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Ionic conductivity by correlated barrier hopping in NH_4I doped chitosan solid electrolyte

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ABSTRACT

Chitosan–NH_4I and chitosan–NH_4I–EC films have been prepared by solution cast technique. The sample containing 45 wt% ammonium iodide (NH_4I) exhibited the highest room temperature conductivity of $3.7\times10^{-7}\,S\,cm^{-1}$. The conductivity of the sample increased to $7.6\times10^{-6}\,S\,cm^{-1}$ when 40 wt% ethylene carbonate (EC) was added to the 55 wt% chitosan-45 wt% NH_4I sample. The conductivity–temperature relationship is Arrhenian. From dielectric loss variation with frequency, the power law exponent was obtained. The temperature dependence of the power law exponent for chitosan–NH_4I system follows the correlated barrier hopping (CBH) model while conduction mechanism of the plasticized system can be represented by the small polaron hopping (SPH) model.

1. Introduction

Many types of polymers have been studied in the pursuit to develop solid electrolyte systems. These include PVA [1–3], PVC [4,5], PVDF [5,6] and PEO [7,8]. These polymers have been complexed with various salts to provide the ions for conduction. Chitosan is a polymer derived from chitin [9,10]. It has high mechanical strength [11]. Some ion-conducting polymer electrolytes based on chitosan have been reported, e.g., chitosan:NH_4NO_3 [12], chitosan:$NH_4CF_3SO_3$ [13], hexanoyl chitosan:$LiCF_3SO_3$ [14–17] and chitosan blend with PEO and complexed with LiTFSI [18]. Donoso et al. [19] have carried out NMR studies on PEO–chitosan blend polymer electrolyte doped with $LiClO_4$. They have shown that the amine group in chitosan participates in the coordination of lithium ion. These results are in agreement with FTIR observations in which the amine band at $1590\,cm^{-1}$ shifted to lower wave numbers in lithium acetate [20,21] and lithium triflate-chitosan [22] complexes indicating Li–N coordination. Impedance spectroscopy has been applied to understand the dependence of complex conductivity on frequency in many polymer electrolyte systems. The variation of conductivity on frequency can be divided into two parts viz., the frequency independent and the frequency dependent regions.

Conductivity in the frequency dependent region increases in a power-law trend becoming almost linear at high frequencies. Polaronic conductors also exhibit behavior similar to ionic conductors [23]. Hence, in this work models based on polarons such as quantum-mechanical tunneling (QMT) [24], small polaron hopping (SPH) [25], large polaron tunneling (LPT) [26] and correlated barrier hopping (CBH) [27] models will be applied to determine the conduction mechanism in two chitosan-based electrolyte systems viz., chitosan–NH_4I electrolytes (System 1) and ethylene carbonate (EC) plasticized chitosan–NH_4I electrolytes (System 2).

2. Experimental

2.1. Preparation of electrolyte

The electrolyte films were prepared by the solution cast technique. 0.5 g chitosan (Fluka) was dissolved in 50 ml 1% acetic acid solution. To this solution, 5–50 wt% ammonium iodide (NH_4I) were added separately and the mixtures continuously stirred until complete dissolution. The solutions were cast in different petri dish and left to dry for films to form. To the highest conducting chitosan–NH_4I sample different amounts of EC (in wt%) were added.

2.2. Impedance spectroscopy

The polymer electrolyte films were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrodes under spring pressure. The impedance of the sample was determined using the complex impedance technique. The conductivity of the electrolyte can be calculated from the

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equation

$$\sigma = t/R_b A \quad (1)$$

Here, A is the area of the film and t its thickness. 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.

3. Results and discussion

3.1. Conductivity studies

The conductivity of the chitosan–NH_4I and chitosan–NH_4I–EC systems at room temperature is illustrated in Fig. 1. From Fig. 1a, it can be observed that conductivity of the sample increases with increase in salt content. The highest conductivity is observed for the sample containing 45 wt% NH_4I at $3.7 \times 10^{-7}\,S\,cm^{-1}$. As the salt content increases, the number density of mobile ions, η in the electrolyte increases and from the Rice and Roth model [28] that expresses the conductivity, σ as

$$\sigma = \frac{2}{3}\left[\frac{(Ze)^2}{kTm}\right]\eta E_A \tau \exp\left[\frac{-E_A}{kT}\right] \quad (2)$$

the conductivity is expected to increase when η increases. In Eq. (2) Z, E_A and m is the valency, activation energy and mass of the conducting ion, respectively. T is absolute temperature, k is Boltzmann constant and e is electron charge. τ is time to travel between sites. Above 45 wt% NH_4I the conductivity decreases and can be attributed to the reassociation of the ions into neutral aggregates [29,30]. Fig. 1b, shows the effect of EC on the conductivity of the highest conducting chitosan–NH_4I sample. EC does not supply ions to the electrolyte system. It is a plasticizer that is able to dissociate more salt into ions and has a low viscosity that can increase ionic mobility. It can be observed that conductivity of sample increases to $7.6 \times 10^{-6}\,S\,cm^{-1}$ at 40 wt% EC. Beyond 40 wt% EC, the conductivity decreased.

