Identification of Volatiles Generated by Lithium-Ion Battery Failure

Identify a wide range of organic and gaseous species within a single data set without requiring a library of prepared standards.

Introduction

Rechargeable lithium-ion batteries (LIBs) are reliable and energy-dense power sources with established usage in a wide range of portable electronics. With expanding applications, research and product testing are focused upon battery longevity and electrical output, as well as potential degradation pathways undermining their performance characteristics.

Swelling is a common and irreversible degradation process of LIBs, indicating internal gas evolution as the battery's electrolyte solution decomposes. Typical root causes vary, and may include physical defects or damage, overcharging, overheating, parasitic reactions between electrolyte components or with other internal components, extensive cycling lifetime (age), or any combination of these factors.[1] Chromatographic analysis of the subsequent gas formation can fingerprint the substances evolved during failure and reflects the electrolyte composition, potential mechanisms of failure (leading to gas evolution), and safety implications for similar cells.

The range of additive components deployed in LIBs increases substantially with ongoing research, and correspondingly, so do the potential degradant structures. Most commonly, residual gas analysis (RGA) or gas chromatography with thermal conductivity detection (GC/TCD) are the choice techniques for targeted or semi-quantitative analyses, but they are not as commonly used for purely qualitative analyses. RGA is very capable with permanent gases and smaller organic

molecules, but has limitations with analyzing higher-molecular weight volatiles. TCDs are non-specific GC detectors, relying upon an internally-built library of historical data to assign peak identities. Responses which do not sufficiently separate and are not individually known cannot be identified.

Gas Chromatography with Mass Spectrometry (GC/MS) is the gold standard technique in identifying a wide range of gases and volatile organic components. After chromatographic separation, the mass spectrometer breaks molecular components into a characteristic pattern of fragment ions. These patterns are identified using commercial spectral databases and interpretation, without strict reliance on an internal library of historical chromatography data. An added benefit of mass spectrometry is that method modifications will not affect the ability to identify the components, and so the general method may be optimized to better target one or more components. Limitations of the technique include GC/MS's inability to detect hydrogen or hydrogen fluoride gases, and possible concerns regarding the reliability of quantitative analysis.

This application note describes the general screening approach of analyzing the gas within a swollen LIB pouch cell and identifying the chemical species present by headspace GC/MS.

Experimental

The battery used in the analysis was a pouch-cell LIB with minor swelling. It was discharged to low voltage immediately prior to gas sampling. The battery was laid flat on a lab bench, and one half of

1 Garcia-Araez, N.; Rowden, B. Energy Reports. 2020, 6, 10-18.

the top face was pressed with a weight to slightly adjust the headspace towards the other half of the battery for ease of sampling.

Two gastight syringes were used to simultaneously penetrate the outer pouch of the battery at the most obtuse angle possible, and to subsequently withdraw portions of the gas occupying the internal headspace. The two syringes differed in volume to match the corresponding instrument methods:

- A smaller volume designated for the separation and identification of permanent gases and light organics ("gas analysis").

- A larger volume designated for the separation and identification of volatile and semi-volatile organics ("volatiles analysis").

The headspaces within each syringe were manually injected onto an Agilent 6890 GC. As part of a typical analysis, a blank of analytical-grade (i.e., 5N) helium is also analyzed using each method to understand the extent to which environmental gases and vapors (e.g., O_2, N_2, Ar, H_2O) are observed due to the injection process.

Results and Discussion

The instrumental methods are designed to overlap in their results such that a wide range of chemical species, evolved by and within the battery, can be determined. For example, the gas analysis method is capable of resolving permanent gases and very light organics (e.g., Ar, O_2, N_2, methane, etc.), which are less commonly associated with GC/MS analysis, while the volatiles method is better suited for larger organic molecules (e.g., solvent species, formates, acetates, and some aromatics). However, certain components (e.g., carbon dioxide, ethane, ethylene, and propane) may be visible by either method depending on response intensity or concentration.

