Application News

GC-MS GCMS-QP2020 NX

GC/MS Analysis of Fluorophosphates as Decomposition Products in Lithium Battery Electrolyte

Yu Nagao [1], Nerea Lorenzo Parodi [2], Waldemar Weber [2], Xaver Mönnighoff [2]
[1] Shimadzu Corporation. [2] Shimadzu Europa GmbH

User Benefits

- A routine and fast GC/MS method for detection of LIB decomposition products.
- Monitoring of the LIB electrolyte after manufacturing, storage and transport.
- Fluorophosphates can be considered as markers for a started electrolyte decomposition.

Introduction

The electrolyte solution is a crucial part of a typical Lithium-ion battery, consisting Li salt (f.e. $LiPF_6$), organic carbonates and additives to ensure a stable transport of Li ions during charging and discharging processes. A significant part of battery aging can be considered as a result of the decomposition of the electrolyte. At the end of this chemical and electrochemical processes oligomeric organic compounds (Fig. 1) [1] and organophosphates [2,3] could be detected. Especially fluor containing organophosphates are of interest due to their potential neurotoxicity [4,5,6].

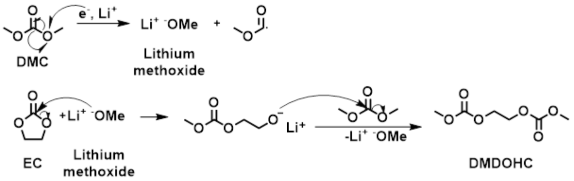


Fig. 1 Formation of lithium methoxide and further reaction with EC leading to DMDOHC [1]

While the electrochemical aging takes place in a battery itself, the chemical aging starts already during manufacturing, storage and transport of the electrolyte. Typical factors that influence this are: exposure to air and moisture, too high temperature at manufacturing/storage, long term storage in general. Wrong materials in the production pipeline like glass are problematic as well due to a catalytic reaction of the fluoric acid traces with SiO_2 as follows: $SiO_2 + 6HF \rightarrow H_2[SiF_6] + 2H_2O$. This application examples of analysis of the electrolyte solution for qualitative determination of fluorophosphates as a possibility for an early-stage quality control.

Sample preparation and measurement

25 µl LIB electrolyte consisting Ethyl methyl carbonate and Ethylene carbonate 1:1 with 1M $LiPF_6$ has been diluted with 1 mL dichloromethane and centrifuged for 5 min at 8500 rpm to remove the solid $LiPF_6$. The centrifuged solution was transferred into a 2 mL GC glass vial and measured by GCMS-QP2020 NX (Fig. 2).

Fig. 2 Shimadzu GCMS-QP2020 NX with AOC^{TM}-30i liquid sampler

Method details

The analytical conditions are listed in detail in Table 1.

Table 1 GC/MS analytical conditions

System Configuration		
Model	GCMS-QP2020 NX	
Autosampler	AOC^{TM}-30i	
GC parameter	Injection mode	Splitless
	Column	SH-Rxi-5MS
	Lin. velocity	36.8 cm/s
	GC oven method	35 °C for 1 min, 3 °C/min to 60 °C, 30 °C/min to 210 °C, 210 °C for 1 min
	Transfer line temperature	210 °C
	Carrier gas	He
MS parameter	Ion source temperature	180 °C
	Ionization mode	EI
	Measurement mode	SIM/Scan
	Solvent cut time	2 min

Decomposition mechanism of LIB electrolyte

The electrolyte used for this experiment was stored for around 1 year at -30 °C in a refrigerator, any aging processed are under such conditions should be extremely slowed down. Nevertheless, such a long storage has already an influence on decomposition, as it is shown in the Fig. 3, a chemical rearrangement of Ethyl methyl carbonate (EMC, 2) to Dimethyl carbonate (DMC, 1) and Diethyl carbonate (DEC, 3) could be observed.

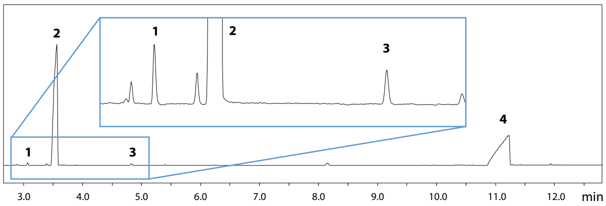


Fig. 3 GCMS chromatogram of the standard LIB electrolyte. **1**: Dimethyl carbonate (DMC), **2**: Ethyl methyl carbonate (EMC), **3**: Diethyl carbonate (DEC), **4**: Ethylene carbonate (EC)

The decomposition of $LiPF_6$ salt under reaction with traces of water and the corresponding electrolyte solvent can be influenced by electrochemical and chemical processes. The reaction mechanisms are basically identical, the content of the produced organophosphates is strongly dependent the aging stage of the electrolyte/LIB [2,3].

