

**Effect of phosphonium based Ionic liquid on structural, electrochemical and thermal
behaviour of polymer poly(ethylene oxide) containing salt lithium
bis(trifluoromethylsulfonyl)imide**

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Supporting information:

FTIR analysis :

FTIR spectroscopy has been used to investigate the interaction of IL cation and salt (LiTFSI) with polymer backbone and to observe the conformational change in PEO polymer matrix due to incorporation of IL. The FTIR spectra of PEO, IL and PEO + 20wt% LiTFSI + Xwt% IL (for X = 0, 10) are given in region 3200-400 cm⁻¹ as shown in Fig.S1. For present discussion, two regions (1000-1200 cm⁻¹ and 2800-3000 cm⁻¹) of FTIR spectra are of particular interest. As we found some significant changes only in these regions. The expanded region 1000-1200 cm⁻¹ is given in Fig.S2. In this region, the peak related to C-O-C stretching of PEO was found at 1060 cm⁻¹ and 1146 cm⁻¹.^[R(1)-R(2)] When 20wt% salt LiTFSI was mixed in polymer (PEO) to obtain polymer electrolyte film (PEO + 20wt% LiTFSI), the interaction of LiTFSI salt cation (Li⁺) occurred with five ether oxygen of PEO chain as depicted in Fig.S3.^[R(3)] Li⁺ moves in polymer matrix by two processes (1) by hopping mechanism, (2) by diffusion mechanism. In hopping mechanism, Li⁺ interacts with five ether oxygen of PEO and moves in polymer matrix by hopping at ether oxygen as shown in Fig.

S3. In diffusion mechanism, Li^+ does not attach with ether oxygen of PEO matrix.^[R(4)] Due to the interaction of LiTFSI salt cation (Li^+) with the ether oxygen (C-O-C group) of PEO, shift in C-O-C related band of PEO was observed. It was found that C-O-C related peak of PEO shifted at 1054 cm^{-1} and 1033 cm^{-1} respectively when 20wt% of LiTFSI salt was incorporated in polymer matrix PEO as shown in Fig.S2. This shows the interaction of salt cation (Li^+) with C-O-C group of PEO. The above observation suggested that the Li^+ moves in polymer matrix by hopping mechanism. When 10wt% IL was incorporated in PEO + 20wt% LiTFSI, the cation of IL (Trihexyltetradecylphosphonium) is most likely to interact with ether oxygen belonging to C-O-C group of polymer PEO. Due to the interaction of cation ring of IL with the ether oxygen of PEO, C-O-C related peak was shifted at 1054 cm^{-1} and 1033 cm^{-1} respectively as given in Table T₁. This shows the interaction of IL cation ring with ether oxygen of PEO. Due to the IL cation interaction with PEO, shift in peak related to the C-H stretching of IL cation has also been observed. C-H stretching vibration related to the cation ring of IL was observed in the region $2800\text{-}3000\text{ cm}^{-1}$ as given in Fig.S4. In this region, peak related to the C-H stretching of IL cation was found at 2855 cm^{-1} , 2873 cm^{-1} , 2926 cm^{-1} and 2958 cm^{-1} . When IL was incorporated in polymer matrix (PEO + 20wt% LiTFSI), C-H stretching peak of IL cation is shifted to 2856 cm^{-1} , 2873 cm^{-1} , 2925 cm^{-1} and 2957 cm^{-1} respectively as shown in Table T₁. The shift in peak position of C-O-C group of PEO and C-H stretching of IL cation, when IL was incorporated in polymer matrix, conforms the interaction of IL cation to C-O-C group of polymer matrix.

References:

- R(1). S. S. Rao, M. J. Reddy, E. L. Narsaiah and S. Rao, *J. Mater. Sci. Eng. B*, 1995, **33**, 173-177.
- R(2). T. Rajkumar and R. Rao, *Mater. Chem. Phys.*, 2008, **112**, 853-857.
- R(3). K. Xu, *Chem. Rev.*, 2004, **104**, 4303-4417.
- R(4). O. Borodin and G. D. Smith, *Macromolecules*, 2006, **39**, 1620-1629.

Figure caption :

Fig.S1: FTIR spectra of (a) pure PEO, (b) PEO + 20wt% LiTFSI, (c) pure IL and (d) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 4000 – 400 cm^{-1} .

Fig.S2: FTIR spectra of (a) pure PEO, (b) PEO + 20wt% LiTFSI and (c) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 1000 - 1200 cm^{-1} .

Fig.S3: Schematic representation of attachment of Li ion with ether oxygen of polymer chain PEO.

Fig.S4: FTIR spectra of (a) pure IL, (b) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 2800 – 3000 cm^{-1} .

Table caption :

Table T₁: Change in C-O-C band of pure PEO, PEO + 20wt% LiTFSI and PEO + 20wt% LiTFSI + 10wt% IL with C – H stretching of IL cation.

