

Investigations on Electrolyte Decomposition during Aging via Headspace GC-MS

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The decomposition of the electrolyte has a high influence of the electrochemical performance of lithium ion batteries [1,2]. Only during the formation of the SEI layer electrolyte decomposition is intended [3,4]. In all other cases it leads to negative effects, such as pressure build-up because of gaseous decomposition products, loss of lithium due to formation of organic lithium salts and excessive filming on anode and cathode resulting in higher resistance. Beside a higher leakage current these side reactions lead to a reduced cycle life and rate capability.

A detection of the species and the amount of the decomposition products can give hints of the decomposition mechanism and the cause and progress of cell aging.

In the present work a method was developed to extract electrolyte out of aged cells and analyse it via gas chromatography. The electrolyte was cycled in pouch full cells to assure an authentic battery environment. Headspace injection was used due to several crucial advantages as against liquid injection. Detection via mass spectrometry allowed the identification of the components. The analytical results were related to the electrochemical measurements of the cells.

Figure 1 shows the chromatogram of an aged standard electrolyte (1M LiPF₆ in EC:EMC (3:7) + 2% VC) obtained out of a NMC/Graphite pouch cell. Beside the main components several decomposition products could be separated and identified. Especially low boiling components can be detected even in very low concentration.

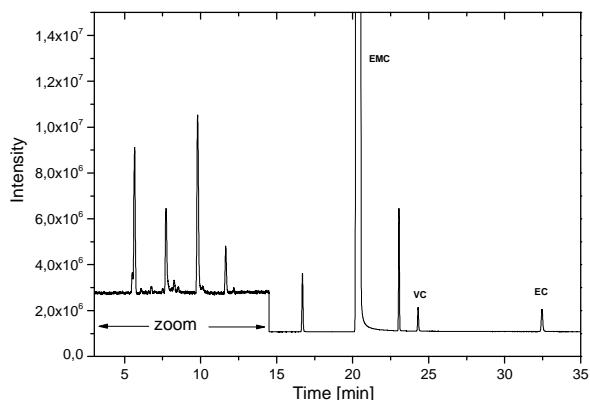


Figure 1: Chromatogram of an aged electrolyte (1M LiPF₆ in EC:EMC (3:7) + 2% VC) using headspace injection

To investigate the relationship between cell aging and electrolyte decomposition, cells with different electrochemical behaviour have been analysed.

Figure 2 shows the capacity and efficiency curves of two NMC/Graphite cells, built under same conditions and

cycled for the same time. The higher capacity fading of cell B is linked to higher electrolyte decomposition, shown by the GC analysis (Figure 3).

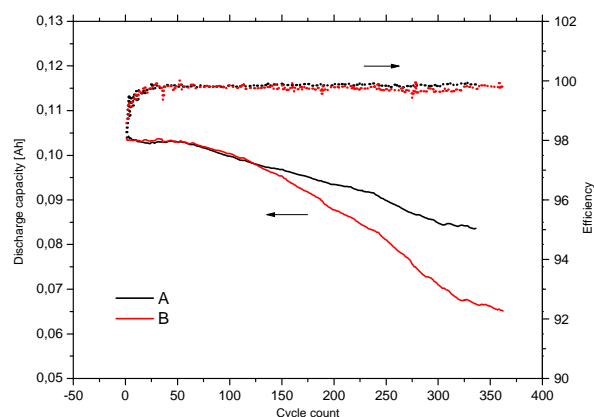


Figure 2: Discharge capacity and efficiency of two NMC/Graphite pouch cells, both cycled for 700 h.

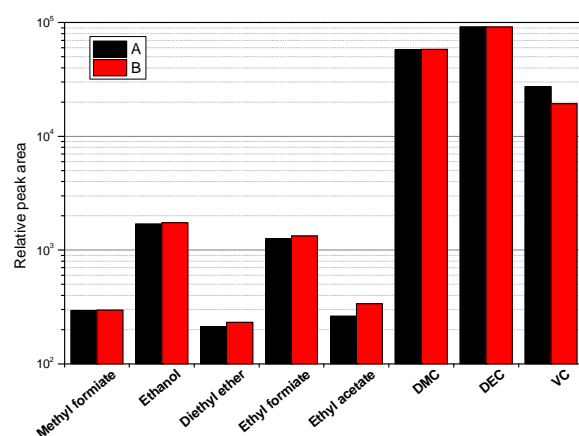


Figure 3: Certain decomposition products measured in aged electrolyte extracted from 2 similar cells

Furthermore electrolytes containing different solvent species and additives were aged in similar cells and subsequently analysed.

In addition the electrode materials have been varied. On the anode side graphite was replaced by titanate, on the cathode side NMC was replaced by LFP. Furthermore first test with high voltage spinel were carried out.

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References:

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