For the dissolved $LiPF_6$ salt a thermodynamic equilibrium $LiPF_6 \leftrightarrow LiF + PF_5$ is considered as a starting point for its destruction, where the PF_5 is forming POF_3 under reaction with traces of water followed by a chain of reactions of POF_3 with organic carbonate solvents. The exact reaction mechanisms are still a point of intensive research. One of proposed mechanisms from POF_3 to fluorophosphates is shown in the Fig. 4.

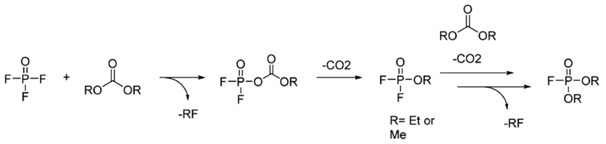


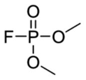
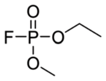
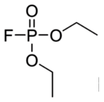
Fig. 4 Proposed formation mechanism of fluorophosphates

Summarizing the destruction process can be divided in four steps, 1: creation of POF_3, 2: creation of difluorophosphate, 3: creation of monofluorophosphates, 4: creation of trialkylphosphates

■ Results and Discussion

To analyze the high volatile destruction products from the step 1 and 2 a headspace-based injection for GCMS is required due to a coelution with the solvent. A liquid based injection applied for this application allow the analysis of the products in step 3 and 4. The used electrolyte consists of ethyl methyl carbonate, therefore methylated, ethylated and mixed ethyl methyl phosphate species can be expected. A SCAN/SIM mode for detection allows a clear identification of compounds by a mass spectra and a sensitive and selective detection using SIM traces. The applied *m/z* values for SIM detection are collected in the Table 2.

Table 2 Chemical structures and the used *m/z* SIM traces for detection

Compound	Chemical structure	*m/z* for SIM	Ret. Time [min]
Dimethyl fluorophosphate (DMFP)		97, 98, 128	4.44
Ethyl methyl fluorophosphate (EMFP)		97, 115, 127 ,141	6.3
Diethyl fluorophosphate (DEFP)		101, 113, 129	9.0

For the analyzed electrolyte only dialkylated species could be detected (Table 2), not the tri- alkylated. The reason is a decomposition at the very early stage as a just long-term stored electrolyte was used, where the creation of tri alkylated species is not started yet. The obtained mass spectra is shown in the Fig. 5 and the corresponding chromatograms in the Fig. 6. The problem in general for identifying such compounds is the absence of M^+ peak in the spectra (except DMFP) and their absence in typical GCMS libraries (except DEFP). To identify the spectra researches used synthesized standards and for more complicated species NCI with CI GCMS detections in addition [3].

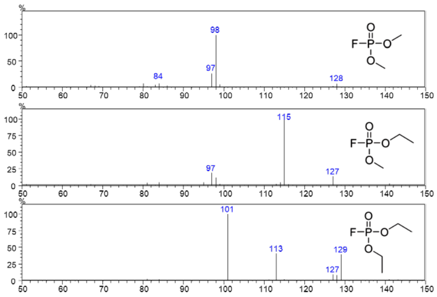


Fig. 5 Mass spectra of the detected fluorophosphates, DMFP (top), EMFP (middle), DEFP (bottom)

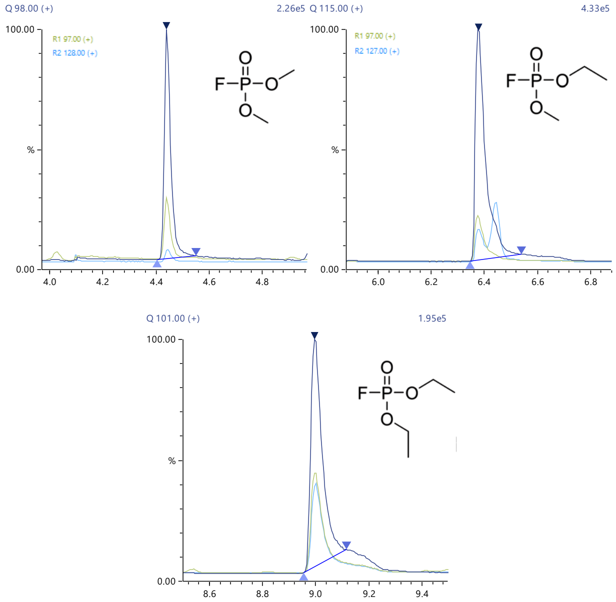


Fig. 6 MS chromatogram of the DMFP, EMFP and DEFP in LIB electrolyte

■ Conclusion

$LiPF_6$ based LIB electrolyte degrade during chemical and electrochemical processes. With GC/MS based analysis method a clear assignment of tree fluorinated alkyl phosphates has been successfully accomplished in a long-term stored electrolyte showing the suitability of GCMS-QP 2020 NX to offer a reliable and simple way of analysis even at early stages of electrolyte decomposition.

■ References

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