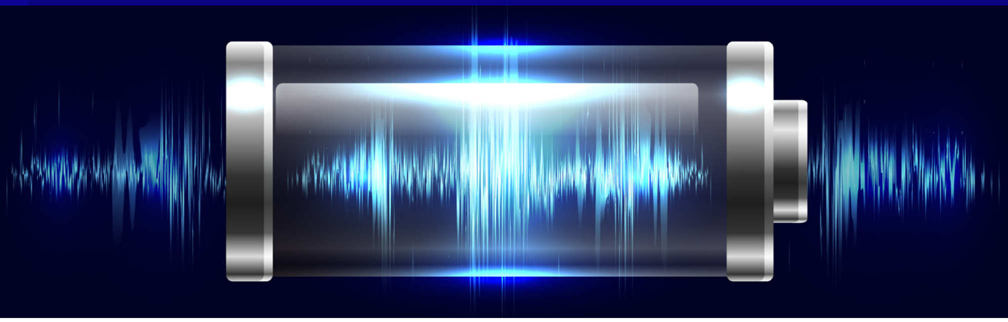
ARTICLE

Bottled Lightning: Researching and Designing Better Batteries with the Help of ICP-OES, ICP-MS, and FTIR Analysis



When discussing the future of the lithium-ion battery (LIB) industry and the role of analytical technologies in staying ahead of the curve, it's difficult to ignore the huge forecasted growth in demand for products such as electric vehicles between 2020 and 2030.[1,2,3] Layered into this dynamic market is the advent of new technologies, such as solid-state batteries, that have the potential to disrupt an already competitive space.

Additionally, regulatory bodies such as the European Commission (EC) and Department of Energy (DOE) are working to ensure that batteries are safe, more sustainable, and perform better to specifications, with clear plans for the regulation of battery materials and supply chains.[4,5]

Given this rigorous environment, participants in the large and complex supply chain for lithium-ion batteries need to be able to leverage analytical techniques and solutions that are geared toward their unique needs – meeting demand, keeping pace with leading-edge materials science, and addressing climate issues and sustainability goals.

Here is a look at three areas in which analysis technologies, including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier transform infrared spectroscopy (FTIR), and others, can add the most value to energy storage analysis and testing.

Elemental Analysis: Providing the Purest Building Blocks for Energy Storage

If we look at the energy-storage supply chain, the first step is extraction of natural resources to be used upstream for the manufacture of components. The lithium-ion battery market faces a specific challenge here as requirements for purity can be higher than is seen for raw materials in other markets. For example, it's not unusual for the expected purity of lithium salts used in cathode production (namely lithium carbonate and lithium hydroxide) to be more than 99.9%. Due to the adverse effects the presence of some ions can have on the electrochemical performance and safety of lithium-ion batteries, it's easy to see why, even without regulation in many geographies, the ability to determine the concentration of these elements in the mining or extraction stage is critically important.[6,7] There are two main techniques that can be used in the

PerkinElmer
For the Better

determination of impurities in the raw materials, and further along the supply chain in cathode active materials such as lithium nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP), and lithium cobalt oxide (LCO). These are ICP-OES and ICP-MS.

ICP-OES is an ideal technique for the determination of major components and impurities present down to the ug/L level. When we think about implementing a QA/QC system in any industry, one of the most important factors is the accuracy and repeatability of the analysis to ensure the data supplied with a product or to regulatory agencies is consistent. Figures 1 and 2 show results from 10 analyses of a battery cathode sample showing the RSD and percentage of recovery, respectively.

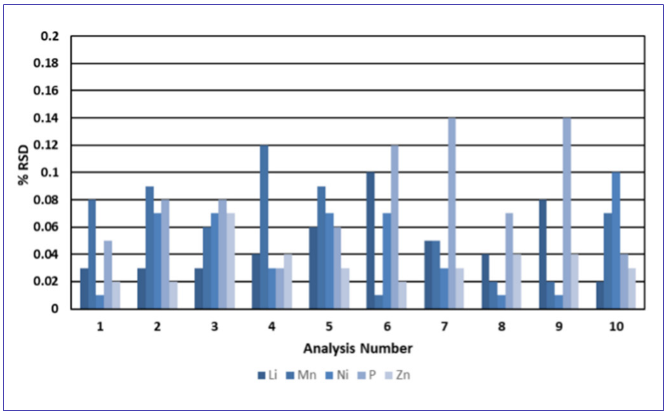


Figure 1. Precision (%RSD) for major elements during 10 analyses of a solution containing 1000 mg/L Mn & P; 500 ppm Li and 100 ppm Ni & Zn.

