

Structural and Dielectric Behaviour of Blend Polymer Electrolyte based on PEO-PAN + LiPF₆

Anil Arya¹, Sweety Sharma¹, A. L. Sharma^{1*}, Dinesh Kumar² and Mohd Sadiq^{1,3}

¹Centre for Physical Sciences, Central University of Punjab, Bathinda, India

²School of Materials Science and Technology (Banaras Hindu University), Varanasi, India

^{1,3}Department of Physics, IIT (BHU), Varanasi, India

Abstract - Solid polymer electrolytes (SPEs) have recently gained more research interest in the area of materials science due to their wide application range in energy storage/conversion devices like batteries, supercapacitors, solar cells and sensors. A blend polymer electrolyte based on polyethyleneoxide (PEO) and polyacrylonitrile (PAN) doped with Lithium Hexafluorophosphate (LiPF₆) has been prepared by solution casting technique using Dimethylformamide (DMF) as a solvent. The complex formation has been studied using X-ray diffraction (XRD). The decrease in intensity and broadness in peak reveals the amorphous phase formation. The dielectric study of PS films has been done which gives the two order decrement in relaxation time (i.e. 10⁻⁴ - 10⁻⁶) which is directly related to faster ion dynamics in polymer electrolytes. The analysis has shown the dielectric polarization at low frequencies. The dielectric peak has been observed to shift toward the higher frequency side with the addition of salt, suggesting the low sample viscosity and faster conduction of ions.

Keywords: Conductivity, Dielectric Permittivity, Electrolyte, Polyethylene oxide, Relaxation Time

I. INTRODUCTION

Research on solid polymer electrolyte is focused since 1973 when Wright [1] first time reported the ionic conduction in polymer/salt complex. At present solid polymer electrolytes are receiving great attention in order to meet the ever-growing demands of technologies ranging from portable devices and electric vehicles to energy storages. To develop the appropriate electrolyte/separator for energy storage devices there has been various approaches done over three decades [2]. The polymer electrolyte must have an advantage as flexibility, mouldability of shape and high electric properties for application purpose. There are various approaches that are being used as blending, copolymerization, composite formation to eliminate the crystallinity of the PEO-based electrolyte while upholding their required flexibility and mechanical stability. One of the most effective approaches has been made in the preparation of polymer blends which offers comfort preparation and easy control of physical properties within the compositional regime. Blended solid polymer electrolyte (SPE) systems obtained by the mixture of PEO with different polymers give rise to the reduced crystalline phase of the polymer. These could improve flexible amorphous content required for faster ion transport, thus exhibiting higher ionic conductivity in contrast to pure PEO complex polymer electrolytes [3].

Polyethylene oxide (PEO) is the best candidate to use as a host polymer for SPE due to the benefits structure of PEO having ether group, also it provides the faster ionic transport. A focused requirement for a high conductivity of the polymer electrolyte demands easy dissolution and coordination of cation with host polymer. The polymer having a Lewis base, typically etheric oxygen, can serve to coordinate the cations, and leads to the dissolution of the salt. Polyethylene oxide is the semi-crystalline polymer possessing both amorphous and crystalline phases at ambient temperature range. It can solvate a wide variety of salts. As the PEO is a linear polymer, the regularity of the structure of the unit allows a high degree of crystallinity [4]. Polyacrylonitrile (PAN) was chosen as a secondary polymer for making the blend polymer along with PEO for the present polymer electrolyte. PAN is a special conjugate polymer because of its high amorphous nature, which can permit faster ionic mobility, and it is easily soluble in PEO.

The conductivity of this solid polymer electrolyte depends on the molecular mobility and transport of ions. Dielectric properties (dielectric permittivity and dielectric loss) are also used for obtaining information about the characteristics of ionic interaction and relaxation time in polymer electrolytes. Dielectric relaxation is of particular interest in ionic conductivity, and the value of dielectric constant provide evidence of desolation of salt in polymer salt. [5]. In the present paper studies of structural and dielectric properties on PEO-PAN + LiPF₆ based solid polymer electrolyte and variation of dielectric permittivity and ac conductivity as a function of frequency have been carried out. Such properties could be helpful for finding a suitable electrolyte for energy storage devices.

