

SYNTHESIS AND ION CONDUCTION STUDIES OF A NEW K⁺ ION CONDUCTING NANO-COMPOSITE POLYMER ELECTROLYTES

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ABSTRACT

Synthesis and ion conduction studies of a new K⁺ ion conducting nano-composite polymer electrolytes (NCPEs): (1-x) [80PEO:20KI] + x TiO₂ where 0 < x < 20 wt. %, are reported. NCPEs were cast using a recently developed hot-press method in place of traditional solution-cast technique. Two and half orders of conductivity enhancement were found in NCPEs after the dispersion of TiO₂ inert material in the polymeric host, from the room temperature conductivity measurement. The ion conduction phenomenon have been explained with the help of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) values and various theoretical models. The ionic transference number (t_{ion}) of optimum conducting composition of NCPE was also determined with the help of Transient Ionic Current (TIC) technique.

Keywords: Nano-composite polymer electrolytes, ionic conductivity, ionic transference number

Amongst the known superionic solids, ion conducting nano-composite polymer electrolytes (NCPEs) are recently attracting great deal of technological attentions due to their tremendous scopes in developing wide variety of all-solid state electrochemical devices viz. batteries, sensors, fuel cells, electrochromic displays etc. [1-6]. Solid polymer electrolyte (SPE)/ nano-composite polymer electrolyte (NCPE) films are traditionally prepared by solution cast method. However, this is a time consuming procedure in the sense that it takes few days to weeks to cast completely dry films. In place of solution-cast method, a novel hot-press technique which is relatively a least-expensive as well as much more-rapid procedure is widely being employed to prepare solution free / dry SPE/ NCPE films. Hot-press technique has recently been developed at the present research laboratory and numbers of polymer electrolyte membranes have been hot-press casted [7-10].

The present paper reports the preparation and ion transport behavior of a new K⁺ ion conducting nano-composite polymer electrolytes (NCPEs): (1-x) [70PEO:30KI] + x TiO₂, where 0 < x < 15 wt.%. SPE composition: (70PEO:30KI), identified as the highest conducting film at room temperature, has been used as Ist-phase polymer electrolyte host and nano size (~ 11 nm)

TiO₂ filler particles as IInd dispersoid phase. The ion transport properties of NCPE membranes have been investigated studying some basic ionic parameters viz. conductivity (σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) etc. NCPE film exhibiting Optimum Conducting Composition (OCC) has been identified and the activation energy values, involved in ion transport through NCPE/ SPE materials, have been computed by least square linear fitting of the respective 'log $\sigma - 1/T$ ' Arrhenius plots.

EXPERIMENTAL SECTION

AR grade chemicals: poly (ethylene oxide) PEO (10⁵ MW, Aldrich, USA), KI (purity > 98%, Reidel, India), TiO₂ (> 99.8%, size ~ 8nm, Sigma, USA) were used for preparation of a new K⁺ -ion conducting NCPE films: (1-x) [70PEO: 30KI] + x TiO₂, where 0 < x < 15 wt. %. The details on hot-press procedure have been given earlier in our earlier communications [10-12]. The highest conducting Ist-phase SPE host: (70PEO: 30KI) was identified from salt concentration dependent conductivity studies, while study of 'log $\sigma - x$ ' variation at room temperature revealed NCPE OCC film. An LCR-bridge (HIOKI 3520 - 01, Japan) has been employed for σ -measurements at a fixed frequency (i.e. 5 kHz). The ionic mobility (μ) and ionic transference number (t_{ion}) in both SPE and NCPE OCC membranes were directly determined at room temperature using a dc polarization Transient Ionic Current (TIC) technique [13]. Subsequently, mobile ion concentration (n) was evaluated from ' σ ' & ' μ ' data. The experimental

details regarding dc polarization measurements have appeared elsewhere [8-12]. The temperature dependent conductivity measurements were also carried out on both SPE & NCPE OCC films and the activation energy (E_a) values were computed from the respective Arrhenius plots.

