The Power Is In Your Hands

UNDERSTANDING BATTERIES

Batteries and energy storage are dynamic and fast-changing markets. Therefore, having powerful and robust solutions for analysis in this area 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 used in batteries across the supply chain can allow 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, focusing on the current market leader, lithium-ion batteries. Innovative analytical solutions for testing every part of the battery, including the anode, cathode, binder, separator, and electrolytes, are demonstrated. Here, we provide easy-to-use links which will allow you to get to the information you seek quickly, and it is easy to see the value in the data generated from the variety of applications addressed and the outstanding performance of the instrumentation used. Moreover, the applications cover the breadth of requirements – from R&D to QA/QC settings.

We are confident that this guide will provide you with valuable insights about batteries and energy storage solutions.
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.

**Anode Analysis**
- General Impurities in Copper
- Bromine Impurities in Copper
- Moisture on Electrodes

**Cathode Analysis**
- Analysis of Aluminum Alloys
- Analysis of Nickel
- Analysis of Lead
- Impurities in Cobalt
- Elemental Impurities in Lithium Cathode Materials

**Binder Analysis**
- Characterization of PVDF (Polyvinylidene Fluoride)

**Electrolyte Analysis**
- Quantification of Carbonates
- Identification of Electrolyte Raw Materials
- Thermal Analysis of Electrolyte Raw Materials
- Thermal Degradation of Ionic Liquids
- Quantification of Conducting Salts
- Thermal Stability of Electrolyte Solvents and Additives
- Monitoring Degradation in Electrolyte Additives

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- Thermal Characterization of Separator Materials
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- Cooling Rates in Separators

**Contact and Support for Solutions**

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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.

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)**
- Determine the quality of raw materials
- Measure ratio compositions and impurities of lithium
- Characterize and develop optimum 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 (FT-IR)**
- 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
INTRODUCTION

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 its 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:

- 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.

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https://www.targray.com/li-ion-battery/anode-materials#:~:text=The%20anode%20(or%20negative%20electrode),Graphite%2C%20coated%20on%20Copper%20Foil.&text=Graphite%20is%20commonly%20used%20as,ions%20between%20its%20many%20layers. (accessed 25/10/21)
Copper (Cu), an important component of most lithium-ion battery anodes, can be found in many minerals in Cu sulfide deposits. This variety of source materials leads to a diversity of impurities, some at very high levels, found in the resulting Cu concentrates. Some of these impurities, such as high levels of arsenic in concentrates from the Pacific Rim, can render the concentrates unsaleable in certain countries. To measure the lowest possible levels of impurities, ICP-MS is required, as it is capable of accurate measurements in the parts per trillion (ppt) range. However, both polyatomic and doubly charged interferences must be dealt with to achieve these levels. These interferences originate from both the plasma and the sample itself. This work describes the challenges encountered in analyzing impurities in metallurgical concentrates, accuracy, and precision comparisons for external calibration versus method of standard addition (MSA). It also documents the importance of reaction management when using reactive gases, specific ammonia, in this application. This work builds on previous work done using an ICP-MS with a single analyzer quadrupole running in Reaction mode. The unique capabilities of the NexION® 5000 Multi-Quadrupole ICP-MS and Universal Cell Technology were proven to be effective at removing spectral interferences, as demonstrated for the removal of the polyatomic CuAr+ interference on Rh+. In addition, the method detection limits obtained to permit the determination of extremely low-level impurities in Cu concentrates. In contrast, excellent spike recoveries demonstrate the accuracy and reliability of the method. These factors are essential in driving process control and increasing the yield and value of the copper end-products.
APPLICATION NOTE

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

Copper (Cu) is frequently used as a current collector for the anode of lithium-ion batteries due to its favorable properties such as high stability and low potential. However, the presence of impurities, such as bromine (Br), in high-purity copper can reduce the thermal and electrical conductivity of the material and, therefore, the battery’s overall performance.

Bromine has two naturally occurring isotopes at m/z 79 and 81, both suffer from copper oxide interferences. Coupled with the low ionization efficiency of Br (5%), the determination of bromine in copper is extremely challenging. Therefore, having an ICP-MS that can effectively remove the oxide interferences, prevent additional interferences from forming, and accurately quantify at low analyte signals would be a significant advantage.

