Lithium Ion Conduction in Solid Polymer Electrolyte Containing Borate Ester Groups

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Compared with the batteries using usual organic liquid electrolyte, all-solid-state polymer lithium batteries should have excellent properties such as safety, ease to scale-up, application of laminate package, and high energy density. However, the polyethers are flammable, it is desirable to improve their thermal stability especially for large-scale batteries in electric vehicle or in load leveling. For overcoming this problem, we have presented details of the preparation of a novel polymer electrolyte containing low molecular weight of poly(ethylene glycol)-borate ester which have excellent thermal stability and good fluidity as plasticizer in our previous report [1].

In the present work, we report on the preparation of solid polymer electrolyte having borate ester groups, which are fixed to the backbone chain of the polymer. The backbone polymer was synthesized by reaction between polyethylene glycol and boric acid anhydride.

The backbone polymer was prepared from polyethylene glycol and boric acid anhydride. The reaction scheme is shown in Fig. 1. Various molecular weights of the polyethylene glycols [diethylene glycol, triethylene glycol, PEG200, PEG400, PEG600, PEG1000, PEG2000 (polyethylene glycol whose average molecular weight is 200, 400, 600, 1000, 2000, respectively)] were supplied from NOF Co. Ltd.

Figure 2 shows the temperature dependence of ionic conductivity for the polymer electrolytes. The molar ratio for ether oxygen to lithium atom (EO/Li) is 32. The ionic conductivity increases with increasing molecular weight of the starting polyethylene glycol. The Arrhenius plots of ionic conductivity are not straight lines. This behavior is often observed for amorphous solid polymer electrolyte systems and is better described by an equation of the WLF type. The segmental motion of the solid polymer electrolytes prepared from the polyethylene glycol having small molecular weight is suppressed by cross-linking of borate ester, because the electrolyte from the small molecular weight polyethylene glycol has large amount of the cross-linking point (borate ester groups). Therefore, the apparent activation energy decreases with increasing molecular weight of the starting polyethylene glycol.

Figure 3 shows TG curves of polymer electrolyte samples. The polymer electrolyte samples were observed thermally stable up to about 200˚C. As shown in Fig.3, the thermal stability decreases with increasing the molecular weight of the starting polyethylene glycol. This phenomenon indicates that the electrolyte made from the polyethylene glycol with small molecular weight is stable because of their large amount of cross-linking point and/or large content of thermally stable borate ester.

The lithium ion transference number and concentration of the borate ester groups (Lewis acid) will be presented.

References

Y. Kato, S. Yokoyama, H. Ikuta, Y. Uchimoto and M. Wakihara, *Electrochem. Comm.*, 3 (2001) 128.

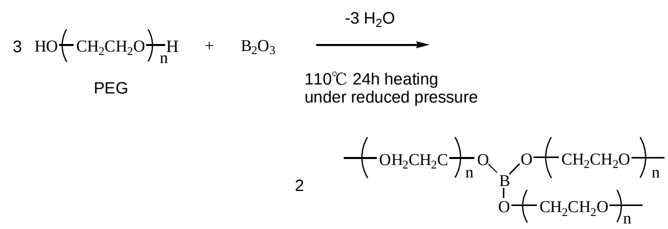

Fig. 1
Reaction scheme for preparation of backbone polymer from polyethylene, glycol and boric acid anhydride.

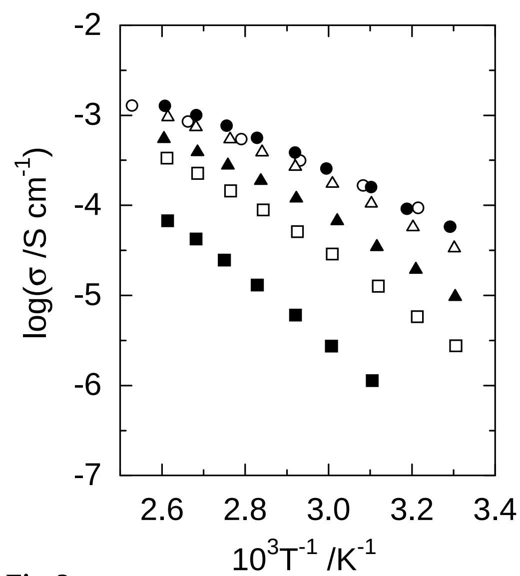

Fig. 2
Temperature dependence of ionic conductivity of solid polymer electrolyte prepared from boric acid anhydride and ■: diethylene glycol, □: triethylene glycol, ▲: PEG200, △: PEG 400, ●: PEG600, ○: PEG1000. The molar ratio for ether oxygen to lithium atom (EO/Li) is 32.

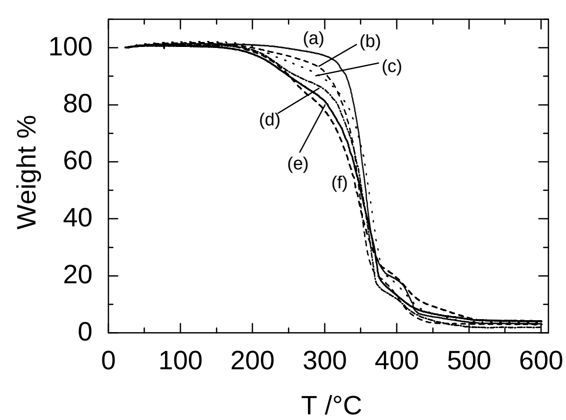

Fig. 3
Thermogravimetry curve for solid polymer electrolyte prepared from boric acid anhydride and (a) diethylene glycol, (b) triethylene glycol, (c) PEG200, (d) PEG 400, (e) PEG600, (f) PEG1000. The molar ratio for ether oxygen to lithium atom (EO/Li) is 32.