BATTERY ANALYSIS GUIDE

Experimental Results & Conclusions for Research Applications

Edition 2

PerkinElmer®
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The Power Is In Your Hands

UNDERSTANDING BATTERIES

Having powerful and robust solutions for analysis in battery and energy materials is of the utmost importance, especially in light of the increase in the production of electric vehicles (EVs), the continued high demand for consumer electronics such as smartphones, and the forecasted growth in the use of electronic medical devices.

Understanding materials and components across the supply chain allows manufacturers and those working on the development of new technologies to not only ensure the quality of the final product but gain valuable insights which may inform design decisions.

This guide offers an overview of the analyses required throughout the value chain. Innovative analytical solutions for testing every part of the battery, including the anode, cathode, binder, separator, and electrolytes, are demonstrated.

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Testing Needs At Every Step

Different analytical techniques can be used at different stages of battery manufacture and recycling to detect and measure performance and safety properties such as impurities and material composition.

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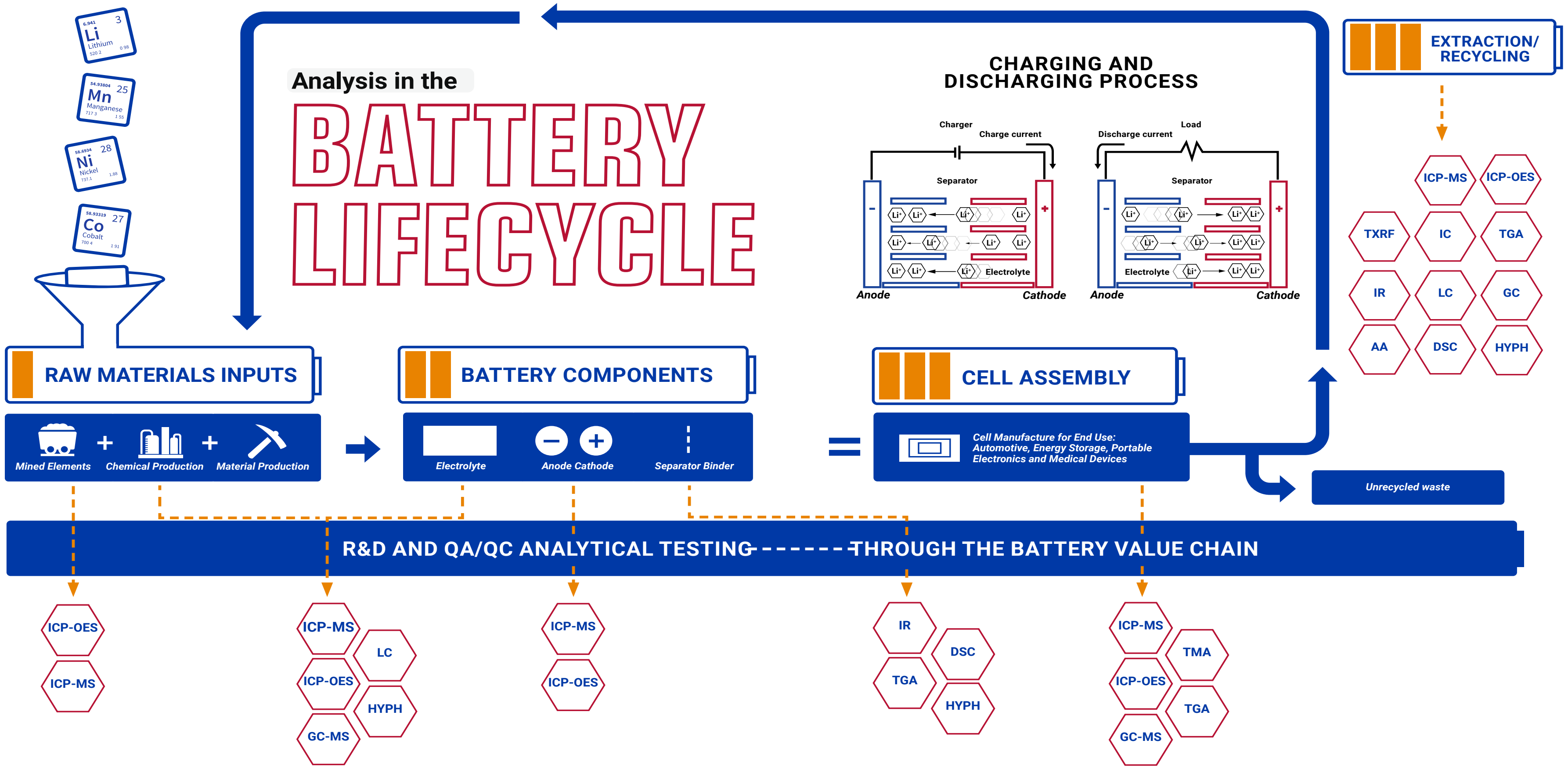

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
- Determine the quality of raw materials
- Measure ratio compositions and impurities of lithium
- Characterize and develop optimal electrode materials.

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)
- Quantify impurities
- Characterize the content of REE

Gas Chromatography Mass Spectrometry (GC/MS)
- Identify possible volatile chemical compounds
- Off-gassing measurements

Fourier-transform Infrared Spectroscopy (FTIR)
- IR can be used to identify and characterize advanced materials

Thermogravimetric Analysis (TGA)
- TGA provides important information about thermal properties

Differential Scanning Calorimetry (DSC)
- DSC provides important information about thermal properties

Hyphenation
- Hyphenation combines two or more technologies for greater analytical depth - know what gases evolved and when

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Anode Analysis

The anode is the negative electrode in a battery. In the vast majority of batteries, graphite is used as the main material in the anode, due to it's ability to reversibly place lithium ions between its many layers. While fully charged, the graphite is 'lithiated' with Li^+ ions being positioned between the graphite sheets. During use (discharging), electrons move from the anode through the components being powered by the battery to the cathode. To stabilize the now negatively charged cathode, Li^+ ions move from in between the graphite sheets in the anode, to the cathode.

The anode (or negative electrode) in a lithium-ion battery is typically made up of graphite, binder and conductive additives coated on copper foil.

One of the requirements for this application is that the graphite surface must be compatible with lithium-ion battery chemistry (salts, solvents and binders).

As previously mentioned, the most essential material in the anode is graphite. To be suitable for lithium-ion battery manufacturing, the material used should have the following characteristics[1]:

- Excellent porosity and conductivity
- Good durability
- Low cost
- Voltage-matched with preferred cathode

There are a number of analytical techniques which may be used to ensure the quality of materials being used. These methods span from using ICP-MS to measure impurities in the copper used in the current collector to downstream methods such as TG-MS, which detects small molecules adsorbed to the surface of electrodes.

Using these analytical techniques can aid in ensuring the quality of battery materials and components thereby improving the battery's overall performance.

1. https://www.targray.com/li-ion-battery/anode-materials

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APPLICATION NOTE

Measurement of Impurities in High-Purity Copper Concentrate Using the NexION 5000 ICP-MS

Sample Material	Copper (Cu)
Battery Component	Current collector
Type of Analysis	Copper concentrate purity test to parts per trillion (ppt) range
Benefits of Analysis	▪ Anode viability ▪ Detect arsenic for removal ▪ Increasing the yield and value of the copper end-products
Technologies Used	▪ ICP-Mass Spectrometry (NexION 5000) ▪ Consumables: Peristaltic Pump Tubing, 17-Element Solution, 10-Element Solution, Silicon
Learnings and Insights	▪ Removal of spectral interferences ▪ Measure to lowest possible levels of impurities ▪ Deals with polyatomic and doubly charged interferences ▪ Removal of the polyatomic CuAr+ interference on Rh+
Authors	▪ Ruth Merrifield, PerkinElmer, Canada ▪ Chady Stephan, PerkinElmer, Canada

SEE THE FULL APPLICATION NOTE

NexION 5000 Multi-Quadrupole ICP-MS

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APPLICATION NOTE

Determination of Bromine in Ultra-High Purity Copper Using the NexION 5000 ICP-MS

Sample Material	Copper (Cu)
Battery Component	Current Collector
Type of Analysis	Determination of Bromine in Copper using Hydrogen Reaction Gas
Benefits of Analysis	■ Anode viability ■ Detect bromine as a potential contaminant ■ Reducing bromine content improves electrical and thermal conductivity of copper
Technologies Used	■ ICP-MS (NexION 5000)
Learnings and Insights	■ Removal of spectral interferences using hydrogen gas to mass shift CuO+, preventing interference on Br+ ■ Use of rejection parameter to prevent further side reactions taking place in the cell ■ High precision test - ± 0.026 ppb shift from initial Br concentration over a four-hour period
Authors	■ Xiaoling Ma, PerkinElmer, Shanghai, China

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NexION 5000 Multi-Quadrupole ICP-MS

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Analysis of Water and Carbon Dioxide Adsorbed to Electrodes using TG-MS

Sample Material	Electrode
Battery Component	Anode and cathode
Type of Analysis	Analysis of small molecules adsorbed to the electrode surface
Benefits of Analysis	■ Electrode quality control ■ Detect the presence of small molecules on electrode surface ■ By reducing incidences of small molecules adsorbed to anode/cathode, side reactions in finished cell may be reduced
Technologies Used	■ TG-MS
Learnings and Insights	■ No sample preparation required unlike current techniques such as K-F titration ■ Gravimetric data from TGA ■ MS can be set to measure single ions or a spectrum
Authors	■ Kieran Evans, PerkinElmer, Seer Green, UK

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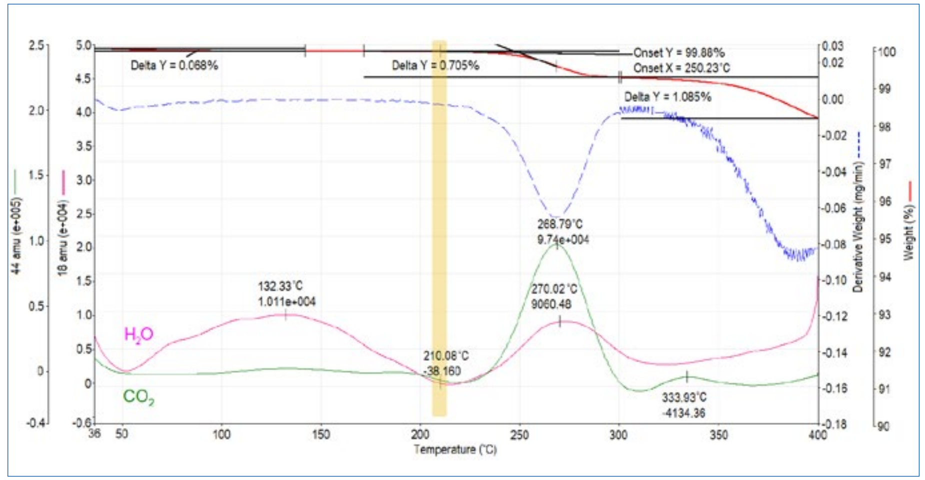

TG-MS Data demonstrating water and CO_2 desorption from an electrode sample.

