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Synthesis and Solid State NMR Studies of the Ionic Conductivity in Blends of Lithium Salts with Cyclotriphosphazene- and Hexaphenylbenzene-Model-Compounds

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Efficient energy storage and conversion is playing a key role in overcoming the present and future challenges in energy supply. In view of energy density and energy drain, the development of rechargeable lithium-ion batteries has to be considered as a milestone for the internal power supply of mobile and portable electric and electronic devices (1). In such batteries lithium ions are solvated by an organic solvent and diffuse freely between the anode and cathode which are physically separated by a separator membrane.

Solutions of Li-salts in highly polar ethylene carbonate (EC) and propylene carbonate (PC) have proven to fulfill the requirements of market concerns of small battery packages. In these cases a high conductivity in the order of 10^{-3} S cm^{-1} at RT is combined with chemical stability, high boiling and a low melting point. However, the usage of organic liquids in large batteries poses potential safety hazards in the case of abrupt leakage (e.g. in car accidents) or in the case of overheating as a course of sudden and uncontrolled discharge (“short circuits”). As a consequence, technical measures as hermetic metal encasements or relief valves are necessary, leading to a decrease in the effective energy density of the battery.

Therefore, over the last 35 years major efforts have been made to develop solvent-free ion-conducting polymer electrolytes starting with P.V. Wright’s discovery in 1973 that alkali metal salt complexes of poly(ethylene oxide) (PEO) show substantial ionic conductivity.

In order to improve the current electrolytes it is critical to understand how the transport of the lithium ions in the matrix is hindered or facilitated by their interactions with solvating moieties. Model substances with a well-defined chemical structure qualify optimally for these studies. Since EC has proven to be an excellent solvent for Li-salts we were tempted to tether the structural element of EC and modifications of it to the side chains of model compounds either with a cyclotriphosphazene- or a hexaphenylbenzene-(HBP)-core. This approach follows our general line of “immobilizing” ion solvents (2). To study the influence of the local mobility of the solvating units, the spacer length between the cyclic carbonate and the cyclotriphosphazene core is varied as well.

The series of model compounds which has been synthesized is shown in fig. 1. In all cases we started with the commercially available phosphorinurilic chloride trimer and reacted it with the alkoxide of an appropriate alcohol containing a carbon-carbon double bond. The cyclic carbonate is then built up by epoxidizing the carbon-carbon double bond with m-chloroperbenzoic acid followed by transition metal catalyzed insertion of CO2 in the epoxide ring. According to the different epoxide intermediates the CO2-insertion has to be performed in an autoclave under high partial CO2-pressure to gain full conversion. DSC/TGA studies of the cyclotriphosphazene model compounds point out a high thermal stability and relatively low kind of glass transition temperatures.

The HBP-compounds have been recently synthesized starting from hexakis-(4-hydroxyphenyl)-benzene (3), followed by an esterification with acid chlorides, e.g. 10-undecenoic chloride, and an analogous build-up of the cyclic carbonate as described for the cyclotriphosphazene compounds. These compounds have also been studied. All these compounds are good solvents for Li-salts, e.g. LiN(CF3SO2)2. Ion conductivities of these blends with different Li-salts and different LiO-ratios have been measured by complex impedance spectroscopy. The conductivity values of the model compound blends gave promising ion conductivities (fig. 1); however, they are not achieving the desired level of an ion conductivity better than 10^{-3} S cm^{-1} in the complete temperature range from -20 °C to +60 °C.

Fig. 1: Temperature dependent ion conductivity of blends of Li-salt with cyclotriphosphazenes tethered with 2,6-dioxolane substituents.

In order to obtain information on the interactions and the mobility of the lithium ions, which is of fundamental interest regarding transport and conductivity in lithium polymer electrolytes, solid state NMR measurements of the blends are performed. Temperature dependent 1H and 13C solid state NMR experiments provide information of the molecular dynamics of the model compound depending on the amount of lithium salt in the sample. Accordingly, solid state 1H NMR experiments are carried out to acquire evidence of diverse lithium species due to different potential coordination sites in the blends e.g. the oxygen atom of the cyclic carbonate or the cyclotriphosphazene nitrogen atoms.

Another important variable in understanding the mechanism of conductivity in a given system is the so-called transference number, describing the ratio between the partial current carried by the lithium ions and the total current.

Overall, the investigations in this work are providing important information on the conductivity mechanism in lithium electrolytes and giving indications for improvements to reach higher conductivities.

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