Optimization of methylalumoxane based composite polymeric electrolytes for lithium battery applications

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ABSTRACT

Composite polymer electrolytes are developed towards nanosized fillers to improve electrochemical properties upon the decrease of the size of the filler grain. Further improvement can be achieved by means of chemical incorporation of the inorganic part into the polymeric backbone. By these means both branched and crosslinked structures can be achieved with strict control of crosslink density. The paper presented shows the possibilities of tailoring the properties of organic–inorganic composite towards its application in lithium batteries. The increase of conductivity has been proved together with the improvement of material homogeneity, lack of crystallization, improved thermal stability of the electrolyte and improved salt dissociation, efficient stabilization of lithium-CPE SEI and promising cycling properties.

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1. Introduction

Ionic conductivity in polymer electrolytes was discovered and proposed for practical usage almost forty years ago. Despite promising beginning there is still no practical/commercial application. The most popular electrolytes based on polyethylene oxide PEO and shorter analogs such as polyethylene glycol PEG have some limitations. Since polymer electrolytes were discovered there has been an increasing amount of modifications to improve electrochemical and mechanical properties of those materials. A significant effort has been made to improve properties of electrolytes based on PEO by the creation of branched and crosslinked structures [1–3]. These techniques can significantly increase ionic conductivity in wide temperature region by the decrease of the PEO crystallization and by improvement in hopping transport of ions. Thermal properties can be also significantly improved by these means of modification. Among others one can find creation of hybrid materials and nanocomposites where inorganic fillers such as SiO_2, Al_2O_3, and TiO_2 are present in the electrolyte [4–11]. It was proved that higher surface to mass ratio of filler affects stronger conductivity enhancement. This observation becomes valid when the ceramic filler is smaller than 10 μm [12]. An increase in conductivity at lower temperature for composite electrolytes and an increase in lithium transference number (LTN) are caused respectively by PEO–ceramic filler and ion–filler interaction. Also an interfacial stabilizing effect has been observed by scavenging liquid impurities and shielding of the electrode surface. Marcinek et al. [9] proved a significant impact of Al_2O_3 on low molecular weight PEGME and PEGDME and proposed competitive interaction

between filler, ions and polymer matrix. In contrast with solid materials the addition of the filler basing on surface modified aluminum oxide to the liquid PEG-based electrolyte leads to a less prominent increase of the overall ionic conductivity observed only for high salt concentrations [9,13]. Independently of the effort made to obtain homogenous composite electrolyte some level of filler sedimentation and/or filler grain agglomeration cannot be avoided. The chemical bounding of filler with the polymer matrix was introduced as a successful countermeasure for this drawback. A new generation of hybrid organic–inorganic polymer electrolytes has been investigated recently, in which different inorganic parts are chemically bonded with polymer matrix.

M. Jeyapandian proposed hybrid inorganic–organic network where Zr atoms are bridged together through glycerol molecules [14]. A three dimensional network was obtained in a sol–gel reaction. These materials with LiTFSI as a dopant salt are electrochemically and thermally stable with conductivity value at 25 °C of 9.3×10^{-6} S cm^{-1}.

Another interesting solution as it comes to hybrid electrolytes was proposed by J. Zhang et al. They synthesized microspheres with active hydroxyl groups [15]. This material has properties analogous to the surface of modified inorganic filler with hydroxyl groups on it. Synthesized microspheres incorporated in PEO with salt improved their mechanical and electrochemical properties in comparison with classic electrolytes with the inorganic additive. The improvement is due to the Lewis acid–base activity of the additive. Ionic conductivity value at 20 °C is equal to 3.36×10^{-5} S cm^{-1} as well as an increase in lithium transference number was observed for these novel materials.

Various materials were synthesized and investigated in [16] where the authors propose a matrix based on di-urethanesils combined with PEO. These so called ormolytes (organically modified silicate electrolytes) preserve thermal stability up to 200–225 °C and are fully amorphous and

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electrochemically stable with a conductivity value of 7.4×10^{-5} S cm^{-1} at room temperature. Moreover, the matrix can be easily modified by substitution of one PEO part for the different ones between di-urethanesil blocks.

Many other similar reagents such as alkoxysilanes [17] were used to obtain an inorganic–organic electrolyte, also $Al((OCH_2CH_2)_nOCH_3)_3$ was used as an additive to solid polymer electrolytes [18], or triethyl-aluminum and poly(ethylene glycol) methyl ethers were reacted together and added to PEO [19]. In paper [20] aluminum carboxylates were the starting point to obtain hybrid electrolytes. The properties of all these hybrid materials are similar to composite matrices with the addition of at least some extra features. It is also worth stressing here that it is very difficult to predict properties of this kind of materials in detail.

This work is a continuation of an earlier research in the field of hybrid materials based on methylalumoxane (MAO) as a product of AlMe$_3$ and itaconic acid reaction (for the structure see Fig. 1a) and various poly(ethylene glycols). We proved in an earlier study that a substitution reaction between methyl groups from MAO at PEG-originated hydroxyls is possible [21]. Due to 12 easily substitutable methyl Al–CH$_3$ groups and one or two hydroxyl C–OH groups in PEG there are a lot of possibilities of modifications and matrices of various constructions (branched and crosslinked) that can be obtained (see reaction scheme in Fig. 1). The vanishing of signals originating from the –OH moieties together with the changes of Al atom coordination number observed in ^{1}H and ^{27}Al NMR and FT-IR measurements prove that the reaction is effective up to substitution of 8–10 methyl groups with practically 100% yield. This was as well confirmed by the volumetric determination of the amount of the evolved methane. Mechanical properties can be easily controlled by changing the mole ratio of branching substituents such as PEGMME and crosslinking substituents as PEG. Moreover, as no more than ten substituents are typically used the remaining free –CH$_3$ groups in matrix can be easily exchanged in reaction with traces of water present in electrolytes. Unfortunately, the water content cannot be directly determined by Karl Fisher titration (Al–C bonds react with the reagent) but in synthesized samples no traces of water were observed at least at concentration levels affecting the lithium electrode electrochemistry [22]. This paper shows as well the improvement of electrochemical properties of electrolytes containing MAO. This paper correlates salt–matrix interaction, their influence on mechanical and electrochemical properties with data obtained by spectroscopic techniques and thermal methods such as DSC and TG.

