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Transport Mechanism of Polythiophene-LiCl Polymer Composite

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Abstract:

Polythiophene-Polyethylene oxide (PTh-PEO) polymer composites doped with LiCl were synthesized at room temperature via chemical oxidative polymerization. Iron(III) chloride ($FeCl_3$) was used as the oxidant, and methanol served as the solvent. The properties of the resulting PTh-PEO composite films were characterized using a range of analytical techniques. The time-dependent polarization current was measured to investigate the effect of varying LiCl weight percentages on the composite's electrical behavior. Transference number analysis revealed that ionic transport is the dominant mechanism within the polymer composites.

Keywords: Polymer composite, Polythiophene (PTh), Polyethylene oxide (PEO) and Lithium Chloride (LiCl).

Introduction:

Recently, Polythiophene composite have received a great deal of attention due to its flexibility, ease of doping, and good thermal and electrical stability that exhibit some unique advantages of PTh for the development of various applications [1-2] While Polyethylene oxide (PEO) based polymer electrolyte has involved excessive attention for high energy density and high power lithium-ion batteries because of its ease formation of complex with lithium salt, flexibility, stable mechanical properties, comparatively high mobility of charge carriers, etc. Among the polymeric materials reported, polyethylene oxide (PEO) based polymer electrolytes are the most commonly studied. The purpose of this investigation is to synthesize a composite material with good environmental and thermal stability and higher conductivity so that it would be useful for human being in developing and sustaining life.

In the present work PTh-PEO Polymer composite films doped with Lithium chlorate (LiCl) were synthesized by *in situ* chemical oxidative method. Transport properties on synthesised composited were investigated with an intension to adventure Polythiophene composites for numerous applications.

Experimental:

1. Materials:

Thiophene (Th), Polyethylene oxide (PEO, Mw 100,000) were obtained from Acros organic, New Jersey, USA. Lithium chlorate (LiCl), was purchased from Loba Chem Mumbai. Methanol and Anhydrous $FeCl_3$ were acquired from S.D. fine, Mumbai. All the chemicals were used as received.

2. Synthsis of PTh-PEO polymer Composite doped with LiCl:

PTh-PEO composite doped with *LiCl* was synthesized at room temperature (303 K) by *in situ* chemical oxidative polymerization method [3]. Anhydrous $FeCl_3$ was used as a oxidizing agent. A solution of PEO was first prepared in methanol by stirring for 6 hours and kept over a night. Appropriate amount of Anhydrous $FeCl_3$ and LiCl were added and stirred for 15 minutes. 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 (Petri dishes), to prepare the composite films. The thiophene polymerization progresses because the evaporation of the solvent increases the oxidation potential of cast solution. After evaporation of the solvent, the composite films were formed.

3. Measurement of Transference Number:

The transference number gives qualitative information of the extent of ionic and electronic contribution to the total conductivity.

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 $\sigma_{ion}/\sigma_{e,}$ and $I_{e,}/I_T$ are the conductivity and current contributions due to ions/ electrons respectively. The ionic / electronic transference number was measured by using dc polarization technique in which PTh-PEO composite film is sandwiched between blocking (graphite) and non blocking (silver) electrodes. A constant dc voltage (0.5V) is established across the sample and the resultant current was measured as a function of time.

Results and Discussion:

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 calculated transference number for different wt. % of LiCl is shown in table 1. The values of transference number, for sample synthesized with different wt. % of LiCl are found to be in the range of 0.83 to 0.90. [4-5]. This suggests that the charge transport in the PTh-PEO Composite doped with different wt. % of LiCl is predominantly due to ions only. [6-8]

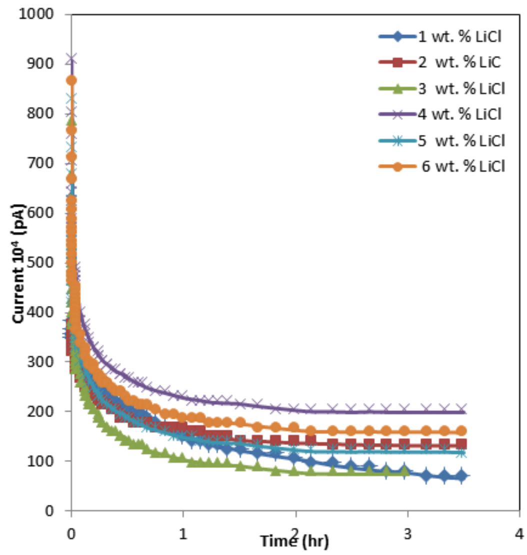

Fig. 1 Variation of polarization current as a function of time for PTh-PEO Composite Doped with different wt. % of LiCl

Table 1: Ionic transference number for PTh-PEO composite doped with with different wt. % of LiCl

Sr. No.	LiCl wt. %	t_{ion}
1	1	0.83
2	2	0.84
3	3	0.90
4	4	0.86
5	5	0.85
6	6	0.82

Figure 2. shows the variation of ionic transference number (t_{ion}) with different wt. % of LiCl. It shows that ionic transference number (t_{ion}) increases with increasing the LiCl concentration, obviously it is due to the increase of lithium ions concentration in the PTh-PEO composite. Up to 3 wt. % of LiCl it increases then slightly decreases and again increases. The ion mobility depends on segmental motion of polymer chain. In this case due to increase in wt. % LiCl, PTh-PEO composite become more rigid this ultimately reduces the segmental motion. [9-10].

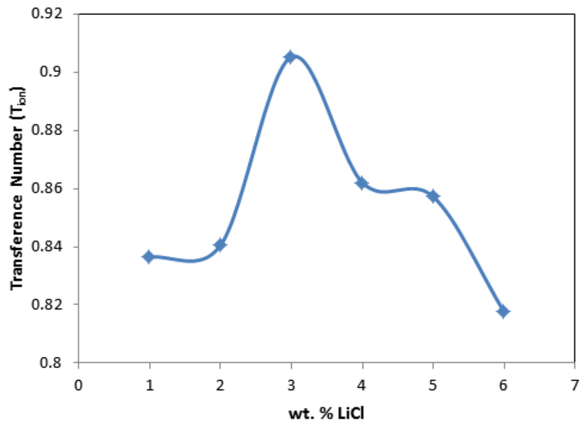

Fig.2 Variation of ionic transference number with different wt. % of Lithium chloride (LiCl)

Concussions:

Polythiophene (PTh) polymer composites were successfully prepared via in situ chemical oxidative polymerization of thiophene doped with LiCl. The transference number of the synthesized PTh-LiCl composites ranged from 0.82 to 0.90, indicating predominantly ionic conduction. As the LiCl concentration increased up to 3 wt%, the transference number initially increased, then slightly decreased, and subsequently increased again. Ion mobility is dependent on the segmental motion of the polymer chain, suggesting that charge transport in these PTh-LiCl composites is primarily ionic.

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