In this application note, PerkinElmer’s NexION® 5000 Multi-Quadrupole ICP-MS was used for the quantification of Br impurities in ultra-high purity copper (approx. 99.999%). This application also demonstrates the high stability of results, with a highly concentrated Cu solution providing results over 4 hours which are shown to be within +/- 0.026 ppb of the initial reading.

SEE THE FULL APPLICATION NOTE
APPLICATION NOTE

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

The presence of water on either the anode or cathode in a lithium-ion battery can seriously hinder its performance. Water may react with the conducting salt (usually LiPF₆) via a hydrolysis reaction or cause swelling, contributing to reduced performance. Therefore, it is important to have a method whereby water on electrodes may be measured. A common method currently used is a Karl Fisher titration. However, this requires several reagents and therefore has a high continuous cost to the user carrying out the analysis.

Thermogravimetric analysis hyphenated to mass spectrometry (TG-MS) provides accurate data on the water absorbed to the surface of an electrode and provides information on other small molecules based on molecular weight. Furthermore, information about the temperature at which these molecules desorb can also be found.

The data obtained from TG-MS may be used to inform decisions regarding the processing of electrodes to ensure minimal water content and thus maximize performance.

TL8500e system allows for 'On-Line' TG-MS analysis

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The data obtained from TG-MS may be used to inform decisions regarding the processing of electrodes to ensure minimal water content and thus maximize performance.
INTRODUCTION

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 Aluminium Oxide (LiNiCoAlO$_2$)
- LMO – Lithium Manganese Oxide (LiMn$_2$O$_4$)
- 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.

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.

APPLICATION NOTE

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

Because of its unique characteristics, aluminum (Al) is used in a wide variety of commercial and industrial applications. However, the utility of Al can be enhanced by combining it with other metals to create aluminum-based alloys, where the non-aluminum additives can make up to 15% of the total alloy by weight. The primary elements added to Al are silicon (Si), iron (Fe), copper (Cu), and zinc (Zn), to improve the alloy’s strength compared to pure Al and also enhance the physical characteristics, such as better conductivity and welding capabilities. Other elements can also be added in various quantities to vary the alloy’s characteristics further.

Because of its popularity and multiple compositions, the London Metal Exchange (LME) lists four different specifications for Al alloy compositions which are primarily used in Europe, Asia, and North America. Si, Cu, Zn, and Fe are considered major additions in these specifications, as they are mostly greater than 1% composition by weight. Therefore, these four elements must be determined with greater accuracy (± 2%) than the others.

Most commercial aluminum applications are aluminum alloys due to their enhanced characteristics compared to pure aluminum. Therefore, PerkinElmer’s Avio® 220 Max hybrid simultaneous ICP-OES is the ideal choice for laboratories performing this application. The Avio 220 Max ICP-OES uses a CCD detector, providing simultaneous background and analyte measurement, which is important when dealing with complex matrices, such as alloys.

This work describes the determination of additives to Al in aluminum alloys at the LME specifications, using the Avio 220 Max ICP-OES.

SEE THE FULL APPLICATION NOTE
APPLICATION NOTE

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

Nickel (Ni) is one of the most widely used metals due to its corrosion resistance and strength at high and low temperatures. While it is most frequently used in the production of steel, it is also an important component in a variety of other alloys and is commonly used in electronics, plating, and rechargeable batteries. These varied uses require nickel of different purities or grades. In some applications, high-purity nickel is required, while lower-grade nickel will suffice for others. The London Metal Exchange issues impurity identity and concentration specifications for various Ni grades in their publication “Special Contract Rules for Primary Nickel.” This work demonstrates the ability of PerkinElmer’s Avio® 550 Max fully simultaneous ICP-OES to analyze solutions of 1% nickel for elements at the levels specified by the London Metal Exchange. Spectral interferences from high matrix samples were overcome using MSF, allowing all defined elements to be measured at their specified concentrations.
APPLICATION NOTE