TL8300e system allows for 'On-Line' TG-MS analysis

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Cathode Analysis

The cathode is the positive electrode in a battery and acts as the source of lithium ions in a lithium-ion battery. Common materials used in cathodes include the following:

- NMC (NCM) – Lithium Nickel Cobalt Manganese Oxide ($LiNiCoMnO_2$)
- LFP – Lithium Iron Phosphate ($LiFePO_4$)
- LNMO – Lithium Nickel Manganese Spinal ($LiNi_{0.5}Mn_{1.5}O_4$)
- NCA – Lithium Nickel Cobalt Aluminum Oxide ($LiNiCoAlO_2$)
- LMO – Lithium Manganese Oxide ($LiMn_2O_4$)
- LCO – Lithium Cobalt Oxide ($LiCoO_2$)

This section will cover the analytical techniques needed to analyze some of the raw metals used in constructing battery cathodes and applications demonstrating analysis of finished cathode powders and other materials used in this component, such as binders[1].

The inorganic methods in this section will demonstrate procedures whereby impurities can be detected and accurately quantified. This will provide analysts, in both R&D and QA/QC settings, with the ability to ensure the high quality of cathode materials and thus improve the overall performance outcomes while reducing the number of failures further downstream.

1. https://www.targray.com/li-ion-battery/cathode-materials/cathode-active-materials

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Analysis of Aluminum Alloys with the Avio 220 Max Hybrid ICP-OES Following London Metal Exchange Guidelines

Sample Material	Aluminium
Battery Component	Current collector
Type of Analysis	Determination of impurities present in aluminium
Benefits of Analysis	■ Current-collector quality control ■ Detect impurities that can have detrimental effects on mechanical or electrical properties of the aluminium current collector
Technologies Used	■ ICP-OES
Learnings and Insights	■ High accuracy for both major and minor components ■ Simultaneous background and analyte measurement – ideal for complex matrices such as alloys
Authors	■ Ken Neubauer, PerkinElmer, Shelton, USA ■ Chenjia Jiao, PerkinElmer, Shanghai, China

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Avio 220 Max Hybrid Simultaneous ICP-OES

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APPLICATION NOTE

Analysis of Impurities in Aluminum with the Avio 550 Max ICP-OES Following London Metal Exchange Guidelines

Sample Material	Nickel
Battery Component	Cathode
Type of Analysis	Determination of impurities present in nickel
Benefits of Analysis	▪ Raw material quality control ▪ Detect impurities that may have detrimental effects on performance of final cell
Technologies Used	▪ ICP-OES
Learnings and Insights	▪ High accuracy for all impurities measured ▪ Matrix interference removed by applying a multicomponent spectral fitting model
Authors	▪ Aaron Hineman, PerkinElmer Shelton, USA ▪ Ken Neubauer, PerkinElmer, Shelton, USA

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Avio 550 Max Fully Simultaneous ICP-OES

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Analysis of Impurities in Lead with the Avio 550 Max ICP-OES Following London Metal Exchange Guidelines

Sample Material	Lead
Battery Component	Electrode (lead acid battery)
Type of Analysis	Determination of impurities present in lead
Benefits of Analysis	▪ Raw material quality control ▪ Detect impurities that may have detrimental effects on performance of final cell
Technologies Used	▪ ICP-OES
Learnings and Insights	▪ High accuracy for all impurities measured ▪ Matrix interference removed by applying a multicomponent spectral fitting model
Authors	▪ Aaron Hineman, PerkinElmer Shelton, USA ▪ Ken Neubauer, PerkinElmer, Shelton, USA

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Avio 550 Max Fully Simultaneous ICP-OES

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Analysis of High Purity Cobalt using ICP-OES

Cobalt is one of the most important metals associated with lithium-ion batteries. It is present in three of the five most common materials used in Li-Ion battery cathodes; lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt oxide doped with alumina (NCA).[1] Unfortunately, cobalt is considered to the highest supply chain risk of all raw materials used in EVs.[2] The PerkinElmer Avio® 550 ICP-OES may be utilized to determine the concentration of impurities in high purity lithium-ion battery raw materials such as cobalt oxide. The Avio 550 has the following advantages, making it the ideal solution for the analysis of high purity materials used in battery manufacturing:

- Ability to select 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

Avio 550 ICP-OES

Example results obtained from a sample of cobalt oxide are shown below.

Analyte	Concentration (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

1. Chapter 12 - Li-Secondary Battery: Damage Control, Editor(s): Jürgen Garche, Klaus Brandt, Electrochemical Power Sources: Fundamentals, Systems, and Applications, Elsevier, 2019, Pages 507-629
2. https://www.energy.gov/eere/vehicles/articles/reducing-reliance-cobalt-lithium-ion-batteries

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APPLICATION NOTE

Determination of Elemental Impurities in Lithium Battery Cathode Materials Using the NexION 1000 ICP-MS

Sample Material	Cathode powder
Battery Component	Cathode
Type of Analysis	Determination of impurities present in cathode materials
Benefits of Analysis	▪ Raw material quality control ▪ Detect impurities that may have detrimental effects on performance of final cell
Technologies Used	▪ ICP-MS
Learnings and Insights	▪ High accuracy for all impurities measured ▪ Low detection limits to meet requirements of manufacturers ▪ Robust sample preparation method used to achieve high-quality results
Authors	▪ Guanyu Chen, PerkinElmer, Shanghai, China ▪ Shaoxia Liang, PerkinElmer, Shanghai, China ▪ Xiaoling Ma, PerkinElmer, Shanghai, China

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NexION 1000 ICP-MS

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INTRODUCTION

Binders

Binders are found in both the anode and cathode of batteries. Their main purpose is facilitating the adhesion of the active material to the current collector or separator in the cell. However, they also serve several other functions including:

- Improving dispersion of the active particles in solvent, producing a more homogeneous slurry
- Aiding film formation to improve uniformity
- Improve adhesion of the active material to the current collector

Depending on the solvent and the desired properties of the finished cell, there are two materials frequently used as binders:

- Polyvinylidene fluoride (PVDF)
- Styrene Butadiene copolymer

Considering the important role they play in batteries, analysis of binders is of upmost importance. Manufacturers and researchers alike stand to gain important insights by understanding the chemical, thermal and mechanical properties of binders.

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Characterization and Analysis of Polyvinylidene Fluoride (PVDF)

Sample Material	Polyvinylidene fluoride
Battery Component	Binder
Type of Analysis	Chemical and thermal characterization
Benefits of Analysis	▪ Raw material quality control ▪ Verification of material identity ▪ Thermal characterization
Technologies Used	▪ IR ▪ DSC ▪ TGA
Learnings and Insights	▪ Fast, turnkey solutions for polymer analysis ▪ Ability to understand thermal effects of different materials-processing parameters ▪ Little to no sample preparation required
Authors	▪ Kieran Evans, PerkinElmer, Seer Green, UK

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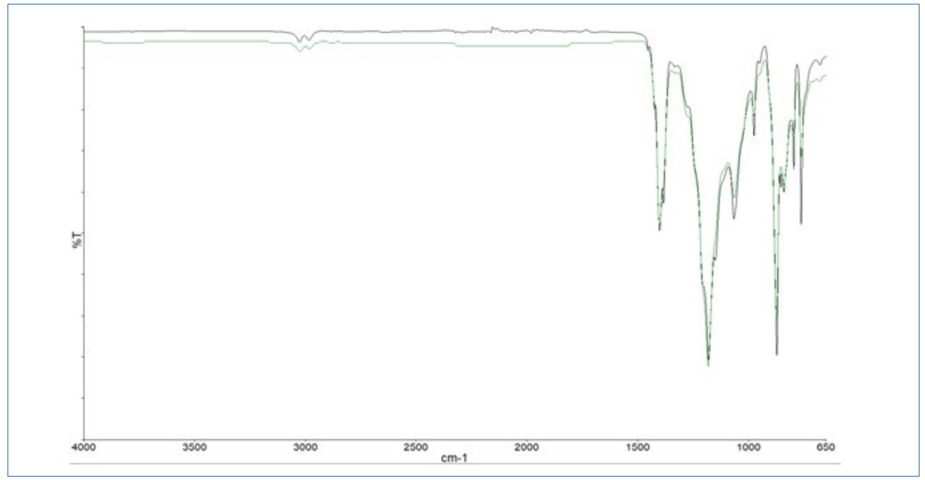

ATR-IR spectrum of PVDF (Black) overlaid with library best hit (Green).

Spectrum Two

DSC 8500

TGA 8000

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INTRODUCTION

Electrolyte Analysis

The main role of the electrolyte in a lithium-ion battery is the transport of lithium ions from the cathode to the anode during charging (and vice versa during discharging). The most common electrolyte solution used in Li-ion batteries is $LiPF_6$ in an organic solvent. The solvent is commonly either one or a mixture of organic carbonates. In addition to the ionic salt and the solvent, a wide variety of additives may also be added to these solutions to improve parameters such as:

- Formation of the Solid-Electrolyte Interface (SEI)
- Safety
- Chemical Stability
- Transport of Ions
- Wetting

A battery's electrolyte may also consist of acids or other bases in liquid, gel, or dry formats. Electrolytes are also available as polymers, as used in the solid-state battery, solid ceramics, and molten salts, as in the sodium-sulfur battery. Electrolyte solutions must enable the Li-ions to transport freely, requiring high dielectric constant and low viscosity.

The major problems associated with electrolytes is their high flammability and slow diffusion. These can be ameliorated using electrolytes based on solid-state materials with higher diffusivity and low flame susceptibility.

