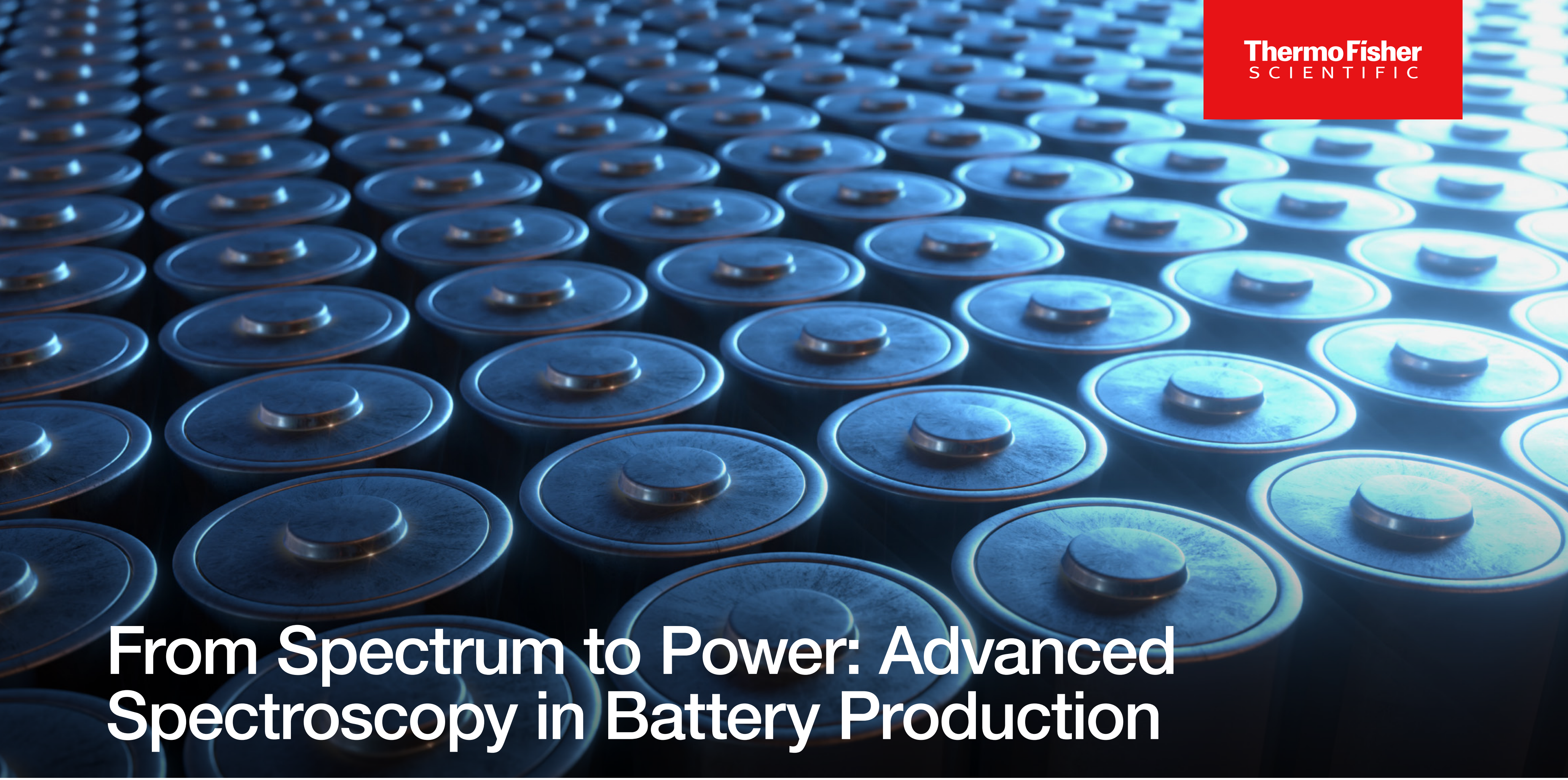


From Spectrum to Power: Advanced Spectroscopy in Battery Production

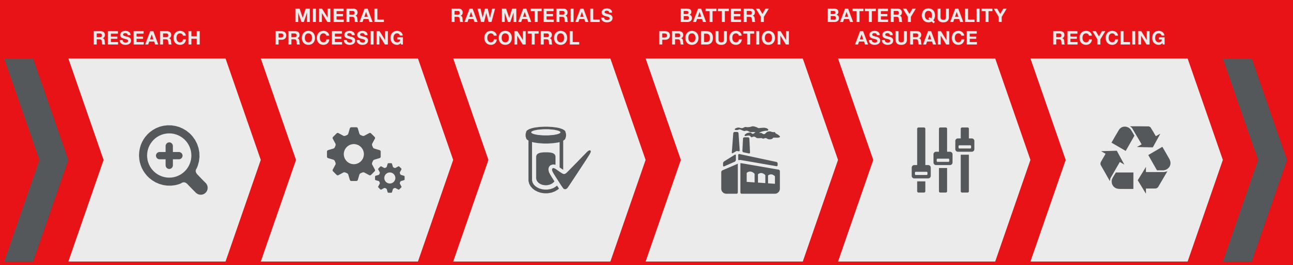
A Deep Dive into Raman, FTIR, and Near-Infrared Analysis in Manufacturing Workflows

Introduction

The production of high-performance batteries requires a thorough understanding of their component materials and chemical processes. By analyzing the vibrations of molecules, vibrational spectroscopy provides essential insights into the composition, structure, and bonding characteristics of battery materials.

Vibrational spectroscopic techniques of FTIR and Raman have emerged as valuable tools in the analysis of everything from raw materials in lithium mines to sophisticated internal electrodes and even the components of recycled battery cells. The real-time analyses provided by these instruments help researchers and manufacturers monitor the chemical and physical changes occurring during battery development or operation.

This eBook describes many of the ways that vibrational spectroscopy tools developed by Thermo Fisher Scientific can be used to enhance the efficiency and safety of lithium-ion battery manufacturing at all stages of battery production.



RESEARCH

MINERAL PROCESSING

RAW MATERIALS CONTROL

BATTERY PRODUCTION

BATTERY QUALITY ASSURANCE

RECYCLING

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Accelerate your battery research and development

With growing needs for next-generation battery technology that features improved performance and reduced costs, the U.S. Department of Energy has outlined research goals for the battery industry. These goals center around new materials, new chemistries, and better diagnostics for battery testing. Spectroscopic analysis, and specifically vibrational spectroscopy, is a powerful tool that can move research forward and accelerate the development of more advanced batteries.

Spectroscopy basics

Spectroscopy is the study of how matter interacts with light. The electromagnetic spectrum encompasses the range of all types of light, with visible light being one small segment of the electromagnetic spectrum. Other types of radiation that make up the spectrum are microwaves, infrared (IR) light, ultraviolet (UV) light, X-rays, and gamma rays. (See Figure 1a, below.)