Figures :

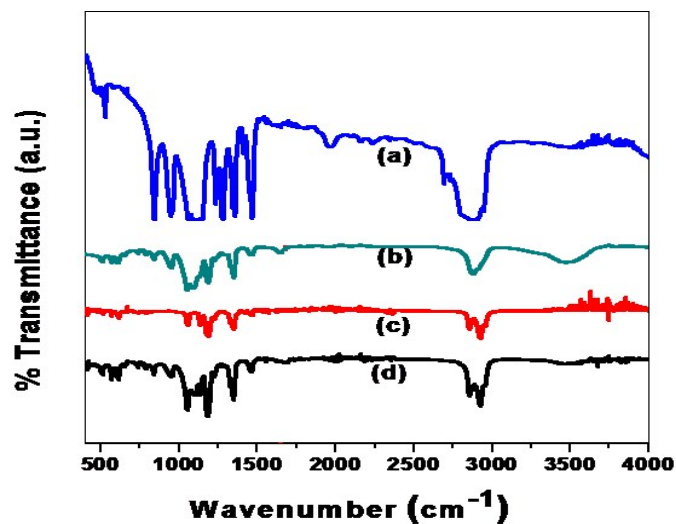


Fig.S1: FTIR spectra of (a) pure PEO, (b) PEO + 20wt% LiTFSI, (c) pure IL and (d) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 4000 – 400 cm⁻¹.

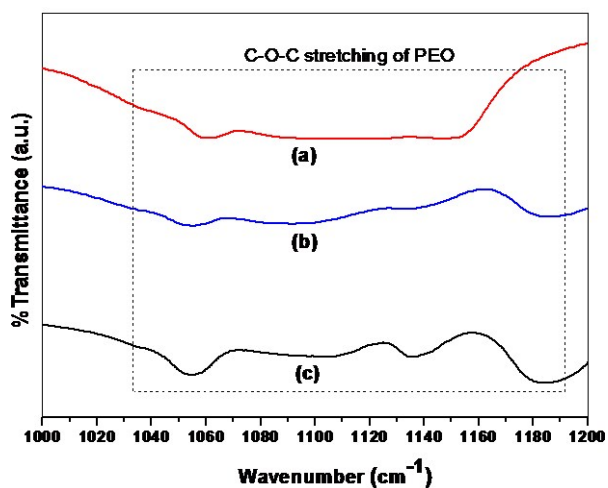


Fig.S2: FTIR spectra of (a) pure PEO, (b) PEO + 20wt% LiTFSI and (c) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 1000 - 1200 cm⁻¹.

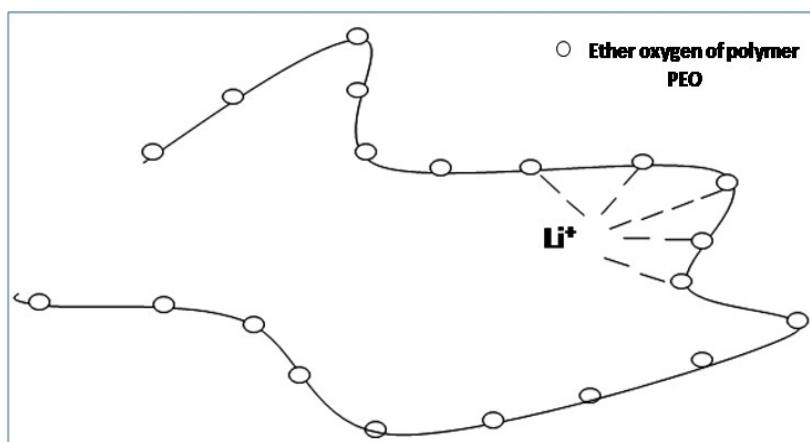


Fig.S3: Schematic representation of attachment of Li ion with ether oxygen of polymer chain PEO.

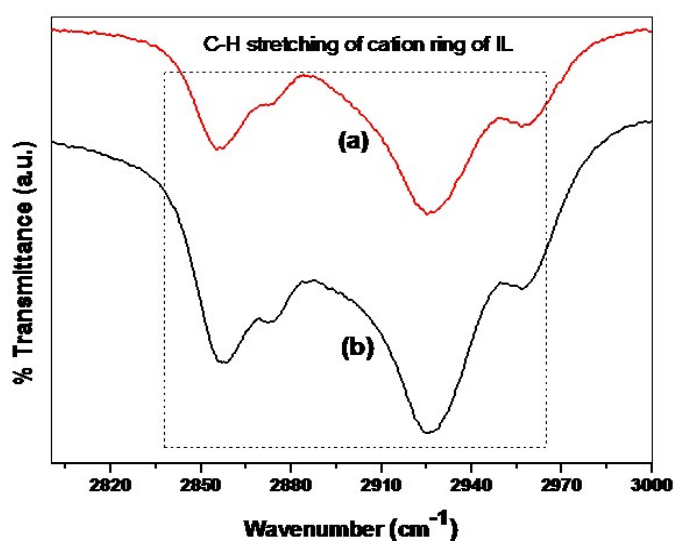


Fig.S4: FTIR spectra of (a) pure IL, (b) PEO + 20wt% LiTFSI + 10wt% IL electrolyte membrane in the region 2800 – 3000 cm^{-1} .

Table :

Vibration mode	Pure PEO	Pure IL	PEO+20%LiTFSI	PEO+20%LiTFSI +10%IL
PEO related CH₂ vibration	843	absent	841	841
	947	absent	948	945
PEO related C-O-C vibration	1060	absent	1054	1054
	1146	absent	1133	1135
IL related C-H stretching	absent	2855	absent	2856
	absent	2873	absent	2873
	absent	2926	absent	2925
	absent	2958	absent	2957

Table T₁: Change in C-O-C band of pure PEO, PEO + 20wt% LiTFSI and PEO + 20wt% LiTFSI + 10wt% IL with C – H stretching of IL cation.