Research on the electrolyte solution is generally focused on one of three areas: functional electrolyte additives, flame-resistant or non-flammable electrolyte solutions, and new electrolyte salts.

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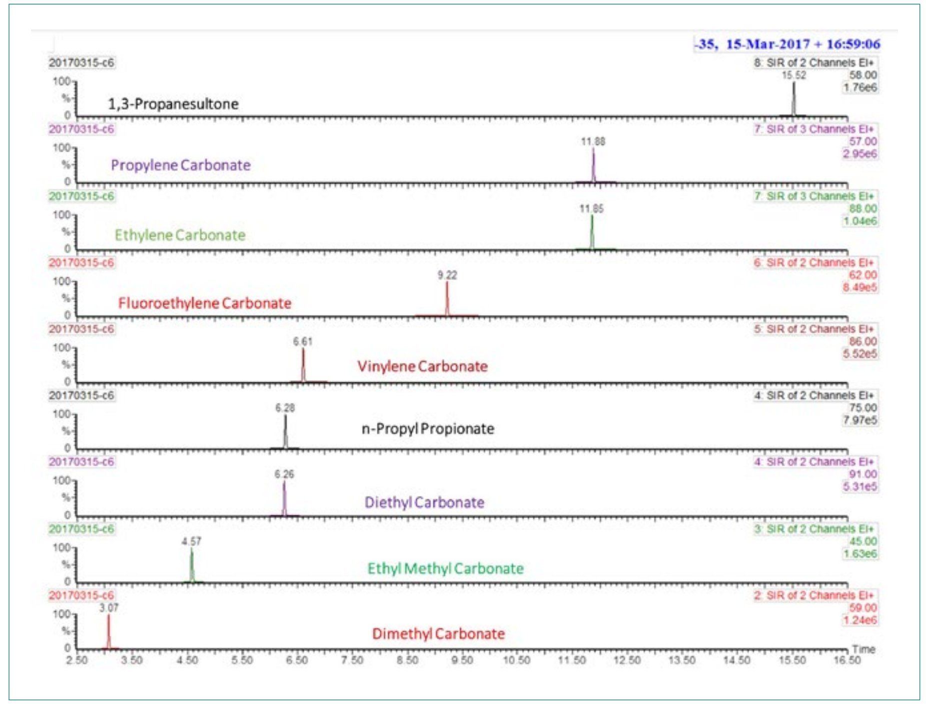
Determination of Nine Carbonates in Lithium-Ion Battery Electrolytes by GC/MS

Sample Material	Liquid electrolyte
Battery Component	Electrolyte solvent
Type of Analysis	Quantification of carbonate solvents
Benefits of Analysis	■ Determination of carbonate ratio – an important parameter affecting energy density, cycle life, and safety
Technologies Used	■ GC/MS
Learnings and Insights	■ A sensitive, simple, efficient method for quantification ■ Low detection limits if contamination is a concern
Authors	■ Kira Yang, PerkinElmer, Shanghai, China



Chromatograms of nine common carbonate solvents used in battery electrolytes. With electron ionization (EI) source and selected ion recording (SIR)

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Image of GC 2400 GC/MS System which would provides comparable data to the Clarus SQ8 GC/MS on which this application is based.

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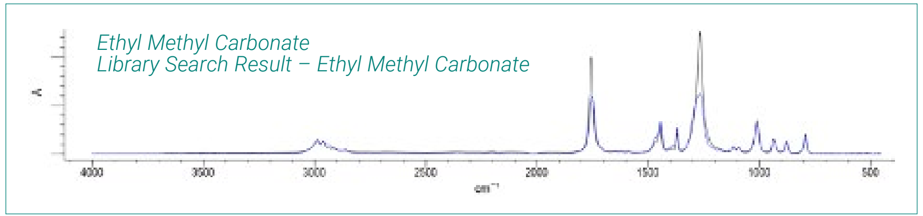
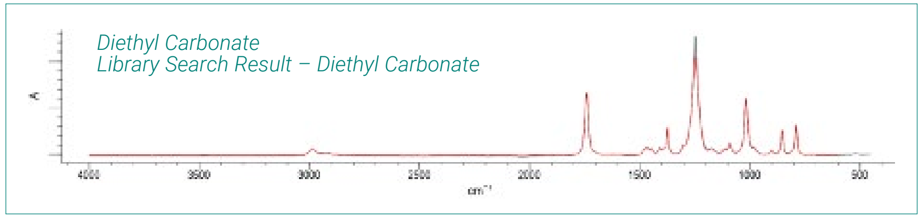
Analytical Summary – Identification and Verification of Electrolyte Raw Materials

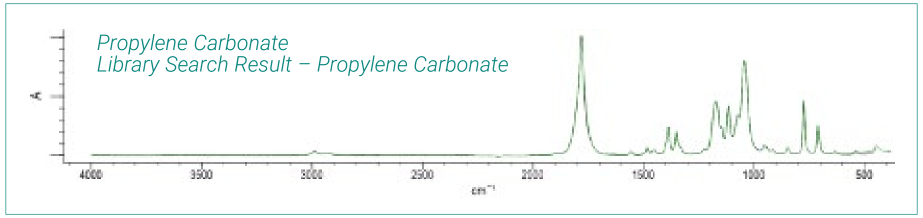


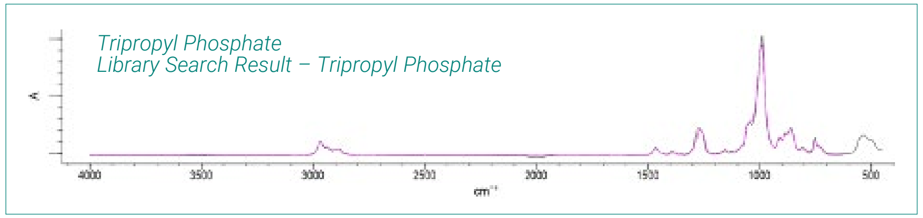
The identification and verification of raw materials is important in a wide variety of industries, from pharmaceutical to polymer manufacturing. The Li-Ion battery market is no different. The challenges facing battery manufacturers regarding demand and performance will require a fast and simple solution for the identification of raw materials. FTIR spectroscopy can provide a method by which materials are accurately identified in less than 30 seconds using the search function in PerkinElmer's Spectrum 10 software.

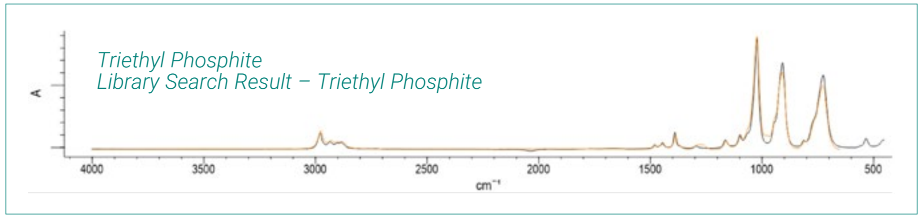
Samples were measured, as received, using a PerkinElmer Spectrum Two™ infrared spectrometer with universal attenuated total reflectance (UATR) accessory. Each sample was measured between 4000 – 450 cm^{-1} with 4 scan accumulations at a 4cm^{-1} resolution. Example results obtained from electrolyte solvents and additives are shown overlaid with library 'best hit' spectra.

Spectrum Two IR Spectrometer with Universal Attenuated Total Reflectance (UATR) Accessory









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APPLICATION BRIEF

DSC Analysis of Binary Carbonate Solvent Mixtures

Sample Material	Liquid electrolyte
Battery Component	Electrolyte solvent
Type of Analysis	Freezing point and eutectic point determination of carbonate mixtures
Benefits of Analysis	▪ Clear understanding of phase transitions in different carbonate mixtures, providing information on ionic conductivity of electrolyte
Technologies Used	▪ DSC
Learnings and Insights	▪ Fast cooling allows for high throughput and greater accuracy when measuring some thermal transitions ▪ Better understanding of how a solvent might behave in low-temperature applications
Authors	▪ Kieran Evans, PerkinElmer, Seer Green, UK

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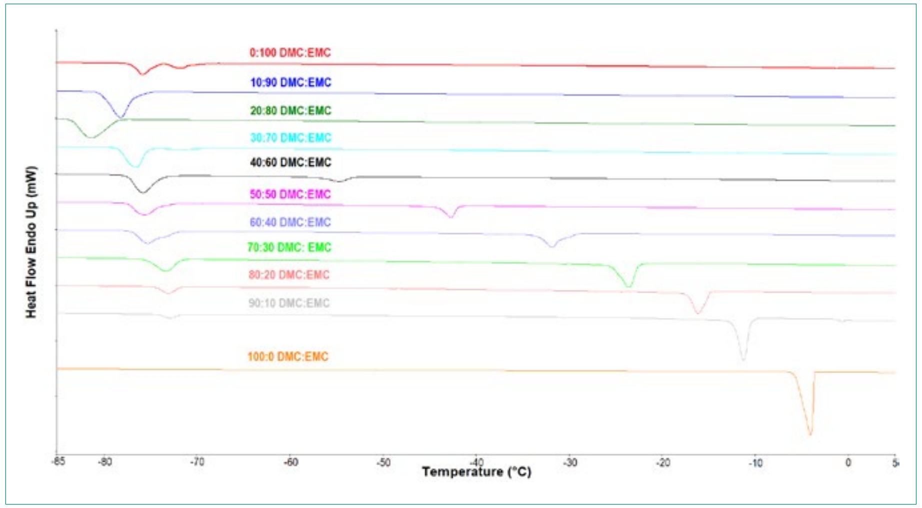

Heat flow curves for 11 DMC/EMC mixtures.

