Non-Target Screening of Battery Aging Products Using the ecTOF

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Electrolytes and Battery Aging

Due to their high energy density, lithium-ion batteries are commonly used in laptops, cell phones, and other electronic devices. Growing interest in green energy and more sustainable transportation options has increased the demand for better, longer lasting batteries. Electrolyte solutions are a critical component of batteries as they facilitate the ion transport between cathode and anode [1]. Aging of electrolytes negatively impacts the lifespan of batteries and is therefore a major issue in this field.

Electrolytic solutions in commercial lithium batteries usually consist of lithium salts, organic solvents, and additives. Organic solvents play an important role in energy density, life cycle, and safety of the final product. Cyclic carbonates are commonly included to increase the solubility of the conducting salt and linear carbonates are mixed in with cyclic carbonates to reduce their viscosity (such as that of ethylene carbonate) [1,2]. At present, the most used conducting salt is lithium hexafluorophosphate ($LiPF_6$). $LiPF_6$ has advantages as a protector of aluminum current collectors but is chemically and thermally unstable in organic carbonates (towards the P-F bond). Therefore, the lithium salt can create phosphate- and carbonate-based aging products. These can have negative effects on the performance and lifetime of the battery [1]. Identifying known and unknown battery aging products is therefore critical for the development of longer lasting batteries.

Identification of Battery Aging Products Using the ecTOF

The ecTOF coupled with a gas chromatograph (GC-ecTOF) acquires both chemical ionization (CI) and 70 eV electron ionization (EI) mass spectra quasi-simultaneously in one chromatographic experiment as described in reference [3] (Figure 1).
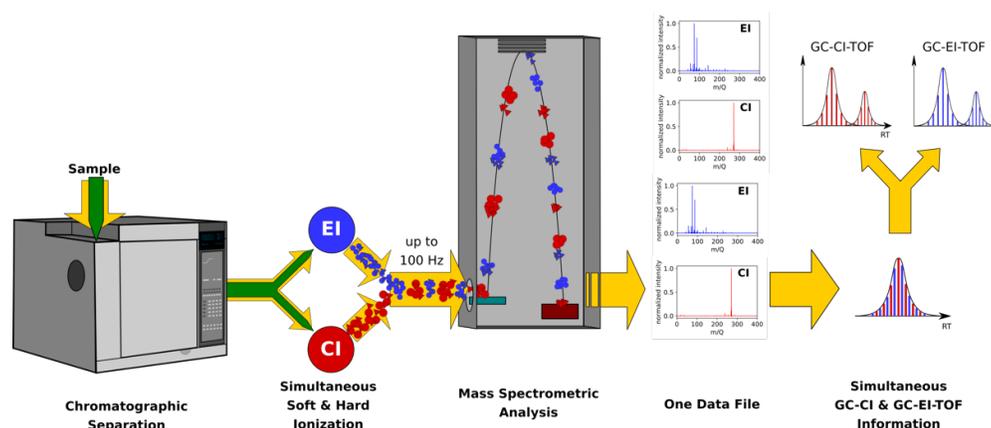
Figure 1. *Schematic illustration of the GC-ecTOF instrument.*

Table 1: Instrumental method.	
Injection	Direct split 1 µL liquid injection (1:50) to Agilent GC 7890A (Agilent Technologies, Santa Clara, CA, USA)
Column	DB-5 MS semi-polar GC column (30 m, 0.25 mm, 25 µm; Agilent Technologies Inc., Santa Clara, CA, USA)
Inlet Temperature	250 °C
Carrier Gas Flow	1.2 mL/min (= sccm) He
Purge Flow	10.0 mL/min
Septum Purge	3.0 mL/min
Temperature Program	40 °C for 2 mins, 3 °C/min to 60 °C. 10 °C/min to 250 °C, 50 °C/min to 320, hold for 1 min
Flow Split	1:1 CI/EI
Source Temperature	EI 280 °C, CI 300 °C
MS	GC-ecTOF Prototype 1- StarBeam70 eV EI source- HRPCI source ($[NH_4]^+$)

A fresh and a twice cycled electrolyte solution were analyzed using the TOFWERK GC-ecTOF system (Table 1). Figure 2 shows EI and CI traces of both the fresh (top) and the aged (bottom) electrolyte. Compared to the fresh electrolyte within the aged electrolyte, additional components were detected (Table 2). Some of the listed substances were identified as common aging products using targeted analysis by comparison with standard mixture. For any additional compounds for which no standard was available, proposed decomposition pathways for electrolytes found in literature enabled suspect screening [4]. Retention time index, NIST library search (EI) and accurate molecular mass and isotopic pattern analysis (CI) were used to tentatively confirm the presence of additional

