thermoscientific

CASE STUDY
MEET Battery Research Center

Orbitrap GC-MS Technology Provides New Insight into Lithium Ion Battery Degradation

"We can see many more compounds that we hadn't seen before—including intermediates from the start of the reaction—which helps us establish reaction mechanisms."

—Dr. Sascha Nowak, Head of the Analytics and Environment Division, MEET Battery Research Center, University of Münster

Advancing lithium-Ion battery technology

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. Münster Electrochemical Energy Technology (MEET), the battery research center at Münster University, aims to address electrolyte aging, a major factor affecting lithium ion battery life. Using the Thermo Scientific™ Q Exactive™ GC Orbitrap™ GC-MS/MS system, MEET's Analytics and Environment division gains a broader and deeper understanding of their samples that in turn provides new insight into the complex reaction mechanisms involved in electrolyte aging. Ultimately these insights will enable the research team to identify additives to curtail, or even halt, electrolyte aging.

ThermoFisher
SCIENTIFIC

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 solids, which are highly fluorinated, and various solvents. Lithium hexafluorophosphate ($LiPF_6$)-based electrolytes with mixtures of aprotic organic carbonate solvents are commonly used. As the electrolyte degrades, several decomposition complex products are formed, such as fluorophosphates and organoflurophosphates. 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.

> "We have solvents that are highly concentrated, and the Q Exactive instrument is robust enough to handle these very well; such that we can do trace analysis."
>
> —Dr. Sascha Nowak

Research challenges

There are significant challenges associated with this research. To begin, the degradation mechanisms, and the resulting degradation products, are often unknown and not described in published literature. Thus there are no reference materials available, and research published thus far has used low-resolution gas chromatography—mass spectrometry techniques (GC-MS)[1, 2], nuclear magnetic resonance (NMR)[3], and other techniques to identify compounds. Often these approaches do not provide sufficient structural information or sensitivity to detect and identify all compounds of interest. Moreover, some of the analytes are very small, low-molecular-weight molecules that, if fragmented, would be below the detection range of standard triple quadrupole GC-MS systems.

Another challenge is the complexity of the sample matrices studied, which are rich in highly fluorinated compounds and concentrated solvents. Matrix effects can lead to interferences, reduce instrument sensitivity, and increase instrument maintenance requirements.

"Because we've seen so many more compounds, the Q Exactive GC reduces the time it takes us to establish complete reaction mechanisms. And though in the future we will spend more time identifying all of these compounds; because we get additional fragmentation information from the Q Exactive, we will be able to do it much faster."

—Dr. Sascha Nowak

Q Exactive GC Orbitrap GC-MS/MS solution

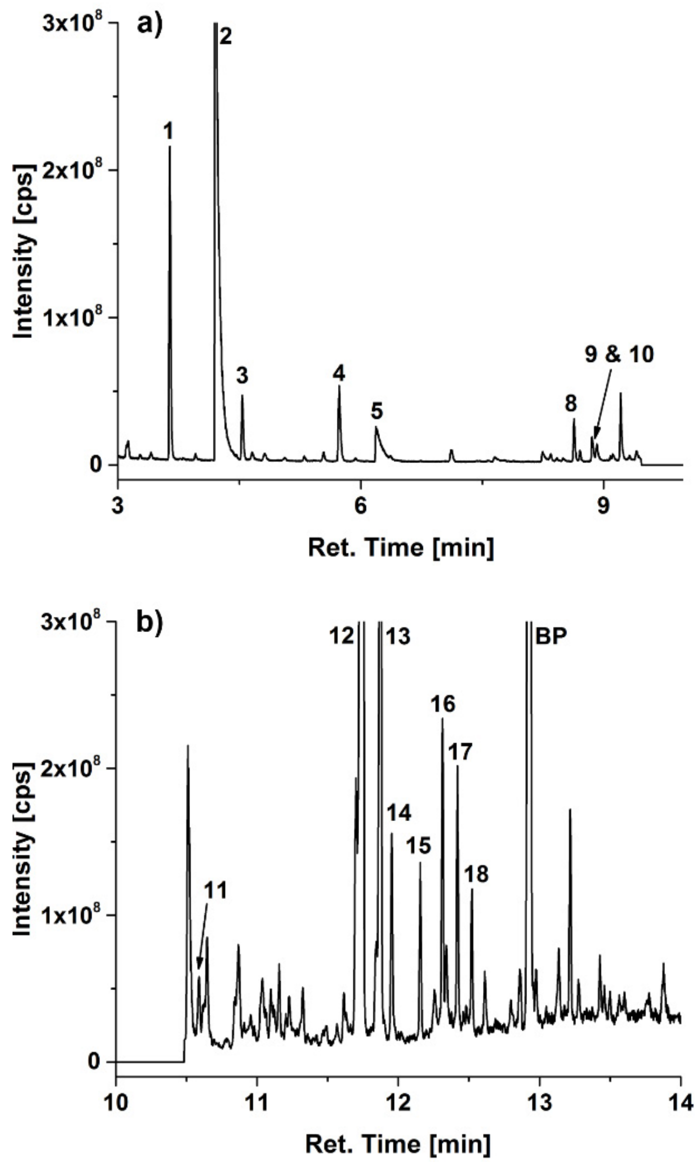
Using the Q Exactive GC Orbitrap GC-MS/MS system, MEET is now able to obtain lower detection limits and richer information in the form of accurate mass fragment ions and molecular ions produced by chemical ionization (CI). Compared to other approaches, this additional information enables MEET to detect and identify many more electrolyte degradation products. This in turn has enabled MEET to determine previously unknown, or confirm suspected, reaction mechanisms.[4]