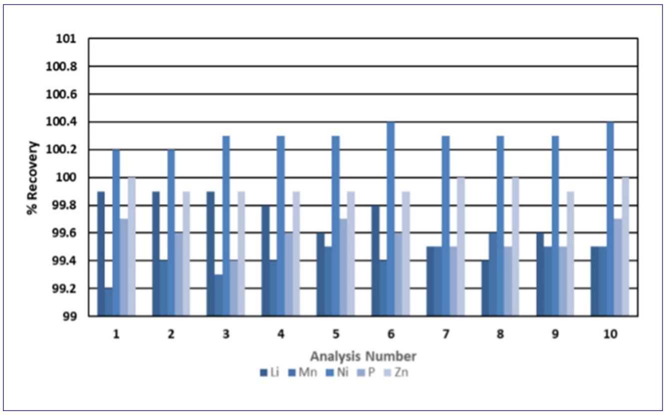


Figure 2. Recovery of major elements over 10 analyses (1000 mg/L Mn & P; 500 ppm Li and 100 ppm Ni & Zn.

Having a method to simultaneously measure matrix components (i.e., the elements forming the cathode active material) and high-level impurities could vastly improve analysis workflow in the upstream stages of the battery supply chain. This type of analysis could also prove invaluable in recycling battery components and meeting upcoming regulatory requirements such as those set out by the EU's battery passport.

For lower-level impurities, ICP-MS may offer the capabilities to ensure that the extremely high purity requirements in the lithium-ion battery industry are not only met but that present elemental impurities are easily identified and quantified.

Two incredibly important materials in the LIB market are lithium carbonate (Li_2CO_3) and Lithium hydroxide (LiOH). ICP-MS may be used to determine the lower-level impurities present in these materials and therefore allow manufacturers to move one step closer to ensuring the quality of their product or incoming raw materials. Figure 3 demonstrates the distribution of impurities in lithium carbonate and lithium hydroxide samples.

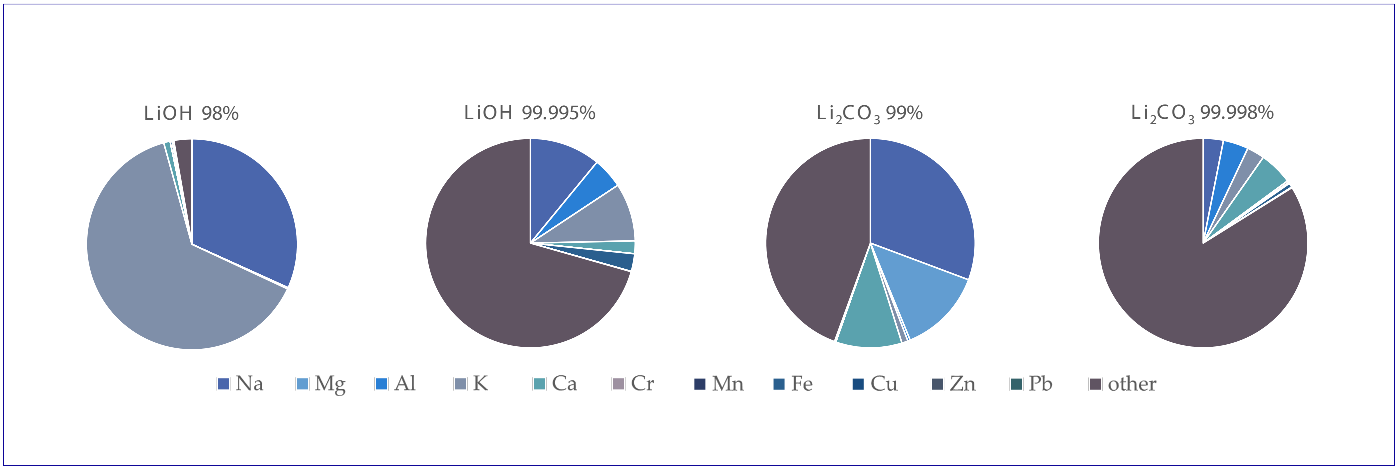


Figure 3. Graphic showing the distribution of impurities.

Hyphenated Power for Performance and Recyclability Testing

The ability to understand the gases evolved under differing thermal conditions provides insights into the safety or performance of a battery component – and the competitive advantage of reverse engineering.

In this instance, hyphenation (also known as evolved gas analysis) refers to techniques wherein a sample is measured using thermogravimetric analysis (measuring the weight of a sample as it's subjected to controlled temperature ramping) and the gases evolved are measured by another technique, such as infrared spectroscopy, gas chromatography, or mass spectrometry.

One area of battery R&D that has been on the rise is exploration of recycling batteries at end of life. Though there can be so-called second-life applications for LIBs – for example, for energy grid storage[8] – there will still be a need for battery recycling to recover and reuse raw materials, especially with the relative scarcity and ethical concerns surrounding the extraction of raw materials such as cobalt.

