

"Mono→Poly"
Polymerization reactions in lithium batteries

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Introduction

Polymers play a major role in lithium metal and lithium ion cells. They are not only used as "hardware" for electrode and cell assembly, e.g., in the form of binders, separators, electrode materials, electrolytes, and electrolyte matrices, but furthermore formation of polymers can be the result of wanted and unwanted chemical and electrochemical reactions in the cell; reactions most often involving electrolyte components.

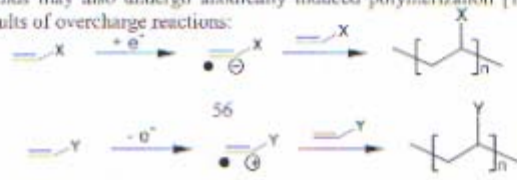
Unwanted polymerization reactions are very often initiated by impurities in the electrolyte, which induce a chain polymerization reaction of electrolyte components, as they are well known for Lewis-acid-type decomposition products of electrolyte salts such as LiBF_4 , LiPF_6 , and LiAsF_6 [1].

Polymerization reactions can be, however, also used to suppress unwanted reactions and processes, which may occur during overcharge or other cell abuse. Typical examples are electrolyte additives. For instance, during overcharge certain electrolyte additives (=monomers) may form a polymeric film on the cathode surface via polymerization. This film is highly resistive to ion transport and thus blocking the overcharge current [2]. Other electrolyte additives can activate the pressure-sensitive current intermittent device (CID) of a cell as they evolve gas when polymerized under overcharge [3]. Finally, but also most important, monomeric electrolyte additives may initiate and/or create highly effective solid electrolyte interphase (SEI) films (cf. below).

Vinylene monomers as electrolyte additives

For vinylene compounds such as vinylene carbonate [4], vinylene acetate [5], acrylic acid nitrile [6, 7], and 2-cyanofurane [8] and many others with well-known SEI-filming function at graphitic anodes in lithium ion cells, we suggested that the first step of the electrochemically induced reduction (= cathodically induced electro-polymerization) of vinylene compounds is the electron transfer from the electrode to the double bond, which starts a chain reaction via addition of the formed reactive species to the double bonds of other monomers or other solvent components present in the electrolyte. Only the first electron transfer step is an electrochemical one, thus a charge consuming step. The subsequent reactions are apparently only of chemical nature [9, 10]. It should be taken care that the functional group "X" is electron-withdrawing, which supports an early additive reduction and thus forms an SEI, which is formed before detrimental side reactions occur.

Vinylene compounds may also undergo anodically induced polymerization [11], that they can inhibit the results of overcharge reactions:



The functional group "Y" in α -position to the vinylene group is electron-donating to promote oxidation.

Isocyanate monomers as electrolyte additives

An electro-polymerization mechanism [14, 15] can be also expected by using isocyanates as electrolyte additives. Both, cathodically and anodically induced polymerization is possible, suggesting the use of isocyanates as SEI additive and for overcharge protection:



Presentation

After a brief overview about polymerization reactions, we will present and discuss recent results obtained with vinylene and isocyanate additives in our laboratory. The underlying reaction mechanism will be highlighted with the help of in situ FTIR spectroscopy.

References

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