LITHIUM ION BATTERY ANALYSIS COMPLETE SOLUTIONS FOR YOUR LAB

Lithium Ion Battery Analysis Guide

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For the Better

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LITHIUM ION BATTERY ANALYSIS

As the landscape of alternate energy methods for high technology and consumer goods such as, electric vehicles (EV) and bikes, smartphones and laptop advances, R&D is increasing to continually develop new types of batteries. In addition, QA/QC methods for lithium ion battery producers are also becoming more stringent. For example, carmakers are increasing their production of electric vehicles, leading to the adoption of rechargeable lithium ion batteries, also known as Li-ion batteries. This trend is giving rise to a host of analyses needed to support the quality and safety of both the battery materials and the end-product. Although there have been significant advances in Li-ion batteries, issues still exist, such as unintended discharge or “self-discharge” and maintaining the integrity of important qualities like energy density, stability, safety, and cost.

Innovative analytical solutions are required to test individual battery components, like positive and negative electrode materials, separator, electrolytes, and more, during the development and quality control in production. In addition, in order to improve battery characteristics and safety, it is also necessary to understand the state of the materials inside the battery over its lifetime, which can be ascertained through multiple analyses.

This compilation covers many of the analytical testing tools that are critical to the Li-ion battery supply industry, as well as those industries that rely on battery quality, safety and technology advancements.

THE CRITICAL TOOLS OF ANALYSIS

FOURIER TRANSFORM INFRARED ANALYSIS (FT-IR)

Fourier Transform Infrared (FT-IR) spectroscopy is a valuable characterization technique for developing advanced lithium batteries. FT-IR analysis provides specific data about chemical bonds and functional groups to determine transient lithium species and impurities during oxidative degradation that impact the performance of lithium batteries. FT-IR spectral analysis and imaging is used to characterize degradation, surface examination of binder and separator materials for chemical bond change during charging and discharging.

PerkinElmer Frontier™ FT-IR spectrometers are loaded with a range of advanced innovations designed to provide superior spectroscopic performance for your product development needs. The Frontier FT-IR system can be upgraded to a Spotlight™ 400 FT-IR imaging system with Attenuated Total Reflectance (ATR) imaging that enables collection of high-resolution infrared images of extremely small samples to visualize the composition of materials based on FT-IR spectral data.

Frontier Series

Spotlight 400 FT-IR Imaging System

Evaluation of Separator by FT-IR Imaging

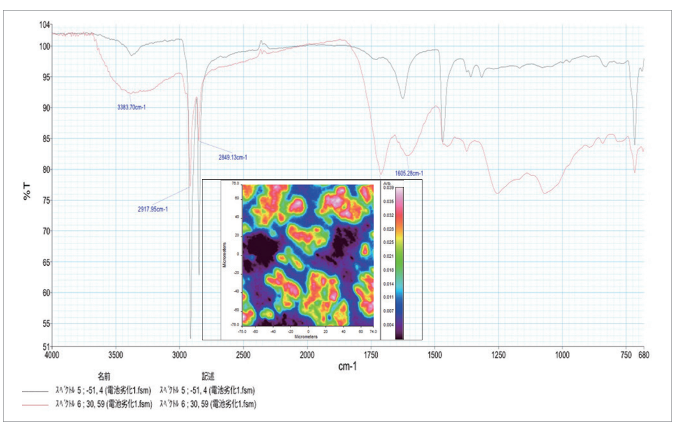

Figure 1. Evaluation of oxidative degradation is shown here through ATR imaging of the separator.

Example of Positive Electrode Active Material

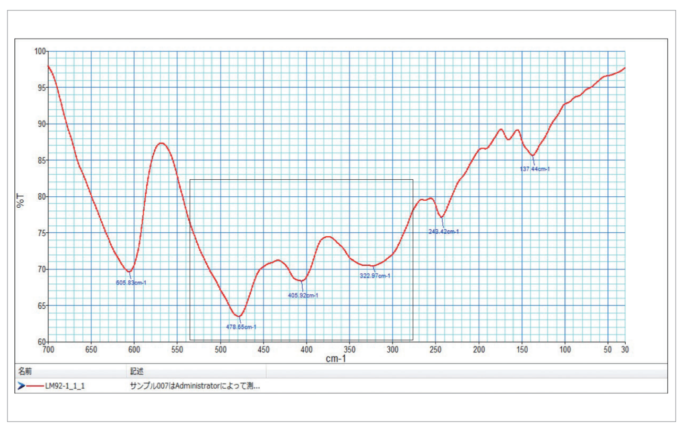

Figure 2. Infrared spectrum of the positive electrode material in the far infrared region is shown here. By using a single reflection ATR accessory using diamond crystal, inorganic oxide information of positive electrodes material can be obtained. One can investigate the qualitative and deteriorated state of cathode material.

GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC/MS)

Gas chromatography mass spectrometry (GC/MS) is an analytical technique well suited for Li-ion battery analyses like compositional testing, as well as other kinds of studies, like analyzing the gasses generated by lithium-ion batteries to generate valuable insights into the degradation of components resulting from repeated charging and discharging. The PerkinElmer Clarus® SQ 8 GC/MS offers uncompromised performance with superior precision, recovery and linearity, delivering consistent ultra-trace detection limits consistently and reliably – time after time.

Determining the composition and ratio of cyclic carbonates, such as ethylene carbonate, propylene carbonate, diethyl carbonate, and ethyl methyl carbonate, has important implications for ensuring optimal battery energy density, cycle life and safety. Systems like the Clarus SQ 8 and its Clarifi™ detector provides the flexibility to choose ideal levels of sensitivity and dynamic range, and eliminates background noise while maximizing analyte signals. The Clarus SQ 8 GC/MS combined with the market-leading TurboMatrix™ sample handling system, user-friendly software, and world-class service from PerkinElmer, form an integrated, complete analytical solution for lithium-ion battery testing.

Clarus SQ 8 GC/MS

GC/MS Application Example: Determination of Nine Carbonates in Lithium Ion Battery Electrolyte by GC/MS

Application Highlights:

- Qualitative and quantitative analysis for the determination of nine carbonates in electrolytic solutions utilizing a Clarus SQ 8 GC/MS with electron ionization (EI) source.
- High reliability and reproducibility of results, as shown by r^2 (determination of coefficients) values over 0.999 for all compounds in the calibration curve range of 1 – 100 mg/L.
- Superior recovery and precision of target analytes, with MDL values at or below 0.176 µg/mL (ppm) for all nine analytes.

Table 1. Calculated Method Detection Limits (MDL) and Method Quantitation Limits (MQL)

Analyte	MDL (µg/mL)	MQL (µg/mL)
Dimethyl Carbonate	0.111	0.444
Ethyl Methyl Carbonate	0.176	0.705
n-Propyl Propionate	0.171	0.684
Diethyl Carbonate	0.172	0.690
Vinylene Carbonate	0.166	0.664
Fluoroethylene Carbonate	0.104	0.415
Ethylene Carbonate	0.146	0.584
Propylene Carbonate	0.086	0.343
1,3-Propanesultone	0.080	0.320

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used for a variety of analyses in the Li battery industry. PerkinElmer's Avio® 500 ICP-OES is a truly simultaneous system that offers high sensitivity and superior resolution, leveraging a host of technological advantages that make it the ideal solution for analyses in the Li battery industry – from Dual View that measures high and low concentrations in the same run, regardless of wavelength, to Flat Plate™ plasma technology which generates a robust matrix-tolerant plasma – you can rest assured that the Avio 500 ICP-OES will meet your analytical needs.

Avio 500 ICP-OES

One of the most important analyses is determining the exact ratios of the main battery components, especially the electrodes. Because of its true simultaneous nature, the Avio 500 ICP-OES can provide the most accurate and precise measurements. In addition, the concentrations of additives and impurities must also be accurately measured. The ability to perform all of the measurements in a single method results in higher sample throughput.

Another important analysis is determining the components of the positive electrodes which have migrated to the electrolyte. This analysis requires the direct introduction of organic solvents, which is possible with the Avio 500 ICP-OES.

ICP-OES Application Examples

Example 1: Analysis of Elements Contained in Positive Electrode Active Material

Avio 500 ICP-OES Application Advantages

- Wide dynamic range allows both major and minor analytes to be measured in the same method
- True simultaneous reads for the ultimate accuracy and precision for major components
- Robust plasma with low argon consumption

Table 2. Major Components of a Positive Electrode Material.