Gas Analysis

From the lower-volume headspace sample, a moderate range of permanent gases and low-molecular weight hydrocarbons were identified. The most predominant species in the total ion (full scan) chromatogram (Figure 1) by response area was carbon dioxide, a common product of electrolyte solution decomposition. Organic gases up to C_3 (as well as alkenes and branched alkanes) were also observed, and their approximate ratios have been reported in early works on battery gas analysis.[2] A listing of components by their retention order is provided in Table 1.

The fingerprint of gases is useful data in battery failure analysis, although certain gases may have a wide variety of possible origins: For example, an abundance of CO_2 may be present due to specific causation such as overheating, overcharging, or other unintended redox processes encouraging carbonate degradation; few distinct generation

---

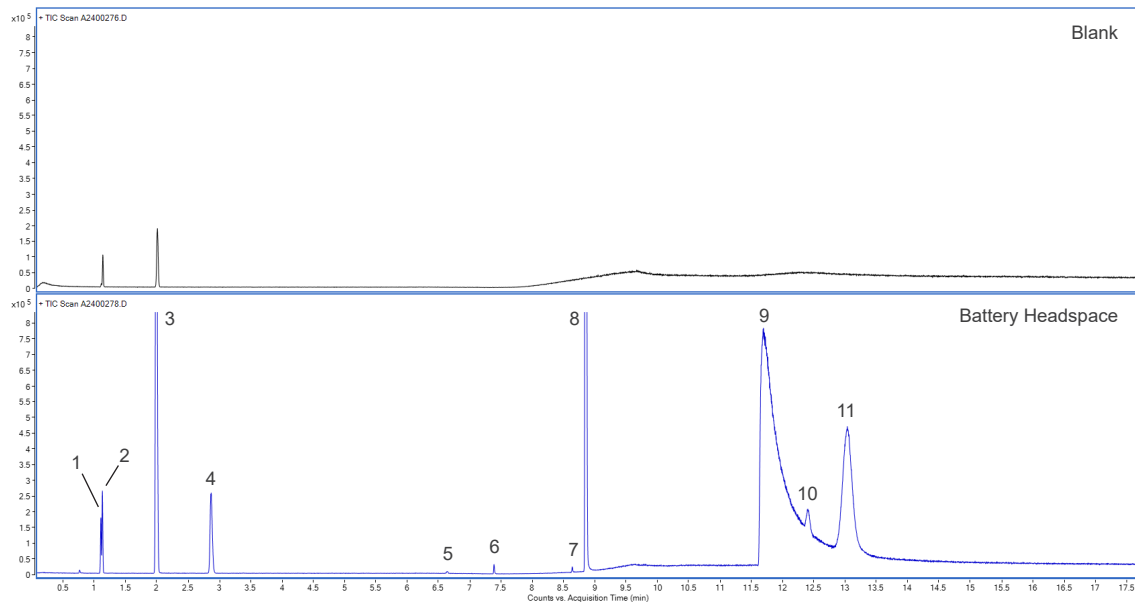2 Yoshida, H. et al. J. Power Sources. 1997, 68, 311-315.

Figure 1: Total-Ion Chromatograms, Helium Blank and LIB Headspace; Gas Analysis

Peak No.	Retention Time (min)	Best Spectral Match*
1	1.10	Argon
2	1.13	Oxygen
3	1.99	Nitrogen
4	2.87	Methane
5	6.64	Carbon Monoxide
6	7.39	Isobutane
7	8.64	2-Methylbutane
8	8.85	Ethane
9	11.70	Carbon Dioxide
10	12.41	Ethylene
11	13.04	Propane

Table 1. Components Detected, LIB Headspace; Gas Analysis
* The tentative structural assignments are based upon mass spectral library matching and interpretation.
For the scope of this application note, analytical reference standards were not analyzed to confirm the presence of any individual components.

mechanisms exist for organic gases, e.g., ethane.[3]

Components with very similar molecular weights (e.g., N_2, CO, ethylene) are separated into discrete responses by the GC and are identifiable by MS using their characteristic fragmentation patterns. Coelution with the full-scan data is also not necessarily a concern for the same reason—a response for ethylene (Peak 10) coelutes with the "tail" of CO_2 but can be resolved with extracted ions.