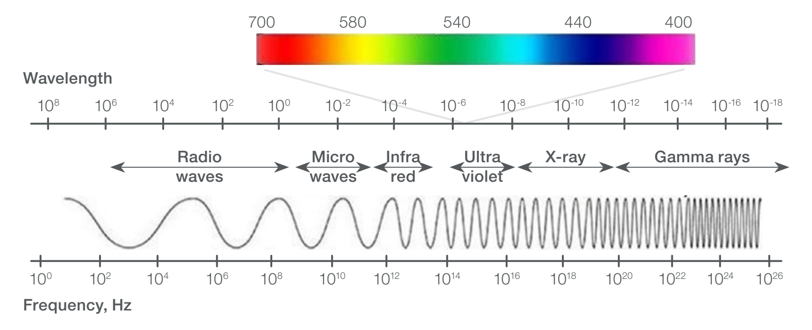


Figure 1a. The electromagnetic spectrum, delineated into sections based on relative energies.

The fundamentals of vibrational spectroscopy

Spectroscopy uses light to excite molecular motion and uses the measured spectrum to learn about the material under study. The part of the electromagnetic spectrum that corresponds to frequencies of molecular vibrations is the infrared, whereas UV-vis probes electronic structure of molecules and microwave spectroscopy excites molecular rotations. (See Figure 1b.) Each interaction and type of spectroscopy provides different information about the material. The peaks in a vibrational spectrum carry information about the molecular structure and can therefore be used for material identification. There are two main vibrational spectroscopy approaches depending on the characteristics of the material of interest: infrared and Raman.

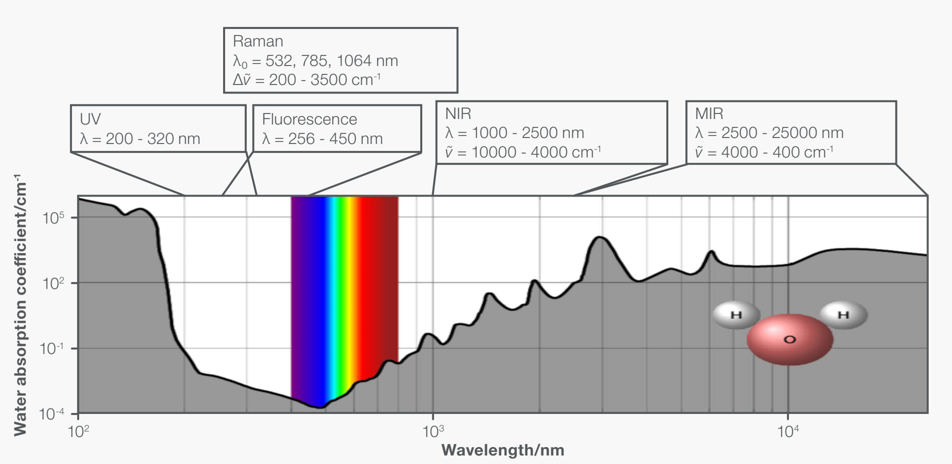


Figure 1b. Electromagnetic absorption spectrum of water.

A wealth of information

Vibrational spectroscopy, which probes molecular vibrations within materials, is an incredibly powerful analytical technique that can help reach these goals.

There is a wealth of information in a vibrational spectrum. Figure 1c highlights some of the knowledge that can be gleaned from the interaction of a sample with light when using Raman spectroscopy, a vibrational spectroscopic technique. The presence and position of peaks can identify materials and can be used to determine the molecular structure of the material, while peak intensity gives information about the quantities present. When comparing spectra, peak shifts or relative peak widths can provide insight about the three-dimensional structure of a material and the relationship between its physical and chemical properties.

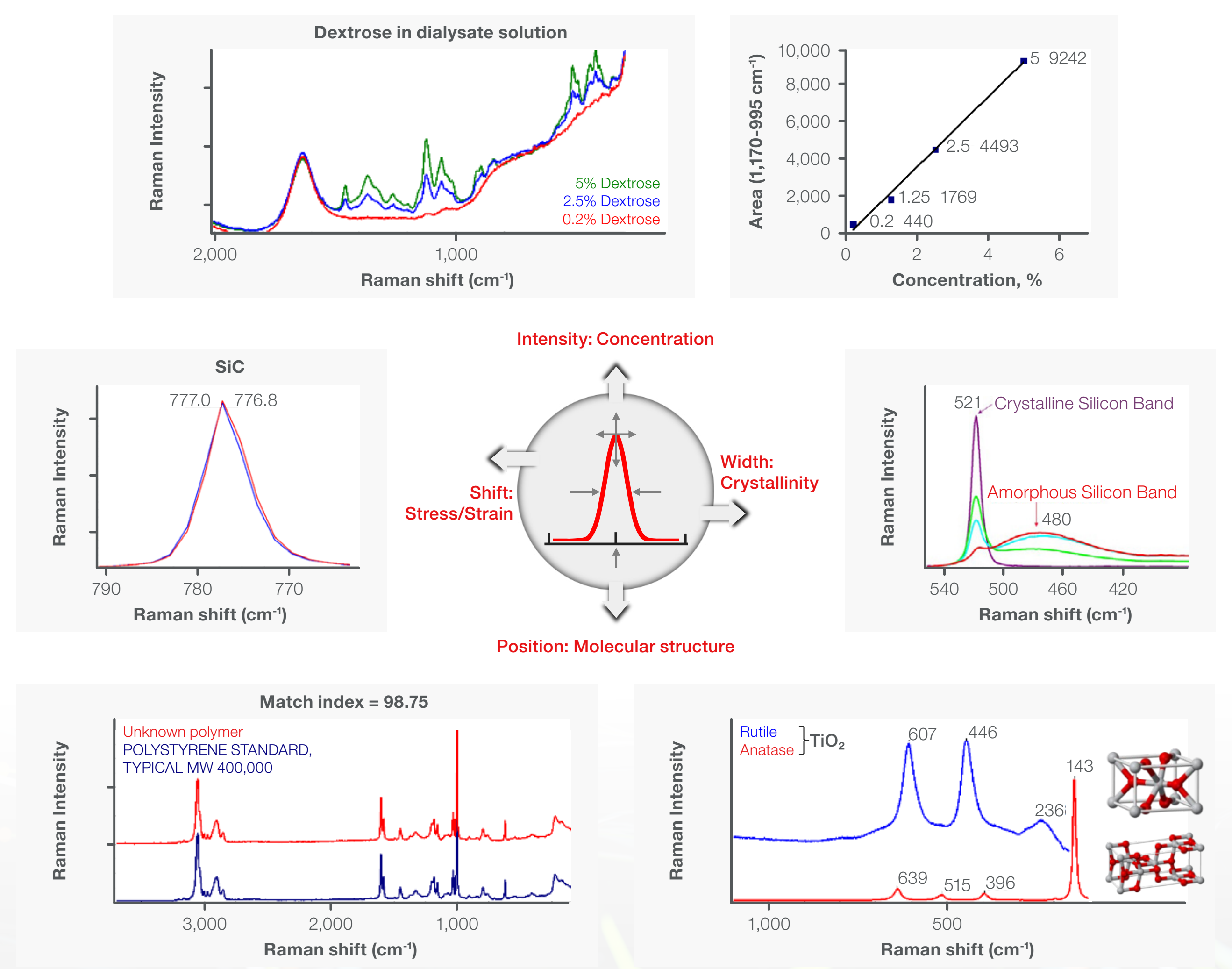


Figure 1c. Information available from analysis with Raman spectroscopy, a vibrational spectroscopic technique.

