

Analysis of Trialkyl Phosphates as markers for Lithium Battery Aging

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User Benefits

- ◆ Lithium Batteries (LIB) decomposition and aging can be evaluated by monitoring Trialkyl Phosphates
- ◆ A routine and fast GCMS method for the detection of Trialkyl Phosphates was developed
- ◆ Trialkyl Phosphates can be detected with high sensitivity and selectivity in commercial liquid electrolytes

Introduction

The electrolyte solution is a crucial part of a typical Lithium-ion battery, consisting of Li salts (e.g. LiPF₆), and organic carbonates. Decomposition and formation of phosphorous-based and other organic products starts already at the production stage of the electrolyte. The formation of such molecules does not affect the electrolyte/battery quality negatively, as long as the quantity is low enough. On the contrary, several decomposition products have a positive effect on the formation of the so-called SEI surface (Solid Electrolyte Interface) on the LIB anodes, which is crucial for the battery functionality. Nevertheless, this is a continuous chemical process and the increasing amount of some of the decomposition products is a clear indicator of the progressive aging of the battery/electrolyte. This application is demonstrating the GCMS analysis of Trialkyl Phosphates as reaction products of carbonates and LiPF₆ salt. The choice of these compounds as markers for electrochemical battery aging is due to the fact, that their formation is very slow and depends only on a few external parameters, allowing to investigate the electrochemical aging (charge/discharge) by a simple comparison of before/after analyte content.

Sample preparation and measurement

The sample preparation and the samples were kindly provided by MEET Battery Research Center. Following procedures were applied: the commercially available 18650 cells, were charged/discharged in a special test chamber at 45 °C and a voltage of 4.2 V. The discharge was performed at a constant current of 2.2 A down to a voltage of 2.75 V. The cycling was stopped at the remaining discharge capacity of 70% (around 1500 cycles). After that, the batteries were opened, and the jelly roll was extracted using Supercritical Fluid Extraction (SFE) and Acetonitrile as co-solvent. Before injection of 1 µl, the extract was dissolved with DCM 1:10.



Figure 1 Shimadzu GCMS QP2020 NX with AOC-30i liquid sampler

The Package

The recommended analytical hardware and software configuration is listed below.

Main Unit

Nexis GC-2030 with QP2020 NX: Gas chromatograph plus mass spectrometer detector

Accessory

AOC-30i autosampler

Main Consumables

SH-I-5MS, 30m × 0.25mm × 0.25µm; P/N 221-75940-30

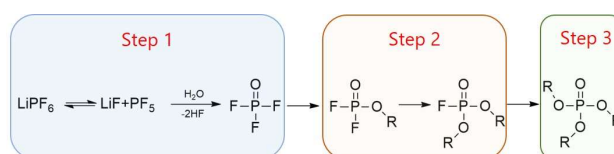
Software

GCMSolution and GCMS Insight Software

A picture of the instrument used, including Main Unit and accessory can be seen in Figure 1.

Decomposition mechanism of LIB electrolytes

The decomposition of LiPF₆ salts under reaction with traces of water and the corresponding electrolyte solvent can be influenced by electrochemical and chemical processes. The formation of tri-alkylated species can be described by a simplified reaction sequence shown in Figure 2. The non-, mono- and di-alkylated phosphates shown on step 1 and step 2 are usually detectable even in new LIB electrolytes. These reactions happen very quickly, therefore the observed content is significantly higher in comparison to the tri-alkylated species shown on step 3. Due to the fact that the tri-alkylated species are formed very slowly through the reaction of organic carbonates with conductive salts, they can be a very useful indicators for battery aging.










R=Alkyl (Et, Me...)

Figure 2 Simplified formation mechanism of Trialkyl Phosphates

■ Results and Discussion

To analyze the phosphate species the SCAN mode on the GCMS was used, which enabled the identification of the different analytes based on their spectra. Since most compounds were not available in the most common libraries the spectra from the available scientific publications were used as a reference [1]. The corresponding retention times, used m/z traces and the detected areas of the different compounds are summarized in the Table 2.

