

Thermal, Conductivity and Morphological properties by the Effect of Lithium dopant in Poly (ethylene oxide) (PEO): An application to Polymer secondary batteries.

Manjunatha V, Devendrappa H

Department of Physics ,Mangalore University, Mangalagangothri-574199, India

Abstract

This paper presents information concerning the thermal, conductivity and miracle morphological properties of lithium doped polymer electrolytes applicable for high-energy density batteries and other solid state electrochemical devices. DSC results show the glass transition temperature decreases from -78.01°C (PEO) to -79.62°C (doped PEO), and decrease in crystalline nature, indicate the amorphous phase becomes more flexible, and the exchange of ions becomes very easy. As a result, activation energy lowers and hence the ionic conductivity increases. The dc conductivity increases from $6.25 \times 10^{-8} \text{ Scm}^{-1}$ to $6.56 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature, reveals the addition of dopant favors to form more transient cross links, with dimensional stable morphology due to large cat ion-anion association effects and decrease in viscosity and, hence, increase in chain flexibility, mobility of Li^{+} , and conductivity. The incorporation of lithium salt into the PEO improves the smooth morphology, with the development of streaks and reduction in crystalline nature. The morphology of the film changes substantially on addition of dopant.

Keywords: DSC, dc Conductivity, SEM, Crystallinity.

1. INTRODUCTION

Solid polymer electrolytes (SPEs) can be obtained by the dissolution of salts in suitable ion-coordinating Polymers [1]. The ion transport properties of lithium ion polymer electrolytes have led to their use in high energy density batteries and other solid state electrochemical devices [2]. Lithium salt complexes have demonstrated a relationship between the motion of the Li^{+} ions and the segmental motion of the Poly (ethylene oxide)(PEO) Chains[3]. Since the discovery of ionic conductivity in PEO complexed with alkali-metal salts, research on this class of materials has grown rapidly[4]. For the polymer electrolytes containing Li^{+} ions, it is believed that Li^{+} ions form both

inter chain and intra chain cross-links through transient coordinative Li-O bonds [5]. In the PEO-salt system the alkali-metal cation and the oxygen atoms in the ether group form complex in which the oxygen atoms form a "cage" around the cation, leading to dissociation of the anion-cation pair. The complexation is reversible, resulting in ionic conductivity. Therefore, studying the complexation is crucial for understanding the ionic conductivity[6]. Polymer-salt complexes show high ionic conductivity of about 10^{-3} – 10^{-5} Scm^{-1} at room temperature. The conductivity is governed by various factors like degree of crystallization, relative values of T_g (glass transition temperature) T_m (melting temperature)[7]. The conductivity about $1.5 \times 10^{-4} \text{ Scm}^{-1}$ has been reported for PEO- LiClO_4 system[8]. Tianbin Ren et.al. have studied on the effects of salt concentration on ion state and conductivity in comb cross-linked polymer electrolytes[9]. Amrta bhide et.al. have reported alkali doped PEO, (PEO) $_n$: NaPO_3 , for which, an increase in conductivity, decrease in T_g and morphological studies[10]. This paper highlights few interesting concepts of those, one is we obtained the porous membrane like SEM results same as that of micro porous membranes obtained by Jingyu Xi et.al[11]. For PVDF-based membranes having improved pore configuration, such as pore size, porosity, and pore connectivity of micro porous membranes, which, results in a high room temperature ionic conductivity. And the other is nano fiber like SEM images obtained by Marc Michel et.al[12] prepared membranes of Pt doped polyaniline, which shows high peak power density. Furthermore, the dependency of the conductivity on amorphosity, glass transition temperature (T_g) of the polymer electrolyte and temperature is explored by DSC, Conductivity and SEM studies.

