New Borate Ester Based Polymer Electrolyte for Battery Application

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Introduction

Safety is an indispensable feature for a battery particularly in large scale applications. In this respect, gel electrolytes are more attractive due to less possibility of electrolyte leakage and safer if abused. Unfortunately, most present gel electrolyte systems are mainly based on polyethers which supposed to be flammable. In addition, PEO and PPO based systems exhibit a low cation transference number. Therefore, the seeking of novel thermally stable and safety polymer electrolytes with improved electrochemical behaviour is crucial. In the present contribution, we propose a series of Li-ion conducting polymer electrolytes based on the poly(ethyleneglycol) (PEG) borate ester (PE-350B) and PEG-methacrylates (PME-400 and PDE-600, respectively) plasticized by M550B100 PEG-borate ester, which can be characterized as a thermally stable solvent with high flash point [1].

Experimental

All polymer samples were supplied from NOF Co (Japan). Scheme 1 shows the structures of PE-350B and M550B100 borate esters. The polymer electrolytes were prepared by radical polymerisation of oligomers mixtures with 1 mol kg^{-1} solution of LiTFSI (Fluka) in M550B100 (Solution I) using AIBN as an initiator. The ionic conductivities of the samples were measured by AC impedance technique using Hewlett-Packard 4192A LF impedance analyzer. Thermal and electrochemical stability of the polymer electrolytes was estimated by TG analysis with TGD-9600 (Shinku-riko) apparatus and cyclic voltammetry using Solartron SI 1287 electrochemical interface. The cation transference number was determined by impedance method [2]

Results and discussion

All polymer electrolytes appeared as self standing transparent films without visible solvent leakage. The high liquid retention ability of the systems may be attributed to high molecular weight of M550B100 used as a solvent. The films of co-polymers of PE-350B AP-400B with PDE-600 and PME-400 are more flexible and mechanically stable than PE-350B and AP-400B polymers itself. The thermal and CV data have shown that all polymer electrolytes are thermally and electrochemically stable up to 200°C and 4.5 V respectively (See example data in Fig. 2).

Systems based on PE-350B:PME-400 and PE-350B:PDE-600 polymer systems in different weight ratio with Solution I were studied. Systems with higher amount of solution exhibited higher conductivity. The activation energy for the above systems is remarkably lower than that for the system without M550B100 (PE-350 with 1 mol kg^{-1} of LiTFSI) due to plasticizing effect of M550B100.

The plasticizing effect of M550B100 is clearly visible in Fig. 3 and enhanced conductivity is resulted by further addition. It is worth noticing that even 80 wt. % M550B100 in the electrolyte gives remarkable mechanical properties.

The cation transference numbers for the studied systems are relatively high and reach 0.5 and this fact can be explained by anion trapping of boron in borate esters, which acts as a weak Lewis acid.

Acknowledgement

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References

1. Y. Kato,S. Yokoyama, H. Ikuta, Y. Uchimoto, M. Wakihara, *Electrochem. Comm.* 3 (2001) 128-130.
2. P. Bruce, C.A. Vincent, *J. Electroanal. Chem.*, 225 (1987) 1.

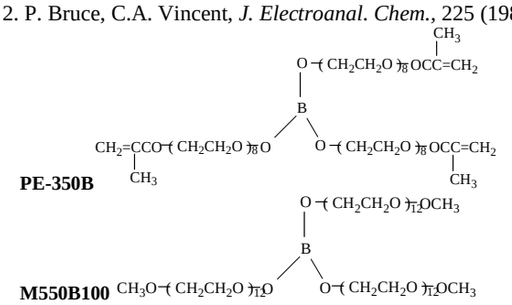


Fig. 1. Formulas of borate esters

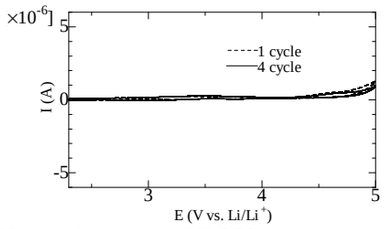
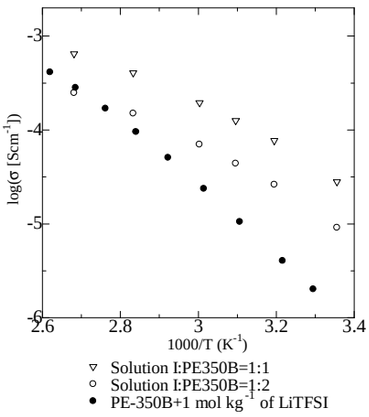


Fig. 2. CV plots for system PE-350 polymer matrix with 50 wt.% of Solution I; scan rate 0.5 mV·s^{-1}



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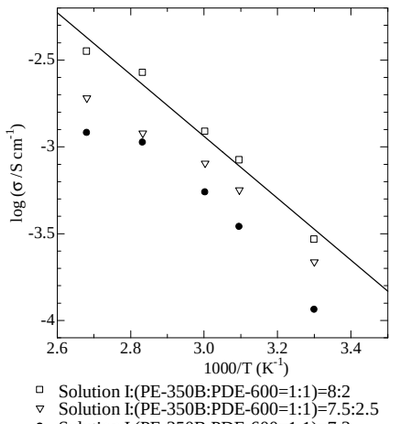

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Fig. 3. Arrenius plots of conductivity for PE-350B based polymer electrolytes with different ratio of Solution I