DSC 8000

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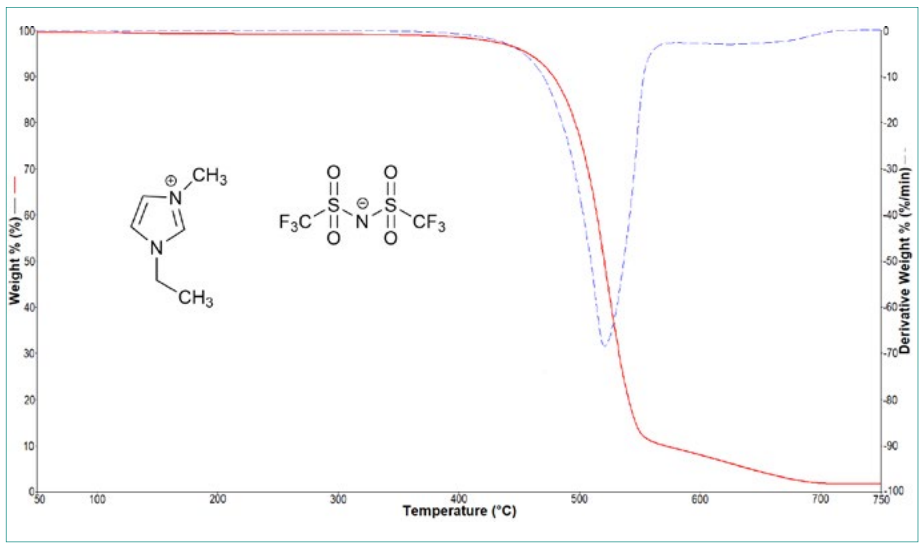
ANALYTICAL SUMMARY

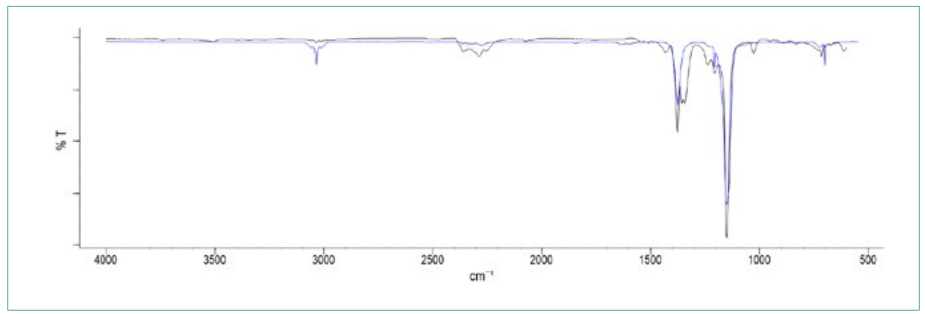
Investigating the Thermal Degradation of an Ionic Liquid Using Hyphenated Techniques

Ionic liquids are becoming more frequently used in battery electrolytes due to their favorable properties, such as large electrochemical window and high thermal stability. Hyphenated techniques, specifically TG-IR and TG-IR-GC/MS, provide information on not only the thermal stability, but the gases evolved during thermal degradation of an ionic liquid. The analytical summary shows the data obtained from the thermal degradation of the ionic liquid EMIM TFSI (Merck, battery grade). This sample was heated from 50 – 750 °C at 20 °C/min under a 40 mL/min nitrogen purge, (60 mL/min nitrogen balance purge). Evolved gases were transferred from the TGA to the FTIR and GC/MS using a PerkinElmer TL9000e transfer line set at 280 °C and a flow rate of 85 mL/min. The TGA data with the chemical structure of EMIM. TFSI is shown below.



TGA curve and structure of EMIM TFSI.

The IR spectra were collected using a PerkinElmer Spectrum 2 FTIR spectrometer. Spectra were collected in continuous mode with 2 accumulations per spectrum between 4000 and 450 cm^{-1} and a 4 cm^{-1} resolution. The infrared spectrum of the gas evolved in the main weight loss at 530 °C is shown below with the best hit from a spectral library (trifluoromethane) overlaid:



IR spectrum (black) and best hit spectrum (blue) for the first weight loss of EMIM TFSI.

TG-IR-GC/MS Hyphenation: Evolved gases transferred from the TGA 8000 to the Spectrum Two FTIR and GC 2400 GC/MS using a PerkinElmer TL9000e transfer line.

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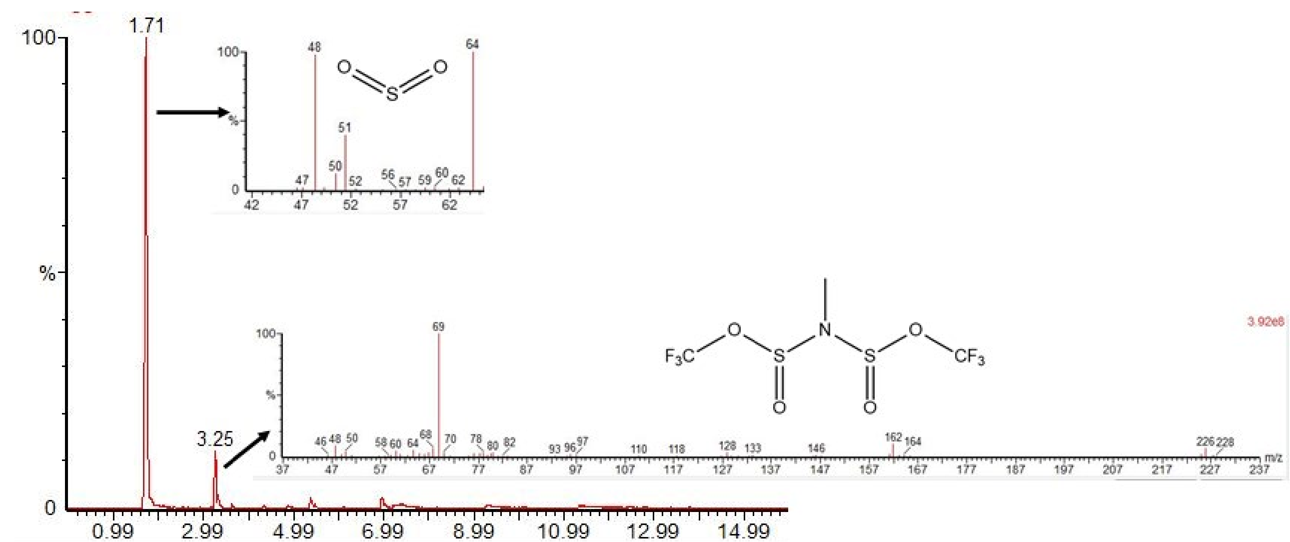
Although there is somewhat of a match between the sample and reference spectrum (a search score of 0.73), there are peaks that are clearly not accounted for by the best hit. The search score is significantly less than what would be required for robust identification. The most significant of these are the peaks at 1357 and 1346 cm^{-1}. These are likely to correspond to an S=O stretch. What is not elucidated by the infrared spectrum is whether the pyrolysis of the material has yielded SO_2 gas alongside a CF_3 containing molecule or whether we are seeing simple evaporation of the ionic liquid. Using TG-IR-GC/MS adds further information which can answer these questions.

The GC/MS data obtained from the main weight loss during the thermal degradation of EMIM TFSI shows that we are seeing partial decomposition of the ionic liquid. The peak at 1.71 min shows the evolution of SO_2 whereas the much smaller peak at 3.25 min shows the evolution of a molecule analogous to the anion of the ionic liquid.

TG-IR-GC/MS provides the ideal solution for elucidation of complex mixtures. The thermogravimetric analysis offers information on thermal stability. Infrared spectroscopy allows for real-time analysis of the bulk gas evolved from the degradation of the material. GC/MS further separates evolved gases which offers separation and more detailed analysis of degradation products.



GC/MS data and results from MS NIST data base for the main weight loss of EMIM TFSI.

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Quantification of $LiPF_6$ in Electrolytes Using FTIR Spectroscopy

The electrolyte in a lithium-ion battery serves as an insulating medium which allows for transport of ions between from the cathode to be intercalated in the anode during charging, and vice versa during discharging. One of the most common electrolyte formulations uses lithium hexafluorophosphate ($LiPF_6$) dissolved in either one, or a mixture, of linear or cyclic carbonates. Additives, such as vinylene carbonate and sulfones, are also added to improve processes such as solid-electrolyte interface (SEI) formation.

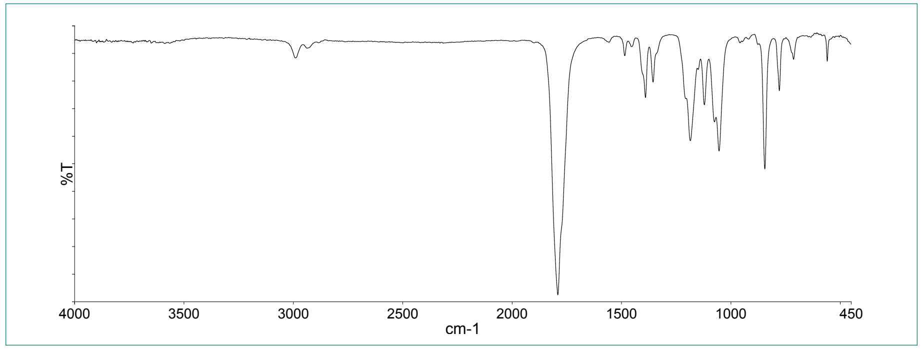
The performance of the battery electrolyte is heavily influenced by the concentration of the conducting salt. Parameters affected by the concentration included viscosity, oxidative/reductive stability, speed of lithium-ion insertion/extraction at the electrodes and the extent to which dendrite formation is suppressed.

Infrared spectroscopy provides a fast and simple technique whereby the concentration of $LiPF_6$ in electrolytes can be determined. By using the SPECAC Arrow™ silicon wafer removable ATR slides, samples can be prepared under inert atmosphere, sealed, and measured outside of a glovebox.

The calibration samples were prepared by volume under nitrogen. Once prepared, 20 µL of solution was pipetted into a Specac Arrow™ slide and sealed. The IR spectra were collected using a PerkinElmer Spectrum Two™ FTIR spectrometer. The accessory used to collect the spectra was a PerkinElmer universal attenuated total reflectance accessory (UATR) with a top plate designed for compatibility with Specac Arrow™ slides. The data was collected between 4000 – 450 cm^{-1} with 4 scans at a 4 cm^{-1} resolution.

Spectrum Two FTIR Spectrometer

Below is an example spectrum showing a 1.00M solution of $LiPF_6$ in propylene carbonate.



IR Spectrum of a 1.00 M solution of $LiPF_6$ in propylene carbonate.