II. MATERIAL PREPARATION AND CHARACTERIZATION

Polymer blend-based solid electrolyte separator films have been prepared by a standard solution cast technique reported elsewhere [6]. In this technique, appropriate amount of polyacrylonitrile (PAN; M/S Aldrich, average molecular weight 1.5×10⁵,(USA); 0.5 gm.) and polyethylene oxide (PEO; M/S Aldrich, average molecular weight 6×10⁵ ,(USA); 0.5 gm.), N,N-dimethylformamide (10 ml), (E-Merck Germany) was used as solvent , Lithium hexafluorophosphate (LiPF₆; Sigma Aldrich) as a conductive species. Although the addition of an appropriate amount salt by stoichiometric ratio has been calculated considering oxygen of PEO [6].

$$\frac{\bar{O}}{\text{Li}^+} = \frac{\text{No. of monomer unit in half a gram of PEO}}{\text{No. of LiPF}_6 \text{ molecular in half a gram of salt}} \times \frac{\text{wt. of PEO taken}}{\text{wt. of salt taken}}$$

The XRD pattern of samples with different salt concentration is recorded at room temperature with an X-ray diffractometer using Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$) over a range ($10^\circ \leq 2\theta \leq 20^\circ$) of diffraction angle. Dielectric properties were measured using electrochemical analyzer on a symmetric cell : SS|SPE|SS (SS stands for steel blocking electrodes) in frequency range from 1 Hz to 1 MHz at AC input signal of $\sim 20.0 \text{ mV}$ applied across blocking electrodes.

III. RESULT AND DISCUSSIONS

The XRD pattern of pure PEO-PAN blend polymer and LiPF $_6$ (O/Li = 6, 8, 10) are shown in Fig. 1. The diffraction peaks of PEO are corresponding to $2\theta \sim 20^\circ, 24^\circ$ and evidence of crystalline nature of PEO. Peaks at $2\theta \sim 13^\circ, 21^\circ$ are for PAN. Blend polymer shows a decrease in intensity of peaks which shows an increase in amorphous content as compared to Pure PEO and PAN [7]. With addition of salt three changes in peak due to coordination interaction between Li $^+$ ion and ether O atoms. Blend polymer shows a decrease in intensity of peaks as compared to XRD of Pure PEO [8], PAN [9] and PEO-LiPF $_6$ [10]. So blending of two polymer blends shows the absence of extra peaks than LiPF $_6$ and PEO and PAN which is evidence of an increase in amorphous content. It does not contain any XRD peak of salt suggesting complete salt dissolution in the polymer matrix via complexations [8].

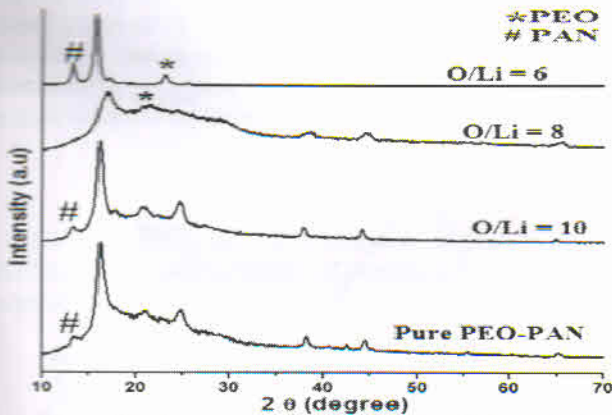


Fig. 1 X-ray diffraction pattern of Pure PEO-PAN and O/Li = 6, 8, 10

As the salt concentration increase it can be seen that there are changes in 2θ from $24.79^\circ \rightarrow 24.65^\circ \rightarrow 25.36^\circ$ for PEO peak and similarly change in the peak for PAN from $13.51^\circ \rightarrow 13.38^\circ \rightarrow 13.94^\circ$. So the angles $2\theta \sim 20^\circ, 24^\circ$ appear to be polymer crystallographic direction whereby and interaction of PEO and salt take place. Variation in intensity of peaks with an increase in salt concentration indicates an increase in a number of free ions for each salt concentration which leads to increase in conductivity [10]. Interaction of salt disturbs the crystalline region and increased amorphous phase of PEO-PAN and hence the intensity of peaks is reduced. It can be interpreted in terms of the criterion of Hodge et al. [11].

