Using GC Orbitrap mass spectrometry for the identification of lithium-ion battery degradation products

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ABSTRACT

Purpose: To demonstrate the identification of characteristic carbonate substructures and electrolyte solvent degradation in lithium-ion batteries using the Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometer.

Methods: Pure aged electrolyte was collected by centrifugation of the separator and negative electrode of the battery after cell formation. The electrolyte was diluted in dichloromethane (1/100; v/v). The supernatant was taken for analysis by gas chromatography high resolution mass spectrometry using Orbitrap technology.

Results: The presence of carbonate substructures is indicative of electrolyte solvent degradation, and information on elemental composition provides information about the possible mechanisms. The electron impact (EI) extracted ion chromatogram of dimethyl, ethyl methyl, and diethyl carbonate structures containing dimers in the aged electrolyte with the marker fragments for methyl carbonate mainly correspond to m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$) and for ethyl carbonate m/z 63.0076 (CH_3O_3). The presence of peaks later in the chromatogram at 13.9, 14.1, and 14.4 minutes with similar fragmentation and elution patterns to known compounds indicates peaks of interest. The two suggested elemental compositions can be reviewed $C_9H_{15}O_9$ fitting with -0.51 ppm and the alternative $C_{10}H_{18}O_3FP_2$ with -0.18 ppm.

INTRODUCTION

From consumer electronics to electric vehicles, the growing demand for better performing, safer, and less costly batteries has led researchers to focus on improving several aspects of lithium-ion battery technology. The experiments shown in this study by Münster Electrochemical Energy Technology (MEET) aim to investigate electrolyte aging, a major factor affecting lithium-ion battery life. Using gas chromatography coupled to high-resolution accurate-mass mass spectrometry (GC-HRAM-MS), MEET's Analytics and Environment division gains the flexibility and data quality to have a deeper understanding of their samples. This in turn provides detailed insight into the complex reaction mechanisms involved in electrolyte aging. Ultimately these discoveries will enable the research team to identify additives to curtail, halt, or even tailor electrolyte aging. Of the basic components of a lithium-ion battery, the electrolyte provides a conductive medium for lithium ions to move between electrodes. It consists of conducting salts, which are highly fluorinated, and various solvents. Lithium hexafluorophosphate (LiPF6)-based electrolytes dissolved in mixtures of aprotic organic complex products are formed, such as carbonate oligomers, fluorophosphates, and organofluorophosphates. Using a variety of analytical approaches, researchers at MEET's Analytics and Environment division identify and quantify these compounds as they are generated during aging.

MATERIALS AND METHODS

Sample Preparation

Pure aged electrolyte was collected by centrifugation of the separator and negative electrode of the battery after cell formation. For precipitation of the GC-harmful LiPF6 conducting salt, the electrolyte was diluted in dichloromethane (1/100; v/v) and stored at 3 °C overnight. The supernatant was taken for analysis.

Test Method

Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH autosampler, and chromatographic separation was performed using a Thermo Scientific™ TRACE™ 1310 GC system fitted with a Thermo Scientific™ TraceGOLD™ TG-5SiMS 30 m × 0.25 mm i.d. x 0.25 µm film capillary column with a 5 m integrated guard. Finally, a Thermo Scientific Orbitrap Exploris GC-MS was used for accurate mass measurements in full-scan mode at 60,000 mass resolution (FWHM at m/z 200). Data processing was performed using Thermo Scientific™ FreeStyle™ software. Further details in tables 1-3.

Table 1. GC and injector conditions.

TRACE 1310 GC system parameters	
Injection volume	1.0 µL
Liner	Thermo Scientific™ LinerGOLD™ Split/splitless with quartz wool (P/N 453A2265)
Inlet	250 °C
Carrier gas, flow	He, 1.16 mL/min
Inlet module and mode	SSL, Split
Split ratio	100 (EI), 10 (PCI)
Purge flow	2 mL/min
Column	TraceGOLD TG-5SiMS 30 m × 0.25 mm i.d. x 0.25 µm film (P/N 26096-1425)

Oven temperature program	Rate (C/min)	Target temperature (°C)	Hold time (min)
Initial		40	1.0
Ramp 1	3.0	60	0
Ramp 2	30.0	260	2.0
Run time	16.3	-	-

Orbitrap Exploris GC mass spectrometer parameters	
Transfer line	250 °C
Ionization type	EI
Ion source	200 °C
Electron energy	70 eV
Acquisition modes	Full-scan
Mass range	35–500 Da
Resolving power	60,000 (FWHM at m/z 200)

Table 2 - Orbitrap Exploris GC-MS parameters (EI).

Orbitrap Exploris GC mass spectrometer parameters	
Transfer line	250 °C
Ionization type	PCI
Ion source	300 °C
CI reagent gas	Ammonia (3.5 purity)
CI gas flow rate	2.5 mL/min
Acquisition modes	Full-scan
Mass range	50–500 Da
Resolving power	60,000 (FWHM at m/z 200)

Table 3 - Orbitrap Exploris GC-MS parameters (PCI).