High-capacity component detection with low limits of detection and matrix tolerance

Using other GC-MS technology, MEET typically detected about eight or nine decomposition products. When the same samples were analyzed with the Q Exactive GC Orbitrap GC-MS/MS system, MEET detected over forty compounds, a remarkable increase. MEET also found never-before-detected non-fluorinated hydrogen, carbon and oxygen-based compounds that improve their understanding of previously unknown mechanisms of solvent decomposition.

The new compounds, many of which were previously unknown early intermediates, were detected due to the sensitivity and selectivity of the Orbitrap GC-MS/MS instrument. Compared to other GC-MS approaches, the Q Exactive GC Orbitrap GC-MS/MS system improved detection limits from low mg/L to low ng/L levels, even in complex lithium-ion battery matrices.

Though the samples are rich in highly fluorinated compounds and concentrated solvents, the Q Exactive GC Orbitrap system provided exceptional robustness for trace-level analysis under these conditions. Continuous operation over the duration of research projects is commonly achieved.



Q Exactive GC Orbitrap GC-MS/MS system chromatograms of electrolyte extracted from an 18650 cell cycled at 20 °C diluted 1:10 in DCM with focus on the retention time from 3 to 10 min (a) and 10 to 14 min (b).

Conclusion

The Q Exactive GC Orbitrap system brings together the power of high-resolution GC and high-resolution accurate-mass (HRAM) Orbitrap MS to provide more comprehensive characterization of samples in discovery analysis. With the Q Exactive GC-MS/MS system, MEET accesses the exact mass information of more compounds, at significantly lower levels. The result is a broader and deeper understanding of the complex reaction mechanisms involved in electrolyte aging.

About Sascha Nowak

Sascha Nowak studied chemistry at the University of Münster, and obtained his Ph.D. in Analytical Chemistry. In 2009, Dr. Nowak joined the working group of Prof. Winter at the MEET Battery Research Center at Münster University as a postdoctoral researcher where he established the Analytical Department. From 2010—2012, he headed the competence areas Analytics and Recycling, and since 2012, has headed MEET's Analytics and Environment division, which mainly focuses on electrolyte aging, transition metal migration, and surface investigations, recycling, second life, and toxicological investigations.

© WWU/MEET

About Münster Electrochemical Energy Technology (MEET)

Münster Electrochemical Energy Technology (MEET) is the battery research center at Münster University. It comprises an international team of about 150 scientists who work on the research and development of innovative electrochemical energy storage devices with high energy density, longer durability, and maximum safety. The aim is to improve batteries for use in electric cars and stationary energy storage systems at the lowest possible cost. MEET strives to further enhance the competitiveness of its partners in battery research—in particular on lithium-ion technology—both regionally and nationally.

The Analytics and Environment division is one of the three divisions at MEET. An important area of research for this division is electrolyte aging, which includes examination of electrolytes and migration of active material into the electrolyte, formation and properties of potentially toxic substances, and re-deposition of the migrated active material on the anode surfaces. The division also deals with the evaluation and development of recycling and second-life procedures to allow recovery and reuse of individual battery components or complete batteries.

References

1. Mönnighoff, X.; Murmann, P.; Weber, W.; Winter, M.; and Nowak, S. Post-Mortem Investigations of Fluorinated Flame Retardants for Lithium Ion Battery Electrolytes by Gas Chromatography with Chemical Ionization. *Electrochimica Acta.* 2017. 246: 1042–1051.
2. Mönnighoff, X.; Friesen, A.; Konersmann, B.; Horsthemke, F.; Grützke, M.; Winter, M.; Nowak, S. Supercritical Carbon Dioxide Extraction of Electrolyte from Spent Lithium Ion Batteries and its Characterization by Gas Chromatography with Chemical Ionization. *Journal of Power Sources.* 2017. 352, 56–63.
3. Wiemers-Meyer, S.; Winter, M.; and Nowak, S. Phys. Mechanistic insights into lithium ion battery electrolyte degradation–a quantitative NMR study. *Phys. Chem. Chem. Phys.* 2016.18, 26595–26601.
4. Horsthemke, F.; Friesen, A.; Mönnighoff, X.; Stenzel, Y.P.; Grützke, M.; Andersson, J.; Winter, M.; Nowak, S.; 2017. Fast Screening Method to Characterize Lithium Ion Battery Electrolytes by Means of Solid Phase Microextraction–Gas Chromatography-Mass Spectrometry. *RSC Advances.* 2017. 7: 46989–46998.

Find out more at **thermofisher.com/OrbitrapGCMS**

ThermoFisher SCIENTIFIC

CS10612-EN 0418M