The dielectric permittivity is the polarizing ability of material when an external field is applied on it and it lead to accumulation of bound charges in the materials. The externally applied field alters the orientation of electric charges and reorientation of dipoles may occur. As permittivity is a function of frequency so it is a complex quantity.

$$\epsilon^* = \epsilon' - j\epsilon''$$

Where

$$\epsilon' = \frac{-Z''}{\omega c_0 (Z'^2 + Z''^2)}, \epsilon'' = \frac{Z'}{\omega c_0 (Z'^2 + Z''^2)}$$

Here ϵ' is related to the stored energy within the medium and ϵ'' is related to the dielectric energy loss of energy within the medium. Both parameters depend on the frequency and ϵ'' also depends on interaction among charge carriers.

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

$$\sigma' = \omega \epsilon_0 \epsilon''$$

$\tan \delta$ is called as the dielectric loss tangent which is proportional to the loss of energy dissipated as heat from the applied field into the sample. Fig 2 show the variation of dielectric constant and tangent loss with frequency for different salt concentration. In all the cases, a strong frequency dispersion of permittivity is observed and frequency independent behavior is seen in high frequency. The decrease of dielectric constant with an increase of frequency may be attributed to electrode polarization effect and dielectric relaxation at high frequencies. At lower frequency electrode polarization dominates and permittivity is high. With the addition of salt and in pure PEO-PAN almost same behavior is seen, that high permittivity at low frequency and independent of a higher frequency. The effect of salt results in an increase in conductivity due to an increase of a number of free ions. Also we can see the presence of a peak in tangent loss curve and it may be due to the presence of relaxing dipoles in in all samples. The tangent loss peaks shifts toward the high frequency side with the addition of salt. This peak shifting is direct evidence of a reduction in relaxation time and fast segmental motion of polymer increase the conductivity.

Figures 3 show the logarithmic plot of the conductivity as a function of frequency for the PNC films at room temperature (30°C). At 30°C , the spectrum for σ' shows two frequency regions: (1) a frequency independent region at a lower frequency, (2) followed by a high frequency dependent region. The observation mentioned in (1) is due to electrode polarization or space charge polarization effect and is a fundamental characteristic of an ionic conductor. In region (1), the lowering in frequency decreases the conductivity value. It is because at lower frequencies, accumulation of more charge occurs at the interface between electrode electrolytes and increase in time for ionic motion leads decrease in conductivity value. This phenomenon becomes dominant at high temperature due to increase in mobility of charge carriers.