FTIR spectroscopy

Fourier transform infrared spectroscopy, or FTIR, measures chemical vibrations. Because each chemical has a unique combination of atoms, each infrared spectrum is a unique combination of vibrations, which results in each chemical having its own “molecular fingerprint.” With FTIR’s broad spectral range, it is possible to measure across a wide portion of energies to excite all IR-active vibrations of a sample to identify its composition.

Spectroscopy connects the structure of materials with function. It provides the link between the composition of the material, or how those atoms and molecules are put together, with how that composition informs what those materials can do. The information in a vibrational spectrum is rich. The peak positions indicate the structure of the molecule, and when compared with library spectra or standards, the material can be identified very quickly. Peak intensities can provide information about how much of a material is present, making it is possible to do quantitative studies with the right calibrations. Additional information in peak shape or the shift of those peaks is can provide important information about the physical and chemical properties of the material under study. With relatively easy to almost no sample preparation, FTIR can rapidly screen materials and identify what the material is, know how much of it there is, and what form is present. This can be done on a wide range of sample types, with almost any kind of material, and at any point in the process. With batteries, as this eBook discusses, it can do this from the incoming raw materials through the research and development process, and all the way to failure analysis and recycling.

Raman spectroscopy

Raman spectroscopy is a spectroscopic technique in which a sample is excited with a laser, and the light scattered by the sample is analyzed. Raman spectroscopy looks at the interactions between the excitation laser light and the covalent bonds within the molecules in the sample. Raman can provide detailed molecular information, although the bonds which will be best represented tend to be highly symmetric bonds like those most commonly found in the backbones of molecules or in a crystal lattice.

Raman is also very sensitive to the slightest changes in bond angle or bond strength, which makes it an excellent means for distinguishing between different molecular morphologies or sensing stress in a crystal lattice. These characteristics make Raman an excellent means of characterizing carbon materials in general and graphene specifically, as those materials are primarily composed of highly symmetric carbon-carbon bonds.

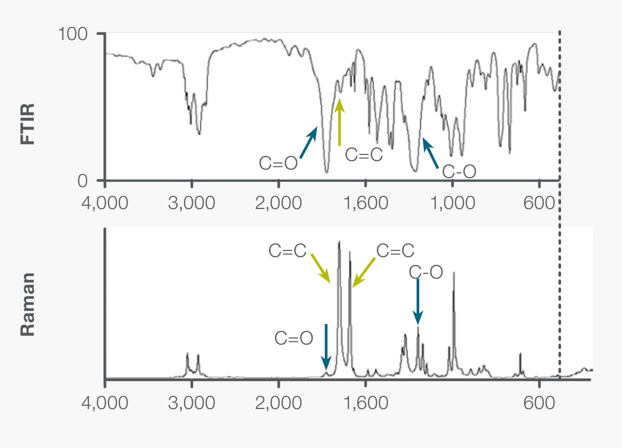


Figure 1d. FTIR and Raman spectra of trans-cinnamyl acetate. Bonds labelled with blue arrows are more prominent in FTIR spectrum and the bonds labelled with green arrows are more prominent in Raman spectrum.

FTIR vs Raman: a brief comparison

FTIR and Raman spectroscopy both probe molecular vibrations, but they acquire information from the molecule differently. FTIR investigates dipole moment changes and Raman probes the changes in polarizability of a molecular vibration. This means that certain motions are better seen in one technique vs the other. FTIR and Raman are considered complementary and the example spectra in Figure 1d illustrates that relationship.

Vibrations, like those generated by carbon-carbon bonds, show up with much greater intensity in the Raman spectrum (bottom image) than they do in the infrared spectrum (top). Notice the intense peaks from the C=C double bond in the Raman spectrum, compared to the relatively small C=C peak on the shoulder of a much larger peak in the FTIR spectrum. Conversely, heteroatomic vibrations between, for example, carbon atoms and oxygen atoms, where there is a dipole moment, are stronger in the infrared spectrum.

When the two techniques are each used to probe a single sample, they generate complementary information. This allows significant information to be generated from a wide range of materials. Thermo Scientific instruments like the Thermo Scientific™ DXR3 Raman Microscope, Thermo Scientific™ DXR3 Raman Flex Spectrometer, Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer and the Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer can be configured with a wide range of sampling accessories to achieve different analytical goals. Certain configurations will even help obtain electrochemical information. On the next page are some examples of how these techniques can be used to address challenging areas of battery research.

Accelerate understanding of battery components

Materials analysis

Vibrational spectroscopy can help understand structural functions and the connection between materials and what they can be used for. It does so easily and rapidly—often with very little to no sample preparation. The technique can be applied to a wide range of sample forms. For example, Raman spectroscopy can distinguish between similar battery materials like lithium oxide, lithium peroxide, lithium hydroxide anhydrous, lithium carbonate, and lithium hexafluorophosphate. (For further discussion, see in Section 4.) Almost any material imaginable can be studied with vibrational spectroscopy!

Cathodes

Conventional cathode materials currently being used are associated with high cost, have safety and toxicity issues or have capacity fade issues. Because of this, researchers are looking at innovative new composites or high-surface area nanomaterials to develop better cathodes. Raman spectroscopy can be used to analyze graphene to assess its potential use in cathodes (See Section 3). Additionally, thermogravimetric analysis coupled with infrared spectroscopy (TGA-IR) is a great tool to evaluate why a multi-component cathode material might fail. (See Section 5.)

Anodes

With respect to the anode, graphitic materials are commonly used today, but the theoretical capacity is limited for graphite. One very attractive alternative as an anodic material is silicon. Silicon has a very high theoretical capacity; however, a current barrier to implementing silicon as an anode material is that it undergoes expansion—volume changes that occur as the battery cycles—that can lead to degradation. Controlling this aspect could be one opportunity for research advancements with respect to using silicon. Researchers are trying to address this by looking at nanocrystalline silicon, and Raman spectroscopy is a great tool that helps study different forms of silicon at the microscopic level.

Electrode chemistry

A battery's electrodes are an incredibly important component of the electrochemical cell, and in commercially available lithium-ion batteries, the traditional electrode materials have very nearly reached their limits in terms of their ability to provide better performance with desired cost reduction. Because of this, researchers are looking into new materials that can allow battery technology to leap into the next level of capacity.

