Conductivity Studies Of Chitosan Based Solid Polymer Electrolyte Incorporated With Ionic Liquid

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Abstract

Chitosan:NH_4I + 1-butyl-3-methylimidazolium iodide [BMIM][I] ionic liquid (IL) based polymer electrolyte were prepared by solution cast technique. The ratio of chitosan and ammonium iodide (NH_4I) salts was fixed at 55:45 (wt. %). Various concentrations of ionic liquid incorporated into the chitosan:NH_4I films have been studied. The highest room temperature ionic conductivity was obtained for the sample containing 80 wt. % IL with the value of 8.47×10^{-4} S cm^{-1}. Dielectric properties of this film have been studied in the temperature range 303 K to 343 K. The AC conductivity was found to increase with increasing frequency and temperature. The plot of AC conductivity versus frequency follows the Jonscher power law $\sigma_{AC} = A\omega^s$.

Keywords: chitosan, ionic liquid, polymer electrolyte

1. INTRODUCTION

Ionic liquids are organic salts that exist as liquid at room temperature and contain essentially ions. Ionic liquids (ILs) have become a part of the "green chemist ry" [1-2] due to unique properties such as non-volatility, non-flammable, high thermal stability and high ionic conductivity [3-7]. These unique properties of IL has led to applications in areas such as chemical sensor, electrochemical capacitors, polymer batteries, solar cells, fuel and water electrolysis cells and electrochromic systems [8-13].

In this work, the electrical behavior of chitosan with ionic liquid has been investigated. Chitosan is a natural polymer synthesized by the deacetylation of chitin [14-15]. Various models such as correlated barrier hopping (CBH) model, quantum mechanical tunneling (QMT) model and small polaron hopping (SPH) model will be applied to determine the AC conduction mechanism for this system.

2. EXPERIMENTAL

The polymer electrolytes were prepared by solution cast technique. Chitosan and ammonium iodide (NH_4I) salts were dissolved in 50 ml dilute acetic acid with ratio 55:45 (wt. %). The solution was stirred for 24 h at room temperature. After the solution was dissolved in dilute acetic acid, 1-butyl-3-methylimidazolium iodide [BMII] ionic liquid (IL) were added to the solution and the mixtures were continuously stirred until complete dissolution. The solutions were cast in different petri dish and allowed to evaporate at ambient temperature for films to form.

The polymer electrolyte films were cut into suitable sizes and sandwiched between two stainless steel electrodes under spring pressure. The impedance of the sample was determined by the complex impedance technique using a HIOKI bridge in the frequency range between 50 Hz to 1 MHz at different temperatures.

3.0 RESULTS AND DISCUSSION

3.1 Conductivity Studies

Fig. 1 shows the Cole–Cole plot (Nquist plot) of chitosan:NH_4I doped with 60 wt. % IL at selected temperatures. The conductivity of the electrolyte can be calculated from the equation

$$\sigma = \frac{t}{R_b A} \quad (1)$$

Here, A is the area of the film, t is its thickness and R_b is bulk resistance. R_b was obtained from the complex impedance plot at the intersection of the plot and the real impedance axis. The disappearance of semicircle in high frequency region indicates that the conduction is mainly due to the ions [16].

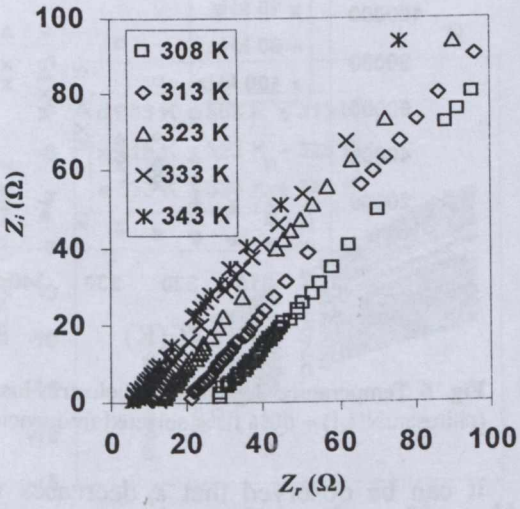

Fig. 2 Impedance plot of (chitosan:NH_4I) + 60% IL

Conductivity at room temperature of the electrolyte with different concentrations of ionic liquid (IL) is shown in Table 1.

Table 1 Conductivity at room temperature for all sample studied

Samples	Conductivity, σ (S cm^{-1})
(Chitosan:NH_4I) + 0% IL	3.73×10^{-7}
(Chitosan:NH_4I) + 20% IL	1.27×10^{-6}
(Chitosan:NH_4I) + 40% IL	1.20×10^{-5}
(Chitosan:NH_4I) + 60% IL	8.50×10^{-5}
(Chitosan:NH_4I) + 80% IL	8.47×10^{-4}

It can be observed that the conductivity increases with the increase in IL content. The increase in conductivity with IL content implies that the number density of mobile ions, n in the electrolyte and/or the mobility of the ions has/have increased since

$$\sigma = nq\mu \quad (2)$$

where n is number density of mobile ions, q is electron charge and μ is mobility of ions. The highest conductivity can be observed at 80 wt. % IL with the value of 8.47×10^{-4} S cm^{-1}. However at this ratio, the polymer electrolyte is not completely dry compared to the film with 40 % (chitosan:NH_4I) + 60 % IL that exhibits conductivity of the order 8.5×10^{-5} S cm^{-1}.