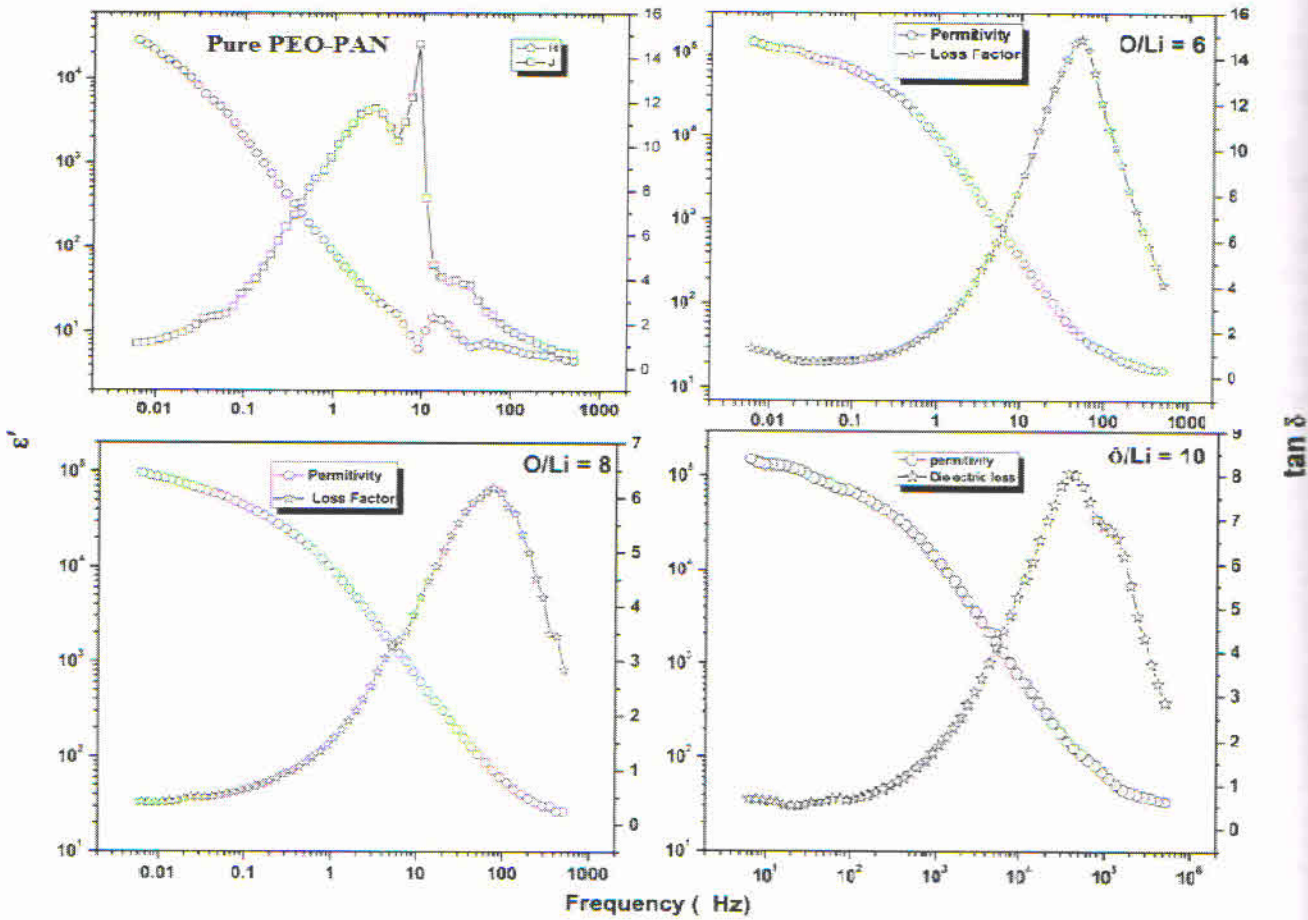


Fig. 2 VARIATION of dielectric constant and tangent loss with frequency for different salt concentration