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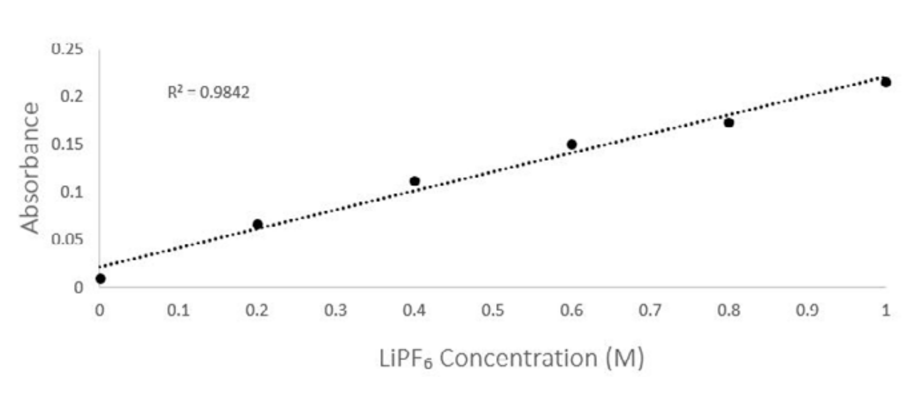
For this application, the height of the peak at 842 cm^{-1} (corresponding to the P-F stretch in $LiPF_6$) was used for quantification. A Beers Law calibration was applied to produce a calibration curve, shown below.



Plot of absorbance at 842 cm-1 against $LiPF_6$ concentration.

To validate this method, two samples were used. The concentrations of these samples were chosen to represent two potential 'problem' samples that would be encountered within a QA/QC laboratory. The first, a 0.98M sample, is indicative of a slight shortfall in $LiPF_6$ concentration, which could have significant effects over the life of the battery. The second, a 0.55M sample, is intended to represent an electrolyte which has seen significant degradation of the conducting salt. This concentration may be encountered during the recycling process when a recycler is attempting to recover the electrolyte.

The results from the validation samples are shown below:

Actual Concentration (M)	Predicted (M)	Error (M)
0.55	0.61	0.06
0.98	0.97	0.01

This work demonstrates the use of FTIR spectroscopy as a screening method for the quantification of $LiPF_6$ in lithium-ion battery electrolytes before the use of a confirmatory technique such as ICP-OES. FTIR could be implemented as a simple 'yes/no' method to understand whether the concentration of the conducting salt is within an acceptable range before moving onto other analyses.

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Thermal Stability of Electrolyte Solvents and Additives

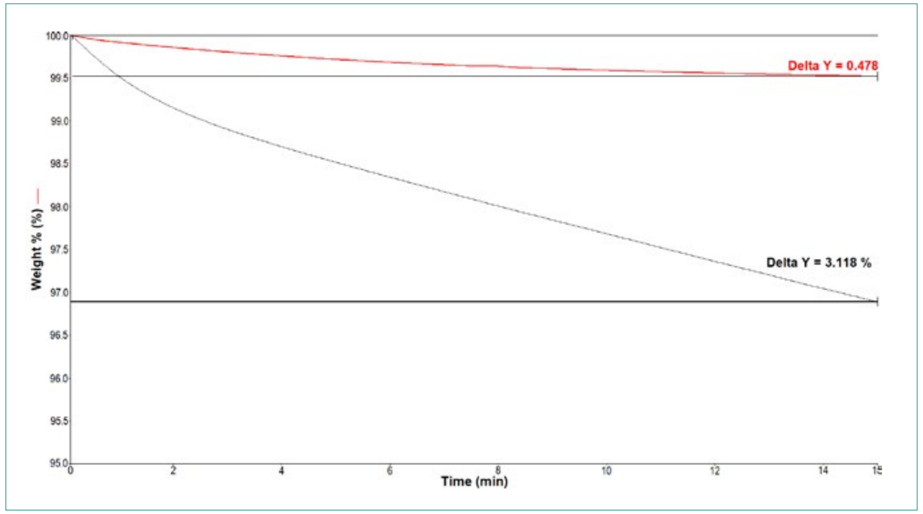
Liquid electrolytes in lithium-ion batteries pose several issues from a safety standpoint. Some of these issues are due to the volatile and flammable carbonate solvents often used which, especially in hotter climates, can lead to hazards stemming from evaporation or even combustion of the solvent in instances of thermal runaway. Thermogravimetric analysis provides a method whereby the thermal stability of a material can be assessed either at a fixed temperature (isothermally), or during an experiment where the material is heated at a controlled heating rate.

This application demonstrates how the stability of a carbonate solvent and an ionic liquid may be investigated using thermogravimetric analysis. The volatility of the solvent will have a huge impact on the pressure that builds up in a cell when it is exposed to high temperature. For example, in an electric vehicle used in a warm climate.

In this experiment, propylene carbonate (Merck, battery grade), a common solvent used in lithium-ion battery electrolytes and EMIM TFSI (Merck, battery grade), a common ionic liquid used in electrolytes, were held isothermally at 50 °C for 15 minutes under a 40 mL/min nitrogen purge. All measurements were carried out using a PerkinElmer TGA 8000

TGA 8000

The data obtained from this experiment is shown below.



Isothermal data for propylene carbonate (black) and EMIM TFSI (red).

It can be seen from the TGA data that there is significantly more evaporation seen in propylene carbonate than in EMIM TFSI, signifying their differences in volatility at raised temperatures.

TGA data such as this may be used to inform decisions on which solvents or additives are used in battery electrolytes for markets where high temperatures may be experienced on a regular basis.

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ANALYTICAL SUMMARY

Detection and Monitoring of Degradation in Electrolyte Additives

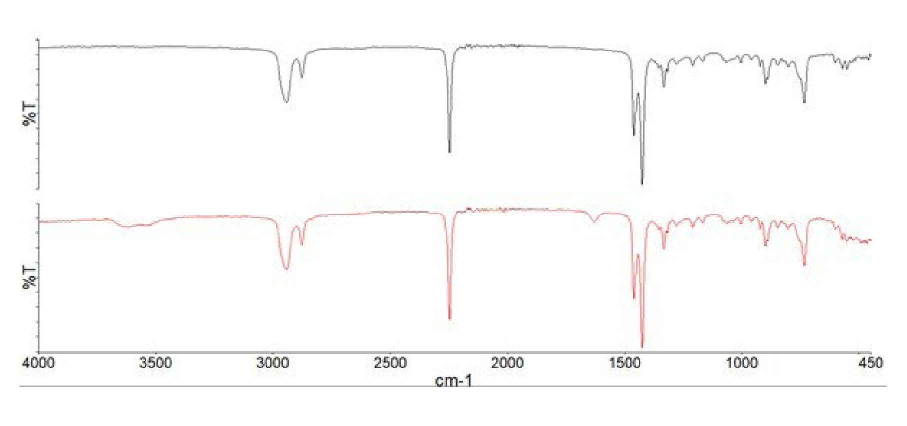
The presence of moisture in any battery component can have significant detrimental effects on the overall performance. This is due to side reactions occurring between the water and the electrolyte as well as the production of hydrogen from the electrolysis of water at the electrodes.

FTIR spectroscopy provides a fast and simple method in which degradation of in an electrolyte component can be detected. In this work, adiponitrile (battery grade, Merck™) was used to demonstrate the speed with which a hygroscopic material may absorb moisture if stored incorrectly i.e., in ambient conditions rather than under an inert atmosphere.

The FTIR spectra of adiponitrile were measured using a PerkinElmer Spectrum Two™ IR spectrometer with universal attenuated total reflectance accessory (UATR). The spectra were measured between 4000 – 450 cm^{-1} with 4 scan accumulations at a 4 cm^{-1} resolution.

Spectrum Two IR Spectrometer With Universal Attenuated Total Reflectance Accessory (Uatr).

Spectra taken at the start of the experiment and at 20 minutes are shown below.



IR spectra of adiponitrile after exposure to air for 0 minutes (black) and 20 minutes (red).

Characteristic amide peaks may be seen in the spectrum after 20 minutes which are not present at 0 minutes. These are the two peaks around 3575 cm^{-1} which corresponds to the N-H stretch in a primary amide and 1627 cm^{-1} which corresponds to the C=O stretch in an amide. This provides a clear indication of degradation.

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APPLICATION NOTE

Direct Analysis of Impurities in Lithium Hexafluorophosphate Battery Electrolyte with the Avio 220 Max ICP-OES

Sample Material	Lithium carbonate and lithium hydroxide
Battery Component	Raw and recycled materials
Type of Analysis	Determination of impurities in products from the recycling process
Benefits of Analysis	▪ Determination of trace impurities in LiOH and Li_2CO_3 ▪ Ensuring a high-performance final product
Technologies Used	▪ ICP-MS
Learnings and Insights	▪ Direct analysis of $LiPF_6$ battery electrolytes ▪ Simple sample preparation ▪ High accuracy and precision for a range of potential elemental impurities
Authors	▪ Ruth Merrifield, PerkinElmer, Woodbridge, Canada

SEE THE FULL APPLICATION NOTE

Avio 220 Max ICP-OES

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INTRODUCTION

Separator Analysis

Most conventional batteries use separators – gelatinous membranes that prevent short-circuiting of the electrodes. Separators should have uniform thickness, adequate mechanical strength during cell fabrication, and chemical and electrochemical stability. Smart separator materials have been developed that melt in situations like an accidental short circuit, overcharging/discharging, or thermal runaway.

In lithium-ion batteries, dendritic formations can short-circuit electrodes, which can ignite flammable electrolytes. Rigorous material characterization technology tests for properties such as;

- Mechanical strength during cell fabrication
- Chemical and electrochemical stability
- Heat and degradation resistance

The separator segregates the anode from the cathode, forming an isolator for electrons but allowing ions to pass through. The separator in an electrochemical battery system is typically a porous polymer membrane that is wetted by the liquid electrolyte and located between the cathode and the anode.

This section will focus mainly on polymer separators, demonstrating primarily how materials characterization techniques (IR spectroscopy, TGA, and DSC) can be used to obtain valuable information. Thermal techniques will play a major role in investigating parameters such as crystallinity and melting point, which can have a huge impact on the performance and safety of a battery.

