

POLYMERIZING ELECTROLYTE ADDITIVES FOR LITHIUM ION BATTERIES

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Liquid nonaqueous solvents have found numerous applications in electrolytes for lithium ion batteries. The choice of solvent mixtures is usually a compromise between the desired physical (e.g. electrolyte conductivity, volatility, flammability, wetting ability, etc.) and electrochemical properties (reduction and oxidation at the respective electrode/electrolyte interfaces, solid electrolyte interphase (SEI) formation behaviour, etc.). An elegant way to overcome the inevitable limitations of this compromise is the use of electrolyte additives, which even in small amounts improve the electrolyte properties in the desired direction. Among many additive applications, such as overcharge protection and cell safety improvement, electrolyte additives for improved film formation processes at anode and cathode have found particular interest.

A well known example for an electrochemical polymerization is the reduction or oxidation of vinylene monomers^[1]. The basic principle of an electrochemically induced reduction process (= cathodically induced electropolymerisation) of vinylene compounds is shown in Fig. 1.

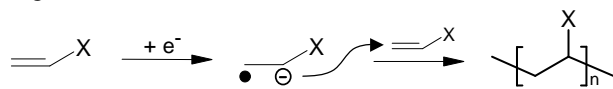


Fig. 1: Cathodic, i.e., by reduction induced polymerization of vinylene monomers.

During reduction, the first step is the electron transfer from the electrode, which starts a chain reaction via addition of the formed reactive species (in this case a radical anion) to the double bonds of other monomers (shown in Fig. 1) or other solvent components present in the electrolyte. Only the first electron transfer step is an electrochemical one, thus charge consuming step. The subsequent steps are of chemical nature. The oxidation or reduction potentials can be simply adjusted via the substitution pattern at the double bond, e.g., by using different functional groups "–X" (cf. Fig. 1).

Acrylic acid nitrile (AAN) has already been presented^[2] as a novel example out of the large class of vinylene group containing film forming additives for anodes in lithium ion batteries. We suggest that an electro-polymerization is the main electrolyte reduction mechanism for vinylene group containing electrolyte additives. The outstanding filming properties of vinylene compounds such as AAN allow to use graphitic carbon anodes in propylene carbonate based electrolytes even whilst only 1 % of the additive.

A laterally reversed reaction mechanism of compounds containing double bonds may be proposed for an anodically induced electro-polymerization at cathodes for lithium batteries.

In constant current overcharge experiments a LiMn_2O_4 cathode was investigated in a PC/LiClO_4 electrolyte. Without additive the cut-off potential of 4.75 V was reached immediately after the complete charge of the electrode, i.e. exhaustive lithium extraction. The addition of only 1 % of cyclohexene allowed a tenfold overcharge without an increase of the potential to more than 4.4 V.

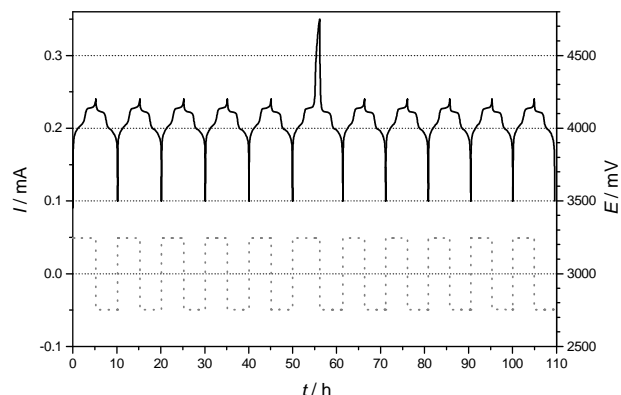


Fig. 2: Charge/discharge study with overcharge step of a LiMn_2O_4 composite cathode in PC/LiClO_4 without additive.

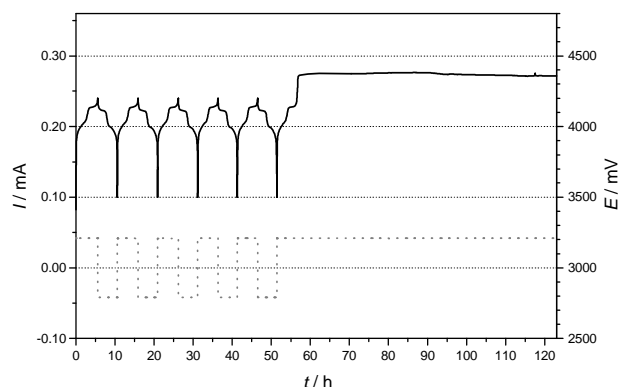


Fig. 3: Charge/discharge study with overcharge step of a LiMn_2O_4 composite cathode in PC/LiClO_4 with 1 % cyclohexene.

The establishment of SEI-like interphases for protection of the cathode against dissolution or the formation of shut-down films at the cathode surface as protection against overcharge will certainly be an important application for the polymerizable electrolyte additives. The design of electrolyte salts, solvents and additives which can be combined in a way that very specific requirements on the electrolyte are fulfilled, will be crucial to the future development of "functional electrolytes".

- [1] J. W. Breitenbach, O. F. Olaj, F. Sommer, *Adv. Polym. Sci.* **1972**, 9, 47.
- [2] K.-C. Möller, S. C. Skrabl, M. Winter and J. O. Besenhard, *Filming Properties of New Electrolyte Additives for Graphitic Anodes for Lithium Ion Cells*, 3rd Hawaii Battery Conference, Hawaii, **2001**.

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