

Electrochemical and infrared spectroscopy analysis of hybrid polymeric electrolytes based on aluminum-oxygen core and PEGs.

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Hybrid polymer electrolytes based on methylalumoxanes (MAO)-containing core being an analog of aluminum oxide and polyethyleneglycols (PEG) of various chain length were successfully synthesized and already pre-characterized. The presence of the methyl groups bonded to the aluminum atoms belonging to the aluminum-oxygen core of the precursor gives a possibility of easy substitution with e.g. hydroxyl groups. Moreover, the remaining after synthesis free methyl groups can easily scavenge impurities e.g. traces of water.

Sample constitution varies from highly viscous liquid (branched structures), to rubbery or even brittle solids (for crosslinked ones). Crosslinked electrolytes are obtained through partial exchange in the reaction mixture of PEG's with one hydroxyl terminal group for ones possessing them on both ends of the oligomer chain. No matrix freezing is observed in DSC thermogram and FT-IR vs temperature spectrums contrastively to electrolytes without the MAO content. This observation suggests existence of interactions of PEG ether oxygens with the MAO core. Some non-prominent changes were observed in the FT-IR spectra in the area characteristic for C-O-C moiety vibrations upon salt addition. Additional entities of acidic and basic character appear then in the electrolyte. According to the Pearson theory ether oxygens should compete with anions in interactions with electron-deficient aluminum atoms being finally expelled by them from the vicinity of core. We believe that softer Lewis bases (salt anions) are more competitive in interactions with the MAO core (soft Lewis acid center) in comparison with the hard bases (oxygen). The latter should rather interact with lithium cations being the hard acidic entity. Finally, this phenomenon should lead to an increase of salt dissociation rates with increasing MAO content in the matrix. This assumption is here confirmed by the FT-IR data. Moreover, thermal dependent FT-IR in range 70 to -20°C confirmed a higher dissociation rate for electrolytes with MAO content in comparison with the pristine ones. Additionally, an increase of the salt dissociation with decreasing temperature was observed (Figure 1). Changes of signals attributed to the free ions are not so prominent for samples with MAO in comparison with ones without MAO.

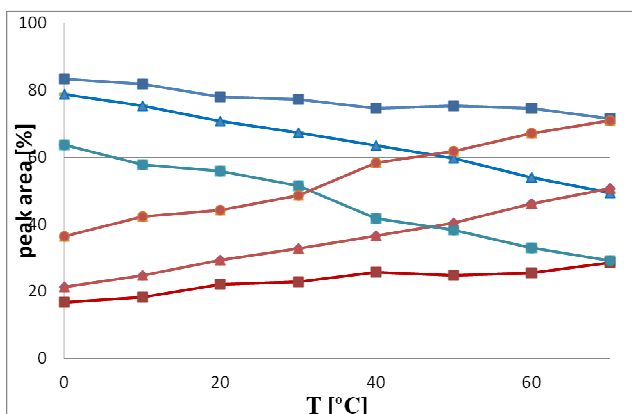


Figure 1 Dependency of intensity of bands for free ions and ion pairs, in temperature range 0°C – 70°C for electrolyte with high, medium and no MAO content. All the samples contain 1mol of salt per kg of polymer .
■ 1MAO10PEGMME350, ▲ 1MAO10PEGMME750, • PEGDME500,

blue lines - free ions , red lines - ion pairs

The obtained conductivity values were in range of 10^{-4}S/cm at temperature 20°C . Moreover, fully amorphous systems were obtained with homogeneity confirmed by TEM with resolution 100 nm. Later the passivation layer formation was studied using a Li|LiX|Li symmetrical cell. When the passivation layer was formed during annealing of the system without a current flow a stable state was achieved with no further changes during electrochemical measurements. No changes of the SEI layer were observed for a current flow or voltage applied (chronopotentiometry and chronoamperometry regimes). The experiment was carried on up to 400 cycles each lasting 15 minutes being preceded and succeeded by EIS experiments. The second semicircle of the spectra here is a superposition of two semicircles observed for medium and low frequencies correlated with the passivation layer and resistance of charge transfer. Evolution in time and temperature dependencies allows us to distinguish between charge transfer and layer formation phenomena attributing the latter to the mid frequency range. To correlate the conductivity values with the viscosity measurements the product of these two parameters (a pseudo Walden product) can be presented as a function of temperature. The value for the reference sample is much lower in comparison with electrolytes with MAO (figure 2). These data can be explained by the increased number of free ions observed above in the mathematical deconvolution of the infrared data.

All the electrolytes studied follow the VTF model in terms of conductivity and viscosity. The data from these calculations are comparable within the analyzed group of samples. The diffusion coefficient measurements were considered as well for VTF model calculations but discrepancies of the results suggest properties of the measured cells to be different than expected.

Additionally, the cyclic voltametry data will be discussed. In this experiment several various salts were considered as additives to the matrices. In all the cases the hybrid polymer electrolytes were electrochemically stable in the battery-applicable potential range.

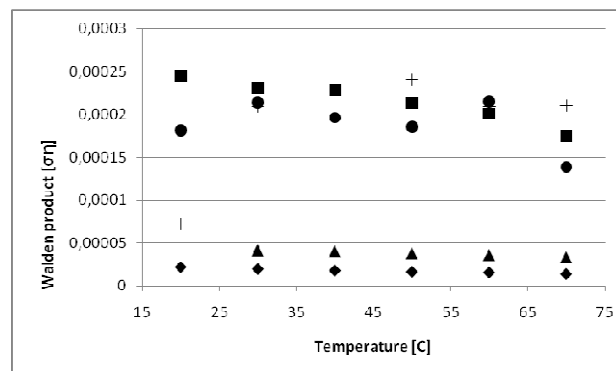


Figure 2 Pseudo Walden product of electrolytes based on MAO and MAO free electrolyte. ▲ PEG MME750; ◆ PEGDME500; ■ 1MAO10PEGMME750 +1MAO6PEGMME350; ● 1MAO6PEGMME750; All the samples contain 1mol of salt per kg of polymer

References:

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