The Pure PEO & doped PEO (PEO + Li_2SO_4) in 10, 20, 30, 40, and 50 wt % were prepared using the solution-cast technique. The Polyethylene oxide (PEO) ($M_w=5 \times 10^6$), white powder had been procured from M/s. Shanghai Research Institute, Shanghai, China. Li_2SO_4 , H_2O (Loba chemical M.W.127.96) and

Methanol (AR, M.W.32) were used. DSC analysis was performed in a Mettler DSC-20 analyzer. The samples were heated from -80°C to 80°C at a heating rate of $15^{\circ}\text{C}/\text{min}$. Electrical conductivity measurements were performed by using the standard two-probe-method with the help of PC based Keithley Electrometer (Model 6514) in the temperature range from 303 -333K for PEO+Li₂SO₄ doped pellets, which were coated with silver paste on either side for good electrical contact. Scanning electron microscope (SEM; JEOL Model JSM, 6390LV) was used to obtain the SEM images of the films.

The effect of dopant on the physical properties of the polymer materials can be best analyzed by studying the thermal characteristics [13]. DSC was used to characterize the effect of the dopant upon the morphologically based thermal behavior of the composite polymer Electrolytes. The glass transition temperature (T_g) and the crystalline melting temperature (T_m) were determined from the DSC. The thermograms of lithium doped samples are as shown in the figure 1. In figure1, the area under the curve for the melting endotherm in DSC data is related to the crystallinity in the specimens. The degree of crystallinity (χ) of the PEO fraction in the matrix is calculated from the equation.

$\chi = \Delta H_m(\text{PEO})/\Delta H_m^0(\text{PEO})$ Where $\Delta H_m^0(\text{PEO})=205 \text{ Jg}^{-1}$ is the heat of melting per gram of 100% crystalline PEO and $\Delta H_m(\text{PEO})$ is the apparent enthalpy of melting per gram of the PEO.

The values of T_g, T_m and degree of crystallinity (χ), as determined from the thermograms, are summarized in Table 1. In semicrystalline polymers, the T_g is a characteristic feature of the amorphous phase, for the parent PEO system the T_g was found to be at -78.01°C . With an increase in dopant content up to 50 wt% in the PEO, the T_g is observed to decrease form -78.65°C to -79.62°C .

The decrease[14] in the T_g, as increase in the concentration of the dopant, from -78.65°C to -79.62°C can be interpreted

Table 1. The glass transition temperature of the polymer electrolyte(T_g), melting temperature (T_m) and melting enthalpy (ΔH_m)of PL10(PEO:Li₂SO₄=90:10), PL20(PEO:Li₂SO₄=80:20), PL30(PEO:Li₂SO₄ =70:30), PL40(PEO:Li₂SO₄=60:40), PL50(PEO:Li₂SO₄ = 50:50)wt %.

Sampl e	T _g (°C)	T _m (°C)	ΔH_m (Jg ⁻¹)	X %	Conductivity At 300K (Scm ⁻¹)
PEO	-	67.2	188.0	91.7	$6.25 \cdot 10^{-8}$
	78.0	7	0	0	
PL10	-	75.4	180.9	88.2	$3.77 \cdot 10^{-5}$
	78.6	7	0	4	
PL20	-	72.5	141.1	68.8	$5.38 \cdot 10^{-5}$
	78.7	7	6	5	
PL30	-	72.4	135.6	66.1	$1.80 \cdot 10^{-5}$
	78.7	7	2	5	
PL40	-	73.8	138.6	67.6	$7.20 \cdot 10^{-5}$
	79.6	2	4	2	
PL50	-	71.2	145.7	71.0	$6.56 \cdot 10^{-4}$
	79.6	8	3	8	

as “The addition of Li-salt weakens the hydrogen bond interactions of the Polymer chains and improves the segmental motions of the polymer chain. Higher segmental motion of polymer electrolyte lowers the glass transition temperature.” As, “the glass transition temperature lowers, the amorphous phase becomes more flexible and the exchange of ions becomes very easy, resulting, activation energy lowers and hence the ionic conductivity is enhanced”[15]. The increased conductivity is confirmed from the conductivity plots and decrease in the crystalline is also correlated and seen in the SEM images