In polymer electrolytes, there are two possible mobile ionic species, i.e., cations and anions. The type of cation responsible for the ionic conductivity in polymer–ammonium salt system has been identified by coloumetric investigation [31] to be H^+. Srivastava and Chandra [32] and Hashmi et al. [33] have reported that in poly(ethylene succinate) complexed with ammonium perchlorate and PEO–NH_4ClO_4 systems, the conducting species is H^+ ion. Following these authors, for the present polymer–salt system, the NH_4^+ ions of NH_4I will be coordinated to the N atom of the amine group in chitosan. The NH_4^+ cations have ideal tetrahedral structure. One of the four hydrogen atoms in NH_4^+ ions is most weakly bound and can dissociate easily under the influence of an electric field. This H^+ ion can hop from one site to another leaving a vacancy which will filled by another H^+ ion from a neighboring site. Thus, the charge transport is carried out by structure diffusion or better known as Grotthus mechanism, i.e., the conduction occurs through proton exchange between chitosan–NH_4I complexed sites. Proton conduction by the Grotthus mechanism involves intermolecular proton jump creating a vacant site followed by reorientation to occupy the vacant site. Therefore, protonic transport in System 1 (conventional polymer electrolyte) is by Grotthus mechanism. Majid and Arof [12] have also inferred that H^+ is the conducting species in chitosan acetate–NH_4NO_3 sample and the proton conduction of polymer electrolyte film occurs by Grotthus mechanism.

The $\log\sigma$ versus $1000/T$ plot for both systems in Fig. 2, confirms that the temperature dependence of ionic conductivity obeys Arrhenius rule,

$$\sigma = \sigma_0 \exp[-E_A/kT] \quad (3)$$

Here σ_0 is the pre-exponential factor. The activation energy, E_A can be obtained from the slope of the $\log\sigma$ versus $10^3/T$ graphs. Activation energy is the energy required for an ion to begin movement. In the context of polymer electrolytes, the ion is usually "loosely bound" to a site with donor electrons. When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site. The movement from one site to another results in the conduction of charge and the energy for this conduction is the activation energy. According to the Anderson–Stuart model [34], the activation energy is the sum of the binding energy of the ion to its site and the kinetic energy for migration. If the energy of the ion is only sufficient to overcome the binding energy, then it will be dislocated from its site but will still be at the same location. Only if it has more energy than this binding energy will it be a free ion. It can be observed that E_A decreases as conductivity of sample increases implying that the ions in highly conducting samples require lower energy for migration. Table 1 lists the activation energy value for all samples studied. As a note, the E_A value for the sample without plasticizer in System 1 ranges from 0.77 to 0.46 eV. PVP doped with NH_4SCN [35] exhibits a decrease in activation energy from 0.74 eV when the NH_4SCN content is 15 mole% to 0.52 eV at 20 mole% NH_4SCN and rises again to 0.54 eV when the salt content is 25 mole%. This trend also exists in the range of E_A values for our samples. The sample with lowest E_A in the case of PVP–NH_4SCN system also has the highest conductivity at room temperature. In our earlier work [12] the sample 90 wt% CA–10 wt% NH_4NO_3 exhibits an activation energy of 0.79 eV. This is almost similar to

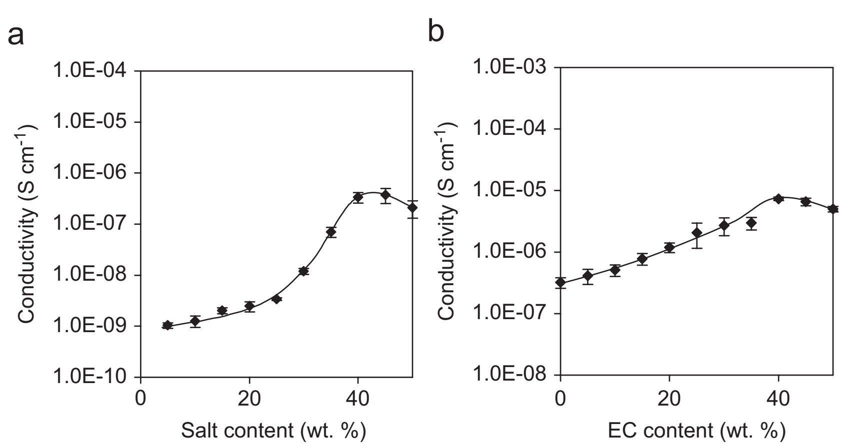

Fig. 1. The ionic conductivity of: (a) chitosan with various concentrations of NH_4I and (b) of 60 wt% chitosan-40 wt% NH_4I with various concentration of EC.