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Research Article

Synthesis and Ion Conductivity Studies of Na^+ Ion Conducting Nano Composite Polymer Electrolytes

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Abstract

Synthesis and ionic conductivity studies of a new Na^+ ion conducting nano-composite polymer electrolytes (NCPEs): (1-x) [70PEO:30NaBr] + x SiO_2, where $0 < x < 20$ wt%, are reported. NCPE films have been synthesized using a recently developed hot-press technique in place of the traditional solution cast method. The highest ionic conductivity (σ) (~ 6.3×10^{-5} $S.cm^{-1}$) has been determined at room temperature of the composition: [93(70PEO:30NaBr) + $7SiO_2$] and this has been referred to as optimum conducting composition (OCC). To explain the conductivity enhancement in the present NCPEs, ionic mobility (μ) and mobile ion concentration (n) measurements carried out with the help of dc polarization method. The ionic transference number (t_{ion}) of NCPE OCC only determined at room temperature to explain the ionic nature of the present systems.

Keywords: *Nano composite polymer electrolytes, ionic conductivity, ionic mobility, ionic transference number*

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Introduction

The ion conducting superionic solids or solid state ionic materials are new class of solid systems which exhibit high ionic conductivity comparable to liquid/ aqueous electrolytes. These materials, widely known as ‘Superionic Solids’ or ‘Solid Electrolytes’, show great technological promises as potential electrolyte systems to fabricate all solid-state electrochemical devices viz. batteries, fuel cells, super-capacitors, memories electrochromic displays etc. [1-6]. Among the known superionic solids, ion conducting polymer electrolytes (PEs) is one of the important areas of research in the last 30 years. Ion conducting PEs shows great technological promises to develop all-solid state devices viz. sensors, fuel cells and flexible thin film batteries in desirable shapes/ sizes [7-11]. The conventional solid polymer electrolyte films are found to be poor conductivity, less flexibility and less mechanical stability. Very recently, the nano-composite polymer electrolytes (NCPEs) are shows technological importance over the SPEs. The recent technique developed for solid polymer electrolytes is the dispersion of nano-size inorganic ceramic filler particles such as Al_2O_3, SiO_2, TiO_2, SnO_2, ZnO etc. in the electrolyte systems [12-15]. Sodium salts exhibit several advantages such as these are available in low cost, this can be potentially used for industrial applications [16-19]. Hence in the present investigation, a new Na^+ ion conducting salt NaBr has been selected as a dopant-salt to prepare the NCPEs. The SPE/ NCPE films are traditionally prepared by solution-cast/ sol-gel method. However, this is a time consuming procedure in the sense that it takes few days to weeks to cast completely dry films. Recently, for casting of ion conducting SPE/ NCPE films, a hot-press technique has been developed which shows several advantages such as it is relatively a least-expensive, much more rapid procedure etc. [20-24].

The present paper reports the synthesis and ionic conductivity studies of a new Na^+ ion conducting nano-composite polymer electrolytes (NCPEs): (1-x) [70PEO:30NaBr] + x SiO_2, where $0 < x < 20$ wt%. The ion conductivity enhancement in the present NCPEs are reported with the help of experimental measurement of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}).

Experimental Details

The AR grade precursor chemicals: poly (ethylene oxide) PEO (10^5 Mw, Aldrich, USA), NaBr (purity > 98%, Merck, India) and nano filler SiO_2 (> 99.8%, size ~ 8nm, Sigma Aldrich, USA) have been used for synthesis of the present Na^+-ion conducting NCPEs: (1-x) (70PEO: 30NaBr) + x SiO_2, where 0 < x < 20 wt%. These NCPEs were casted by using hot-pressed method in place of traditional solution-cast technique. The SPE composition (70PEO:30NaBr) was identified as the highest conducting composition from the salt-concentration-dependent conductivity study in previous communication [25]. This highest conducting composition has been used as a host matrix for casting the present NCPEs. The dry powders of PEO: NaBr in 70:30 (wt%) (as the first-phase) and nano-sized SiO_2 in different wt% ratios (as the second phase dispersoid) were mixed homogeneously, heated at ~70 °C in SS blocks and then pressed. A thin hot-pressed polymeric film with thickness ~ 0.016 cm. has been obtained in the present NCPE systems.

