Li^+ Transference Number Enhancement in Polymer Electrolytes by Incorporation of Anion Trapping Boroxine Rings into the Polymer Host

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Polymer electrolytes incorporating boroxine rings with pendant oligoether side chains and a variety of dissolved lithium salts were prepared. High ionic conductivities and Li^+ transference numbers were observed, the latter being ascribed to the anion trapping ability of the boroxine ring.

Recently emphasis has been put on the development of polymers which exhibit high Li^+ conductivity for use as the separator in lithium rechargeable batteries.[1-3] In addition, materials with high Li^+ transference numbers are being sought to reduce the problem of cell polarization which arises during charging when simple bi-ion conductors are used. Although there have been many reports of polyelectrolytes where the anion is immobilized on the polymer chain, elaborate and costly synthetic techniques are often necessary.[4-6] Here we present a new series of polymer electrolytes where high Li^+ transference numbers are achieved by the incorporation of anion trapping boroxine rings into the polymer structure.

Host polymers were prepared by adapting the method of Steinberg as shown in Scheme 1.[7] Solutions in tetrahydrofuran (THF) of poly(ethylene glycol) monomethyl ether (M.W. 350) [PEGMME] and tetraethylene glycol (TEG) were added to boric oxide. After prolonged heating at 120 °C (4 – 6 h under N_2 flow, 4 h under vacuum) to remove THF and water, an extremely viscous transparent liquid (**1**) was obtained. This polymer was dissolved in THF containing the calculated amount of lithium salt to give the required boroxine ring: Li^+ ratio and was stirred overnight to obtain a homogeneous solution. Evaporation of the solvent gave the polymer electrolyte in almost quantitative yields. IR data was consistent with that expected for a system containing boroxine rings.[8-9]

Ionic conductivities of samples sandwiched between blocking stainless steel electrodes were determined by the ac impedance method. Since preliminary experiments indicated that maximum conductivity was obtained for a boroxine ring: $LiCF_3SO_3$ ratio of 2:1 this composition was used to investigate the effect of using different salts as illustrated in Figure 1. In addition, Li^+ transference numbers (t_+) were measured by the ac impedance/ dc polarization method[10] and are listed in Table 1. It was of particular interest to note that significant conductivity was observed for the system containing LiCl. Low conductivities have been observed for systems formed by the dissolution of salts containing small polarizing anions such as LiCl and LiBr in poly(ethylene oxide).[11] This was ascribed to incomplete

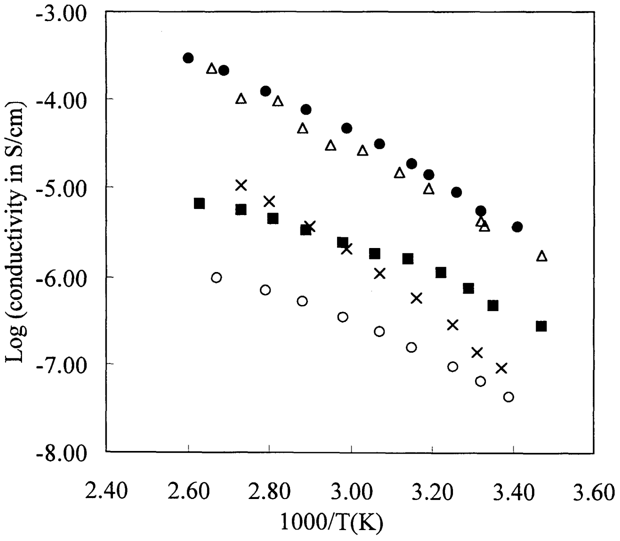
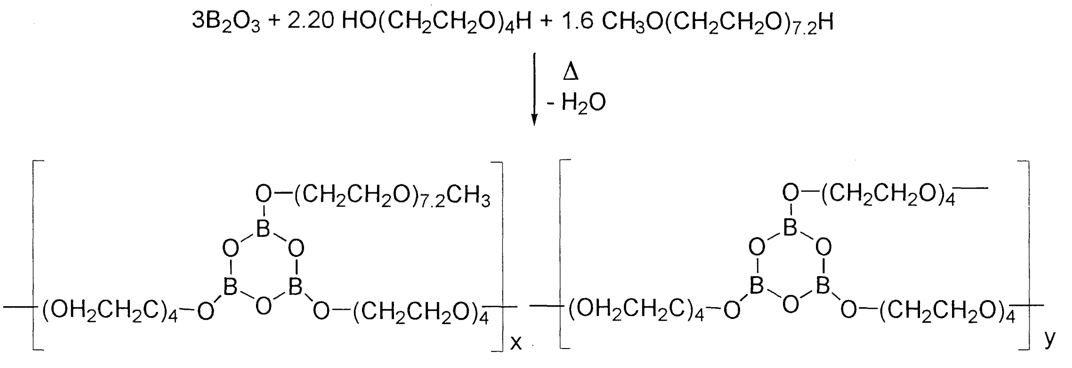


