Lithium Tetrakis(pentafluorobenzenethiolate) Borate and Poly(ethylene oxide) Based Polymer Electrolytes

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Recently we reported lithium ion conducting ionic liquid which contain two methoxy [oligo (ethyleneoxide)] and two electron withdrawing groups bonded to aluminate or borate complex center.[1,2] Borates exhibited higher ionic conductivities than aluminates due to weaker ion pairing between lithium ion and borate anion.[3]

We wish to report here ionic conductivities of polymer electrolytes based on a novel lithium salt, lithium tetrakis(pentafluorobenzenethiolate) borate (LiTPSB) (Fig. 1) and poly(ethylene oxide) (PEO, Mw $5x10^6$). LiTPSB is insoluble in polar or less polar solvents. Weaker ion pairing between lithium ion and TPSB anion is expected based on the small partial negative charges on sulfur atoms obtained from MOPAC calculations (PM5).

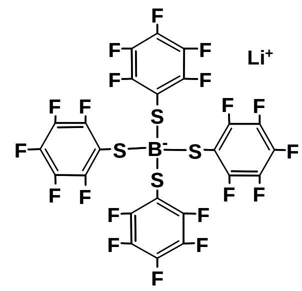
LiTPSB was synthesized by refluxing in THF from lithium borohydride and pentafluorobenzenethiol. LiTPSB exhibited good thermal stability up to 200^0C by TGA measurement. Polymer electrolyte films were obtained by hot pressing after mixing of LiTPSB powder with PEO.

Ionic conductivity of PEO-LiTPSB is shown in Fig.2. LiTPSB is not soluble in any solvents and polymers and exhibited very low ionic conductivity ($<10^{-9}$ Scm^{-1} at 200^oC) alone. However it's composites with PEO exhibited ionic conductivity at room temperature and good ionic conductivity at higher temperature than melting point of PEO. PEO-LiTPSB (salt 50wt%) was optimized for ionic conductivity which exhibited ionic conductivities of 2×10^{-8} Scm^{-1} at 30 ^oC. Ionic conducting mechanism is suggested in Scheme1. LiTPSB is insoluble in PEO and exhibited very low ionic conductivity alone. Therefore, lithium ion transport at the interface between LiTPSB and PEO can be proposed. Glass transition temperature (Tg), melting point (Tm) and crystallinity of PEO are shown in Table1. PEO-LiTPSB (salt 80wt%) had higher Tg than PEO-LiTPSB (salt 20wt%) and PEO-LiTPSB (salt 50wt%). PEO-LiTPSB (salt 20wt%), PEO-LiTPSB (salt 50wt%) and PEO-LiTPSB (salt 80wt%) had similar Tm and crystallinity.

LiTPSB is attractive lithium salt because it is insoluble in solvents and polymers but gives lithium ion conductivity when it mixes with appropriate host materials. Characterization and electrochemical properties of LiTPSB will be presented in detail.

References

1. T. Fujinami and Y. Buzoujima, J. Power Sources, **119**, 438 (2003).
2. T. Fujinami and K. Miyamoto, 8th IUMRS, B5-12-O13 (2003).
3. T. Aoki, A. Konno and T. Fujinami, J. Electrochem. Soc., accepted.



LiTPSB

Fig. 1 Structure of lithium tetrakis (pentafluorobenzenethiolate) borate (LiTPSB)

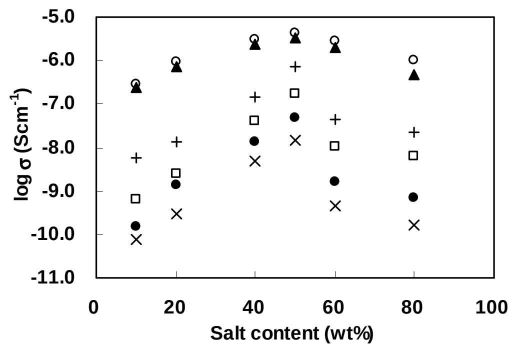
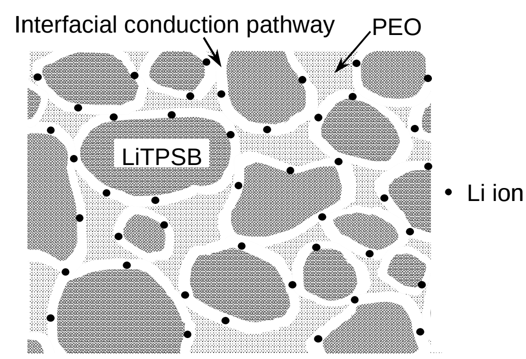


Fig.2 Ionic conductivity of polymer electrolytes based on PEO and LiTPSB
(○) 80^{o}C, (▲) 70 ^{o}C, (+) 60 ^{o}C,
(□) 50 ^{o}C, (●) 40 ^{o}C, (x) 30 ^{o}C



Scheme1 Ionic conducting pathway suggested for polymer electrolytes based on PEO and LiTPSB

Table1 Thermal properties and crystallinity of PEO for polymer electrolytes based on PEO and LiTPSB

PEO-LiTPSB	Tg (^{o}C)	Tm (^{o}C)	Crystallinity (%)
salt 20wt%	-53.5	62.6	63
salt 50wt%	-53.8	61.9	62
salt 80wt%	-48.8	61.8	65