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oligocarbonates (Table 2). An example of the EI and CI mass spectra of an additional oligocarbonate as well as its isotopic ion distribution comparison can be found in Figure 3. Oligocarbonates up to diethyl-2,5-dioxahexane carboxylate (DEDOHC) have previously been described [5,6] and standards are available for these compounds, yet the identification of higher oligocarbonates has only been reported using liquid chromatography analysis [7].
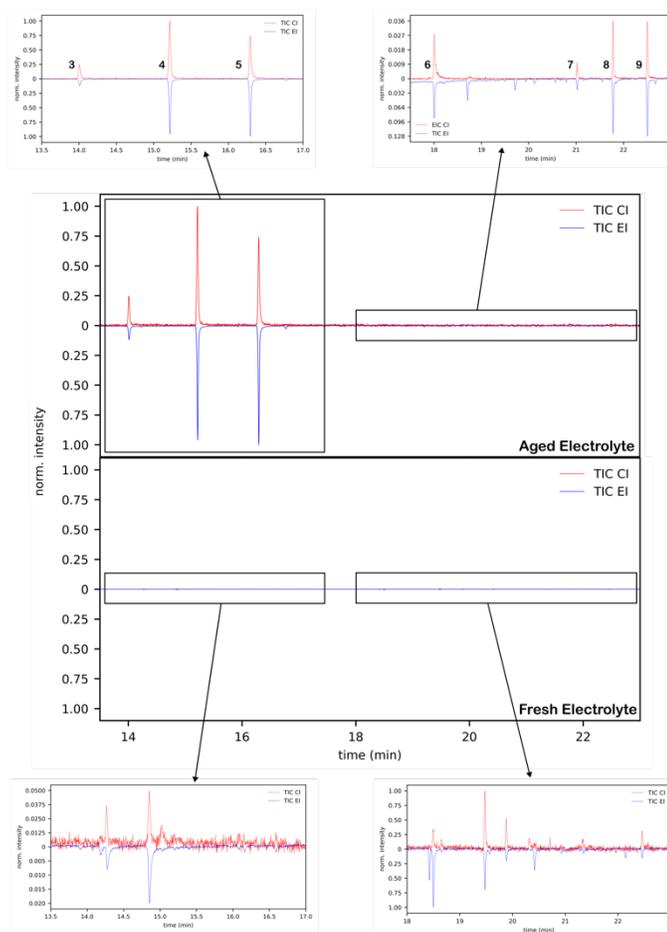

Figure 2. Total ion chromatogram (TIC) of a region of interest for EI and CI traces of aged (top) and fresh (bottom) electrolyte. For the aged electrolyte solution larger additional peaks are found. A zoom in for some of these regions of interest is provided, highlighting detected compounds 1-9. Here, the extracted ion chromatogram (EIC) of the CI is shown for clarity of some of the compounds. The [M+NH$_4$]$^+$ of the possible compounds described in Table 2 were chosen as the extracted ions for the CI trace. For comparison purposes, the chromatogram of the fresh sample is also shown with the same normalization. A zoom in for some of the small additional peaks found in the fresh electrolyte are also provided. Some of these are due to the extraction method used for the electrolyte solution and are also seen in the aged solution.

Table 2: Aging products identified in the aged electrolyte solution. Ion species [M+NH₄]⁺.

| Peak No.	RT (min)	m/Q (Th)	Predicted [M+NH₄]⁺	Rel. Mass Accuracy (ppm)	Predicted Compound M
1	1.6	108.0640	$[C_3H_6O_3+NH_4]^+$	5.2	Dimethyl Carbonate (DMC)
2	3.2	136.0972	$[C_5H_{10}O_3+NH_4]^+$	4.1	Diethyl Carbonate (DEC)
3	14.0	196.0764	$[C_6H_{10}O_6+NH_4]^+$	2.2	Dimethyl-2,5-dioxahexane carboxylate (DMDOHC)
4	15.2	210.0936	$[C_7H_{12}O_6+NH_4]^+$	3.9	Ethyl methyl-2,5-dioxahexane carboxylate (EMDOHC)*
5	16.3	224.1098	$[C_8H_{14}O_6+NH_4]^+$	4.3	Diethyl-2,5-dioxahexane carboxylate (DEDOHC)
6	18.0	252.1421	$[C_{10}H_{18}O_6+NH)]^+$	1.1	Dibutyl peroxy dicarbonate*
7	21.0	284.0952	$[C_9H_{14}O_9+NH_4]^+$	1.3	Higher oligocarbonates*
8	21.7	289.1117	$[C_{10}H_{16}O_9+NH_4]^+$	2.5	Higher oligocarbonates*
9	22.5	312.1267	$[C_{11}H_{18}O_9+NH_4)^+$	1.4	Higher oligocarbonates*