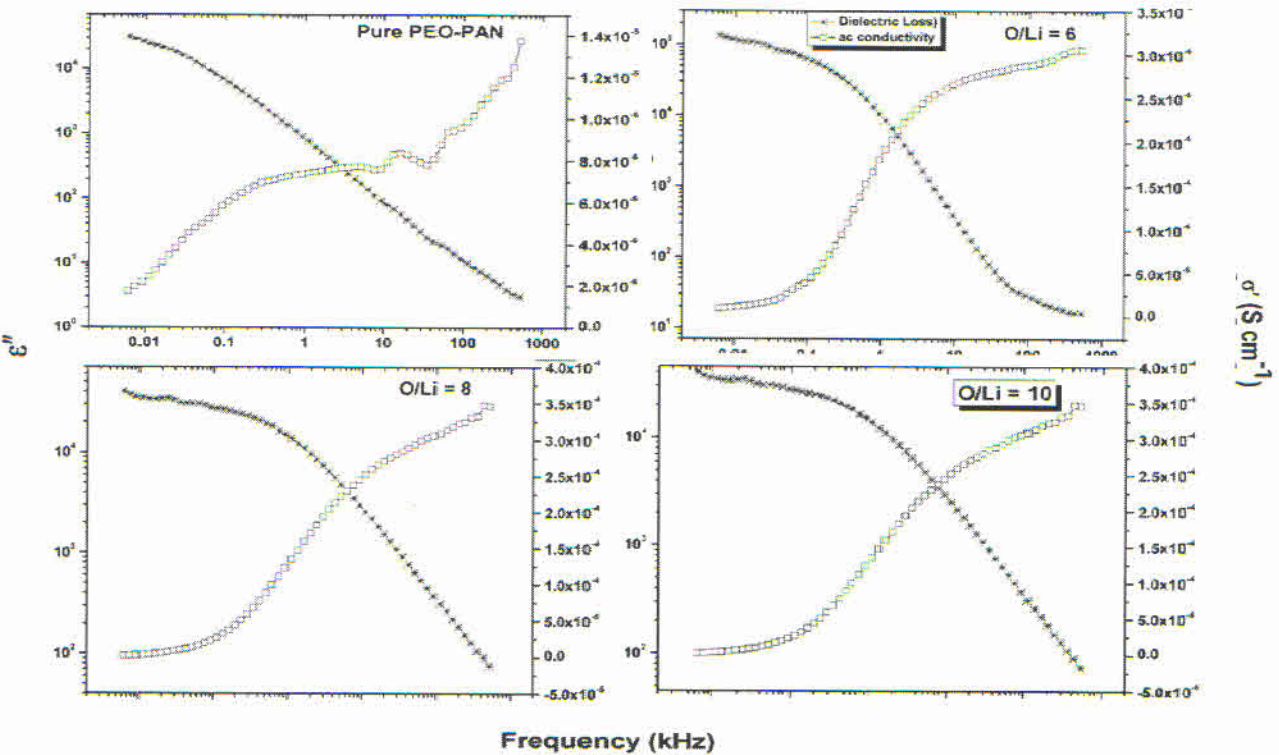


Fig. 3 Variation of imaginary part of permittivity and ac conductivity with frequency for different salt

At low frequency the applied electric field forces the charge carriers to drift over large distances and increase in time for ionic motion takes place which directly affects the conductivity value. It is observed from the figure that both real and imaginary parts of dielectric constants as well as dielectric loss of the samples have been decreased exponentially with frequency and showed the frequency independent behaviour at a higher frequency. The higher value of dielectric loss at a lower frequency is due to free charge motion in polymer electrolytes. In the high frequency region, σ_{ac} increase with increasing frequency, primarily due to the dielectric contribution. It refers to the region in the conductivity spectrum where strong frequency dependence of conductivity is a generally observed. The slope of the low frequency dispersion curve is different for pure PEO-PAN and O/Li = 6, 8, 10. The decrease of relaxation time from 10^{-6} to 10^{-4} with an increase in salt content shows enhancement of ac conductivity.

IV. CONCLUSION

Solid Polymer blend electrolytes consisting of Polyethylene oxide (PEO) as host polymer and lithium hexafluorophosphate (LiPF₆) as salt have been prepared by solution cast technique. The sample was prepared by taking a different concentration of O/Li ratio i.e. (O/Li = 0, 6, 8, 10) and structural and dielectric properties are studied. At low frequency, the variation of dielectric constant shows polarization effect. Shifting of tangent loss peak suggests the presence of relaxing dipoles and reduction in relaxation time. Conductivity is dependent on lower frequency and frequency independent region at a higher frequency. Decrease in relaxation time with the addition of salt shows enhancement in conductivity.

ACKNOWLEDGMENT

Authors would like to appreciate support of research facility of Central University of Punjab and partial financial support from UGC Start up Grant [GP 41].