To explain the ion conduction behavior in the present system, ionic conductivity (σ) -measurements were carried out by using the following equation:

$$\sigma = \frac{l}{R_b.A} \qquad [S.cm^{-1}] \qquad (1)$$

where R_b is the bulk resistance, l is the thickness and A is the cross sectional area of the polymeric sample material. The bulk resistance R_b was determined from the impedance analysis by using an LCR- bridge (model: HIOKI 3520-01, Japan). The ionic mobility (μ) and ionic transference number were also determined by using transient ionic current (TIC) technique [26, 27] with the help of following equations:

$$\mu = \frac{d^2}{V.\tau} \qquad [cm^2V^{-1}s^{-1}] \qquad (2)$$

and

$$t_{ion} = 1 - \frac{I_e}{I_T} \qquad (3)$$

where I_e is the electronic current and I_T is the total current of the cell: [SS // NCPE OCC // SS]. Subsequently, the mobile ion concentrations were also determined from the well-known relation:

$$\sigma = n.q.\mu. \qquad (4)$$

Results and discussion

The salt/ filler SiO_2 concentration dependent ionic conductivity (σ) of hot-pressed nano-composite polymer electrolytes (NCPEs): (1-x) (70PEO: 30NaBr) + x SiO_2, where 0 < x < 20 wt% is shown in **Figure 1**. The ionic conductivity (σ) of NCPE increases with increasing the nano-filler SiO_2 concentration and two maximum values of conductivity 6.3×10^{-5} $S.cm^{-1}$ and 3.0×10^{-5} Scm^{-1} observed at 7 and 13 wt% of SiO_2. The approximate two orders of conductivity enhancement were observed from that of pure SPE host: (70PEO: 30NaBr). However, the maximum conductivity of 6.3×10^{-5} Scm^{-1} has been observed at 7 wt% of SiO_2 (i.e. the composition: 93(70PEO: 30NaBr) + $7SiO_2$) and this composition is known as optimum conducting composition (OCC). The ionic conductivity enhancement in NCPE is also due to the Lewis acid-base reactions and increase in degree of amorphicity. The decrease in room temperature conductivity at higher filler concentration is due to the ion-ion association (pairing) effect, as reported in by various workers [28-30].

To explain the conductivity enhancements in the present system, ionic mobility (μ) and mobile ion concentration (n) of NCPEs were also determined directly at room temperature using dc polarization TIC technique. **Figure 2** shows 'log μ-x' and 'log n-x' plots for NCPEs: (1-x) (70PEO: 30NaBr) + x SiO_2. It is obvious from the figure that the increase in room temperature conductivity of NCPE OCC is due to the increase in both μ and n and this is due to the available of more numbers of mobile Na^+ ions and free conduction paths in the system. The room temperature values of some of the ionic parameters: σ, μ, n and t_{ion} are listed in **Table 1**, for direct comparison.

Table 1 Some important ion transport parameters of hot-pressed SPE host, NCPE OCC and ionic conductivity of pure PEO at room temperature

Systems	σ (Scm^{-1})	μ ($cm^2V^{-1}s^{-1}$)	n (cm^{-3})	t_{ion}
Pure PEO	3.2×10^{-9}	---	---	---
SPE host: (70PEO:30NaBr)	7.5×10^{-7}	7.2×10^{3}	6.5×10^{14}	0.95
NCPE OCC: [93 (70PEO: 30NaBr) + 7SiO_2]	6.3×10^{-5}	2.3×10^{2}	1.6×10^{15}	0.95

