Organization of the Polymer Matrix in Solid Polymeric Electrolyte by Lithium Salts Bearing Chiral Anion

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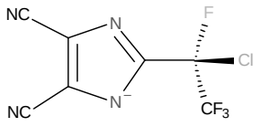
Solid Polymeric Electrolytes (SPEs) are systems in which salts are dissolved in polymeric matrix (usually PEO-polyethylene oxide). This type of electrolyte can be possibly used in several commercially important systems, such as lithium batteries, electrochromic cells as well as fuel cells. Of course, the main interest is put on the lithium batteries. Up to now, SPE-containing batteries can be used only applications in which high energy density, low power density as well as low self-discharge of the battery is needed. In order to make the range of application wider, the conductivity and lithium transference number should be enhanced [1].
Armand proposed organization of the membrane at the molecular level by the use of the lithium salt bearing chiral anion, i.e. given enantiomer of the anion which has at least one asymmetric carbon. Such application resulted in noticeable increase of the ionic conductivity, especially between 30 and 60°C. It is worth to remark that this temperature range is especially interested when application of the SPE-containing battery in biological systems is considered. The studies conducted by Armand were, however, limited to PEO-lithium 10-camphorsulfonate systems. Fortunately, this acid is commercially available, however, the degree of dissociation of its salts is low. In consequence, systems containing such salts exhibit poor conductivity [2]. This was improved by using asymmetric imide-type salt in which imide nitrogen was linked to 10-camphorsulfonyl and trifluoromethylsulfonyl groups [3] . Unfortunately, up to now, other chiral systems were not synthesized and studied.



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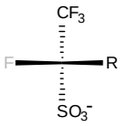

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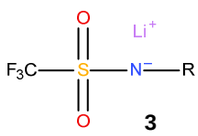
Therefore, we decided to study the ion transport properties of other chiral salt-PEO systems. The main interest is to synthesize salts of low tendency to anion pairing. Some of such salts is relatively easy in synthesis, e.g. compound **1**- derivative of dicyanobezoimidazole- can be synthesized from diaminomaleodinitrile (DAMN) and 2-chlorotetrafluoropropionyl chloride in two-step synthesis. Fluorinated sulfonic acids of formula **2** can be obtained by hydrolysis of commercially available 1-trifluoromethyl-trifluoroethanesultone.



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Other idea is synthesis and studying of the sulfonamides **3** obtained from trifluoromethylsulfonic anhydride and chiral amines. This class is interesting as large number of salts of similar structure can be synthesized. Moreover, this class of the salts exhibit relatively high lithium transference number due to existing anion-polymeric matrix interactions [4].
In the presentation, the effect of chirality on ion transport properties of the SPE will be presented. Also the dependency between the chemical structure of the salt used and effect observed will be discussed.

References

[1] K. Xu, Chem. Rev. 104 (2004) 4303.
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[3] S. Beranger, M.-H. Fortier, D. Baril, M. B. Armand, Solid State Ionics 148 (2002) 437.
[4] E. Paillard, F. Toulgoat, C. Iojoiu, F. Alloin, J. Guindet, M. Medebielle, B. Langlois, J.Y. Sanchez, J. Fluorine Chemistry 134 (2012) 72.