

Effect of LiCl Doping on Transport Properties of PTh-PEO Polymer Composite

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Abstract— Lithium Chloride (LiCl) has been used as dopant in PTh-PEO Polymer composite to improve the transport properties of polymer composite at ambient temperature. Polymer Composite membrane comprising polythiophene (PTh), Polyethylene oxide (PEO) and different wt. % of LiCl were prepared by *in situ* chemical oxidative polymerization method using FeCl₃ as a oxidant in methanol. The effect of lithium salt on the transport properties of the PTh-PEO polymer composite is discussed. The ionic transference numbers for the PTh-PEO composite films, synthesized with different wt. % of LiCl were determined by dc polarization techniques. The value of transference number for samples was found to be in the range of 0.90 to 0.91. The conductivity studies of these PTh-PEO composite films are carried out as a function of temperature in ranging of 303 K to 338 K. The maximum value of ionic conductivity is found to be -3.97 Scm^{-1} for the film containing 4 wt. % LiCl. The temperature dependence of the conductivity of polymer composite films seems to obey the Arrhenius relation.

Keywords: Lithium Chloride (LiCl), Transport Property, Ionic conductivity

I. INTRODUCTION

In the last two decades there is an explosive increase in the demand for composite materials, which are now available as materials with unique combination of properties. The electronic properties of conducting polymer and insulating polymer matrix combined with attractive mechanical properties and processing advantages of the polymers has now attained a level of maturity consistent with a new set of opportunities to develop a wide range of application based conducting polymer composites. Thus, the composites based on conducting polymers have been studied as materials for industrial products [1]. Polythiophene and its derivatives have been often considered as a model for the study of charge transport in conducting polymers and the high environmental stability of both their doped and undoped states [2]. There are many application areas of the conductive polymers. The most exciting developments are the new class of semiconducting devices such as plastic batteries, sensors, conductive surface, magnetic recording [3-5]. Recently we have discussed the electrical properties PTh-PEO polymer composites doped with Li₂SO₄. Here we report a detailed study of synthesis and characterization of PTh-PEO composites [6].

In the present work, the Polythiophene-Polyethylene oxide (PTh-PEO) composite doped with LiCl were prepared by *in situ* chemical oxidative polymerization method. The effect of various concentrations of LiCl on the transport properties of the PTh-PEO polymer composite films was investigated, with an intension to exploit these composites for various applications such as batteries and sensors.

II. EXPERIMENTAL

Polythiophene-Polyethylene oxide (PTh-PEO) polymer composite doped with LiCl was synthesized at ambient temperature (303 K) by *in situ* chemical oxidative polymerization method. Anhydrous FeCl₃ was used as an oxidizing agent. A solution of PEO was first prepared in methanol by stirring for 6 hr. and kept over a night.

Appropriate amount of Anhydrous FeCl₃ and LiCl were added and stirred for 15 min. When monomer thiophene was added drop by drop to the solution a dark brown homogeneous solution was obtained. The solution was then poured on a polypropylene dishes, to prepare the composite films. The wt. % of LiCl was changed from 1 to 6. For each wt. % of LiCl, quantity of thiophene was kept constant at 0.5 ml. The thiophene polymerization progresses because the evaporation of the solvent increases the oxidation potential of cast solution. After evaporation of the solvent, the polymer composite films were formed. The thickness of all films was measured using the Digimatic Micrometer (Milutoyo Make, Japan) with least count 1 μm ; all the films have thickness in the range 150 – 250 μm .

III. RESULTS AND DISCUSSION

The addition of LiCl to PTh- PEO polymer composite has induced improvement in the transport properties. The ionic / electronic transference number was measured by using dc polarization technique [7]. The ionic and electronic transference number can be defined as:-

$$t_{ion} = \sigma_{ion}/\sigma_T = I_{ion}/I_T \quad (1)$$

$$t_{e,h} = \sigma_e/I_e/I_T \quad (2)$$

where σ_{ion}/σ_e , and I_e/I_T are the conductivity and current contributions due to ions/ electrons respectively.

Figure 1 shows the variation of polarization current as a function of time for PTh-PEO composite doped with different wt. % of LiCl. As seen from fig.1 the total current becomes nearly constant at some non –zero value after some time. The final residual current is mainly due to electrons/holes. The ionic and electronic transference numbers are calculated separately from the polarization current verses time plot using the Equ (1) and (2). The values of transference number, for sample synthesized with different wt. % of LiCl are found to be in the range of 0.81 to 0.93. This suggests that the charge

transport in the PTh-PEO Composite doped with different wt. % of LiCl is predominantly due to ions only.

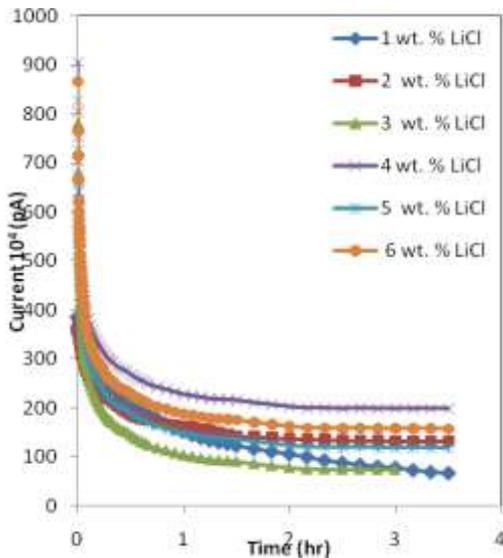


Fig. 1 Variation of polarization current as a function of time for PTh-PEO Composite Doped with LiCl.