3 Zheng, T. et al. ChemElectroChem. 2024, 11, e202400065.

This would be particularly useful in attempts to estimate concentrations, where resolution of one component from another in the chromatogram is critically important. From the full-scan data, ions representative of CO_2 (44 m/z) and of ethylene (27 m/z) and unique from each other are extracted, and the resolved responses are shown in Figure 2.

Semi-Volatiles Analysis

From the higher-volume headspace sample, a wide range of organics were determined, extending from those identified in the gas analysis to the expected
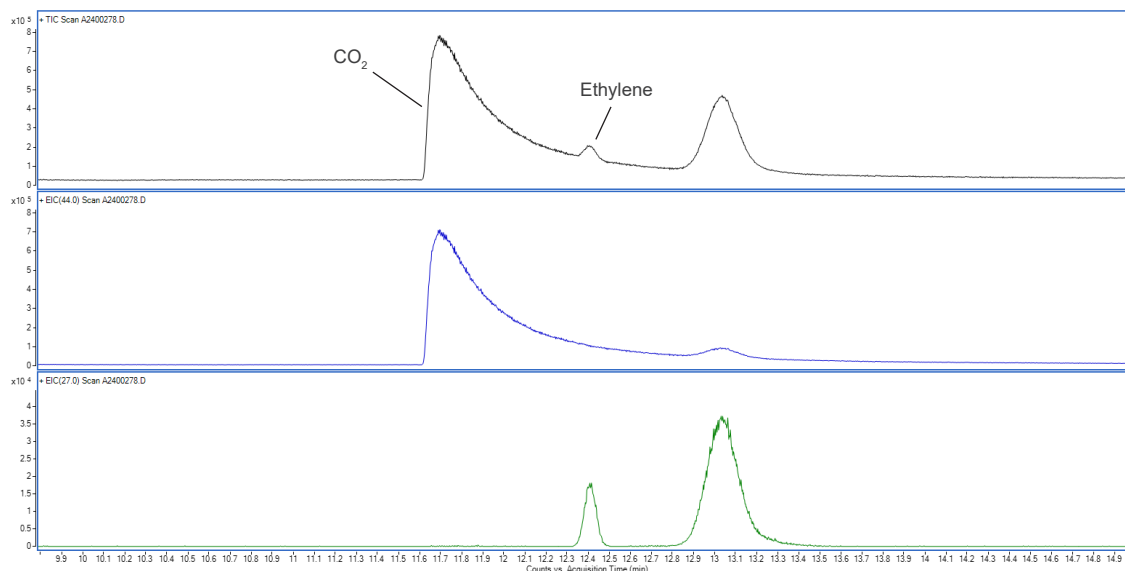

Figure 2: Full-Scan (CO_2 + Ethylene) and Extracted-Ion Chromatograms (CO_2 and Ethylene, Separated)

electrolyte solvent vapor and its degradants. Among the most intensely detected components in the sample chromatogram (Figure 3) were carbonates (e.g., diethyl carbonate, DEC; propylene carbonate, PC) and esters (e.g., ethyl propionate, EP; propyl propionate, PP) which are consistent with the electrolyte solvent. PC shows a relatively weak response, most likely due to its lower volatility compared to other carbonates, making it unlikely to be an electrolyte degradant. Other species from the same families which were detected at much lower level are probable indications of transesterification of the components brought about by degradation.[4] The response list, in Table 2, focuses on these products as well as any other relatively intensely-
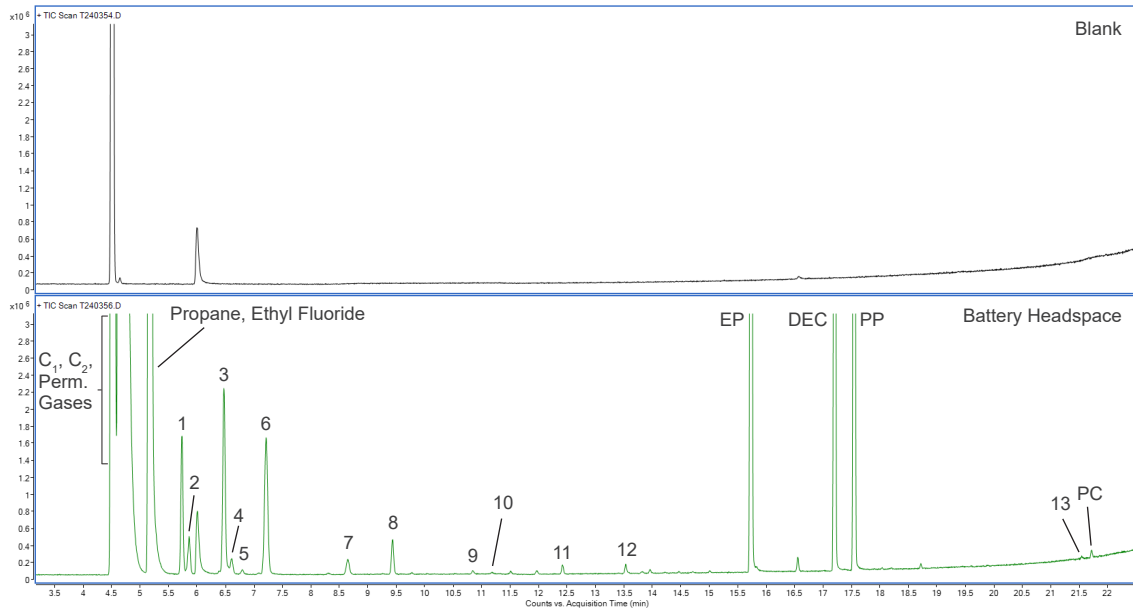
4 Xu, K. Chem. Rev. 2004, 104, 4303-4417.