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ANALYTICAL SUMMARY

Thermal Characterization of Materials Used in Polymeric Separators

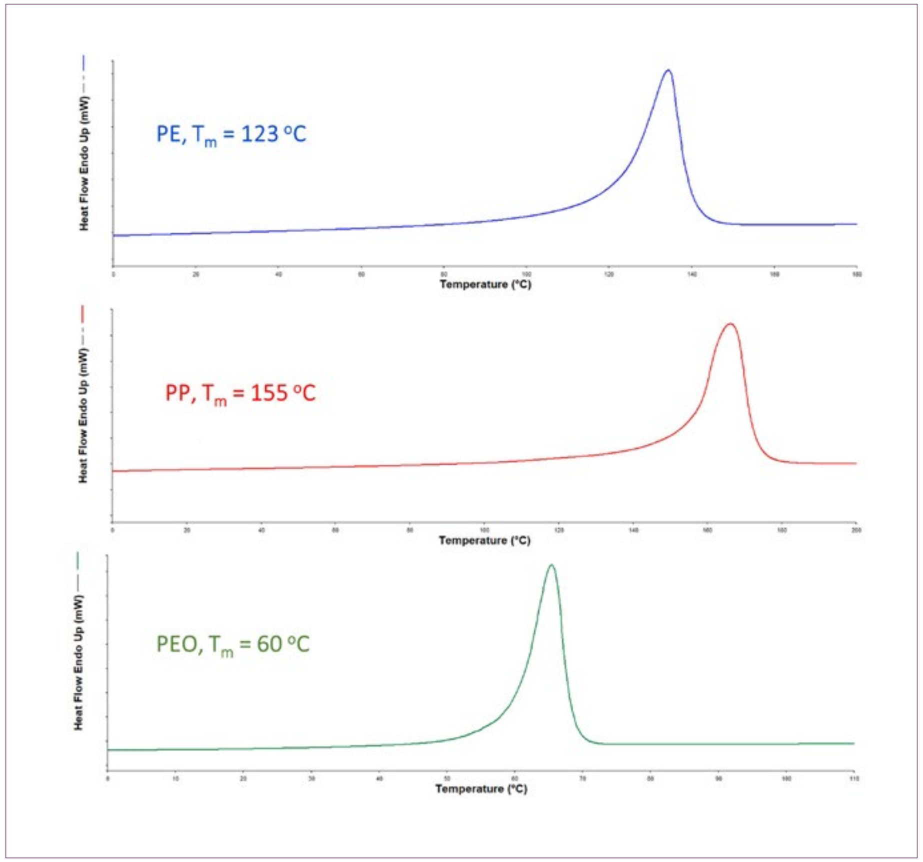
A wide range of polymers are commonly used in separators for lithium-ion batteries. Some of the most common include: polyethylene (PE), polypropylene (PP), poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA), polyethylene oxide (PEO), poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-hfp).

Understanding the thermal characteristics of these polymers can help inform design decisions based on melting point, decomposition temperature, and other phase transitions. Differential Scanning Calorimetry (DSC) may be used to determine the melting point of a polymer, among other parameters such as glass transition temperature.

To the right are three examples of DSC data collected for polymers commonly found in separators.

DSC 4000

STA 6000



DSC Data for polyethylene (blue), polypropylene (red) and polyethylene oxide (green).

KEEP READING >

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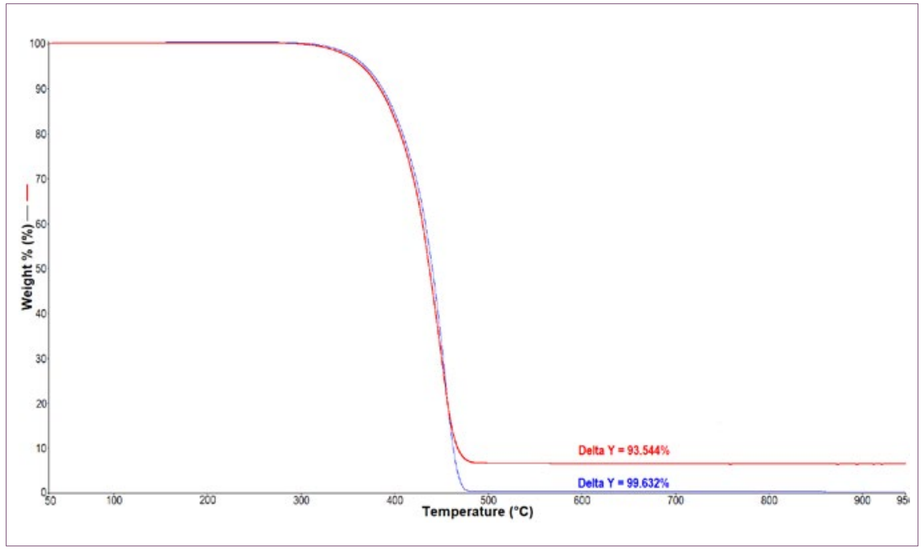
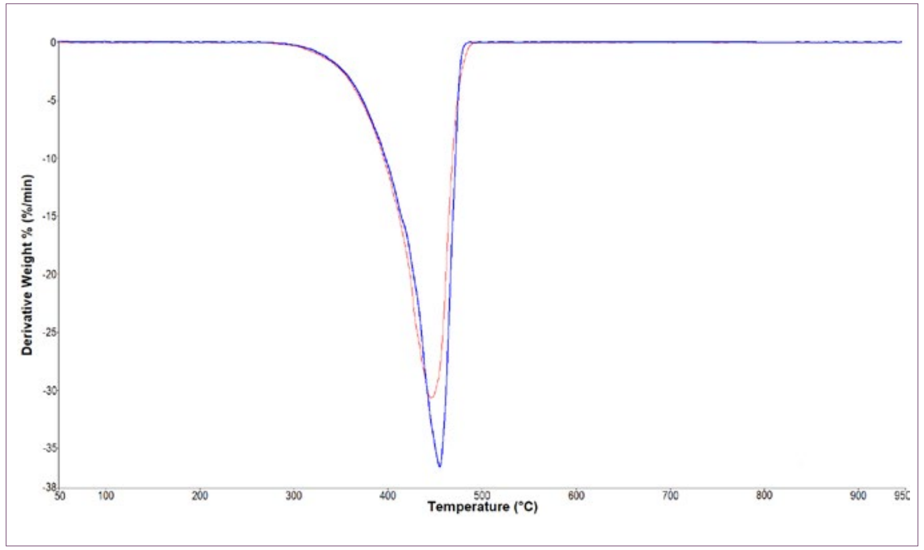
In addition to understanding the melting point of polymers used in separators, thermal techniques such as thermogravimetric analysis (TGA) provide more information. In this case, TGA can be used to understand the temperature at which a material begins to decompose. It can also be used to quantify the inorganic filler present in a polymer. The amount and type of filler used in a polymer can greatly influence important parameters such as ion conductivity, cycle life, and mechanical strength. The example below shows the weight loss curves of two samples of polypropylene with very small differences in filler content. These samples were heated from 50 °C to 800 °C under nitrogen at 20 °C/min, then from 800 °C to 950 °C under air using a PerkinElmer STA 6000.



TGA data for higher (red) and lower (blue) filled samples.

The total weight loss of the more filled sample (red) was found to be 6.09% less than that for the less filled sample (blue). This demonstrates the ability of thermogravimetric analysis to detect differences in sample composition.

Investigation of the derivative weight loss curves reveals the more significant effect this small difference in filler has on the pyrolytic behavior of these samples.



DTG data for higher (red) and lower (blue) filled samples.

Using the 'Peak Area' function in Pyris™ software, the onset of pyrolysis can be calculated for each sample. This was found to be 408 °C for the less filled sample and 399 °C for the more filled sample, providing a clear indication of the effect filler content has on the thermal behavior of materials used for separators.

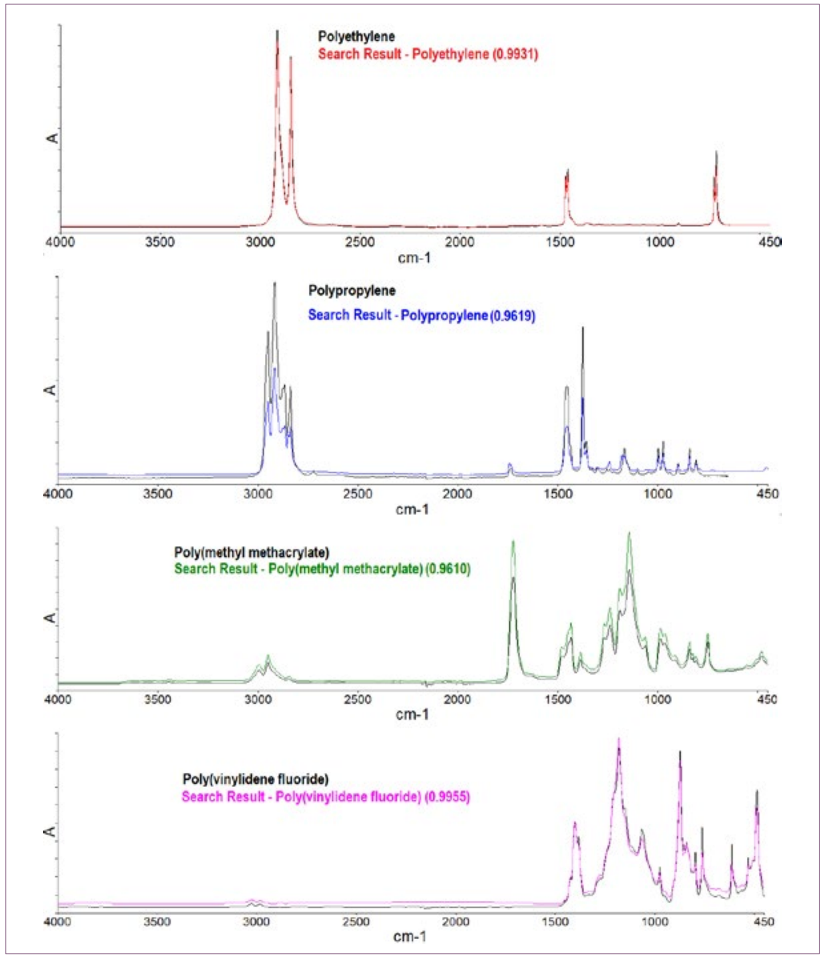
ANALYTICAL SUMMARY

Identification of Polymer Raw Materials Used in Separators

Verification of incoming raw materials is an important step in any manufacturing process. Infrared spectroscopy provides a simple and fast method for the identification of polymer raw materials by searching sample spectra against readily available commercial libraries.

