

Salt Effects on Ionic Conductivity and Electrochemical Properties of Polymer Electrolytes

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Comb-shaped polymers with different structures have been designed to replace crystalline polyethylene oxide (PEO) as the hosts to dissolve lithium salts and higher ambient temperature ionic conductivities in the range of 10^{-6} - 10^{-5} S cm^{-1} have been reported^{1, 2, 3}. Aiming at further improving the ionic conductivity, new perfluorinated lithium salts with larger anions, such as LiTFSI, LiBETI and lithium methide have also been synthesized and tested in both liquid and polymer electrolytes during the last ten years⁴. Recently a non-fluorinated cheaper salt, lithium bis(oxalato)borate (LiBOB) has emerged as a promising lithium salt for applications in lithium ion batteries⁵. In our lab we have synthesized LiBOB along with two other boron containing lithium salts, Lithium bis (malonato) borate (LiBMB) and lithium bis(allylmalonato)borate (LiBAMB). The latter salt (LiBAMB) has been mainly used to synthesize network single ion conductors, which showed good cycling profile under different current densities^{6, 7}. The focus of this paper is to compare these lithium borate salts with those commercially available lithium salts in terms of ionic conductivity and electrochemical performance. The polymer matrix used here is the one that used in the synthesis of network single ion conductor, which is a four ethylene oxide (EO) based comb shape polyepoxide ether⁷. This can facilitate the comparison between the single ion conductor and those of bi-ion conductors.

At the same salt concentration of EO/Li=20, all the binary salt electrolytes were viscous liquids and showed glass transition temperatures 10-15°C higher than that of pure polymer, which is mainly due to the physical complexation of lithium cation by the polymer chains. It is interesting to note that at the same salt concentration the single ion conductor, which is a self standing film, showed a glass transition temperature 5-10°C higher than those of binary salt solutions, clearly indicated the effect of chemical crosslinking effect (network formation)⁷. The ionic conductivity of single ion conductor (LiBAMB based) is one and half order of magnitude lower than that of the un-tethered LiBAMB solution, which can be ascribed to both higher glass transition temperature (low mobility) and no contribution from the anion for the former (fewer charge carrier number) (Fig.1). For non-fluorinated lithium salts the conductivity of LiBOB is the highest, followed by LiClO₄ and LiBAMB. The abnormal lowest conductivity of LiBMB solution is believed to be due to its poor dissociation in the ether media, since it can not be dissolved in dimethoxyethane while other lithium salts can be readily dissolved in. The conductivity order (not shown) for perfluorinated lithium salts is as following: LiTFSI, LiBETI > LiPF₆ > Li methide > LiBF₄ > LiTf.

All the binary salt solutions were used to build symmetric lithium cells, which were cycled at 85°C under the current density of 0.1mA cm^{-2} and a cycling sequence of 1hr relaxation, 2hr charge, 1hr relaxation and 2hr discharge. A typical cycling profile is shown in Fig. 2 for LiTFSI solution. The cell potential does not change too much

with cycling, indicating the electrolyte was stable against lithium electrodes. This was consistent with the impedance spectra measured at different cycles. As shown in Fig. 3. both the bulk and interfacial impedance did not change with cycling. However, it was noted in Fig. 2 that the concentration polarization was built up with cycling, as reflected in the relaxation profile after charge/discharge, which took longer time for the cell to reach the equilibrium. Overall the charge/discharge current density is below the critical level and no dendrite was observed so far. Similar results were obtained for other lithium salts, except that the cycle number and impedance spectra varied with lithium salts. The best results were obtained for cells based on Li methide and LiClO₄ solutions, which were cycled up to 450 cycles without dendrite formation.

Acknowledgements: This work was supported by the US department of Energy under contract No SE-AC03-76SF0098.

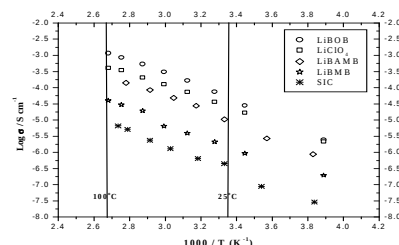


Fig.1. Ionic conductivities for the non-fluorine-containing salts in PEPE₄-co-AllylE₂ system (EO/Li=20).

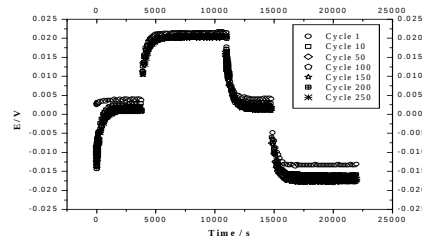


Fig. 2. Li cycling profile for the lithium cell based on LiTFSI /PEPE₄-co-AllylE₂ electrolytes at 85 °C.

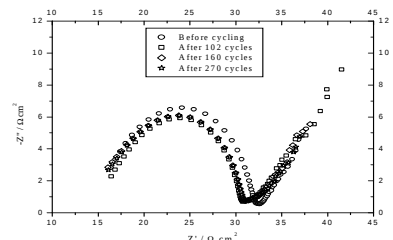


Fig. 3. Impedance of the lithium cell based on LiTFSI /PEPE₄-co-AllylE₂ electrolyte at 85 °C at different cycles.

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