RESULTS

Figure 1. Overlaid EI extracted ion chromatogram of m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$), and m/z 63.0076 (CH_3O_3). Peaks labelled (A) dimethyl carbonate, (B) ethyl methyl carbonate, and (C) diethyl carbonate. For ethyl methyl species both m/z 103.0389 and m/z 63.0076 are detectable.
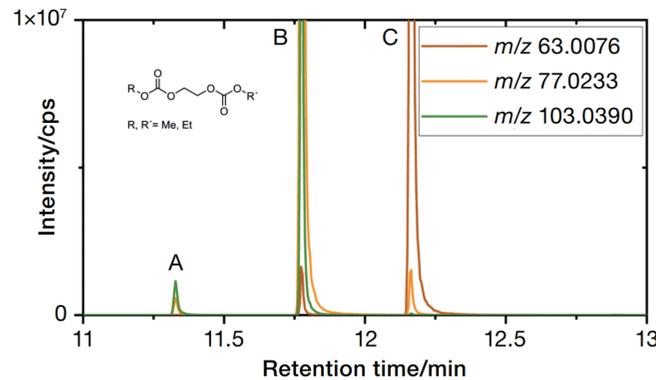
Targeted carbonate substructures

Figure 1 shows the EI extracted ion chromatogram of dimethyl, ethyl methyl, and diethyl carbonate structures containing dimers in the aged electrolyte. The marker fragments for methyl carbonate mainly correspond to m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$) and for ethyl carbonate m/z 63.0076 (CH_3O_3). The accurate mass fragmentation patterns observed in the full scan data in Figure 2 provides reliable confirmation of which substructure is present. When determining these compounds in unknown samples, these accurate mass ions provide the selectivity to extract against a complex chemical background and certainty in the detection. The mass accuracy of the ions in the spectra in Figure 2 are all < 2ppm even at these relatively low masses.

Figure 2. Full scan accurate mass spectra of dimer peaks at 11.3 and 12.2 minutes, peaks A and C. Upper spectrum shows characteristic fragmentation for methyl carbonate (m/z 103.0390), and lower spectrum for ethyl carbonate (m/z 63.0076).
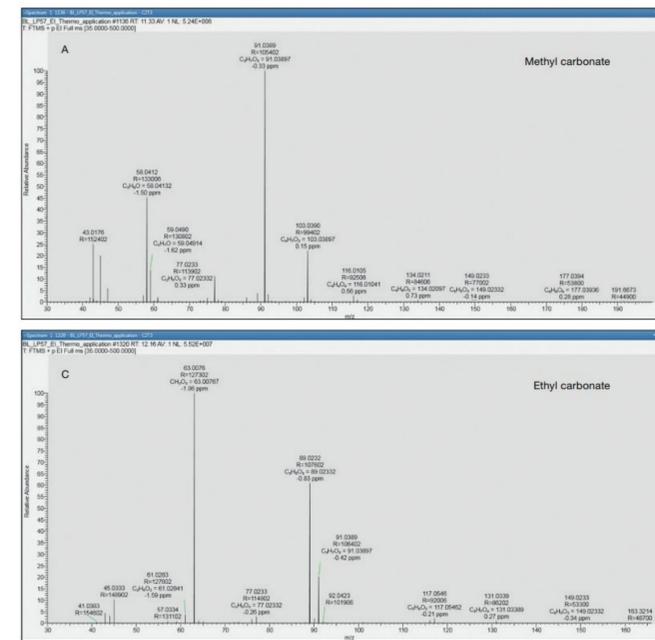
Identification of unknown carbonate substructures

The extraction of the accurate mass ions in the targeted analysis of methyl and ethyl carbonate revealed the presence of peaks later in the chromatogram at 13.9, 14.1, and 14.4 minutes (Figure 3) with similar fragmentation and elution patterns. This similarity led to the suspicion that these were structurally related to the known compounds and therefore of interest in the context of electrolyte degradation. Due to strong fragmentation behavior of organic carbonates with electron ionization, molecular ion information was not obtained by this analysis. Furthermore, carbonate dimers and trimers also fragment when methane is used as a chemical ionization reagent gas. Therefore, soft PCI with ammonia was performed as it was critical to identify the molecular ion of the peaks through a chemical ionization acquisition. The zoomed spectrum of the peak at 13.9 minutes is reproduced in Figure 4 (upper), showing the [M+H]+ and [M+NH4] + ions at m/z 267.07106 and m/z 284.09761, respectively.