RESULTS AND DISCUSSION

The salt concentration dependent conductivity for the hot-pressed conventional solid polymeric electrolyte (SPE) membranes: (PEO:KI) is shown in Fig. 1. Initially, σ increased abruptly after 10 wt.% salt complexation in PEO then relatively slowly upto 30 wt.%, followed by the decrease in conductivity on further addition of the salt. A moderate-sized conductivity maxima with $\sigma \sim 6.3 \times 10^{-7} \text{ S.cm}^{-1}$ occurred for SPE film composition: (70PEO:30KI). The reason for the abrupt increase in σ may be due the complexation of KI in PEO resulted into a large enhancement of the amorphous region in polymeric host which in turn gave rise to a rapid increase in the ionic mobility and hence, the conductivity. SPE films beyond 50 wt.% salt in PEO physically/ mechanically appeared less-flexible/ brittle [11]. SPE film composition: (70PEO:30KI), has been chosen as 1st - phase polymer electrolyte host for the synthesis of nano composite polymer electrolytes (NCPEs): (1-x) [70PEO:30KI] + x TiO₂, as mentioned.

Fig. 2 shows TiO₂-filler particle dependent room temperature conductivity plot for NCPE membranes: (1-x) [70PEO:30KI] + x TiO₂. The dispersal of nano-size (~ 11 nm) TiO₂ filler particles in the polymeric electrolyte host: (70PEO:30KI), resulted in 'log σ - x' variation containing two σ -maxima occurring at x = 7 & 12 wt.%. The appearance of two σ -peaks, noticed in most of the NCPE membranes, has usually been attributed to the existence of two kinds of conduction phenomenon and can be explained on the basis of percolation theories suggested for composite electrolyte systems [14]. σ - enhancement of approximately two orders of magnitude ($\sigma \sim 2.0 \times 10^{-5} \text{ S.cm}^{-1}$) could be achieved further in NCPE film composition: 93(70PEO:30KI) + 7 TiO₂ from that of the pure polymer electrolyte host: (70PEO:30KI). This has been referred to as Optimum Conducting Composition (OCC) NCPE film. The reason of σ -enhancement was identified by ionic mobility (μ) and mobile ion concentration (n) measurements.

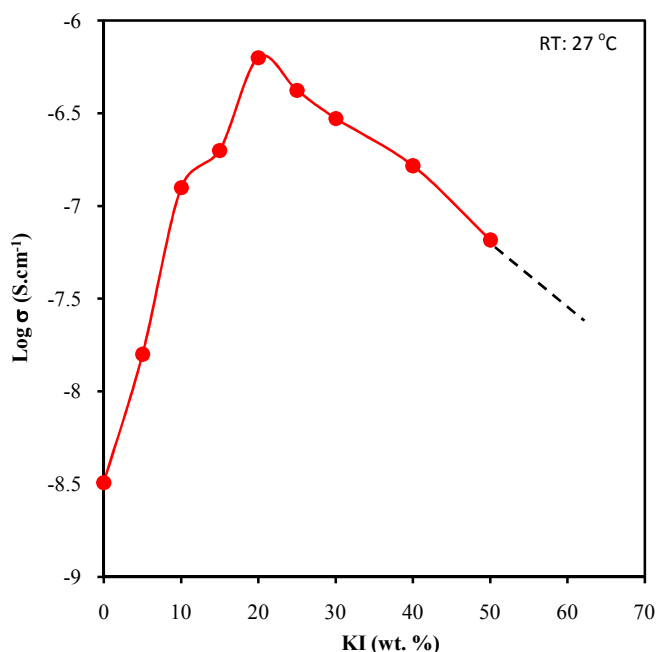


Figure 1: Room temperature conductivity (σ) as a function of salt concentration in wt.% for hot-pressed SPE films: [PEO:KI] [11].

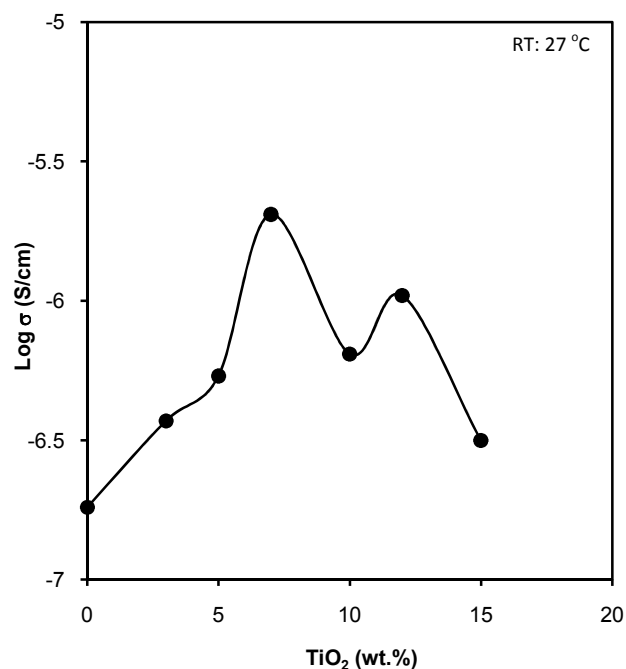


Figure 2: Room temperature conductivity (σ) as a function of TiO₂ filler particle concentration (x) for NCPE films: (1-x) [70PEO:30KI] + x TiO₂.