2. Experimental

The sample synthesis is based on the substitution reaction between methyl groups bonded to the MAO core and hydroxyl groups from PEGs. A more precise description is presented in our earlier work [21].

2.1. Electrochemical analysis

A VMP 3 Multichannel Electrochemical Analyzer was used to determine all electrochemical properties.

Ionic conductivity was determined by means of impedance spectroscopy. The electrolytes were pressed between stainless-steel blocking electrodes for solid samples. In the case of brittle ones they were pelletized by subsequently repeated heating at 80 °C and pressing with 1 ton/cm^2 load between blocking plate electrodes. Liquid electrolytes were measured using specially designed stainless steel covets. In all cases frequency range varied from 100 MHz to 500 kHz. The cells were immersed in a HAAKE DC 50 cryostat to control the measurement temperature in 253–353 K range.

Lithium ion transference numbers (t_{Li+}) of the samples were measured at a fixed temperature (25 °C). The steady state (polarization) technique, which involves a combination of AC- and DC-measurements, was applied [23]. The impedance response of the Li|electrolyte|Li cell was measured prior to the dc-polarization stage, in which a small voltage pulse (ΔV) was applied to the cell until the polarization current reached the steady-state I_{ss}. Finally, the impedance response of the cell was measured again. The double AC test was required to determine solid electrolyte interface (SEI) resistance before (R_0) and after (R_{ss}) dc-polarization.
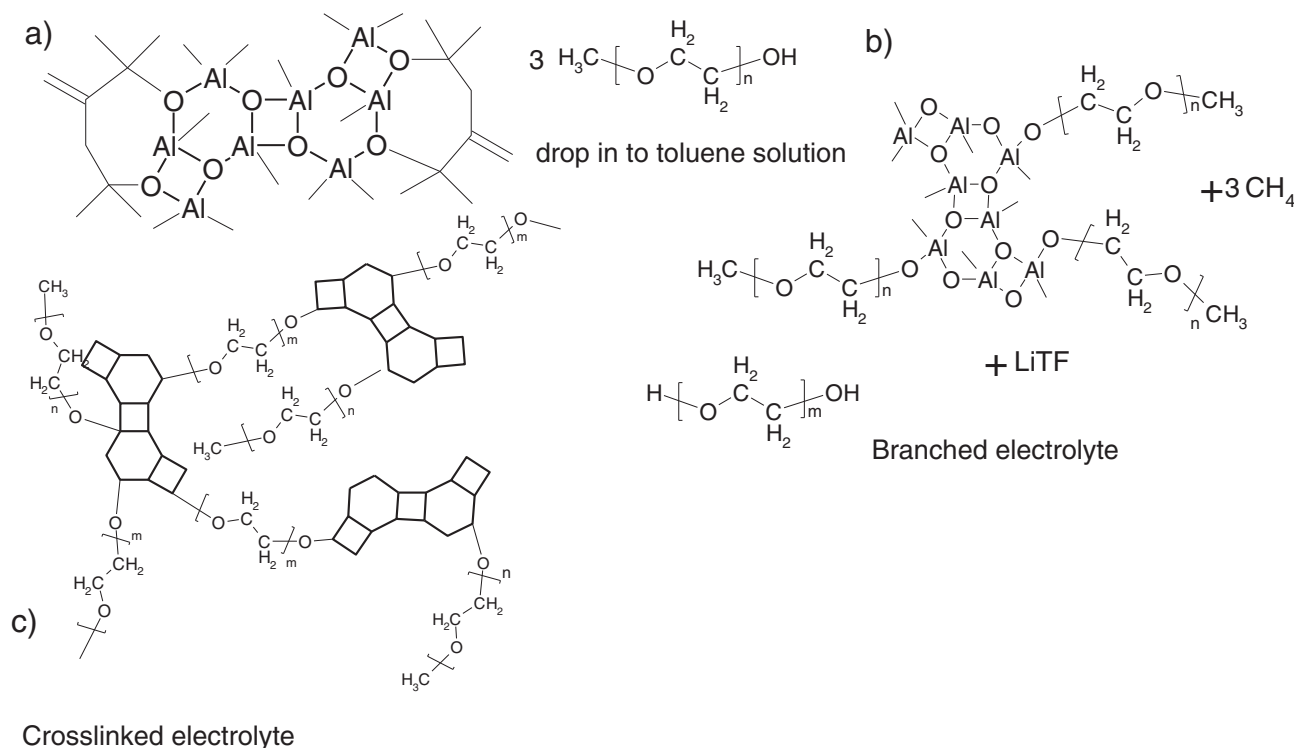

Fig. 1. The structure of the substrate molecule methylalumoxane (MAO) (a) and the reaction scheme leading to the branched (b) and cross-linked (c) structures of the electrolyte matrix.