The key to solving such issues is understanding the electrode chemistry and the overall role it is going to play in the cell. It is critical to be able to measure the composition, the morphology, and all the chemistry that's happening at those electrodes, at the same time. Vibrational spectroscopy is extremely well-suited to meeting those needs. A couple of examples here show the kinds of information that can be generated:

A Raman image map of carbon electrode material alongside plots of Raman spectra for graphite and graphene are shown in Figure 1e. Graphene was grown onto a substrate and then transferred onto silicon. Raman spectroscopy is wonderful in analyzing graphene because of the symmetric vibrations of carbon-carbon bonds in graphene. Raman spectroscopy can be used to probe the broader overall morphology of the material; for example, Raman spectra can distinguish between the different allotropes of carbon, from graphite to single-layer graphene, to carbon nanotubes or buckyballs. The graphs on the right side of Figure 1e show how the spectra of graphite and graphene differ from one another, as indicated by the changes in the relative intensities of the key characteristic peaks. Furthermore, there is also a region in the spectrum where a defect peak will emerge, should any defects be present in the material.

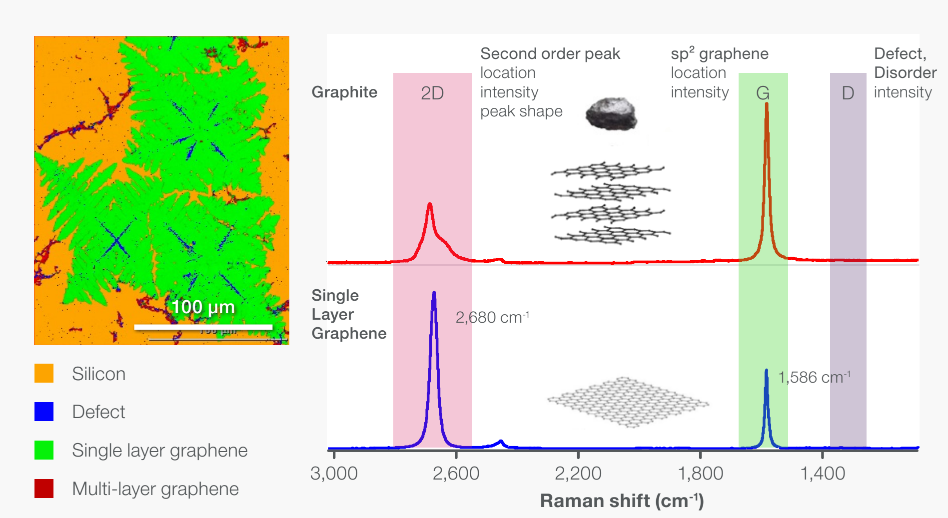


Figure 1e. Graphite and graphene reveal different structures in a Raman image map.

In the Raman microscope image on the right, which is shown as a color coded chemical map, the primary structure (shown in green) is the single-layer graphene that was grown. In blue are the defect regions. There are also little veins of red and blue: those are actually creases in the graphene layer that developed when it was transferred onto the silicon substrate. This demonstrates that a wealth of information can be acquired quickly and easily through non-destructive Raman analysis.

The second example involves silicon expansion. Previously mentioned challenges with silicon—again, a very attractive potential anode material—revolve around understanding how the expansion issue can be minimized, especially during overcharging. One way that researchers are trying to investigate this is by looking at nanocrystalline silicon. Figure 1f shows a Raman image map of a nanocrystalline silicon powder. The Raman spectrum of silicon displays dramatic peak changes between the two forms of the element. The peak shifts and broadens depending on whether the silicon exists in crystalline or amorphous form. The respective colors in the associated Raman map image identify exactly how much and where those different forms of silicon are present.

With both cathodes and anodes, there are many challenges in trying to reach the next generation of materials that are going to push the limitations of current technology. Nanomaterials and other composite materials can be examined, and Raman spectroscopy is a very nice way to quickly screen and get a wealth of information to understand the morphologies, structures and different stoichiometries of the cathode materials that are present. That spectral information can be overlayed with the actual video images to provide even deeper insights. (Section 7 demonstrates this further.)

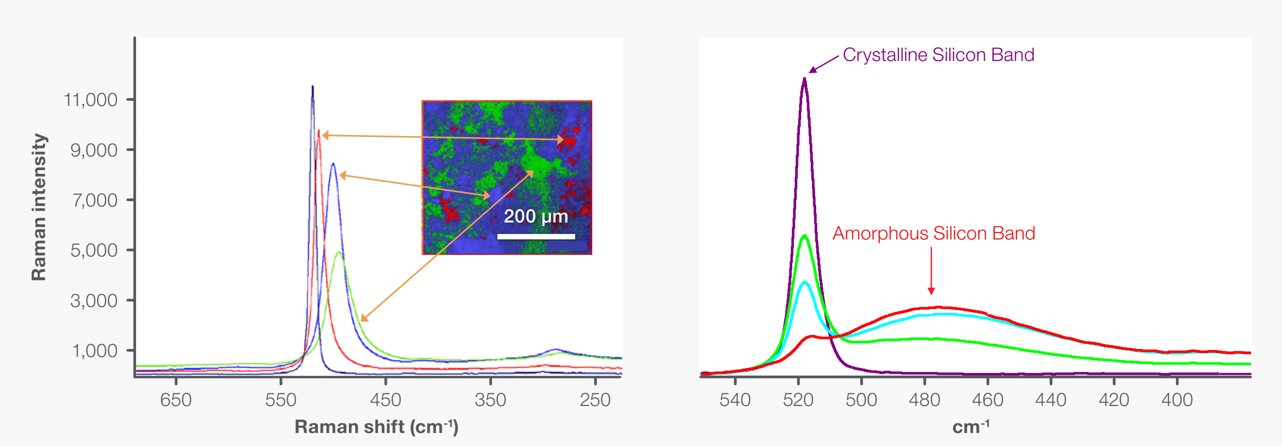


Figure 1f. Raman spectrum and associated image map of nanocrystalline silicon powder.

Electrode coatings

Additionally, electrode coatings or other functional materials that allow for control of the chemistry that's happening in the cell is another area of research. Again, these are attempts to push the limits of the capacities and properties that the batteries have. Some work has been done utilizing an accessory called the Jackfish Spectroelectrochemical Cell from Pike Technologies. The Jackfish Cell fits right into the sample compartment of the Nicolet iS50 research FTIR. With this configuration, simultaneous infrared spectra are obtainable as the potential is swept. This helps obtain sub-monolayer information about the chemistry and the chemical structure at the electrode surface simultaneously. This technique is called ATR SEIRAS, or attenuated total reflection surface-enhanced infrared absorption spectroscopy. The ATR technique is extremely simple to use, and this accessory coupled with the spectrometer provides chemical structure and dynamics of that electrochemical cell. This technique enables surface-selective spectrochemical measurements.