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

Although lead (Pb) is highly toxic to living organisms and has been phased out of a wide variety of products, it is still commonly used in several applications, most notably lead-acid batteries, alloys, radiation shielding, flashing in the construction industry, ammunition, and as lining in industrial pipes and baths carrying corrosive substances. With this assortment of uses, the required purity or grade of lead varies; as a result, lead is produced in various purity levels. The London Metal Exchange lists specifications for various Pb grades in their publication “Special Contract Rules for Standard Lead.” This work demonstrates the ability of the Avio® 550 Max ICP-OES to analyze solutions of 1% lead at London Metal Exchange specifications for purities ranging from 99.97% to 99.994%. Although the high matrix concentration results in spectral interferences for a few elements, these can be overcome by using multicomponent spectral fitting (MSF), allowing all of the specified elements to be measured at their required concentrations. The Avio 550 Max fully simultaneous ICP-OES can easily measure trace elements in the lead to meet the London Metal Exchange requirements.
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). Unfortunately, cobalt is considered to the highest supply chain risk of all raw materials used in EVs. 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

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

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
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</tr>
<tr>
<td>Bi</td>
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</tr>
<tr>
<td>Cu</td>
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<tr>
<td>Fe</td>
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<td>Ni</td>
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<tr>
<td>Te</td>
<td>0.51</td>
</tr>
<tr>
<td>TI</td>
<td>4.20</td>
</tr>
</tbody>
</table>

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#:~:text=Cobalt%20is%20considered%20the%20highest,impurities%20in%20lithium%20ion%20EV%20batteries (accessed 06/12/21)
Determination of Elemental Impurities in Lithium Battery Cathode Materials using the NexION 1000 ICP-MS

The quality of the cathode material of a lithium-ion (Li-ion) battery, especially the ratio of the primary elements and the concentrations of impurities, has a great impact on its charging and discharging performance as well as safety. For example, in the battery formation process, metal impurities such as Fe, Cu, Cr, Zn, or Pb will be oxidized on the cathode and then reduced and deposited on the anode when the applied power reaches the redox potential of the respective metal. This deposition of impurities has two consequences.

First, impurities can block Li ions reducing the coulombic efficiency of the battery, essentially its ability to charge and discharge. Second, impurities can encourage the formation of dendrites, which are microstructures that form on the anode and can pierce the battery’s separator leading to a short circuit. Since conventional liquid electrolytes are flammable, a short circuit is a fire hazard and could also cause some electrolytes to decompose exothermically, adding safety issues. Therefore, it is particularly important to monitor and address the presence of impurities in cathode materials.

Conventionally, inductively coupled plasma optical emission spectrometry (ICP-OES) has been the method of choice for the battery industry to determine the ratios of primary elements and the concentrations of impurities. However, impurity control is becoming more stringent with the development of new battery technologies, leading to the need for ever-decreasing detection limits for metal impurities. Presently, some detection limits have dropped below what is practical to be detected by ICP-OES, particularly for Cr, Cu, Fe, Zn, and Pb. Most manufacturers set the detection limit of these five elements to be <1 ppm, which can be as low as ten ppb in the final solution after sample digestion. While this would be challenging for ICP-OES, inductively coupled plasma mass spectrometry (ICP-MS) is an excellent alternative with higher sensitivity and lower detection limits than ICP-OES.

This work reports the determination of Cr, Cu, Fe, Zn, and Pb impurities in lithium battery cathode materials, namely lithium nickel cobalt manganese oxide (LNCM), as well as two precursor materials, lithium cobalt oxide (LCO) and lithium manganese oxide (LMO), using a PerkinElmer NexION® 1000 ICP-MS. It includes techniques used to address high total dissolved solids (TDS), high acid content, and interferences.
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

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.
APPLICATION NOTE

Characterization and Analysis of Polyvinylidene Fluoride (PVDF)

PVDF, along with other polymers such as SBR and PTFE, is commonly used as a binder in the electrodes of lithium-ion batteries. It is the most common material used as a binder due to its electrochemical and chemical stability and high adhesion to the current collector. The binder serves several purposes, including aiding film formation and improving dispersion of the active material in the solvent. Like many battery components, understanding both the chemical composition and thermal behavior of PVDF is incredibly important for predicting performance, especially under the harsh conditions of a lithium-ion battery.

IR spectroscopy can be used to verify the identity of a sample of PVDF by searching against a commercial spectral library. This provides a fast and simple method for the identification of incoming raw materials.