Spectra were collected using a PerkinElmer Spectrum Two™ FTIR spectrometer with a universal attenuated total reflectance accessory. Each material was measured between 4000 – 450 cm^{-1} with 4 scan accumulations at a resolution of 4 cm^{-1}. Infrared spectra of these materials are shown to the right.

Spectrum Two FTIR Spectrometer



IR Spectra and search results for common polymers used in separators.

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ANALYTICAL SUMMARY

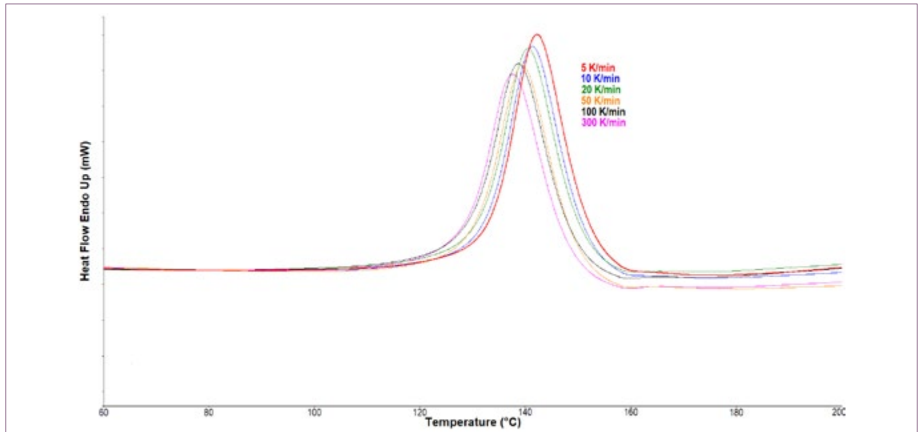
Investigation of Cooling Rate Effect on Polypropylene Separator Properties

The processing conditions used in polymer production has a great effect on the final characteristics of the material. In separators, there are several parameters that have a significant impact on the overall performance of the battery.

Differential scanning calorimetry may be used to investigate the effects of cooling rate on thermal characteristics of materials such as polypropylene, including melting point and enthalpy of fusion.

In this work, a 250 µg sample of polypropylene separator was cooled from 200 °C to -30 °C at different rates, before being heated to 200 °C at 300 °C/min. All work was carried out under a helium purge on a PerkinElmer DSC 8500.

The data obtained from this experiment is shown below.



Heat flow curves for polypropylene after cooling at different rates.

It can be seen from the heat flow curves that the cooling rate has a clear effect on the melting point of polypropylene. The melting point (as calculated by the onset of the melting peak) varies from 128.2 °C for polypropylene cooled at 300 K/min to 133.0 °C for polypropylene cooled at 5 K/min. Furthermore, there is a clear variation in the enthalpy of fusion with the sample cooled at 300 K/min giving a value of 302.7 J/g, and the sample cooled at 5 K/min, a value of 349.6 J/g.

This application demonstrates the use of differential scanning calorimetry for the determination of important thermal parameters in polymeric materials used in separators. Understanding this information can provide insights into how a separator may affect the final performance of a battery. Using a power compensated DSC instrument such as a DSC 8500 provides the user with the ability to heat and cool at much faster rates than would be achievable on a standard heat flux system.

DSC 8500

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INTRODUCTION

Battery Recycling

As battery demand increases due to various applications such as electric vehicles, battery recycling will become more important to reduce the environmental and societal impacts caused by obtaining critical materials such as lithium. Due to the fact the final applications will remain the same, recycled battery materials will need to meet the same strict requirements as those imposed on virgin materials. Furthermore, gaining an understanding of each part of the recycling process in order to optimize them will be of the utmost importance. One key aspect of recycled battery materials analysis is that of black mass. Black mass is a key product obtained during the recycling process and contains elements of interest such as:

- Lithium
- Cobalt
- Nickel
- Manganese
- Aluminum
- Copper

Organic material can result from the electrolyte and binders, which can cause processing issues at later stages.

This section will demonstrate how a selection of analytical techniques may be used to characterize and better understand the impurities present in black mass as well as the utilization of analytical methodologies to optimize the recycling process itself.

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APPLICATION NOTE

Determination of Impurities in Lithium Materials Using the NexION 2000 ICP-MS

Sample Material	Lithium carbonate and lithium hydroxide
Battery Component	Raw and recycled materials
Type of Analysis	Determination of impurities in products from the recycling process
Benefits of Analysis	▪ Determination of trace impurities in LiOH and Li_2CO_3 ▪ Ensuring a high-performance final product
Technologies Used	▪ ICP-MS
Learnings and Insights	▪ Direct analysis of $LiPF_6$ battery electrolytes ▪ Simple sample preparation ▪ High accuracy and precision for a range of potential elemental impurities
Authors	▪ Ruth Merrifield, PerkinElmer, Woodbridge, Canada

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Nexion 2000 ICP-MS

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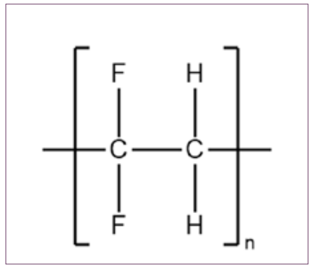
ANALYTICAL SUMMARY

Monitoring Quenching of HF Production from PVDF Pyrolysis Using TG-IR

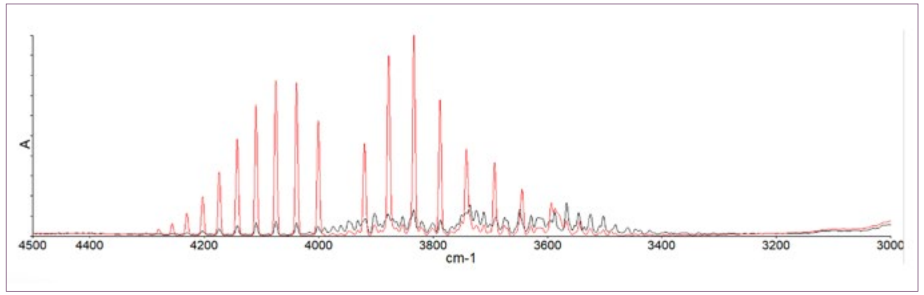
One key step for the processing of spent lithium-ion batteries is to heat them at high temperatures (usually more than 500 °C) to pyrolyze remaining organic and polymeric materials. Along with olefin polymers such as polyethylene and polypropylene in the separator, another frequently occurring polymer is poly(vinylidene fluoride), or PVDF, the chemical structure of which is shown below.



Chemical Structure of Poly(vinylidene fluoride).

One characteristic of PVDF is that it evolves gaseous hydrogen fluoride during thermal decomposition, which can damage equipment and pose environmental and health risks. Recent work demonstrates the use of calcium oxide (CaO) as a sequestering agent to reduce the occurrence of HF formed during pyrolysis. Thermogravimetric analysis coupled with infrared spectroscopy (TG-IR) can be used to demonstrate a reduction of HF present in the gases evolved from the pyrolysis of PVDF. Approximately 3 mg of PVDF was measured into a 50 µL pan in both experiments. In the first measurement, PVDF alone was measured. In the second, a further 3 mg of calcium oxide was added to the pan. Samples were measured from 30 °C to 700 °C at 20 °C/min under a 100 mL/min nitrogen purge using a PerkinElmer TGA 8000 system. Gases were transferred to a PerkinElmer Spectrum™ 3 FTIR spectrometer using a TL 8000e transfer line set to 280 °C with a flow rate of 80 mL/min. FTIR analysis was carried out between 4,500 cm^{-1} and 600 cm^{-1} (to capture the peaks corresponding to H-F) with a resolution of 4 cm^{-1} and two scans per spectrum.

The spectra collected at the point of maximum weight loss are shown below. This demonstrates a clear reduction in the HF evolved during the pyrolysis of PVDF by adding CaO as a reaction medium.



Evolved gas spectrum from the pyrolysis of PVDF with (black) and without (red) the addition of CaO.

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ANALYTICAL SUMMARY

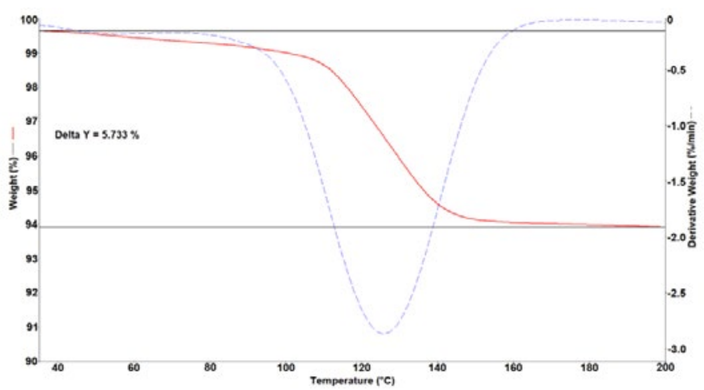
Determination of Residual Electrolyte in Lithium-Ion Battery Black Mass Samples

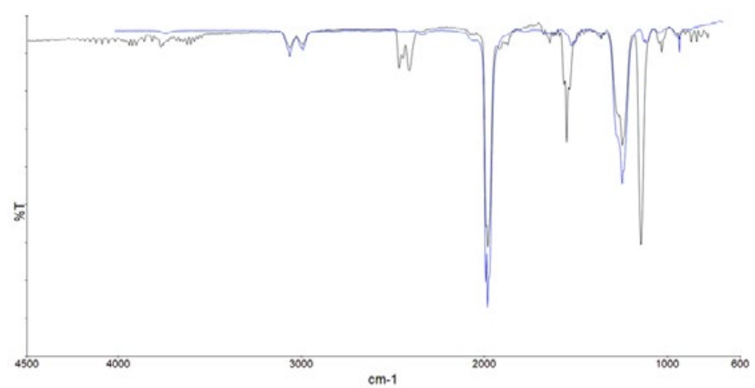
A key aspect of current lithium-ion battery recycling processes is the pre-heating of shredded end-of-life batteries used drive off remaining organic solvents from the electrolyte. Thermogravimetric analysis coupled to FTIR spectroscopy provides a method for not only the quantification of remaining electrolyte in a black mass sample, but also identification of some of the degradation products present in the electrolyte.

