

Homophase model composite polymer electrolytes with triphenylborane additive

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Up to now ceramic particles, sometimes enriched with Lewis acid surface groups, were used as an additive in composite electrolytes. It seemed that the next step in the development of composite polymer electrolytes will be to obtain single cation highly conductive systems. The idea is based on the use of anion-trapping compounds as additives. In the literature studies on the use of cation receptors such as crown ethers, cryptands and calixarenes in low molecular weight non-aqueous solutions [1-4] as well as polymer electrolytes are more widely described. Anion receptors based on boron compounds were applied to the solutions of lithium salts in aprotic (inert) electrolytes based on low molecular weight solvents [5,6] as well as in gel polyelectrolytes [7]. Boron based aza ether compounds (borane, borate complexes) have been studied by McBreen and coworkers [8-11] using mainly Near edge X-ray absorption fine structure spectroscopy (NEXAFS). These studies showed that the degree of complexation of Cl^- or Γ^- anions strongly depends on the structure of the boron compounds. Also, the dramatic enhancement in ionic conductivity upon the addition of boron compounds has been noticed in these electrolytes.

This presentation describes the physicochemical properties of composite electrolytes based on PEODME $M_w = 500$ triphenylborane complexes with different salts LiI , LiCF_3SO_3 , LiNTFSI , LiBF_4 and LiClO_4 (0.2 mol/g of polymer).

On one hand triphenylborane can be used as a homophase anion complexing additive and on the other one (because of its Lewis acid character) as a promoting factor of the lithium cation mobility.

Studies on the use of anion receptors in polymer electrolytes are very limited. Papers dealing with this subject are based on either theoretical predictions [12] or studies on addition of boron family compounds, as well as cyclic or linear aza-ether structures with electron-withdrawing groups to oligoethers [9-11, 13]. The unique features of the new type of ionic conducting polymers with grafting anion receptors based on aza-ether structures are also described in literature.

Upon addition of triphenylborane to the PEODME based model polymer electrolytes an increase in the conductivity in lower temperature range (e.g. below 0°C) is observed (Figure 2).

At higher temperature, upon anion complexation, in some cases (PEODME LiClO_4 , LiCF_3SO_3 electrolytes) the overall conductivity decreases proving that at this concentration (0.2 mol/kg PEODME) and temperature range the ion transport occurs mainly via anions.

The types of interactions between polymer salt and triphenylborane are discussed on the basis of FTIR spectroscopy.

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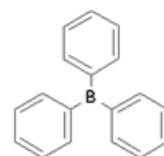


Figure 1. Structure of triphenylborane

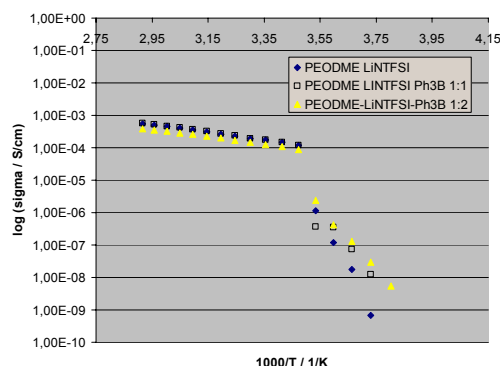


Figure 2. Conductivity vs. reciprocal temperature for PEODME-LiNTFSI and PEODME-LiNTFSI-Ph₃B (1:1 and 1:2, respectively).