Notes: *no standard available
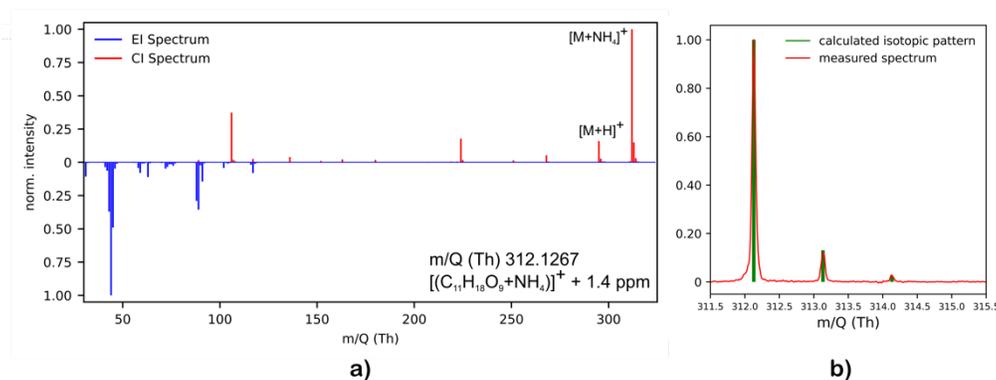
Figure 3. *a) Corresponding EI and CI mass spectra of the chromatographic Peak 9 at 22.5 mins. b) Isotopic ion distribution ([M+NH₄]⁺) of Peak 9 at 22.5 mins with [CH₂₂NO₉]⁺.*

Detailed information on the chemical pathways for the formation of these oligocarbonates can be found elsewhere [4]. These specific identified polymerized aging products change the function of an aged battery by reducing the conductivity in the electrolyte and increasing its viscosity [1,7]. Hence, it is of high importance for scientists and battery manufactures to identify these compounds, especially when standards are not available.

Summary

Nine degradation products in an aged electrolyte solution could be identified, of which three could be confirmed using comparison with standards. For the other six, identification of the compounds was possible by means of combining the

multitude of information provided by the combined EI/CI and chromatographic data gained by the GC-ecTOF. The unique capability of the GC-ecTOF to simultaneously obtain CI and EI data provides this information using completely aligned data, quickly and within one chromatographic run.

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References

[1] Schultz et al. "Quantitative investigation of the decomposition of organic lithium ion battery electrolytes with LC-MS/MS" RSC Adv., **7**, 27853-27862, 2017. https://doi.org/10.1039/C7RA03839A

[2] Stenzel et al. "Chromatographic Techniques in the Research Area of Lithium Ion Batteries: Current State-of-the-Art" Separations., **6(2), 26**, 2019. https://doi.org/10.3390/separations6020026

[3] Klee and Bräkling "Principle of Operation – Simultaneous Electron Ionization & Chemical Ionization with the ecTOF for GC-MS" Tofwerk Application Note, 2021. https://www.tofwerk.com/principle-of-operation-ec-tof-white-paper/

[4] Laruelle et al. "Identification of Li-Based Electrolyte Degradation Products Through DEI and ESI High-Resolution Mass Spectrometry" Electrochem. Soc., **151, A1202,** 2014. https://doi.org/10.1149/1.1760992

[5] Horsthemke et al. "Possible carbon-carbon bond formation during decomposition? Characterization and identification of new decomposition products in lithium ion battery electrolytes by means of SPME-GC-MS" Electrochimica Acta, **295, 401-409,** 2019. https://doi.org/10.1016/j.electacta.2018.08.159

[6] Horsthemke et al. "Fast screening method to characterize lithium ion battery electrolytes by means of solid phase microextraction – gas chromatography – mass spectrometry" RSC Adv., **7, 46989-46998,** 2017. https://doi.org/10.1039/C7RA08599K

[7] Schultz "Anti-aging for batteries? LC-MS method development for battery electrolytes" Shimadzu Magazine Application Note, 2, 2016.

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