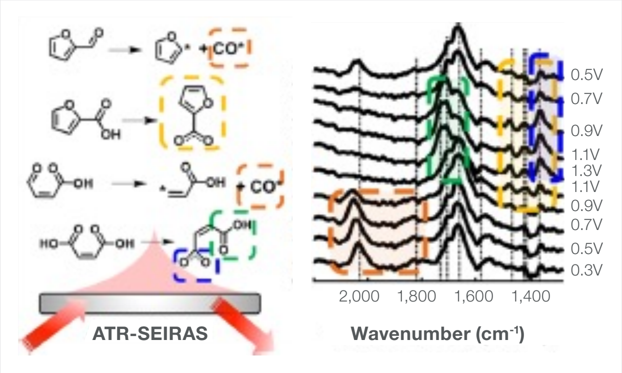


Figure 1g. ATR-SIERAS measurements reveal spectrochemical information about electrode surfaces. (Attribution to: Hasse, J.; Agrawal, N.; Janik, M.; Holewinski, A. *J. Phys. Chem. C* **2022**, 126, 7054–7065**)**

Electrolyte materials and charge transfer analysis

The electrolyte is another critical part of the battery cell. There is a need to move away from the current conventional liquid electrolytes because of potential leakage hazards as well as the limitations in terms of the applications those batteries can support. There is a significant push for moving away from liquid electrolytes completely and instead using solid or semi-solid electrolytes. With solid or semi-solid electrolytes, researchers can start to imagine flexible batteries for use on clothing, toys, smart cards, and smart devices. A few solid electrolyte materials that are of interest are solid polymer electrolytes (SPEs), metal-organic framework materials (MOFs), covalent organic framework materials (COFs), and hydrogels. There is no better tool than vibrational spectroscopy to look at the structure of these materials and assess the charge transfer dynamics that they are enabling in these cells, all with a typical quick screening.

A common challenge with solid polymer electrolytes (SPEs) is that they can exhibit some reduced ionic conductivity. It has been discovered that crystalline regions within the electrolyte are hindering that ionic conductivity. To mitigate this, additives such as dopants have been mixed into the electrolyte to inhibit the formation of those crystalline regions. Raman spectroscopy can be used to probe SPEs and identify regions of crystallinity or amorphous character in the overall electrolyte. The images in Figure 1h show how Raman spectra and Raman mapping can identify different regions, which are color coded for easy recognition.

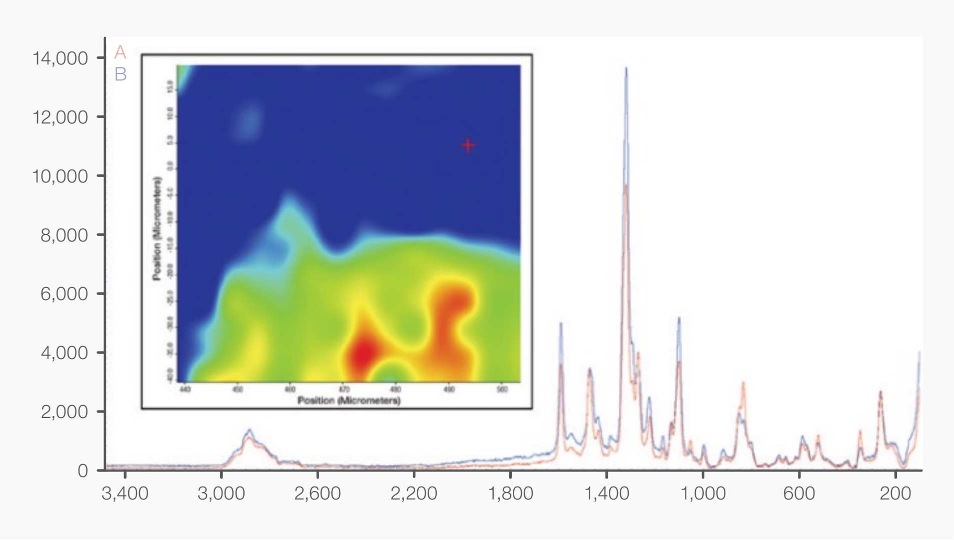
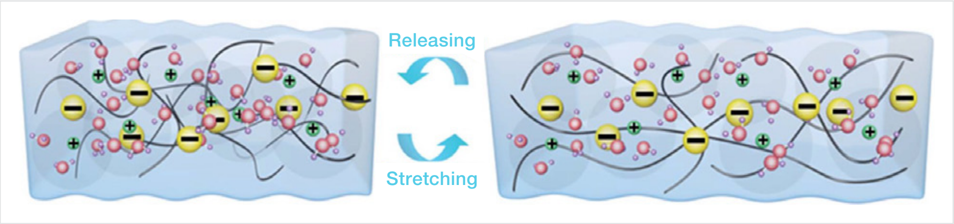


Figure 1h. Raman map of a solid polymer electrolyte (SPE).

Flexible electronics

When it comes to flexible electronic applications, it has been determined that hydrogels have shown promise. The data featured here was collected using a Nicolet iS50 FTIR Spectrometer with the diamond ATR accessory. This work analyzed the cross-linked hydrogels and used the infrared spectrum to verify that the chemical properties of this electrolyte remained unchanged, whether or not this electrolyte is stretched or unstretched. (See Figure 1i.a.) The orange and purple traces shown in the spectra (Figure 1i.b.) are identical, indicating the electrolyte is behaving exactly as it should regardless of the amount of stretching present. In this exciting avenue of research, vibrational spectroscopy is critical in understanding and advancing potential battery-related applications.



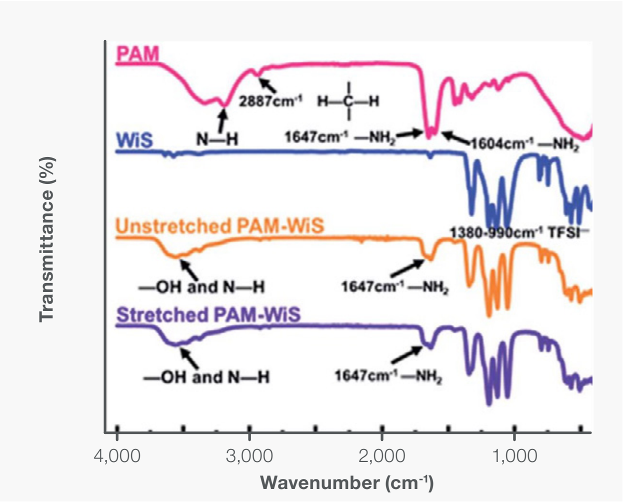


Figure 1i.(a, above) A diagram illustrating cross-links stretched and unstretched flexible hydrogel. (b, below) Spectra for hydrogel in stretched and unstretched conditions reveal their chemical consistency regardless of form. (Attribution to: *J. Mater. Chem. A,* **2022**, 10, 1156**)**

Chemical dynamics

A sampling cell enables *in operando* studies by effectively allowing an electrochemical cell to be built within it. Raman microscopy analysis of the sampling cell allows visualization of the chemistry and the morphology changes happening at the electrode as the battery is cycling.

Figure 1j shows a striking image of an electrode of titanium dioxide. It depicts the study of an electrode that starts off mostly in the anatase form of titanium dioxide. As the battery is cycled, lithium ions move into the titanium dioxide and change it into the orthorhombic structure. The two different forms of titanium dioxide have different Raman signatures.

The Raman maps were collected over time during the cycling of the battery. The color change from mostly yellow (depicting the anatase form) on the left-side images to predominantly red (depicting the orthorhombic form) at the right illustrates that structural change very clearly. This visualization could be done in real time to see the chemical and physical changes at the electrode as the battery is working.