3.2 Dielectric Studies

The real part of complex permittivity or dielectric constant (ε_r) and dielectric loss (ε_i), imaginary part of complex permittivity can be calculated from

$$\varepsilon_r = \frac{Z_i}{\omega C_0 \left(Z_r^2 + Z_i^2\right)} \quad (3)$$

$$\varepsilon_i = \frac{Z_r}{\omega C_0 \left(Z_r^2 + Z_i^2\right)} \quad (4)$$

Here $C_0 = \varepsilon_0 A/t$, ε_0 is permittivity of free space and $\omega = 2\pi f$, Z_i and Z_r is the imaginary and real parts of the complex permittivity, respectively. The dielectric constant was calculated in the frequency range of 50 Hz to 100 kHz. Fig. 2 shows the angular frequency, ω dependence of dielectric constant (ε_r) for (chitosan:NH_4I) + 60 wt. % IL at selected temperatures. It can be observed that ε_r decreases with the increase in frequency and is almost constant at high frequencies. At low frequency, electrode polarization is observed [17-18].

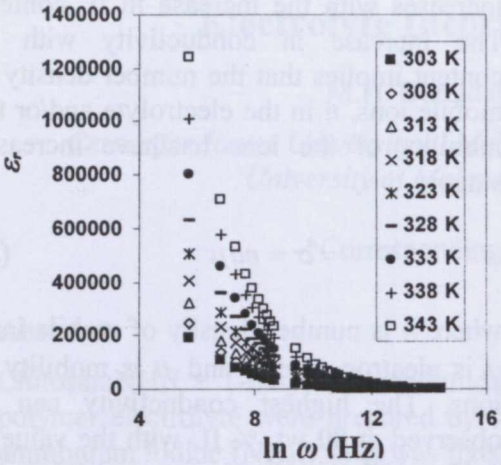

Fig. 2 Frequency dependence dielectric constant for (chitosan:NH_4I) + 60% IL at selected temperatures

Fig. 3 shows the temperature dependence on dielectric constant (ε_r) at certain frequencies. It can be seen from the figure that ε_r increases with the increase in temperature and it shows strong temperature dependence at lower frequencies.

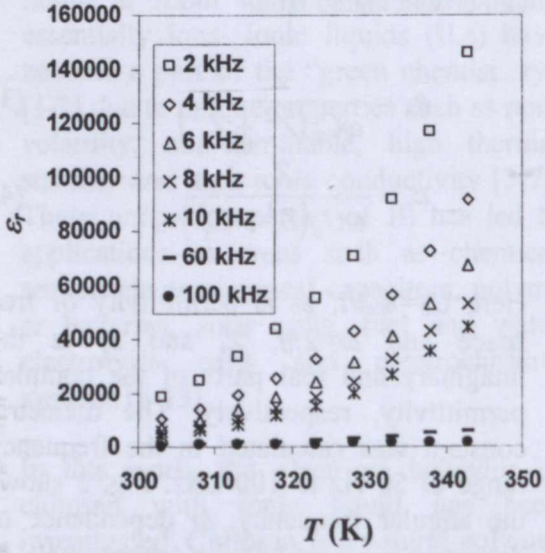

Fig. 3 Temperature dependence dielectric constant for (chitosan:NH_4I) + 60% IL at selected frequencies

Frequency and temperature dependence dielectric loss (ε_i) is shown in Fig. 4 and Fig. 5.

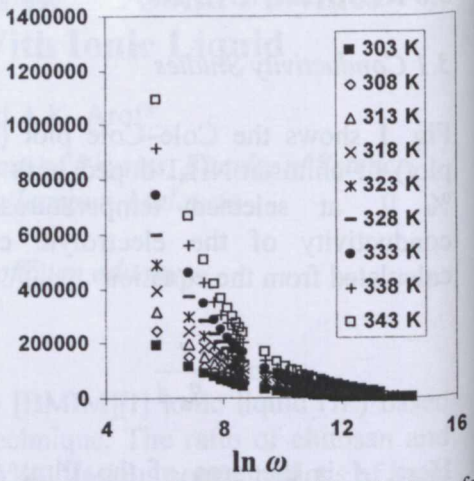

Fig. 4 Frequency dependence dielectric loss for (chitosan:NH_4I) + 60% IL at selected temperatures

