Cyclic Organoboron Electrolytes with High Ionic Conductivity

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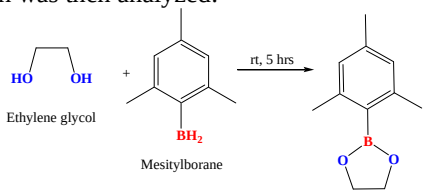
Introduction

Organic liquid electrolytes, for long have been used in Lithium ion Batteries (LiBs) due to their impressive ionic conductivity and practical usage in ambient temperature. However, there are a few reasons to site the need for an alternative electrolyte. Search for a non-flammable and a simple insertion procedure of the electrolyte during the manufacture of LiBs were the two main reasons which triggered the use of Solid Polymer Electrolyte (SPE) in LiBs. Improvement in the conduction of solid polymer electrolyte in Li-ion batteries (LiBs) has been a continuous barrier in their manufacturing. Use of boron moiety in the electrolyte has recently attracted scientists due to its flame retardant nature with significant conductivity [1]. It is widely known that there is theoretical limit in ionic conductivity of solid polymer electrolytes. In order to exceed the expected limitation, there is an urgent need to seek for another ion conductive mechanism that is different from ordinary polymer electrolytes. Herein we report the synthesis of an anion receptor crystalline cyclic organoboron compound that has an anomalous Li-ion conduction behavior under specific composition of Li salt.

Experimental

Novel boric ester type electrolyte bearing mesitylboron unit was prepared by dehydrocoupling reaction of ethylene glycol with mesitylborane at room temperature for 6 hours (Scheme 1). The resultant product was purified by recrystallization using hexane. Characterization of the prepared cyclic organoboron electrolyte was performed by ^{1}H NMR, ^{11}B NMR, DSC and TGA. 1 was doped with LITFSI salt in different molar ratios by grinding them together resulting in a soft solid which was then analyzed.



Scheme 1

Results and Discussions

The synthesized compound was crystalline solid possessing transparent needle like structure.^{11}B and ^{1}H NMR spectra confirmed the successful synthesis of expected compound. The highest ionic conductivity was observed (Figure 1 and 2) for the sample with molar ratio of 1: LiTFSI = 1:3. A unique phenomenon observed in these systems was the Li-salt when mixed with the cyclic organoboron compound with the aid of a solvent exhibited lower ionic conductivity compared to a ground mixture. Further, measurement of Li^{+} transference number was carried out for all the samples. Sample with 1: LiTFSI=2:1 showed t_{Li+} of 0.28. Under low amount of Li salt, Arrhenius plot showed linear profile while curved profiles were observed under rich amount of Li salt. This indicates ion conductive mechanism is different depending on the amount of Li salt in the present systems. These results indicate the prospective application of this cyclic organoboron compound as a viable LiB electrolyte.

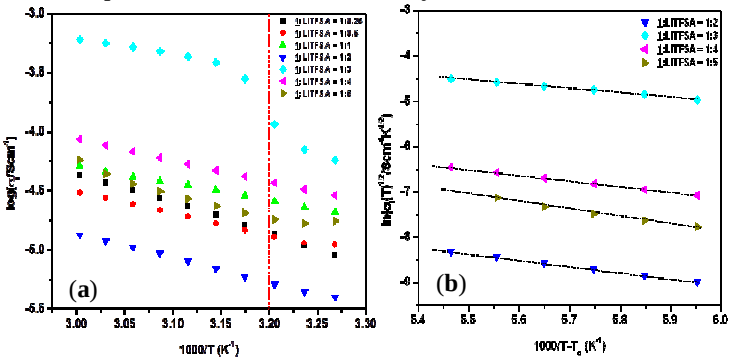


Fig 1.(a)Arrhenius plot and (b) VFT plots for (1) with LiTFSI

References :

1. Noriyoshi Matsumi, Hiroyuki Ohno, "Organoboron Polymer Electrolytes for Selective Lithium Cation Transport", Macromolecules Containing Metal and Metal-Like Elements: Boron-Containing Polymers, 2007, Volume 8, pp 175-196 (John Wiley & Sons Inc.)