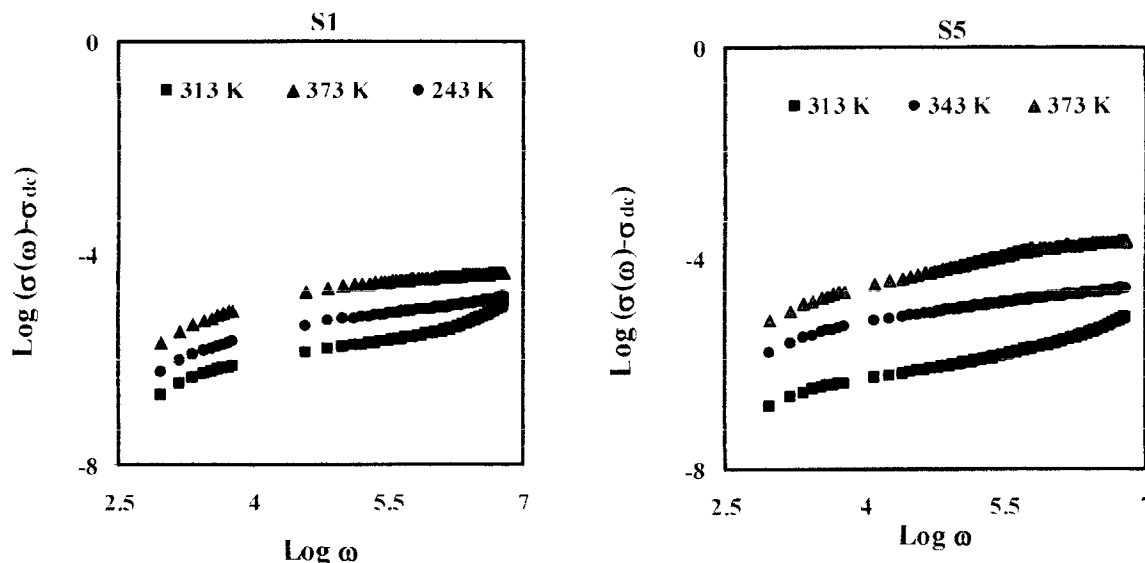

Fig. 4. Plot of log $\sigma(\varpi)$-σ_{dc} versus log f at selected temperatures for S1 and S5.
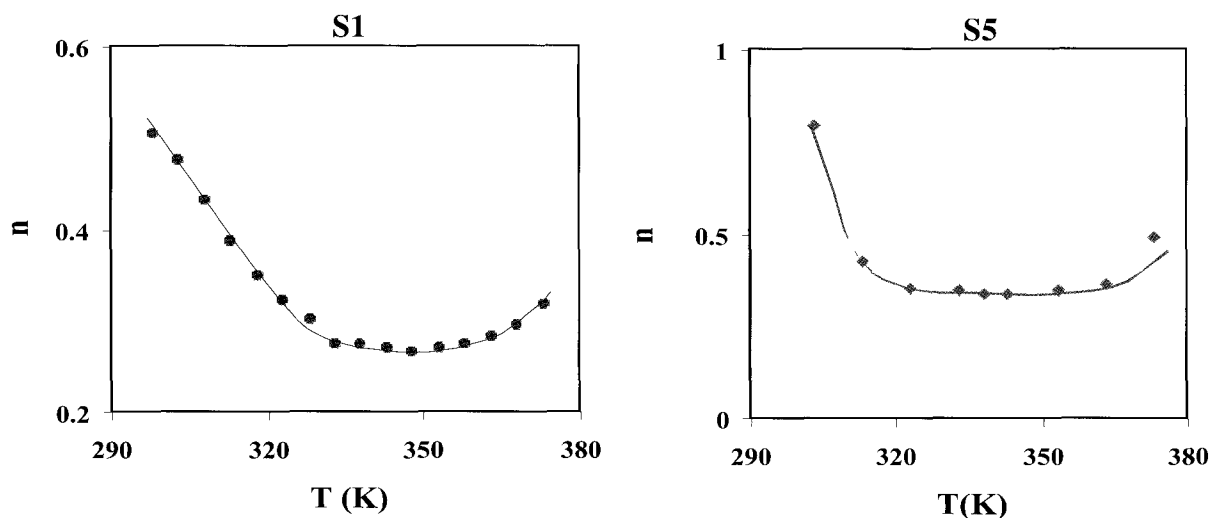
Fig. 5. Variation of exponent n versus temperature for S1 and S5.

with increasing temperature can be attributed to the dissociation of the ionic salt which can be explained by weak electrolyte model. The decreases of mobility, μ, with increasing of temperature from 0.61 to 0.05 $cm^2V^{-1}s^{-1}$ is probably due to the increase in the partial (blocked) pathways and/or decrease in the preferred pathways for ion migration, as suggested in the cluster-by-pass model.

The frequency dependence of a.c conductivity, σ_{ac} at various temperatures is shown in Fig. 3 for samples S1 and S5 respectively as a representative example for the investigated system. It can be noted that values of σ_{ac} of the investigated samples obey the general relation:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n$$

Here A is a parameter dependent on temperature, σ_{dc} is frequency independent and n is the power law exponent (0 < n < 1). The values of the exponent n can be determined from the experiment data using the equation:

$$n = \frac{\log(\sigma(\omega) - \sigma_{dc})}{\log \omega}$$

The plot of log $\sigma(\omega)$-σ_{dc} versus log f at selected temperatures for samples S1 and S5 is presented in Fig. 4.

In order to identify the conduction mechanism, different models have been proposed to explain the a.c.

conductivity in this work. Among these models are the quantum mechanical tunneling (Q.M.T.) [9-10], the correlated barrier hopping (CBH) and the overlapping large polaron tunnelling (OLPT)[11]. The values of exponent n as a function of temperature are plotted in Fig. 5.

The values of n lies between ~0.3 to 0.7 and decreases with increasing temperature until certain temperature after which n increases as temperature increases for all samples under investigation. The behavior shows good agreement with the OLPT model. Since S1 is highest conductivity polymer-salt complex at room temperature and S5 is the highest conductivity polymer-salt-filler complexes at room temperature, the addition of aluminosilicate filler does not in any way change the conduction mechanism of the charge carriers.

4. Conclusion

Transport parameter such as mobility and number of mobile ions has been calculated for filler doped chitosan complexes. Both parameters are temperature dependence. It was clearly seen that the conductivity is dependent on the number of mobile ions. Analysis of the experimental conductivity data shows that the overlapping large polaron tunneling (OLPT) model is the most applicable conduction mechanism for the investigated system. The addition of fillers does not change the conduction mechanism of the charge carriers.

5. Acknowledgment

6. References

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