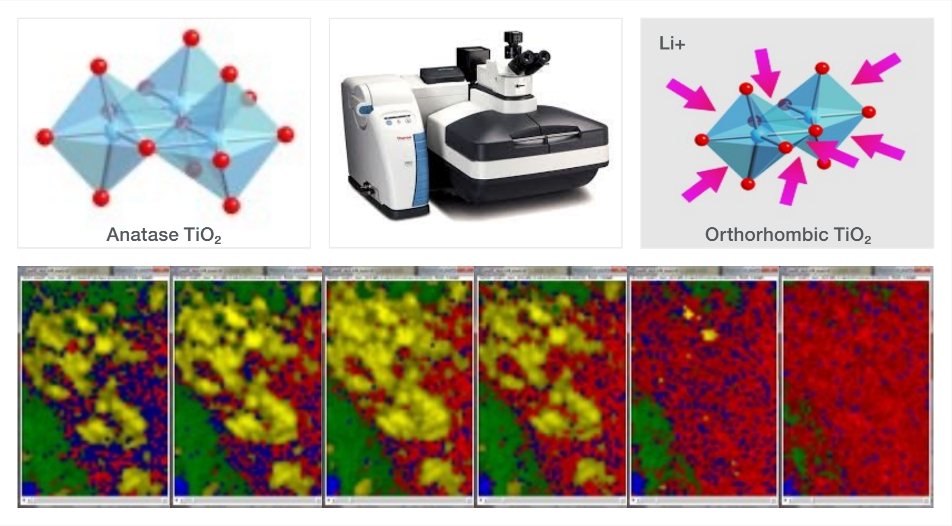


Figure 1j. Raman maps of TiO_2 as it morphs from anatase to orthorhombic form.

Hyphenated analysis

Themo Fisher Scientific’s research FTIR instrument, the Nicolet iS50, can be coupled with other analytical techniques to get even more information out of one cohesive experiment. Infrared spectroscopy can be coupled with gas chromatography (GC-IR), thermogravimetric analysis (TGA-IR), or mass spectrometry (FTIR-GC-MS)—any permutation of these is supported and is being done currently. Each of these options is touched on in other sections within this eBook. Coupling all of this information together really generates a complete picture of the chemical dynamics of a battery. All these options and possibilities surrounding vibrational spectroscopy will hopefully accelerate the advancement of battery technologies and help scientists produce, quickly and safely, the next generation of more powerful and longer lasting batteries.

Real-time monitoring of lithium precipitation, using process and other capabilities of Raman

Raman spectroscopy is utilized heavily in battery research, manufacturing and quality control. This section of the eBook will focus on real-time monitoring of lithium precipitation, using process and other capabilities of Raman. Spectroscopy is well-suited for continuous lithium product monitoring and process monitoring in general. It offers several advantages and establishes itself as great process analytical tool, or PAT.

Raman spectroscopy is very sensitive to small structural changes. Therefore, it is an excellent technique to help understand or monitor the reaction processes. Since it is a technique that provides detailed spectra often referred to as a "molecular fingerprint," it can easily identify and measure multiple products simultaneously. In addition, a typical measurement for Raman only takes a few seconds. In these ways, Raman really establishes itself as a great tool for real-time measurement.

Another great benefit is that there is minimal or no sample preparation needed. For example, if a sample of interest is mixed with contaminants and byproducts, it can still be measured along with all other species without having to do procedures to filter out the sample of interest. Also, it is a nondestructive technique which results in no loss or degradation of samples during measurement. Raman is also very effective at measuring through transparent containers, such as plastic bags, glass windows, and vials. This provides flexibility when samples are inaccessible due to toxicity or for reasons where sample integrity could be disrupted if the container is opened. Raman is a great tool for research and method development, and it has become more accessible as more people are trained on it. As familiarity with the technique grows, organizations are able to use Raman spectrometers to develop their own site-specific and process-specific methods rather than relying on third parties.

It is no surprise that lithium compounds are of immense interest when it comes to lithium ion batteries. Lithium compounds are used as cathodes, and cathodes account to close to 50% of the material cost in batteries. The importance of monitoring such vital products is obvious.

Various lithium salts and lithium compounds are naturally found in lithium-containing brines, and these brines are found in different parts of the world, such as Asia, North America, and South America. These brines are processed to obtain lithium carbonate, an important precursor for cathode materials. The cathodes may be composed of different lithium compounds, such as lithium cobalt oxide or lithium iron phosphate. While discussing the use of Raman spectroscopy to monitor these lithium materials, this section will focus on the analysis of lithium carbonate.

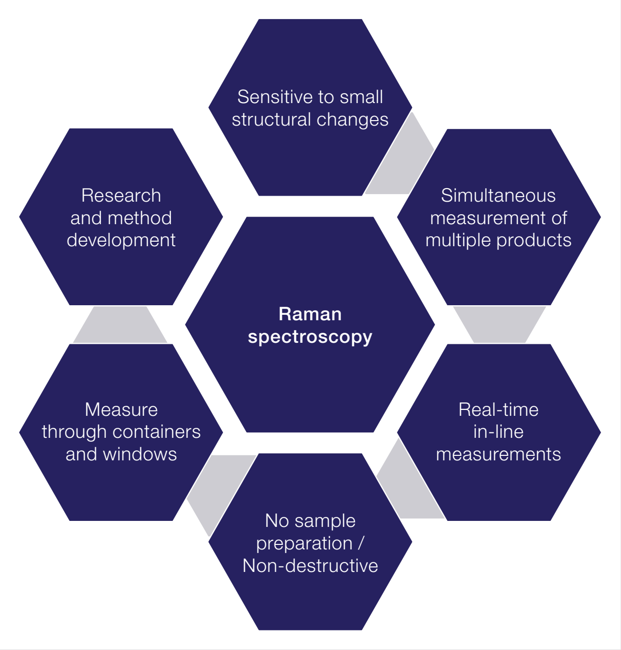


Figure 2a. Benefits of Raman spectroscopy for process control.

Lithium extraction process

The very first steps taken to extract lithium from natural resources focus on lithium brines. (See Figure 2b.) These brines are processed to obtain lithium carbonate. After the naturally-occurring brines are extracted from deposits in the earth's crust, they are put through a drying process—this is often a passive process utilizing shallow pools and the power of the sun. The concentrated brines are then taken through an intensified heating process, bringing them up to a temperature of around 70 to 90 °C, further concentrating the lithium compounds.

In the next step, soda ash (sodium carbonate) is added, which helps to precipitate lithium carbonate. The goal of this process is to produce the maximum yield of lithium carbonate. Continuous monitoring saves costs and time by providing real-time information on concentration, contamination, and yield. The extraction system can be set up to use this monitoring information to continuously fine tune and adjust the process, so it delivers maximum yield.

Using Raman spectroscopy to monitor the extraction process

Each species has unique Raman spectrum, which is also referred to as the "molecular fingerprint" of that species. In Figure 2c, we have excerpts of two Raman spectra of the species, dissolved carbonate (aqueous CO_3^{2-} ions) and precipitated lithium carbonate (solid). The blue spectrum is from dissolved carbonate and the orange spectrum is from lithium carbonate.