Figure 3: Total-Ion Chromatograms, Helium Blank and LIB Headspace; Semi-Volatiles Analysis

Peak No.	Retention Time (min)	Best Spectral Match*
1	5.73	Cyclopropane
2	5.86	Isobutane
3	6.47	Butane
4	6.61	n-Propyl Fluoride
5	6.80	2-Butene
6	7.21	Trimethylsilyl Fluoride
7	8.65	2-Methylbutane
8	9.44	Pentane
9	10.85	Ethyl Formate
10	11.85	Methyl Acetate
11	12.42	Hexane
12	13.53	Ethyl Acetate
13	21.72	Ethylene Carbonate

Table 2: Components Detected, LIB Headspace; Semi-Volatiles Analysis
* The tentative structural assignments are based upon mass spectral library matching and spectral interpretation.
For the scope of this application note, analytical reference standards were not analyzed to confirm the presence of any individual components.

eurofins | EAG Laboratories

detected species presumably created during the electrolyte solution degradation.

These other components beyond the gas profile (the tail end of which are visible, but poorly resolved versus the dedicated gas analysis method) include linear and branched alkenes and alkanes, fluorinated organics, and low-molecular weight esters (acetates, formates). The alkanes and esters are expected products of solvent degradation, and low molecular weight fluorides have been observed in similar GC analyses.[5] Fluorinated analogues of other observed volatile species are indicative of the electrolyte's (i.e., $LiPF_6$, or related) role in the degradation process.

Note that while the syringe is intended to remain solely within the battery's headspace, its exact position is unknown and may contact a surface containing electrolyte solution. As such, this analysis is not meant to specifically characterize the solvent system used, but rather to give any insight into degradant components generated during failure and promoted to the headspace within the battery.

As described for CO_2 and ethylene, a strength of GC/MS is the ability to extract characteristic ions of a chemical species which may not be intensely observed in the full-scan data. 78 m/z, characteristic of benzene, was extracted from the full-scan data and was tentatively identified in the sample at retention time 14.75 min, as depicted in Figure 4. The response is weak, but an assignment as benzene is plausible given the similarity of its most intense ions (i.e., 78 m/z; cluster at 51 m/z) to that of a benzene reference spectrum in Figure 5. Other aromatic hydrocarbons (up to C_8) are generally observable using the method, but were not detected (in the full-scan or using extracted ions) for the battery being analyzed.