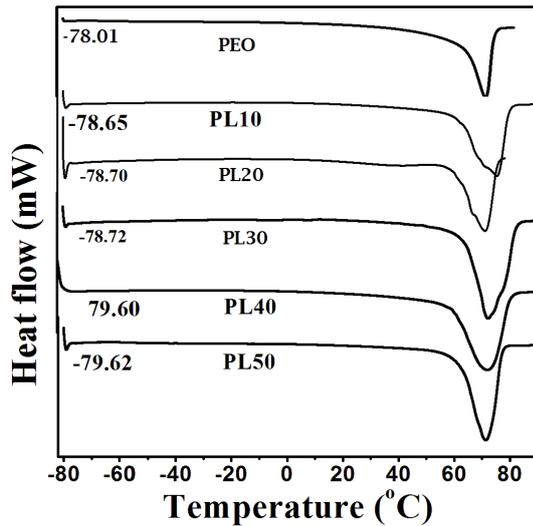


Figure 1

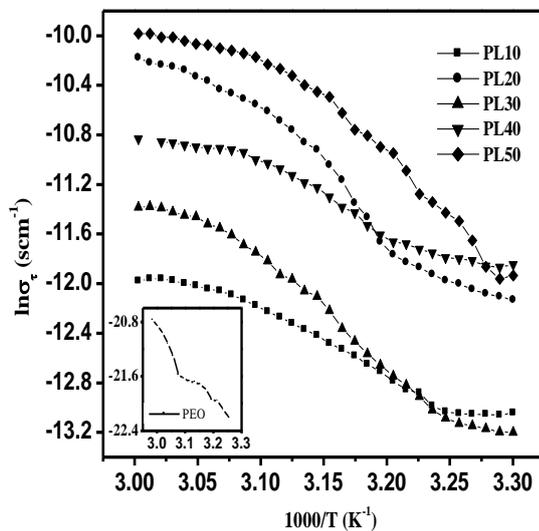


Figure 2

Figure 1 The DSC thermograms of PL10(PEO:Li₂SO₄=90:10), PL20(PEO:Li₂SO₄=80:20), PL30(PEO:Li₂SO₄ =70:30), PL40(PEO:Li₂SO₄=60:40), PL50(PEO:Li₂SO₄ = 50:50)wt %.

Figure 2 Plot of $\ln\sigma_t$ versus $1000/T$ for PEO (100%)(inset), and Li₂SO₄ doped PEO of PL10(PEO:Li₂SO₄ = 90:10), PL20(PEO:Li₂SO₄ = 80:20), PL30(PEO:Li₂SO₄ = 70:30), PL40(PEO:Li₂SO₄ = 60:40), PL50(PEO:Li₂SO₄ = 50:50)wt %.

The Conductivity measurements of pure PEO and Doped PEO at different temperatures are shown in Figure 2. The conductivity of the polymer electrolyte was calculated from the measured resistance, area and thickness of the polymer film. From the figure

2, the conductivity Plots of all polymer films show an increasing nature with temperature and dopant concentration, indicating these electrolytes exhibit a completely amorphous nature.

The Li₂SO₄ doping favoured the formation of complexes with ether or oxygen in PEO. In this case of polymer electrolyte, it favoured to form more transient cross links, with dimensional stable morphology due to large cat ion–anion association effects and decrease in viscosity and, hence, increase in chain flexibility, mobility of Li⁺ and the conductivity”[16]. Since the conductivity–temperature data follow Arrhenius behavior, the nature of cat ion transport is quite similar to that in ionic crystals, where ions jump into neighboring vacant sites.

Scanning Electron Microscope is one of the most versatile instruments available for the examination and analysis of microstructure morphology of the conducting surface. SEM images of pure PEO are as shown in the figure 3(a,b,c). In the figure, distinct spherulites [17] are visualized, which indicates the lamellar microstructure of pure polymer. The micrographs of pure PEO show a rough surface which has several crystalline domains. In the absence of the salt, separate polymer and oxide phase can be easily identified, which indicates the lack of a driving force for miscibility. On blending with lithium salt, the surface morphology of PEO is changed severely and improves the smooth morphology as seen in the figure 3(d,e,f) shows there are large spherulites. In addition, the crystal boundaries connect closely with each other. Only a little continuous amorphous phase among the crystal domain is observed. On further addition of dopant in PL20 i.e. figure3(g,h,i) appearance of number of uniform tracks of few micrometer sizes and porous membrane[18] are responsible for appreciable ionic conductivity of the electrolyte in figure3(g,h,i). Due to increase in the porous to certain extent the interconnectivity increases and the conductivity increases. When the size of the spherulites becomes much smaller, in the diameter, the fraction of amorphous phase increases greatly. In addition, all the amorphous domains form a continuous pathway, where Li⁺cation can move freely and quickly with increase in the concentration of the dopant in polymer electrolyte[19]. In PL30, figure3 (j,k,l), the surface is smoother than PL10 may be due partial solubility of the dopant. But, still we observe little higher conductivity than PL10. with the development of streaks Figure 3(m, n) and reduction of crystallinity. Now we see the interesting point is nano fiber like[20] structures