Figure 3. Overlaid EI extracted ion chromatogram of m/z 103.0389 (C4H7 O3), m/z 77.0233 (C2H5O3), and m/z 63.0076 (CH3O3). The chromatographic pattern at 13.9, 14.1, and 14.4 minutes is similar to the known carbonate dimers, and therefore the peaks are interesting to this study of electrolyte degradation.
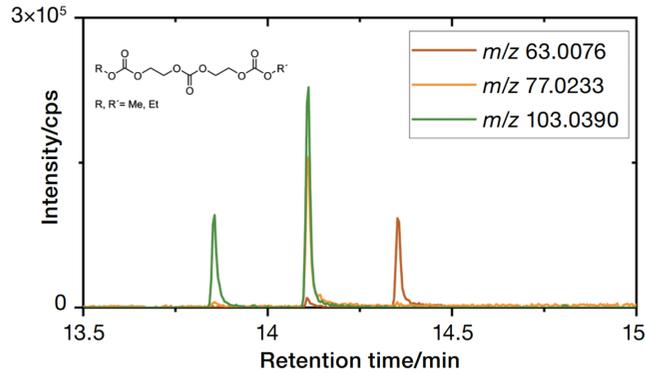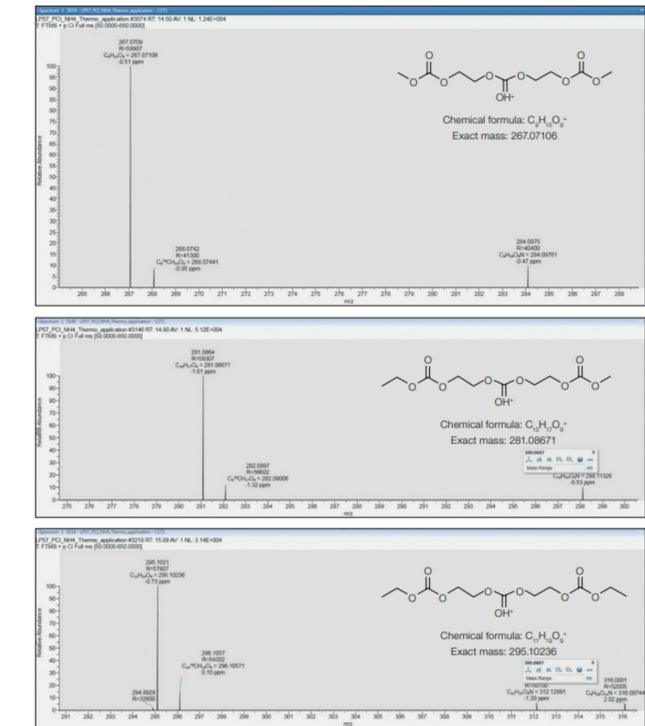

Figure 4. Zoomed positive chemical ionization spectra of peaks at 13.9 (upper), 14.1 (middle,) and 14.4 (lower) minutes. [M+H]+ and [M+NH4] + ions are labeled with theoretical accurate mass, proposed elemental formula, and ppm mass accuracy. The R value corresponds to the mass resolution of the ion.

The importance of good mass accuracy is demonstrated in Figure 5 where < 1 ppm mass accuracy suggests only two possible elemental compositions. Whereas, with poor mass accuracy at 5 or 10 ppm there are up to 11 formulae that would fit.
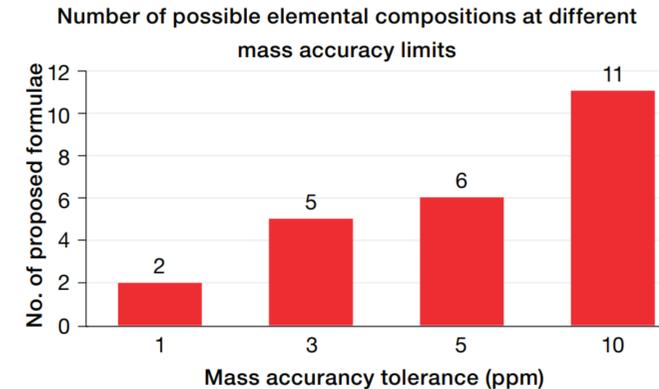

Figure 5. Bar chart showing the number of possible elemental compositions with increasing mass accuracy. The expected sub 1 ppm mass accuracy of the GC Orbitrap system shows only two possible formulae, meaning that identification can be achieved in a shorter time and with a higher degree of confidence.

CONCLUSIONS

- Target compounds, ethyl carbonate and methyl carbonate, could be accurately determined against a complex chemical background through identification of unique fragmentation profiles including m/z 103.0389 (C4H7 O3), m/z 77.0233 (C2 H5O3), and m/z 63.0076 (CH3O3). .

- GC unknown trimer peaks exhibiting similar elution profiles to known compounds could be identified through EI and PCI data acquisitions that provided information on the elemental composition of mass adduct ions in the spectra.

- Good mass accuracy ensured that the correct elemental composition C9H15O9 , C10H17O9 , and C11H19O9 could be proposed for unknowns without an extensive workload and that proposals could be made with a high degree of certainty.

REFERENCES

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TRADEMARKS/LICENSING