Analyte	Wt%
Co	15.4
Li	6.74
Mn	14.0
Ni	31.4

Example 2: Determination of Impurities in High-Purity Metal Raw Materials

Avio 500 ICP-OES Application Advantages

- Capable of selecting interference-free spectral lines from tens of thousands of spectral lines
- Flat Plate™ plasma technology with solid-state RF generator can effectively overcome matrix effects
- High sensitivity to meet the requirements for the determination of impurities in high-purity metals
- Sample introduction systems resistant to high salt matrices, hydrofluoric acid, and highly corrosive samples

Table 3. Analytes in High-Purity Raw Materials Used in Li-Battery Production – Cobalt Carbonate.

Analyte	Cobalt Carbonate (mg/kg)
As	8.03
Bi	1.30
Cu	2.80
Fe	4.74
Hg	3.44
Ni	9.67
P	29.2
S	3.58
Sb	4.48
Se	6.04
Sn	3.22
Te	0.51
Tl	4.20

Table 4. Analytes in High-Purity Raw Materials Used in Li-Battery Production – Lithium Carbonate.

Analyte	Lithium Carbonate (mg/kg)
Al	0.76
Ca	79.5
Cr	0.082
Cu	0.295
Fe	3.86
K	228
Mg	35.5
Mn	0.36
Na	480
Pb	2.75
Zn	2.70

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES) *CONT.*

Avio 500 ICP-OES

ICP-OES Application Examples

Example 3: Main Component Composition and Impurity Analysis of Lithium/Iron/Phosphate Materials

Avio 500 ICP-OES Application Advantages

- Excellent stability ensures precision and data stability for the determination of high concentration elements
- High sensitivity to determine lower-level impurities within the sample
- Dual view capability to simultaneously measure high concentration elements as well as low concentration of trace impurities

Table 5. Impurities in Lithium Cobalt Oxide ($LiCoO_2$).

Analyte	Lithium Cobalt Oxide (%)
Al	112
Ca	45.0
Cd	0.91
Cr	9.43
Cu	0.73
Fe	15.9
Mg	146
Na	228
Ni	ND
Ti	901
Zn	ND

Table 6. Major Components in Lithium Cobalt Oxide.

Analysis	Li (wt%)	Co (wt%)	Li/Co
1	7.043	59.74	1.0012
2	7.032	59.64	1.0012
3	7.055	59.71	1.0033
4	7.048	59.66	1.0032
5	7.047	59.57	1.0045
6	7.011	59.53	1.0001
7	7.009	59.49	1.0004
8	7.007	59.41	1.0015
SD	0.0183	0.1047	0.001457
AVG	7.031	59.592	1.002
RSD	0.26%	0.18%	0.15%

Example 4: Analysis of Electrolyte, Lithium Hexafluoride and Other Materials

Avio 500 ICP-OES Application Advantages

- Simple sample pretreatment with organic solvent instead of complex acid digestion
- Organic sample introduction system for direct analysis of electrolytes in organic solvents

Table 7. Impurities in DMC Electrolyte.

Analyte	DMC Electrolyte (µg/L)
Al	2480
Ca	96.4
Cd	43.6
Fe	158
K	136
Mg	2.20
Na	3172
Pb	192

Example 5: Cathode Material Determination of the Application of Graphite and Hard Carbon

Avio 500 ICP-OES Application Advantages

- High sensitivity ensures lower detection limits
- Unique pretreatment method available for rapid processing of cathode material samples
- High-solids nebulizer can be used to analyze samples containing particulate matter

Table 8. Determination of Impurities in Graphite.

Analyte	Concentration (µg/g)
Al	1.30
B	0.549
Ca	20.8
Cd	0.127
Co	ND
Cr	3.51
Cu	ND
Fe	7.90
K	ND
Li	ND

Analyte	Concentration (µg/g)
Mg	1.38
Mn	0.190
Na	ND
Ni	1.15
Pb	1.13
S	10.1
Sn	ND
Ti	2.72
Zn	ND

THERMAL ANALYSIS (TGA, DSC) AND HYPHENATION

Characterizing safety performance of lithium batteries during non-normal circumstances is mandated by various standards and regulations and becoming increasingly important due to their use in portable electronic devices and electric vehicles. Thermogravimetric analysis (TGA) is a valuable tool in determining thermal stability and the decomposition profile of materials used in lithium batteries under controlled heating conditions. PerkinElmer TGA 8000™ thermogravimetric analyzer gives you complete control over the sample environment to perform complex characterizations and generate accurate results.