The temperature dependant conductivity of PTh-PEO polymer composite was measured by using Ohms law. The variation of ionic conductivity with different wt. % of Lithium chloride (LiCl) at constant temperature 323K is shown in figure (2). As compared to pure PTh-PEO polymer composite, the conductivity of doped polymer composite initially increases up to 4 wt. % LiCl and then decreases. PTh-PEO composite doped with the 4 wt. % LiCl shows the maximum value of ionic conductivity. Addition of LiCl results in decrease in the conductivity value due to the aggregation of excess LiCl salt.

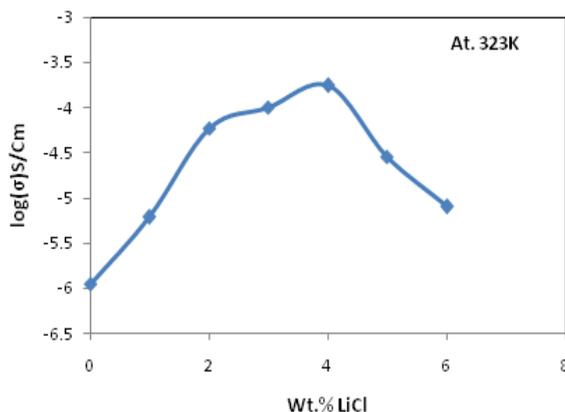


Fig. 2 Variation of conductivity versus wt % of LiCl for PTh-PEO Composite films

The variation of ionic conductivity as a function of inverse temperature for PTh-PEO polymer composite doped with the different wt. % LiCl is shown in Figure 3, over the temperature range 303 to 338K. It can be observed that the ionic conductivity for all the compositions of PTh-PEO

composite doped with the different wt. % LiCl increases with increasing temperature for the entire range.

The natures of the curves are consistent with Arrhenius type charge conduction in polymer composites and the conductivity relationship follows the equation,

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (3)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann's constant. The slope of each straight line gives the activation energy which lies between 0.14 and 0.26eV. the ionic conductivity increases with increasing lithium salt concentration due to the increase in the carrier density. However, the formation of ion-pairs becomes more in the case of high salt concentration than in the case of low concentration, leading to a drop in the ionic conductivity. Many researchers [7,8] reported a similar Arrhenius conductivity isotherm. It can be seen that the Arrhenius plots for all the samples display a similar behaviour. The ionic conductivity value increases with the different wt. % of LiCl at different temperatures.

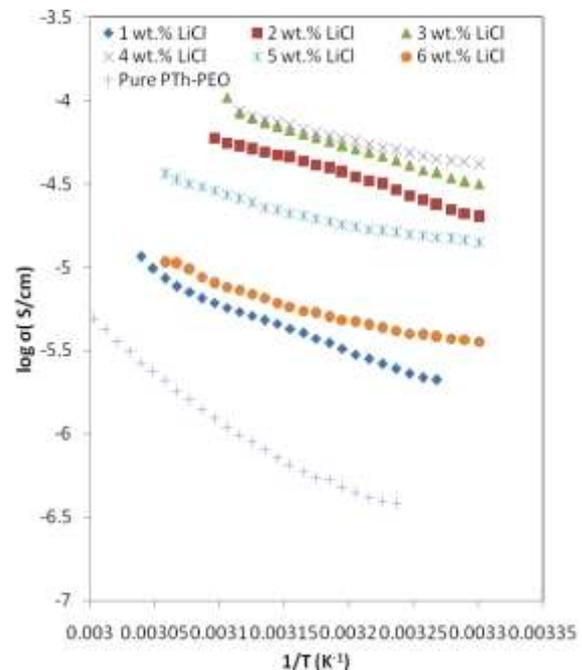


Fig 3 Arrhenius plots of PTh-PEO composite for different wt. % of Lithium chloride (LiCl)

As the temperature increases, mobility of the ions increases, which results the rise in conductivity. Uppermost curve belong to 4 wt % of LiCl for which conductivity is maximum. The conductivity versus temperature curves of all synthesized samples shows that the increase in conductivity. The rate of increase of conductivity is linear for the composite; which may be due to the segmental motion of the ions in the polymer [9].

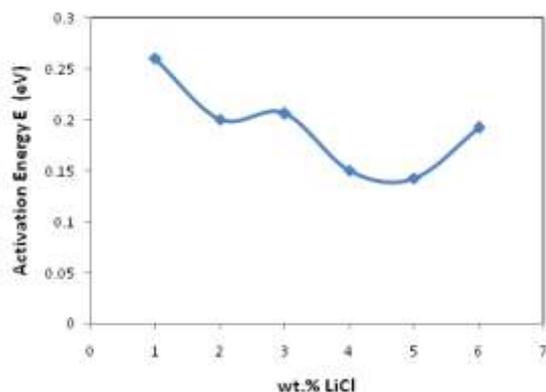


Fig 4. Variation Activation Energy as a function of wt. % of LiCl

Plot of activation energy with different wt. % of LiCl is illustrated in figure 4 and it is similar to mirror image of conductivity plot. Activation energy is large for lower conductivity and is small for higher conductivity [10]. Which shows that activation energy E_a is found to be maximum for the 1 wt % of LiCl. The value of activation energy varies with wt. % and DC conductivity respectively.

IV. CONCUSSION

PTh-PEO polymer composites were prepared successfully by *in situ* chemical oxidative polymerization of thiophene doped with LiCl. The value of transference number of all polymer composite samples was found to be in the range of

0.81 to 0.93. This suggests that the charge transport in the PTh-PEO composite doped with different wt. % of LiCl is predominantly due to ions only. The temperature dependence of conductivity showed Arrhenius behaviour. PTh-PEO composite doped with the 4 wt. % LiCl shows the maximum value of ionic conductivity.

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