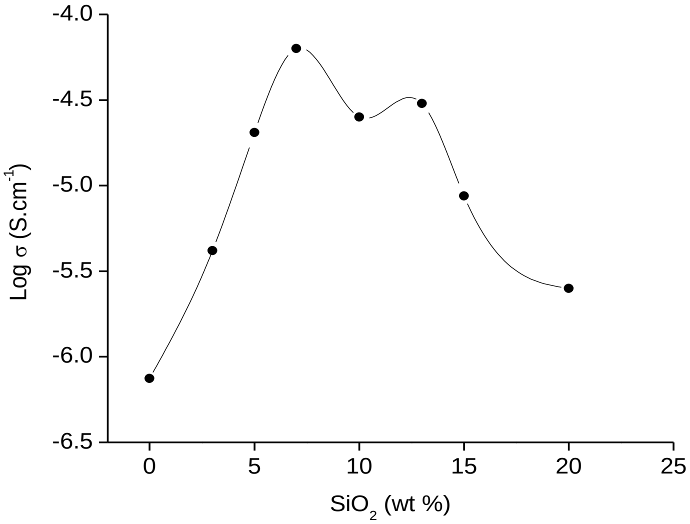

Figure 1 'Log σ – x' plot for NCPEs: (1-x) [70PEO: 30NaBr] + x SiO_2, where x in wt. %

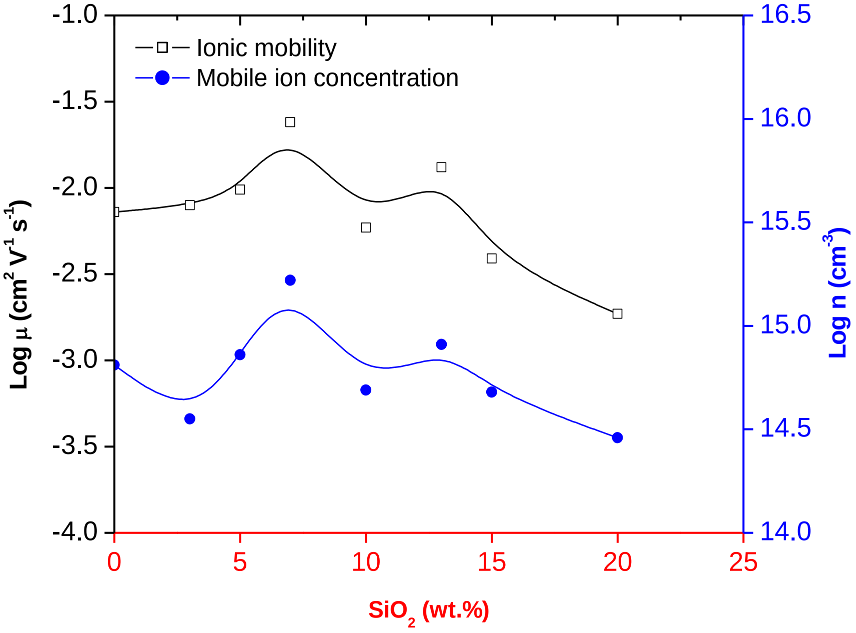

Figure 2 'Log μ–x' and 'log n–x' plots for NCPEs: (1-x) (70PEO:30NaBr) + x SiO_2

Figure 3 shows the temperature dependant conductivity variation of NCPE OCC: 93(70PEO: 30NaBr) + 7 SiO_2. The increase in ionic conductivity with temperature can be interpreted as a hoping mechanism between coordinating sites, local structural relaxation and segmental motions of the polymer electrolyte complexes which result in an increase in free volume, as reported elsevier [31, 32]. The upward changes in slope at ~ 60 °C are observed which is due to the well-known semi-crystalline to amorphous phase change/ melting point temperature of PEO-based polymers The straight line portions of the plot below this transition temperature can be linearly fitted-in very well in the following Arrhenius equation:

$$\sigma\,(T) = 2.28 \times 10^{0} \exp\,(-0.27/\,kT) \qquad [Scm^{-1}] \qquad (5)$$

where k is Boltzmann constant, T is temperature in Kelvin and E_a = 0.27 in eV is the activation energy values for hot-pressed NCPE OCC. The lower activation energy (E_a) indicates that this can be potentially used for solid state device fabrications.