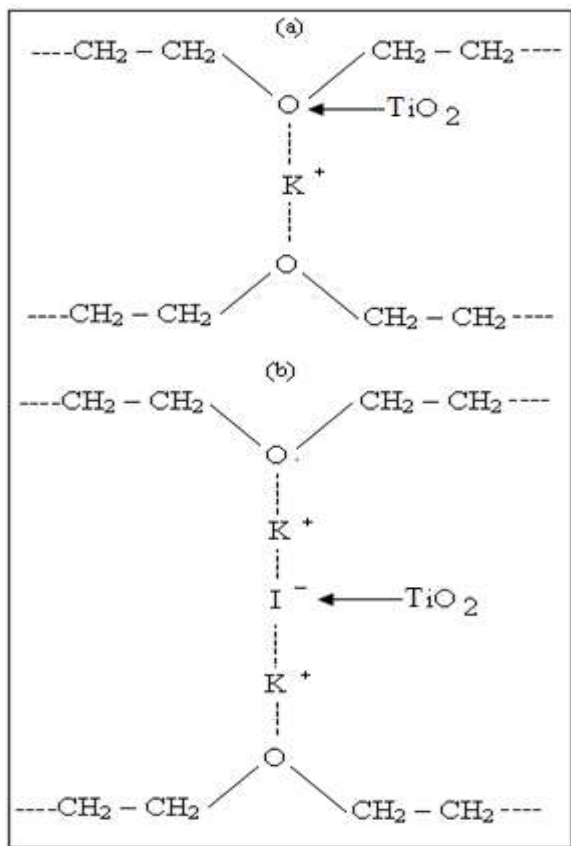


Figure 3: The schematic representation of two kinds of possible configuration of newly synthesized NCPE.

The existence of two maxima in the present NCPE can also be attributed to two separate percolation thresholds involving two different kinds of mobile species: cation (K⁺) and anion (I⁻). The ionic conductivity enhancement in NCPE is also due to the Lewis acid-base reaction [2,15]. The schematic representation of two kinds of possible configuration of newly synthesized hot-pressed NCPE OCC is shown in Fig. 3.

Fig. 4 shows the current vs time plot for NCPE OCC film. The ionic transference number (t_{ion}) of NCPE OCC has been evaluated using dc polarization TIC technique by using the following equation:

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

where I_e is the electronic current and I_T is the total current of the cell: [SS // NCPE OCC // SS]. $t_{ion} \sim 0.92$ clearly indicates that the majority of charge carriers (~ 92 %) are cations K⁺ and only a very small contribution of anions. The higher t_{ion} in the present NCPE also indicated that the more numbers of K⁺ ions are mobile in the system and this is also support the increase in degree of amorphicity as well as available of more numbers of conduction paths by the dispersion of nano filler TiO₂ in the pure host polymers. The room temperature values

of σ , μ , n and t_{ion} obtained for NCPE OCC as well as SPE host membranes are listed below in Table 1 along with the conductivity of pure PEO. It can be clearly noticed that the overall increase in σ of NCPE OCC is due to the increase in both μ & n .

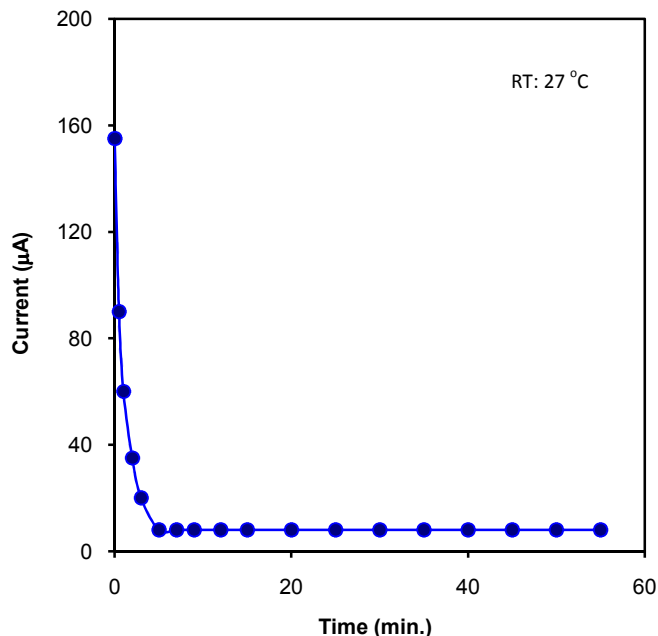


Figure 4: ‘Current vs time’ plot for NCPE OCC: 93(70PEO: 30KI) + 7 TiO₂.