Hyphenated techniques can provide unique insights into the recycling process, as they give us the ability to analyze and identify evolved gases. For example, in pyrometallurgical recycling, the battery is preheated at around 300 °C to remove the electrolyte after dismantling.[9] Thermogravimetric analysis hyphenated to infrared spectroscopy (TG-IR) allows us to identify the gases evolved during this process. This, in turn, can help identify gaseous products before en masse preheating occurs in order to determine necessary safety precautions. It can also be used after preheating to ensure the electrolyte has been successfully removed.

The search score here is 0.55 and does not represent a complete match for the sample measured. The other components can be deduced from visual inspection of the spectrum. For example, the fine band structure between 4300 and 3500 cm^{-1} corresponds to H-F, a common product found from the thermal degradation of one of the most common conducting salts in lithium-ion batteries, LiPF6. By using multicomponent library searching, the sharp, strong peak around 1000 cm^{-1} was found to correspond to dipropyl phosphite, an additive used as a flame retardant and to improve high-voltage stability in lithium-ion batteries.[10]

This work could be expanded by extending the system to include a GC/MS, which would allow for the detection and identification of much lower-level species in the evolved gas. However, that's beyond the scope of this work.

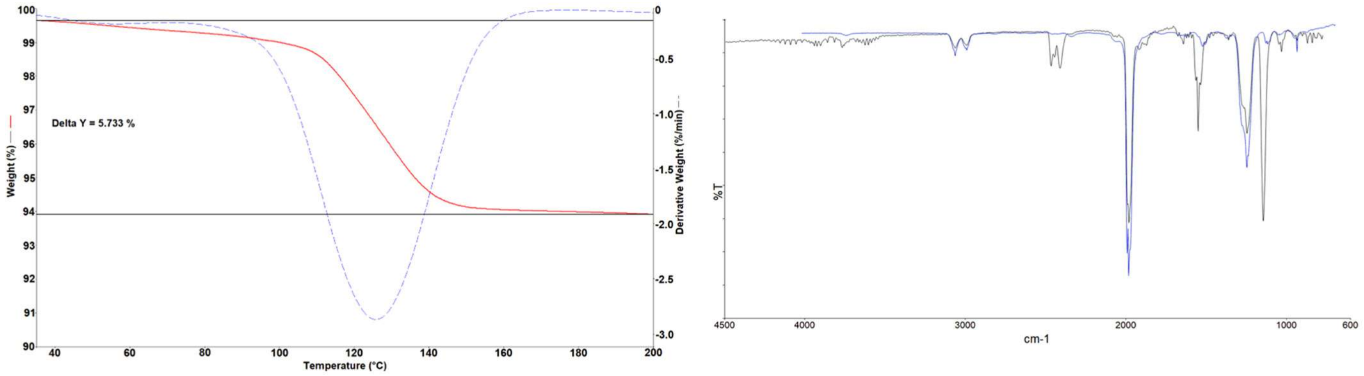


Figure 4. Weight loss curve from 35-300 °C with the IR spectrum of the gases evolved at 130 °C (black) overlaid with the best hit spectrum (blue, ethylene carbonate).

Materials Characterization: Ensuring the Quality of Materials Going In and Components Coming Out

To determine the identity, grade, and additives for LIB materials, technologies widely used in more established and regulated industries such as the polymer industry can be implemented including infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

A key component in a battery is the separator. Often made of a simple thermoplastic such as polyethylene or polypropylene, separators act as a physical barrier between the anode and the cathode, while also allowing for movement of ions. It's important to be able to quickly determine important properties of an incoming product, including identity and thermal characteristics. As one can imagine, melting point is a key thermal parameter of a separator, because if the battery begins the thermal runaway process and the temperature reaches the melting point of the separator, the pores close and electrical current no longer flows.[11] For this reason, having a technique to accurately determine melting point and other thermal transitions could prove to be very valuable. Differential scanning calorimetry can achieve just that. Data collected on two common separator materials, polyethylene and polypropylene, is shown in Figure 5.