observed in figure3 (O). This type of nanofiber structures have shown high peak power density which is confirmed by Marc Michel et.al for Pt doped polyaniline. But, in the dc conductivity and DSC it showed good performance as we expected. Figure3(p,q,r) shows branch and fiber like structure.

The conductivity behavior in these composite system can be solely attributed the highest conductivity for 50wt %. One may assume that the structural modification is induced via Lewis acid (Li^+ cation) – base (ether oxygen of PEO) interactions between the PEO chain and lithium cation [21]. Which led to the maximum ionic conductivity of the polymer electrolyte with segmental motion of the polymer system.

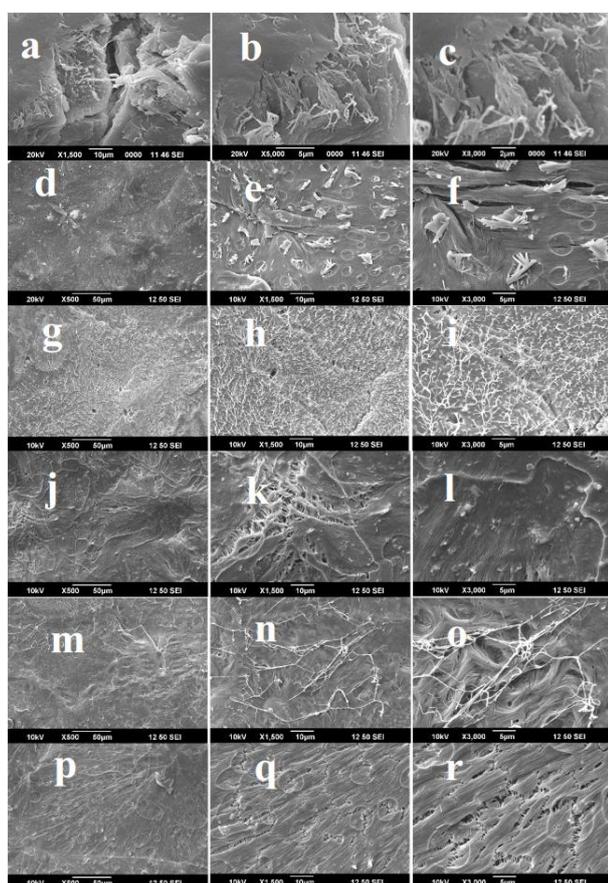


Figure 3 Scanning Electron Microscope micrographs of samples and its resolution of pure PEO at a) $10\mu\text{m}$, b) $5\mu\text{m}$, c) $2\mu\text{m}$ and Li_2SO_4 doped PEO of PL10(PEO: $\text{Li}_2\text{SO}_4 = 90:10$) at d) $50\mu\text{m}$, e) $10\mu\text{m}$, f) $5\mu\text{m}$, PL20(PEO: $\text{Li}_2\text{SO}_4 = 80:20$), at g) $50\mu\text{m}$, h) $10\mu\text{m}$, i) $5\mu\text{m}$, PL30(PEO: $\text{Li}_2\text{SO}_4 = 70:30$), at j) $50\mu\text{m}$, k) $10\mu\text{m}$, l) $5\mu\text{m}$, PL40(PEO: $\text{Li}_2\text{SO}_4 = 60:40$), at m) $50\mu\text{m}$,

n) $10\mu\text{m}$, o) $5\mu\text{m}$, PL50(PEO: $\text{Li}_2\text{SO}_4 = 50:50$)wt %. p) $50\mu\text{m}$, q) $10\mu\text{m}$, r) $5\mu\text{m}$.

