

SYNTHESIS AND CHARACTERIZATION OF COMB SHAPE SINGLE ION CONDUCTORS BASED ON POLYEPOXIDE ETHERS AND PERFLUORINATED LITHIUM SALTS

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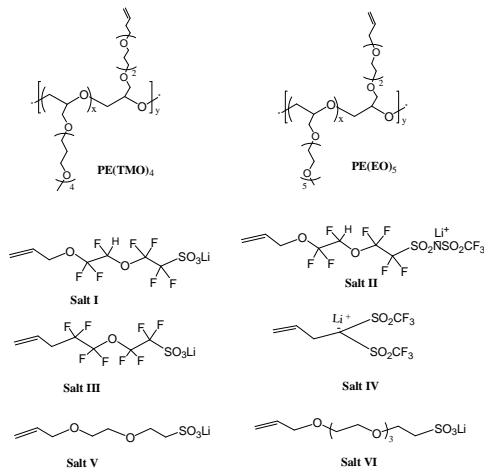
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Most single ion conductors for lithium batteries are synthesized by fixing either alkyl sulfonate or carboxylate to the polymer backbones. However, due to their limited solubility and dissociation in polyether media, their ambient conductivities are usually in the range of 10^{-7} - 10^{-8} S.cm⁻¹.^{1, 2} There are several approaches to improve the ambient conductivities of single ion conductors. One is to modify the structure of the host polymer to lower its glass transition temperature and thus improve ionic conductivity through increased ion mobility. Another is to modify the structure of the anion by putting strong electron-withdrawing atoms, most preferably being fluorine, adjacent to it to decrease the electron density on the anions and thus increase the ionic conductivity through increased number of free conducting lithium cations. The best approach, of course, is to combine the above two favorable changes in one structure.

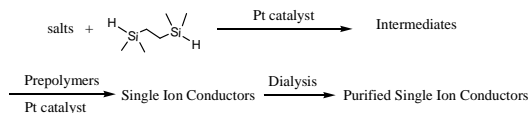
It was shown in our group³ that the comb-shaped polyepoxides with trimethylene oxide (TMO) as side chains have lower glass transition temperatures with increasing lithium salt concentration than those with EO as side chains, which is more effective in providing higher chain mobility especially at lower temperatures. In this paper we synthesized two polyepoxide ether prepolymers, one with four TMO units at the side chain and the other with five EO units at the side chain, and different allyl group containing lithium salts, either perfluorinated or non fluorinated (**Schemes 1 & 2**). The focus of this paper is to compare the effect of the structure of polymer and lithium salts on the ionic conductivities of the resulting single ion conductors.

Figure 1 shows the ionic conductivities of PE(EO)₅ based single ion conductors. The ionic conductivities of perfluorinated salts (I and II) based single ion conductors were more than one order of magnitude higher than those of non-fluorinated salts (V and VI) based ones. This ionic conductivity order falls in expectation and can be well explained by the difference in the number of free lithium cations, since the lithium mobility associated with the polymer in all these single ion conductors are same. The fluorine substituents reduce the electron density of the anion, which allows more lithium cation to dissociate and thus provides higher ionic conductivity.

For a specific lithium salt, the ionic conductivity of PE(EO)₅ based single ion conductor is more than one order of magnitude higher than that of PE(TMO)₄ based single ion conductor. It is noticed from that the glass transition temperature of PE(TMO)₄ based single ion conductor is much lower than that of PE(EO)₅ based single ion conductor. This indicates higher ion mobility for the former case, so the lower conductivity of PE(TMO)₄ system must be due to fewer number of free conducting lithium cation. This is ascribed to a lower dielectric constant for the TMO polymers due to the extra CH₂ group between the oxygens.



Scheme 1. Prepolymers and lithium salts



Scheme 2. Synthesis of single ion conductors

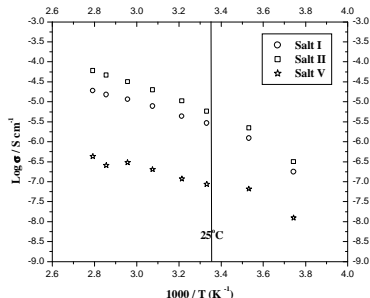


Figure 1. Arrhenius ionic conductivities of PE(EO)₅ based single ion conductors at the salt concentration of EO/Li=40.

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