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Fig. 5 shows the temperature dependant conductivity variations for hot-pressed films of SPE host: (70PEO:30KI) and NCPE OCC: 93[70PEO:30KI] + 7 TiO₂. It is clear from the figure that as the temperature is increases conductivity is increases and ‘log $\sigma - 1/T$ ’ plots exhibited straight line behavior with an upward change in slope at ~ 70 °C which is due to the well-known semicrystalline to amorphous phase change of PEO. The increase in ionic conductivity at higher

temperature is due to the increase in degree of amorphicity and available of free conduction paths which also be explained by free volume model. The straight line portions of both the plots below this transition temperature can be linearly fitted-in very well in the following Arrhenius equations:

SPE Host : $\sigma(T) = 1.44 \times 10^{-4} \exp(-0.34/kT)$ (2)

NCPE OCC : $\sigma(T) = 3.26 \times 10^{-2} \exp(-0.23/kT)$ (3)

where 0.34 and 0.23 in eV are the activation energy (E_a) values for SPE host and NCPE OCC respectively. The slight decrease in the activation energy for NCPE OCC from that of SPE host is indicative of increased mobility as a consequence increase in degree of amorphousity of PEO after TiO₂ dispersal and hence this can be potentially used for solid state device fabrications.

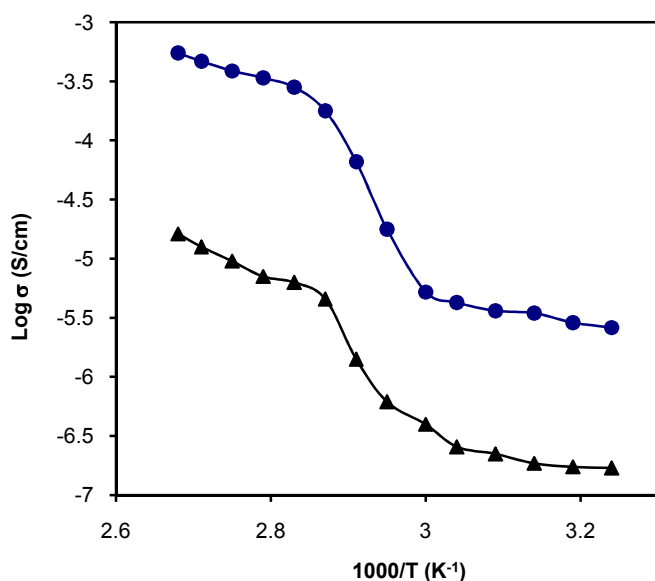


Figure 5: ‘Log σ-1/T’ plots: SPE host: (70PEO:30KI) (▲) and NCPE OCC: 93[70 PEO: 30KI]+ 7TiO₂ (●).

Table 1: Some important ionic parameter: σ, μ, &n for SPE & NCPE OCC membranes along with σ-value of pure PEO.

Systems	σ (S.cm ⁻¹)	μ (cm ² V ⁻¹ s ⁻¹)	n (cm ⁻³)	E _a (eV)
PEO	3.2 × 10 ⁻⁹	---	---	---
SPE host: (70PEO: 30KI)	6.3 × 10 ⁻⁷	2.8 × 10 ⁻³	1.3 × 10 ¹⁵	0.34
NCPE OCC: 93[70 PEO:30KI] + 7 TiO ₂	4.5 × 10 ⁻⁵	2.8 × 10 ⁻²	7.4 × 10 ¹⁵	0.23

CONCLUSION

A new K⁺ ion conducting nano-composite polymer electrolytes: 93[70PEO:30KI] + 7 TiO₂ has been synthesized by a novel hot- press technique. Dispersal of nano sized- TiO₂ filler particles into SPE host: [70PEO:30KI], enhanced the room temperature conductivity by approximately one order of magnitude. The increase in ionic mobility (μ) and mobile ion concentration (n) has been predominantly responsible for the overall increase in room temperature conductivity of NCPE. The ionic transference number measurements indicated the fact that charge transport in both SPE and NCPE materials takes place mainly due to ions and this can be potentially used for solid state device applications.

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