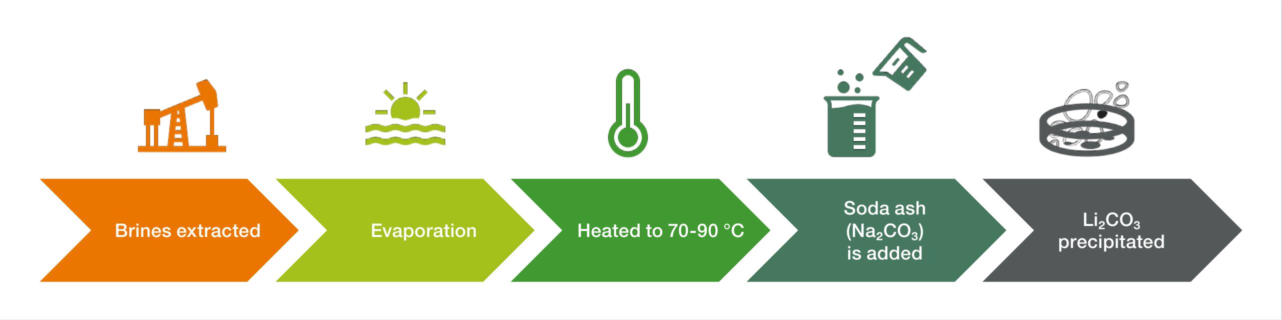


Figure 2b. Diagram of the process flow for lithium mining.

In this example, this continuous testing was done in the last step where the precipitation was happening (represented by the rightmost arrow in Figure 2b's progress diagram). A good separation of peaks resulting from these two species can be seen, and this difference can be utilized to monitor lithium carbonate as it precipitates. In an ideal process where the yield is expected to be maximum, the lithium carbonate peak will become stronger or much more prominent as the dissolved carbonate ions and dissolved lithium ions bond to precipitate solid lithium carbonate. If the dissolved carbonate peak is more prominent, then it is an indication that the process is not working in an optimal way. With Raman spectroscopy, this kind of result is obtained instantaneously. This means monitoring and applying corrective actions can be done immediately as the results are seen, which can lead to savings in time, resources, and costs.

Note that this is just a simple example intended to show how a difference in peak position can be utilized for monitoring products of a particular species using process Raman. More accurate measurements can be obtained by further utilizing chemometrics and advanced data analysis in raw data such as this.

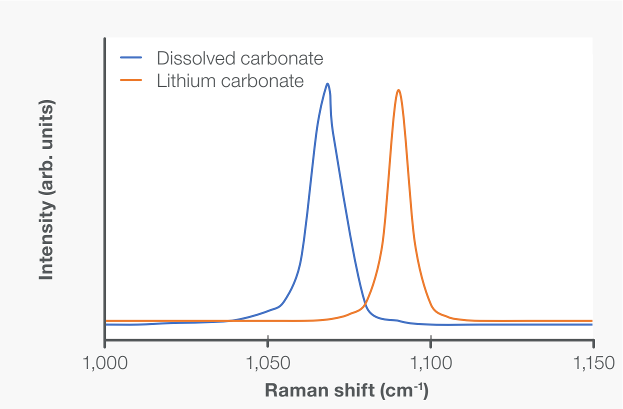


Figure 2c. Raman spectra of dissolved carbonate and lithium carbonate.

Raman identifies unique spectral features

To provide a larger-scale picture, here are two more examples showing how different species have unique Raman spectral features which can be utilized to identify, measure, and monitor species. These examples are not necessarily related to the lithium production process discussed earlier, but are relevant in lithium ion battery research and production in general.

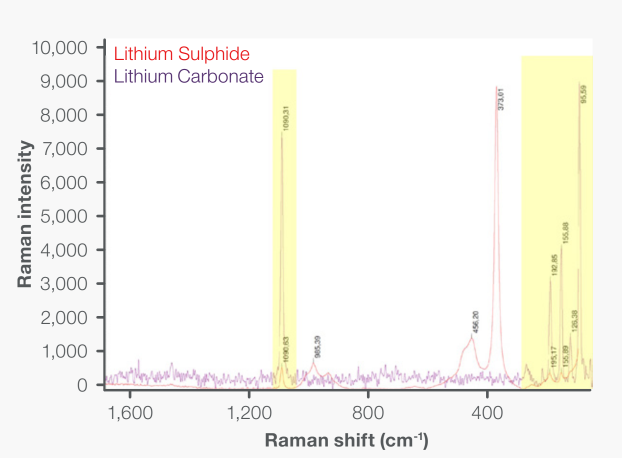


Figure 2d. Raman spectra of lithium sulfide and lithium carbonate.

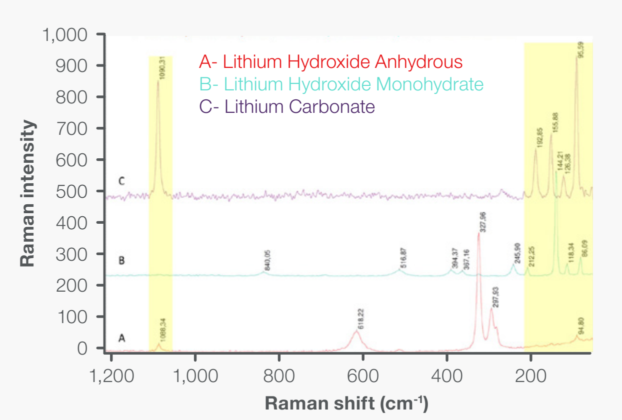


Figure 2e. Comparison of spectra between lithium hydroxide anhydrous, lithium hydroxide monohydrate, and lithium carbonate.

Figure 2d shows example spectra of lithium sulfide (red) and lithium carbonate (purple). A number of peaks are highlighted for both species.

Similarly, Figure 2e shows clear spectral differences between lithium hydroxide anhydrous, lithium hydroxide monohydrate, and lithium carbonate. These examples further show the benefit of Raman spectroscopy as a process analytical tool capable of monitoring several species simultaneously, even when they may be very close in terms of molecular structure.

Raman spectroscopy for laboratory process development

The DXR3 Flex Raman Spectrometer is an excellent tool for laboratory process development—for example, to perform lithium monitoring as discussed in this eBook.

In laboratories, the DXR3 Flex provides Raman measurement capabilities using various types of fiber optic probes. While it can use contact probe for measurement of samples, the DXR3 Flex also can be fitted with an immersion probe for liquid measurements, and or with rugged reaction probes for monitoring ongoing processes in harsher settings.

This instrument is a research instrument that provides great flexibility and multiple sampling options suitable for different kinds of applications. The DXR3 Flex also supports user-swappable lasers with fiber options of 532 nm and 785 nm, and these and other laser options with other sampling accessories. Included is the Thermo Scientific™ OMNIC™ Software that offers extensive data analysis and library search, along with the capability for users to create their own libraries.