TGA 8000

Lithium battery performance degradation and failure is often caused by degradation of the battery separator. Differential scanning calorimetry (DSC) is used to study the melting profile, electrolyte decomposition, and other thermal properties of materials used as separators. The PerkinElmer DSC 8500 double-furnace DSC with controlled heating and cooling offers great sensitivity, accuracy and reliable results which advances product improvement efforts.

DSC 8500

To overcome some of the safety risks posed by lithium-ion batteries such as leakage, burning, and explosions, composite polymer electrolytes (CPE) are considered a promising alternative. With advantages such as low flammability, good flexibility, excellent thermal stability, and high safety, CPEs are being widely investigated to improve their conductivity and performance in polymer-based lithium-ion batteries. DSC 8500 and TGA 8000 from PerkinElmer enable researchers to determine the measurement of changes in melting points, the enthalpy of phase transitions and thermal stabilities of CPEs for use in new and improved polymer-based lithium-ion batteries.

Hyphenated solutions are often used in the lithium battery industry in which two or more instruments are coupled to increase the power of analyses for deeper insights and enhance productivity by acquiring more information from a single run PerkinElmer TGA 8000 and Simultaneous Thermal Analysis (STA) systems coupled with FT-IR, MS,and/or GC/MS instruments represent the industry's most complete and advanced line of hyphenated platforms for materials characterization.

Analysis of Ethylene Vinyl Acetate (EVA) Used as Binder for Lithium-ion Battery Electrodes

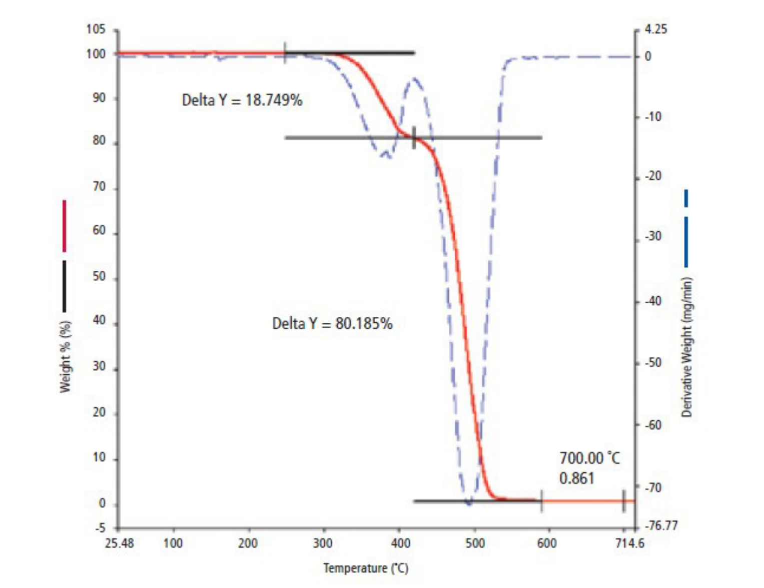

Figure 3. Thermogravimetric data generated from the analysis of EVA sample.

TECHNOLOGY LIST BY TYPE OF ANALYSIS

RESEARCH AND DEVELOPMENT

	Cathode				Anode			Separator	Electrolyte	
	Cathode Composition			Parts	Anode		Part	Qualitative	Composition	
	Positive Materials	Conductive Materials	Binder	Electrode Sheet	Negative Materials	Binder	Electrode Sheet		Solvent	Electrolyte
FT-IR			*			*		*		
AA	•			•			•			
ICP-OES	•			•			•			•
GC/MS									•	
DSC, TGA, TGA-STA/DSC	•	•	•		•	•		•		

Qualitative in Standard Conditions

QUALITY CONTROL

	Battery			Raw Materials	Processing	
	Storage Management	Degradation Analysis	Investigation of Impurity	Composition and Impurity Control	Investigation of Impurity Composition	Contamination Study
FT-IR		*	*	*		*
AA				•	•	
ICP-OES			•	•	•	
GC/MS	•	•		•		
DSC, TGA, TGA-STA/DSC		•				

Qualitative in Standard Conditions

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