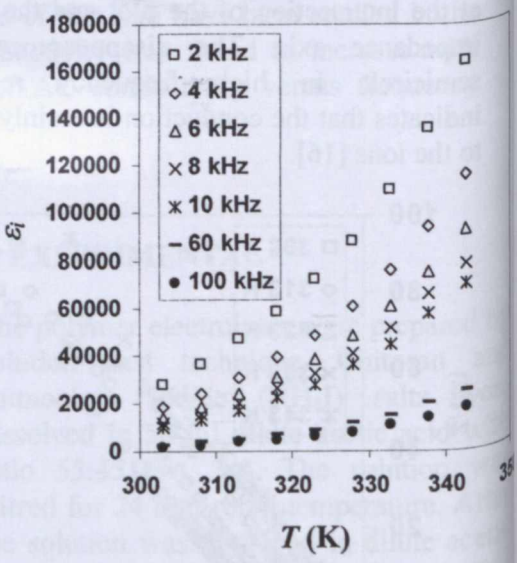

Fig. 5 Temperature dependence dielectric loss for (chitosan:NH_4I) + 60% IL at selected frequencies

It can be observed that ε_i decreases with the increase in frequency for a fixed temperature but increases with increasing temperature for a fixed frequency. Dielectric loss is also observed to show strong temperature dependence at low frequencies.

3.2 Frequency Dependence AC Conductivity

Fig. 6 shows the variation of the AC conductivity (σ_{AC}) with frequency. From the figure, it can be observed that σ_{AC} is

found to increase with increasing frequency. The dependence of the AC conductivity on frequency is given by universal power law [19-20]:

$$\sigma_{AC} = \sigma_{tot} + \sigma_{DC} = A\omega^{s} \quad (5)$$

and

$$\ln \sigma_{AC} = \ln A + s \ln \omega \quad (6)$$

where σ_{DC} is the DC part of the total conductivity σ_{tot}, A is a constant, ω is the angular frequency and s is the power law exponent with the value in the range between 0 and 1. The value of exponent s can be obtained from the slope $\ln \sigma_{AC}$ versus $\ln \omega$ in the high frequency region (f > 28 kHz) where there is no or minimal space charge polarization.

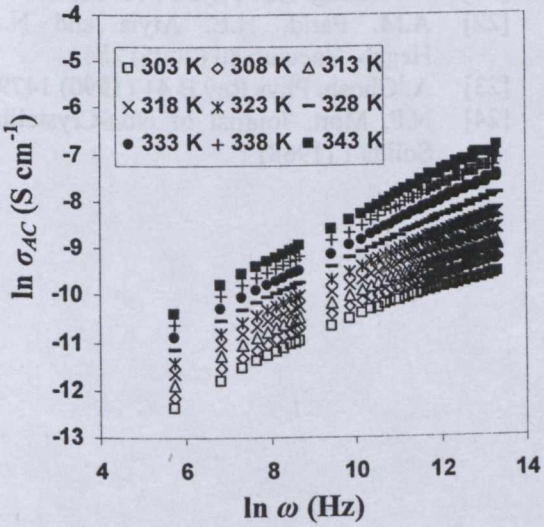

Fig. 6 ln σ_{AC} versus ln ω for (chitosan:NH_4I) + 60% IL at selected temperatures

To determine the conduction mechanism of materials, different theoretical models have been developed such as overlapping large polaron tunneling (OLPT) model, correlated barrier hopping (CBH) model, quantum mechanical tunneling (QMT) model and small polaron hopping (SPH) model. According to OLPT model [21], the exponent s decreases with increasing temperature to a minimum value then it increases with increasing temperature. In CBH model [22], s decreases with increasing temperature but no minimum in s is observed. According to QMT model [23], the exponent s is almost equal to 0.8 and increases slightly with increasing temperature or independent on temperature. In the small polaron (SPH) model [24], s has been observed to increase with temperature. The temperature dependence of s for (chitosan:NH_4I) + 60% IL film is shown in Fig. 7. It can be observed that s increases with increasing temperature. This is in good agreement with the SPH model. Thus the frequency dependence of σ_{AC} can be explained in terms of SPH model.

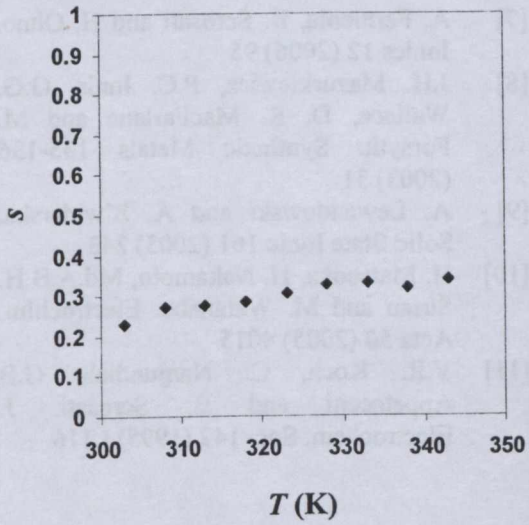

Fig. 7 s versus T for (chitosan:NH_4I) + 60% IL

4. CONCLUSIONS

The electrolyte based on chitosan:NH_4I and chitosan:NH_4I + 1-butyl-3-methylimidazolium iodide [BMII] ionic liquid (IL) were prepared by solution cast technique. The addition of IL into the electrolyte enhanced the conductivity up to 8.47 x 10^{-4} S cm^{-1} at 80% IL and good solid polymer electrolytes are obtained until 60% IL. Conduction mechanism of (chitosan:NH_4I) + IL sample can be represented by SPH model.

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