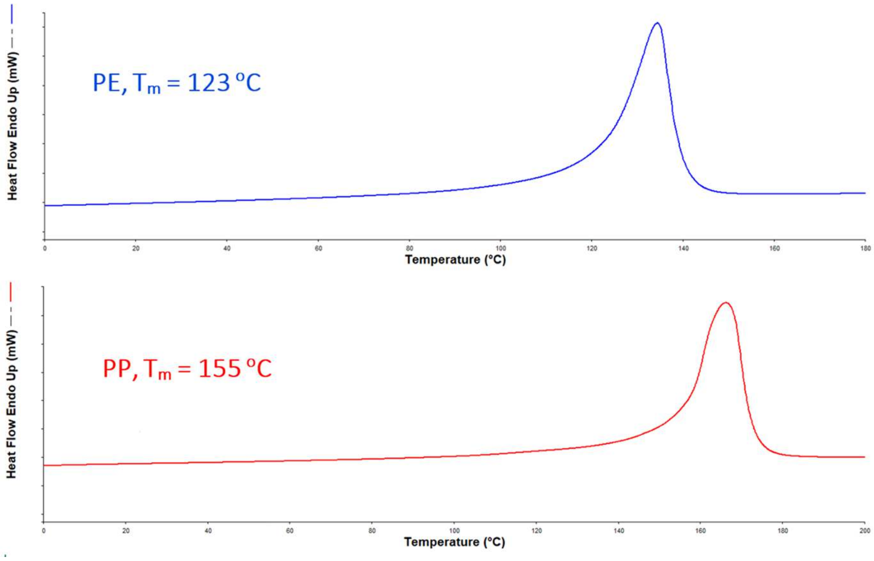


Figure 5. DSC data showing the melting point of polyethylene and polypropylene.

Summary

It's clear that the battery market will continue to grow at a lightning pace over the next decade. This growth is likely to translate into the need for materials analysis in three ways.

First, the introduction of new regulations will require manufacturers of materials and other components to carry out more detailed compositional analysis.

Second, the increased competition will mean that manufacturers must go further to ensure battery performance, safety, and reliability.

Finally, leveraging analytical techniques to improve our understanding of battery recycling processes will assist in bridging the gap that's forecast between the supply and demand of raw materials for lithium-ion batteries.

One way to progress with these three areas is to understand the materials used in the final product and, ideally, detect potential problems with materials and components before they make it into the final battery cell.

This work has described just a few of the many analytical techniques that offer some benefits to the energy storage market. However, all analysis technologies that offer the ability to detect low-level impurities, identify raw materials, and understand electrochemical processes in situ will continue to play an important role.

About the Author

Kieran Evans is a senior applications scientist at PerkinElmer focussing on evolved gas analysis using hyphenated techniques such as TGA-FTIR and TGA-GC/MS. During his time at PerkinElmer, Kieran has worked in a variety of end markets such as polymer, pharmaceutical, and environmental analysis. He has also developed applications for several other techniques including thermal analysis (DSC & TGA) and molecular spectroscopy (FT-IR, FT-NIR, UV/Vis & fluorescence). Kieran obtained a master's degree in chemistry from the University of Surrey with a focus on spectroscopic identification of natural products and is currently pursuing a PhD in environmental analytical chemistry using TGA-GC/MS to detect tire wear particles in the environment.

References

1. The Faraday Institution. (2022). UK electric vehicle and battery production potential to 2040.
2. Department of Energy. (2021). National Blueprint for Lithium Batteries 2021-2030.
3. World Economic Forum, Global Battery Alliance. (2019). A Vision for a Sustainable Battery Value Chain in 2030
4. European Commission. (2020). Proposal For A Regulation of the European Parliament and of the Council Concerning Batteries And Waste Batteries, Repealing Directive 2006/66/EC and Amending Regulation (EU) No 2019/1020.
5. Department of Energy. (2022). Notice of Intent to Issue Funding Opportunity Announcement No. DE-FOA-0002678.
6. D. Shao, D. Rao, A. Wu, X. Luo, How the Sodium Cations in Anode Affect the Performance of a Lithium-Ion Battery, Batteries, 2022, 8, 78
7. R. Zhang, Z. Meng, X. Ma, M. Chen, B. Chen, Y. Zheng, Z. Yao, P. Vanaphuti, S. Bong, Z. Yang, Y. Wang, Understanding fundamental effects of Cu impurity in different forms for recovered LiNi0.6Co0.2Mn0.2O2 cathode materials, Nano Energy, 2020, 78, 105214
8. L. C. Casals, B. A. Garcia, C. Canal, Second life batteries lifespan: Rest of useful life and environmental analysis, 2019, J. Environ Manage. 15, 354
9. L. Zhou, D. Yang, T. Du, H. Gong, W. Luo, The Current Process for the Recycling of Spent Lithium Ion Batteries, 2020, Front. Chem., 8, 578044
10. N. von Aspern et al., Phosphorous additives for improving high voltage stability and safety of lithium ion batteries, 2017, J. Fluorine Chem., 198, 24
11. C. J. Orendorff, The Role of Separators in Lithium-Ion Cell Safety, The Electrochemical Society Interface, 2012.

PerkinElmer U.S. LLC
710 Bridgeport Ave.
Shelton, CT 06484-4794 USA
(+1) 855-726-9377
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

Copyright ©2023, PerkinElmer U.S. LLC. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer U.S. LLC. All other trademarks are the property of their respective owners.