In order to determine the quantity of residual electrolyte and identify volatile components, 11.1 mg of black mass was weighed into a platinum crucible. TGA measurements were carried out between 35 and 200 °C at a heating rate of 20 °C/min under a 30 mL/min nitrogen purge using a PerkinElmer STA6000. Evolved gases were transferred to a FTIR gas cell using a TL8000e transfer line heated to 280 °C at a flow rate of 20 mL/min. IR spectra were collected in continuous mode using a PerkinElmer Spectrum 3 FTIR spectrometer over a range of 4500 – 600 cm^{-1} using a spectral resolution of 8 cm^{-1}.

The TGA data is shown below alongside the mean FTIR spectrum averaged over the duration of the weight loss.

The TGA data allows us to quantify the volatile content remaining in the black mass. In this case we can see that the weight loss, and therefore the volatile content, is equal to approximately 5.7%. The IR spectrum provides evidence that the solvent present is ethylene carbonate, a common solvent used in battery electrolytes. There are peaks which allude to the presence of known degradation products from the extended use of lithium-ion batteries. The fine band structure centred around 4000 cm^{-1} corresponds to the rotational bands in HF. Additionally, the strong band at 988 cm^{-1} and the band at 1413 cm^{-1} correspond to a P-F stretch and a P=O stretch respectively which demonstrates the possible presence of POF_3. Both HF and POF_3 are known degradation products from the degradation of $LiPF_6$, the most common lithium-ion battery conducting salt.





TGA data (left) and FTIR spectrum (right) of initial solvent-evaporation step during heating of black mass.

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APPLICATION BRIEF

The Determination of Major Components in Black Mass with the Avio 550 Max ICP-OES

Sample Material	Black mass
Battery Component	Recycled battery material
Type of Analysis	Determination of major elements in black mass
Benefits of Analysis	▪ Understand major elemental constituents of black mass before further processing ▪ Determine contaminant levels to eliminate potential problems with further processes
Technologies Used	▪ ICP-OES
Learnings and Insights	▪ A clear, effective sample preparation procedure for black mass ▪ Use of SmartQuant™ to provide rapid semiquantitative data for up to 75 elements ▪ Use of at least two wavelengths per element allows for verification of results
Authors	▪ Chenija Jiao, PerkinElmer, Shanghai, China ▪ Ken Neubauer, PerkinElmer, Shelton, USA

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Avio 550 Max Fully Simultaneous ICP-OES

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INTRODUCTION

Emerging Battery Technologies

So far in the electric revolution, the vast majority of batteries have been lithium-ion which uses well established chemistries. However, emerging technologies have started to emerge which promise to solve some of the safety, sustainability and performance issues encountered with lithium-ion batteries. Some of the most prominent of these are solid-state batteries, which use a solid electrolyte rather than the more conventional liquid electrolyte, and sodium-ion batteries, which use much more readily available sodium compounds rather than lithium. As these new technologies become increasingly commonplace, the need for analytical techniques to understand them will become more important. In the case of solid-state materials, thermal and mechanical techniques may be used to investigate structural and chemical properties. For sodium-ion batteries, chromatographic techniques are used to investigate electrolyte degradation.

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APPLICATION NOTE

GC/MS Analysis of Degradation Products in Propylene Carbonate-Based Sodium-Ion Battery Electrolytes

Sample Material	Electrolyte
Battery Component	Sodium-ion battery electrolyte
Type of Analysis	Determination of degradation products in a novel electrolyte
Benefits of Analysis	■ Understand compatibility of various electrolyte mixtures with sodium metal ■ Semiquantitative analysis of the decomposition products
Technologies Used	■ GC/MS
Learnings and Insights	■ Determination of electrolyte/additive mixtures that are stable in contact with a sodium metal anode ■ Determination of decomposition products with a semiquantitative approach
Authors	■ Andreas Hoffman, KIT, Germany ■ Nicholas Lancaster, PerkinElmer, UK ■ Gerlinde Wita, PerkinElmer, UK

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GC/MS

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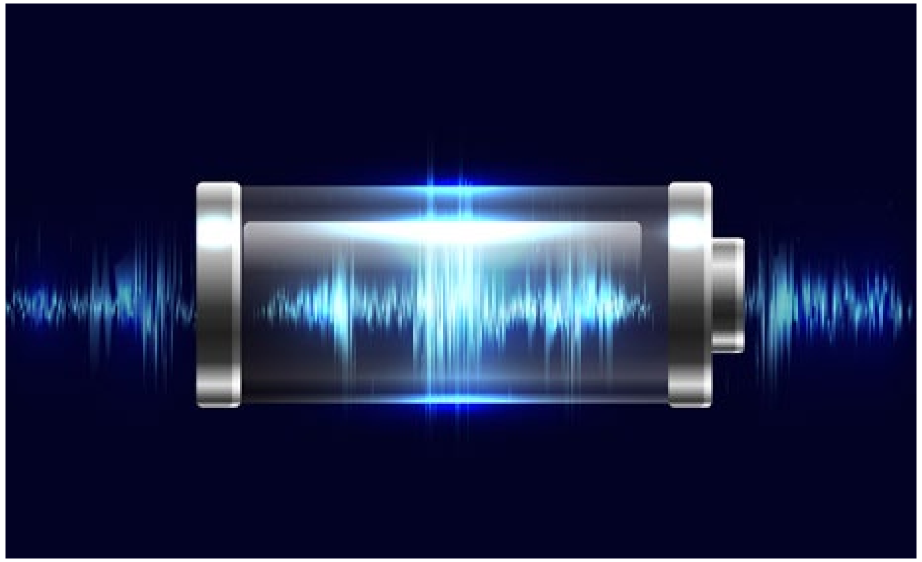
APPLICATION NOTE

Degradation Analysis of a Solid Electrolyte Using TG-IR-GC/MS

Sample Material	Electrolyte
Battery Component	Solid polymer electrolyte
Type of Analysis	Qualitative analysis of degradation products from a solid polymer electrolyte
Benefits of Analysis	▪ *In situ* analysis of evolved gases by coupling of techniques ▪ Determination of degradation products using both FT-IR spectroscopy and GC/MS
Technologies Used	▪ TG-IR-GC/MS
Learnings and Insights	▪ Determination of main polymer backbone ▪ Reverse engineering of polymer electrolyte; understanding which additives and side groups are present
Authors	▪ Kieran Evans, PerkinElmer, UK



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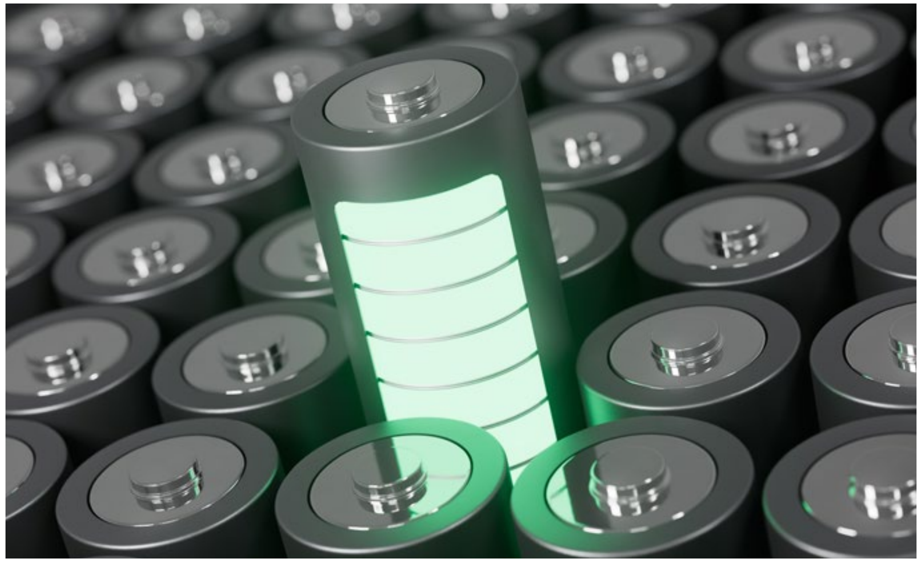
APPLICATION NOTE

TMA and STA to Optimize Sintering Process of Solid-State Electrolyte Used in ASSB

Sample Material	Electrolyte
Battery Component	Solid-state electrolyte
Type of Analysis	Qualitative analysis of degradation products from a solid polymer electrolyte
Benefits of Analysis	▪ By using TMA and STA to understand sintering, the process can be optimized to produce electrolytes with better electrical and mechanical properties
Technologies Used	▪ TMA ▪ STA
Learnings and Insights	▪ Insights into thermal behavior of solid-state electrolyte during sintering ▪ Insights into mechanical behavior of solid-state electrolyte during sintering
Authors	▪ Cheng Hua, PerkinElmer, Shanghai, China



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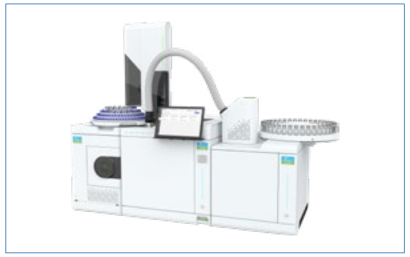
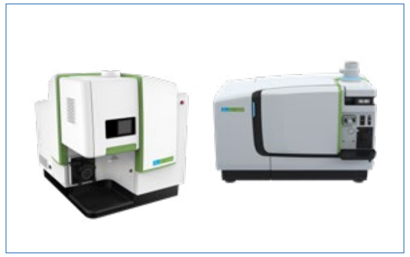


Chromatography



Atomic Spectroscopy

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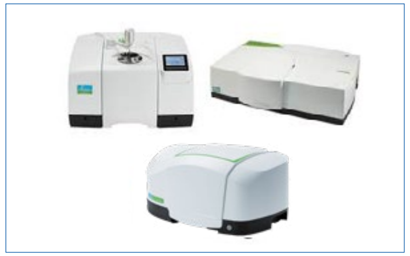
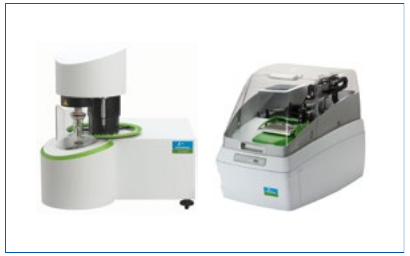


Molecular Spectroscopy



Thermal Analysis

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