_____

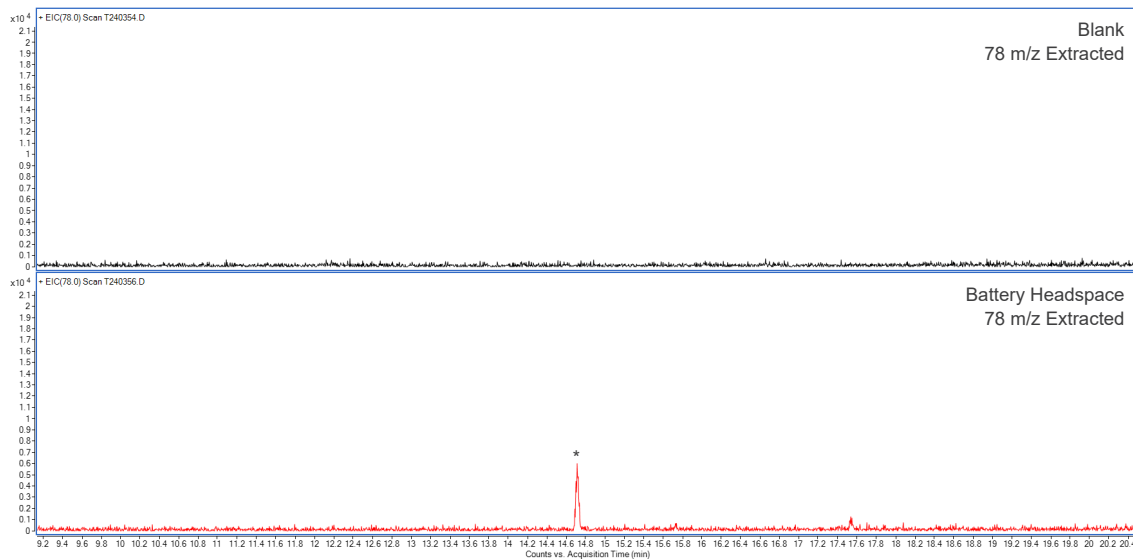5 Gachot, G. et al. Anal. Methods. 2014, 6, 6120.

Figure 4: Extracted-Ion Chromatograms, Helium Blank and LIB Headspace; Targeted Survey
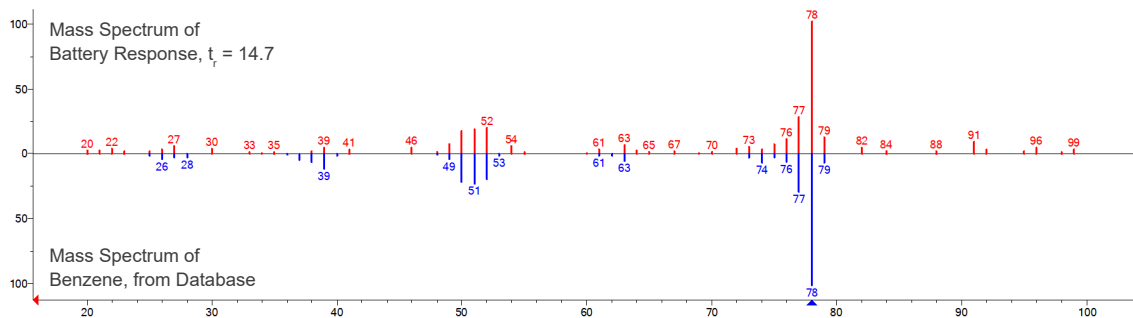

Figure 5: Comparison of Mass Spectra: Benzene Candidate Response from Battery versus Database

Conclusion

The pouch cell was found to contain electrolyte degradation-related hydrocarbons down to C_1 and gases including CO and CO_2. The battery was also found to contain many suspected electrolyte solution degradants in its organic semi-volatile profile, supporting a measurable degree of carbonate decomposition. The strength of headspace GC/MS in this application lies in the simplicity of sampling, the ability to identify a wide range of organic and gaseous species within a single data set without requiring a library of prepared standards, and the ability to quickly survey the data for low-level specific compounds of interest. The methodology demonstrates strong suitability for a wide range of LIBs, including those from a variety of product types.

LIBs are an ever-refining technology whose production and application sees sustained growth. Eurofins EAG offers a comprehensive range of analytical techniques to characterize the material composition of batteries and their components, support their research and development, and assess potential failure points—from raw material to end-of-life. Contact us today to learn how we can help with your next project.

eurofins | EAG Laboratories