Figure 1. Ionic conductivities of boroxine ring containing polymer electrolytes. Boroxine ring : Li^+ = 2:1.
(•) $LiCF_3SO_3$; (Δ) $LiBF_4$; (▪) LiCl; (x) $LiPF_6$; (o) No salt



(1)

Scheme 1. Synthesis of polymer host (**1**) containing boroxine rings.

Table 1. Li^+ ion transference numbers for polymer **(1)** containing lithium salts

Salt	Transference No. (T_+)	Temperature (°C)
$LiCF_3SO_3$	0.75	35
$LiBF_4$	0.75	29
LiCl	0.88	26
$LiPF_6$	-	-

Boroxine ring : Li^+ = 2:1.

dissociation of the salt in the polymer. The extremely high Li^+ transference number for the LiCl system suggests that the anions are immobilised to a high degree. We therefore conclude that strong anion interaction with the boroxine ring causes a reduction in ion pairing and promotes LiCl dissociation in the polymer. The Li^+ transference numbers for all the systems were observed to be greater than those commonly observed in polyether systems [10,12] which can be ascribed to anion interaction with the boroxine ring. The precise nature of this interaction is at present uncertain however, small weakly polarizable anions such as Cl^-, may be expected to interact with a single B atom in the ring to yield tetra-coordinate borate as illustrated in Figure 2a. Easily polarizable anions with the correct geometry may be capable of simultaneously interacting with all three B atoms in the ring as illustrated in Figure 2b. The nature and geometry of the anion will determine the strength of interaction with the boroxine ring and therefore the extent to which the anion is immobilised. This in turn will determine the magnitude of the Li^+ transference number. Segmental motion of the oligoether chains facilitates Li^+ motion.

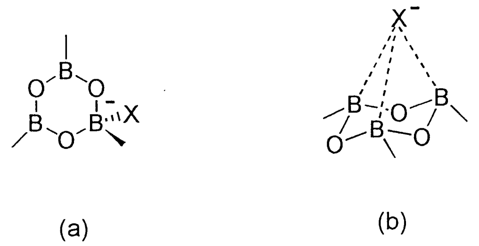

(a) (b)

Figure 2. Anion trapping by the boroxine ring. a) Interaction with one B atom of the ring, b) simultaneous interaction with all three B atoms.

Although the electrochemical stability of the electrolytes has not yet been studied rigorously, samples containing $LiCF_3SO_3$ or $LiBF_4$ sandwiched between lithium electrodes sustained a steady current was over a period of 3 days. When these cells were dismantled, the lithium surface in contact with the polymer remained shiny. This suggests that the polymers are stable with respect to metallic lithium. Their viability for use as separators in lithium rechargeable batteries is currently being assessed.

In conclusion, we have shown that the boroxine ring is an efficient anion trapping system. A new series of anion trapping polymer electrolytes with high Li^+ transference numbers may be simply prepared by incorporation of boroxine rings into the polymer host structure.

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