Table 2 Chemical structures and the specific m/z traces for identification

Compound	Chemical structure	m/z for SIM	Ret. Time [min]	Peak area	
				New battery	After 1500 cycles at 45 °C
Dimethyl fluorophosphate (DMFP)		97, 98, 128	3.83	15304	11406
Ethyl methyl fluorophosphate (EMFP)		97, 115, 127, 141	5.64	7015	14619
Diethyl fluorophosphate (DEFP)		101, 113, 129	8.05	2136	3426
Trimethyl phosphate (TMP)		140, 110, 109, 95	9.12	N.D	3952
Ethyl dimethyl phosphate (EDMP)		153, 139, 127, 110, 109, 96, 95	10.11	N.D	1028
Diethyl methyl phosphate (DEMP)		141, 113	10.77	N.D	588
Triethyl phosphate (TEP)		155, 127, 109, 99	N.D	N.D	N.D

The fluorinated species could be detected in both, the new and the aged battery. The content of EMFP and DEFP in the aged battery is significantly higher in comparison to the new one, and at the same time the content of DMFP is slightly lower. The reason for this result is the very fast formation of fluorinated compounds and their dependence on many external factors (sample preparation, time of storage, moisture). As mentioned above, the fluorinated compounds are more suitable to analyze the quality of the manufactured electrolyte, e.g. to investigate the destruction due to storage conditions like moisture levels. In contrast to the fluorinated compounds, the tri-alkylated phosphates are formed significantly slower and are usually not detectable in a fresh electrolyte, offering the possibility to investigate their formation as an indicator of battery aging. The obtained GCMS chromatograms and the corresponding MS spectra are shown in Figure 3.

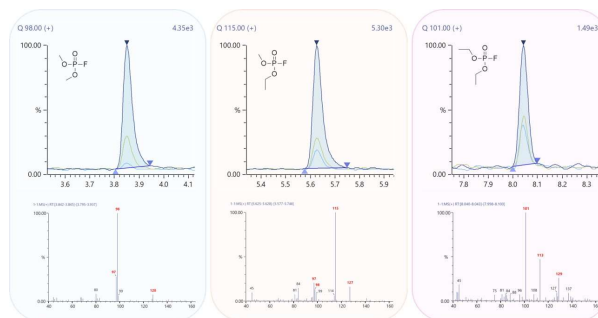


Figure 3 Mass spectra of the detected fluorophosphates in the aged LIB, DMFP (left), EMFP (middle), DEFP (right)

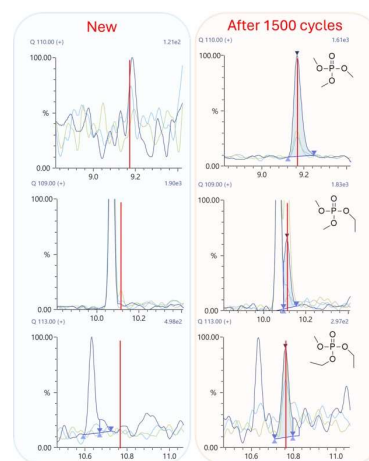


Figure 4 GCMS chromatogram of the TMP, EDMP and DEMP in a new LIB (left) and after 1500 cycles (right)

As it is shown in Figure 4, TMP, EDMP and DEMP could be detected in the electrolyte after 1500 charge cycles, TEP was not observed in this experiment, nevertheless TEP might be detected in a sample with a more advanced aging.

■ Conclusion

The presented application demonstrated the suitability of GCMS to investigate the aging of the LIBs using phosphate-based degradation products. This investigation is based on SCAN measurements. Here, a SCAN/SIM mode would be beneficial offering the possibility to detect the main compounds (carbonated, additives) and the degradation products in one measurement. A further improvement would be a dedicated SIM method for the mentioned phosphates with the highest selectivity and sensitivity.

■ Acknowledgment

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■ Literature

[1] W. Weber, V. Kraft, M. Grütze, R. Wagner, M. Winter, S. Nowak, Identification of alkylated phosphates by gas chromatography-mass spectrometric investigations with different ionization principles of a thermally aged commercial lithium-ion battery electrolyte, 2015, 1394, 128-136.