In conclusions, DSC results showed the glass transition temperature decreased from -78.01°C (PEO) to -79.62°C (doped PEO), and decrease in crystalline nature. As a result, the ionic conductivity increases. The dc conductivity increases from $6.25 \times 10^{-8} \text{ Scm}^{-1}$ to $6.56 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature as the concentration of the dopant increase. The incorporation of lithium salt into the PEO improves the smooth morphology, with the development of streaks and fiber like structures, which give more peak power density and reduction in crystalline nature. The morphology of the film changes substantially on addition of dopant. In all these views and proofs it is an excellent candidate for high energy density secondary polymer batteries.

Acknowledgments: Authors thank to STIC Cochin for DSC and SEM.

References

- [1] Wu-Jyh Liang, Ping-Lin Kuo 2004 *Macromolecules* **37** 840-845.
- [2] Sangamithra Chintapalli, Roger Frech 1996 *Macromolecules* **29** 3499-3506.
- [3] Krishnan M, Balasubramanian S 2003 *Physical Review B* **68** 064304.
- [4] Yang X Q, Chen J M, and Skotheim T A, Okamoto Y, Kirkland J, Denoer M L, 1989 *Physical Review B* **40** 7948-7952.
- [5] Jong Hak Kim, Byoung Ryul Min, Chang Kon Kim, Jongok Won, and Yong Soo Kang 2001 *Macromolecules* **34** 6052-6055.
- [6] Yang X Q, Chen J M, and Skotheim T A 1989 *Physical Review B* **40** 7948-7952.
- [7] Haldar B, and Singru R M, Maurya K K and Chandra S 1996 *Physical Review B* **54** 7143-7150.
- [8] Xiao-Liang Wang, Ao Mei, Ming Li, Yuan-Hua Lin, and Ce-Wen Nan 2007 *Journal Of Applied Physics* **102** 054907.
- [9] Tianbin ren, Xiaobin Huang, Xian Zhao, Xiaozhen Tang 2003 *Journal Of Materials Science* **38** 3007 – 3011.
- [10] Amrtha Bhide, Hariharan K 2006 *Journal of Power Sources* **159** 1450–1457.
- [11] Jingyu Xi, Xinping Qiu, Liquan Chen 2006 *Solid State Ionics* **177** 709–713.
- [12] Marc Michel, Frank Ettingshausen, Frieder Scheiba, Andre Wolz and Christina Roth, 2008 *Phys. Chem.* **10** 3796–3801.

- [13] Hsien-Ming Kao T, Yi-Yuan Tsai, Shih-Wei Chao 2005 *Solid State Ionics* **176** 1261–1270.
- [14] Jing Zhang, Hongwei Han, Sujuan Wu, Sheng Xu, Conghua Zhou, Ying Yang and Xingzhong Zhao 2007 *Nanotechnology* **18** 295606.
- [15] Wen-Shiue Young and Thomas H. Epps III 2009 *Macromolecules* **42** 2672-2678.
- [16] Saibaba G, srikanthand D, Ramachandra reddy A, **2004** *Bull. Mater. Sci.* **27-1** 51–55.
- [17] Kamlesh Pandey, Mrigank Mauli Dwivedi, Mridula Tripathi 2009 *Polymer Composites* **10** 503-509.
- [18] Peter P. Chu , Jaipal Reddy M, Kao H M 2003 *Solid State Ionics* **156** 141 – 153.
- [19] Xueli Li , Yi Zhao, Liang Cheng, Manning YanXuezheng Zheng, Zi Gao, Zhiyu Jiang , 2005 *J Solid State Electrochem* **9** 609–615.
- [20] Marc Michel, Frank Ettingshausen, Frieder Scheiba, Andre Wolz and Christina Roth, 2008 *Phys. Chem. Chem. Phys.* **10** 3796–3801.
- [21] Hsien-Ming KaoT, Yi-Yuan Tsai, Shih-Wei Chao 2005 *Solid State Ionics* **176** 1261 – 1270.