REFERENCES

- [1] Wright, P. V. (1975). Electrical conductivity in ionic complexes of poly (ethylene oxide). *British Polymer Journal*, 7(5), 319-327.
- [2] Sharma, A. L., & Thakur, A. K. (2013). Plastic separators with improved properties for portable power device applications. *Ionics*, 19(5), 795-809.
- [3] Rajeswari, N., Selvasekarapandian, S., Prabu, M., Karthikeyan, S., & Sanjeeviraja, C. (2013). Lithium ion conducting solid polymer blend electrolyte based on bio-degradable polymers. *Bulletin of Materials Science*, 36(2), 333-339.
- [4] Kumar, K. N., Kang, M., Sivaiah, K., Ravi, M., & Ratnakaram, Y. C. (2015). Enhanced electrical properties of polyethylene oxide (PEO)+ polyvinylpyrrolidone (PVP): Li⁺ blended polymer electrolyte films with the addition of Ag nanofiller. *Ionics*, 1-11.
- [5] Shukla, N., Thakur, A. K., Shukla, A., & Marx, D. T. (2014). Ion Conduction Mechanism in Solid Polymer Electrolyte: An Applicability of Almond-West Formalism. *Int. J. Electrochem. Sci*, 9, 7644-7659.]
- [6] Das, A., Thakur, A. K., & Kumar, K. (2013). Exploring low temperature Li⁺ ion conducting plastic battery electrolyte. *Ionics*, 19(12), 1811-1823.
- [7] Sharma, A. L., & Thakur, A. K. (2013). Plastic separators with improved properties for portable power device applications. *Ionics*, 19(5), 795-809.
- [8] Ibrahim, S., Ahmad, R., & Johan, M. R. (2012). Conductivity and optical studies of plasticized solid polymer electrolytes doped with the carbon nanotube. *Journal of Luminescence*, 132(1), 147-152
- [9] Flora, X. H., Ulaganathan, M., & Rajendran, S. (2012). Influence of lithium salt concentration on PAN-PMMA blends polymer electrolytes. *International Journal of Electrochemical Science*, 7(8), 7451-7462.
- [10] Kock, L. D., Lekgoathi, M. D. S., Crouse, P. L., & Vilakazi, B. M. (2012). Solid state vibrational spectroscopy of anhydrous lithium hexafluorophosphate (LiPF₆). *Journal of Molecular Structure*, 1026, 145-149.
- [11] Ibrahim, S., Yassin, M. M., Ahmad, R., & Johan, M. R. (2011). Effects of various LiPF₆ salt concentrations on PEO-based solid polymer electrolytes. *Ionics*, 17(5), 399-405.
- [12] Hodge, R. M., Edward, G. H., & Simon, G. P. (1996). Water absorption and states of water in semicrystalline poly (vinyl alcohol) films. *Polymer*, 37(8), 1371-1376
- [13] Sharma, A. L., & Thakur, A. K. (2013). Plastic separators with improved properties for portable power device applications. *Ionics*, 19(5), 795-809.
- [14] Sharma, A. L., Shukla, N., & Thakur, A. K. (2008). Studies on structure property relationship in a polymer-clay nanocomposite film based on (PAN) 8LiClO₄. *Journal of Polymer Science Part B: Polymer Physics*, 46(23), 2577-2592.
- [15] Shukla, N., & Thakur, A. K. (2009). Role of salt concentration on conductivity optimization and structural phase separation in a solid polymer electrolyte based on PMMA-LiClO₄. *Ionics*, 15(3), 357-367.
- [16] Wang, Y., Chen, K. S., Mishler, J., Cho, S. C., & Adroher, X. C. (2011). A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research. *Applied Energy*, 88(4), 981-1007.
- [17] Yuan, F., Chen, H. Z., Yang, H. Y., Li, H. Y., & Wang, M. (2005). PAN-PEO solid polymer electrolytes with high ionic conductivity. *Materials chemistry and physics*, 89(2), 390-394.
- [18] Shukla, N., Thakur, A. K., Shukla, A., & Chatterjee, R. (2014). Dielectric relaxation and thermal studies on dispersed phase polymer nanocomposite films. *Journal of Materials Science: Materials in Electronics*, 25(6), 2759-2770.
- [19] Mathew, C. M., Kesavan, K., and Rajendran, S. (2015). Dielectric and thermal response of poly [(vinylidene chloride) coacrylonitrile]/poly (methyl methacrylate) blend membranes. *Polymer International*, 64(6), 750-757.
- [20] Michel Armand; (1983). Polymer solid electrolytes-an overview, *Solid State Ionics* 9 & 10, p.745-754.
- [21] Mohapatra, S. R., Thakur, A. K., and Choudhary, R. N. P. (2009). Vibrational spectroscopy analysis of ion conduction mechanism in dispersed phase polymer nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, 47(1), 60-71.
- [22] Noor, S. A. M., Ahmad, A., Rahman, M. Y. A., and Talib, I. A. (2009). Preparation and characterization of a solid polymer electrolyte PEO-ENR50 (80/20) LiCF₃SO₃. *Journal of applied polymer science*, 113(2), 855-859.