Differential Scanning Calorimetry may be used to investigate the effect of cooling rate on important physical parameters in PVDF, which can, in turn, inform important processing parameters.

Thermogravimetric Analysis gives the user information on how PVDF would act at very high temperatures, which may be seen during thermal runaway or a fire.

The data demonstrated in this application note is indicative of one type of binder. It is important to note that these analytical techniques can be successfully applied to any polymer used as a binder, including PTFE and SBR.
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.
APPLICATION NOTE

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

The electrolyte solutions commonly used in commercial lithium batteries consist of lithium salts, organic solvents, and some additives. The organic solvents are mainly cyclic carbonates, such as ethylene carbonate and propylene carbonate, or chain carbonates, diethyl carbonate and ethyl methyl carbonate. The composition and ratio of these carbonates have important implications for energy density, cycle life, and lithium-ion batteries’ safety. Therefore, studying the composition and content of carbonates in the electrolytic solution plays an important role in the development and quality control of lithium-ion batteries.

In this application note, a qualitative and quantitative method for the determination of nine carbonates in electrolytic solutions was established using the PerkinElmer Clarus® SQ 8 GC/MS with electron ionization (EI) source.

Chromatograms of nine common carbonate solvents used in battery electrolytes. With electron ionization (EI) source and selected ion recording (SIR)
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. FT-IR 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 4 cm\(^{-1}\) resolution. Example results obtained from electrolyte solvents and additives are shown overlaid with library ‘best hit’ spectra.
Carbonates are the most common class of solvents used in both primary and secondary batteries. Understanding phase transitions in these solvents is beneficial as freezing, and other changes will have a detrimental effect on the ionic conductivity of the electrolyte.

Differential Scanning Calorimetry (DSC) provides a method to accurately measure thermal transitions. The PerkinElmer DSC 8000 is a power compensated differential scanning calorimeter which provides the benefit of a small, double furnace. This allows for controlled cooling down to lower temperatures than achievable with a traditional, single furnace heat flux system.

DSC allows the user to understand not only at what temperature the eutectic point may occur, but also investigate any other phase transitions taking place. This will provide information on how the solvent will behave when implemented in low-temperature applications. The data below shows the DSC curves for 11 different binary carbonate solvent mixtures.

Heat flow curves for 11 DMC/EMC mixtures.
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 FT-IR 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.

The IR spectra were collected using a PerkinElmer Spectrum 3 FT-IR 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.
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.

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.

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ANALYTICAL SUMMARY

Quantification of LiPF$_6$ in Electrolytes Using FT-IR Spectroscopy

The electrolyte in a lithium-ion battery serves as an insulating medium which allows for transport of ions between 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™ FT-IR 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.

Below is an example spectrum showing a 1.00M solution of LiPF$_6$ in propylene carbonate.

![IR Spectrum of a 1.00M solution of LiPF$_6$ in propylene carbonate.](image-url)
For this application, the height of the peak at 842 cm⁻¹ (corresponding to the P-F stretch in LiPF₆) 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 LiPF₆ concentration.](image)

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 0.98 M sample, is indicative of a slight shortfall in LiPF₆ concentration, which could have significant effects over the life of the battery. The second, a 0.55 M 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:

<table>
<thead>
<tr>
<th>Actual Concentration (M)</th>
<th>Predicted (M)</th>
<th>Error (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>0.61</td>
<td>0.06</td>
</tr>
<tr>
<td>0.98</td>
<td>0.97</td>
<td>0.01</td>
</tr>
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</table>

This work demonstrates the use of FT-IR spectroscopy as a screening method for the quantification of LiPF₆ in lithium-ion battery electrolytes before the use of a confirmatory technique such as ICP-OES. FT-IR 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.
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.

The data obtained from this experiment is shown below. 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.
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.

FT-IR spectroscopy provides a fast and simple method in which degradation of 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 FT-IR 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.

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.
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 and chemical and electrochemical stability are required for separator materials. Research is now focusing on separator materials that offer superior heat resistance and are less prone to degradation.

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

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.

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.

DTG data for higher (red) and lower (blue) filled samples.
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™ FT-IR 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.

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

**Investigation of Cooling Rate Effect on Polypropylene Separator Properties**

The processing conditions used in polymer production have 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.

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.
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