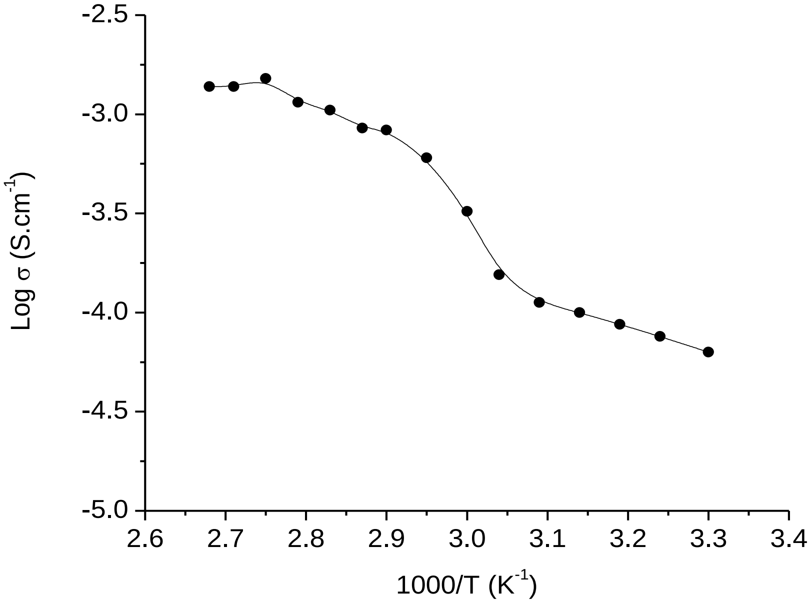

Figure 3 'Log σ – 1/T' plot for NCPE OCC: [93 (70PEO:30NaBr) + 7 SiO_2]

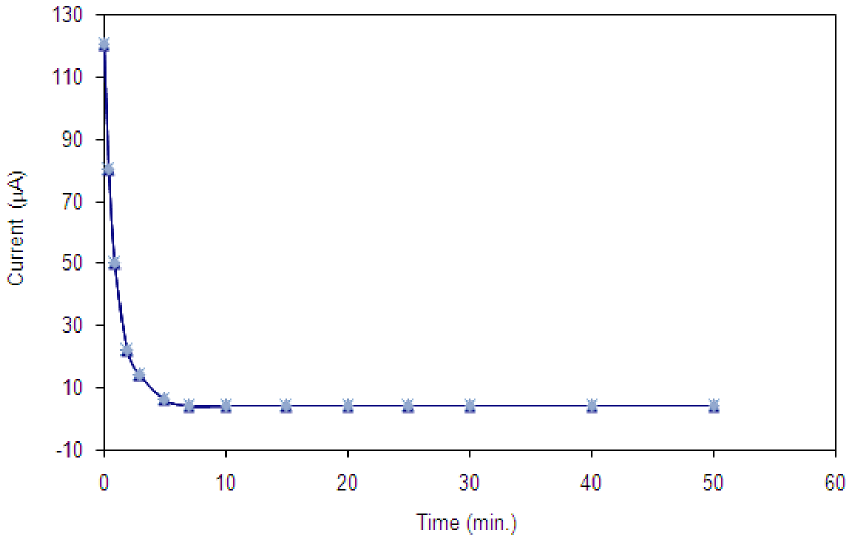

Figure 4 'Total current (I_T) vs time' plot for NCPE OCC: [93 (70PEO:30NaBr) + 7 SiO_2]

To explain the ionic nature of the present NCPE, ionic transference number (t_{ion}) was also evaluated at room temperature by using TIC technique. **Figure 4** shows the 'total current (I_T) versus time' plots for hot-pressed NCPE OCC: 93(70PEO:30NaBr)+ 7 SiO_2. It can be clearly observed in all the plots that the initial total current (I_T) finally approached near to zero with the lapse of time. This is indicative of the fact that the system remained purely ionic $t_{ion} \simeq 0.95$ and hence the charge transport in the present system is predominantly ionic with a negligible contribution (~ 0.05) of electrons.

Conclusions

A new Na^+ ion conducting nano-composite polymer electrolyte (NCPE): [93(70PEO:30NaBr)+ 7SiO_2] has been synthesized by hot-press method. The two orders of conductivity enhancement (~ 6.3×10^{-5} $S.cm^{-1}$) were achieved at room temperature. The ionic mobility and mobile ion concentration both are responsible for the conductivity and stability enhancement in the present NCPE system. The low activation energy in the present system indicates that it can be potentially used for ion conducting solid state device applications.

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