In addition, the fiber probe attachment can be easily replaced with available macro measurement or microscopic measurement accessories, allowing users to perform more conventional Raman measurements. This flexibility is yet another unique feature that could be very useful for R&D.

With its ease of use, quick sampling capabilities and sensitivity to molecular structures, Raman spectroscopy is ideal tool for real-time monitoring of lithium precipitation or for use as a process analytical tool capable of monitoring several species simultaneously.

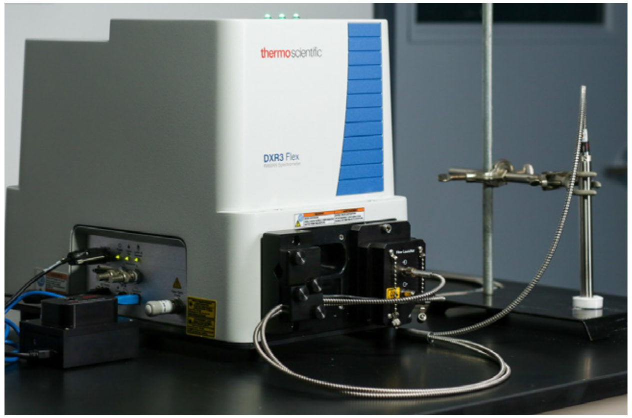


Figure 2f. The Thermo Scientific DXR3 Flex Raman Spectrometer.

Key features of the DXR3 Flex:

- Multiple probes available
- User-swappable lasers
- High resolution parameters
- Ability to optimize parameters
- OMNIC software included

thermofisher.com/flex

Quick screening tools for battery materials

With the proper screening tools, manufacturers can quickly assess the materials used in the production of lithium-ion batteries. “Gigafactories” and other producers of batteries used in automation, power storage, and other applications can take advantage of these tools to improve efficiency, reduce costs, and identify more environmentally friendly methods of manufacturing.

The four main stages of a battery’s life cycle

The life cycle for lithium-ion batteries can be broken down into four distinct categories: upstream, midstream, downstream, and waste or recycling. As the diagram in Figure 3a depicts, each category can be further divided based on different materials or process steps.

In the initial upstream stage, the quality of the raw materials is critical, as impurities can negatively affect the processing steps for midstream materials. During the midstream phase, the correct composition of cathode material and electrolytes comes into focus, as this can affect the cost and performance of lithium-ion batteries. Nevertheless, monitoring of impurities which may be introduced during synthesis or processing is still required as they can affect the battery quality and safety during any downstream applications. And then, at the end of a lithium-ion battery’s lifetime, recycling of the battery components is key to achieving a sustainable and circular economy. Testing for specific impurities and assuring the integrity of the recovered materials is again of wide importance.

Purity, composition, moisture

Certain aspects of the analytical steps taken to assess critical quality attributes during manufacturing processes come to light straight away. For example, when a lithium-ion battery manufacturer purchases different kinds of raw materials like lithium salts and solvents, the critical parameters to consider are purity levels, moisture content, and the identity of any impurities present such as sulfates, carbonates or phosphates.

The precursors that are used for cathode and anode materials can contain many different types of impurities or irregularities that must be accounted for. In cathode materials, the composition and ratios of any metals used along with the possible presence of any residual alkali content formed by surface reactions are of key importance. The purity of the phosphate in LFP (lithium iron phosphate, a common cathode material) is also of concern. In anodes, which often use graphite and graphene, a simple phase impurity (amorphous vs. crystalline) may impact performance. Any moisture present can also have a large impact, which means these two parameters are of utmost importance for efficient battery operation.

In an electrolyte, presence of moisture can create harmful compounds. One of those could be hydrofluoric acid (HF), a very reactive and highly dangerous chemical. Impurities in the composition of the lithium salt used in the electrolyte come into play as another critical parameter.

During assembly of battery, if the separator material contains significant moisture, during the fast charging cycle, that moisture could create unwanted side reactions that have a negative impact. These could cause battery swelling or even more catastrophic failure to occur. Therefore, controlling moisture is a very critical parameter in all the processing steps of raw materials, whether upstream or downstream.

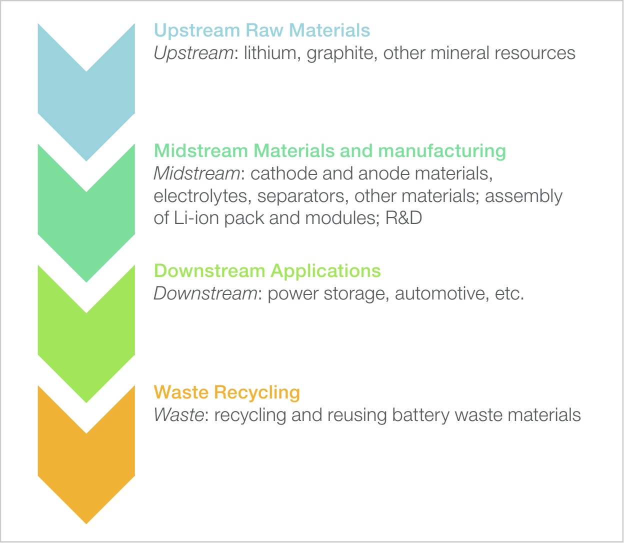


Figure 3a. Categories of the lithium-ion battery life cycle.

Raman spectroscopy can analyze for moisture quickly and safely

In battery manufacturing, and indeed in most any chemical manufacturing process, there are several ongoing needs: There is a need for batch-to-batch material consistency, so that the final product is dependable. There is a need to reduce hazardous solvents in any wet chemistry, to ensure the health of workers and lessen environmental risks. There is a need to improve the efficiency of operations so that a company can be sustainably profitable. Any kind of analysis that could be performed with little or no sample preparation and thus deploy a rapid analysis methods for, say, authentication of solvents, would be helpful. If an analysis of moisture-sensitive lithium salts and electrolytes could be performed directly through glass vials and plastic packaging without the need to open the packaging for sampling, that could be very important. As it so happens, all this can be done using a Raman spectrometer. Raman spectroscopy has a unique ability to perform analyses without requiring sampling. It is even possible to directly measure a sample through a sealed container, providing yet another quick-screening advantage.

With Raman spectroscopy, a sample can be prepared in a dry room, securely packaged into a glass container, and then transported to a standard lab for analysis. Of course, there are general contamination limits that dictate molecular spectroscopy, and analysis will depend on the sample type and the sample form. But as a general idea, it is safe to say that Raman spectroscopy can measure contaminants from the range of 1 to 5%. If the sample being measured has a high Raman cross-section or a high absorbance, this sensitivity can sometimes even go down to ppm levels.

Spectral differences between different grades of lithium salts: a real-word example

Here is a real-world example of the capabilities of Raman spectroscopy involving a large lithium hydroxide supplier: The supplier was worried about the possible formation of metal carbonates, which can happen during any reactions between surface hydroxides and carbon dioxide gas when cathode materials are exposed to the ambient air. This potential surface cap of carbonates, also referred as residual alkali or soluble base content, can lead to formation and subsequent off-gassing of CO_2 and CO. That makes this a very important parameter to manufacturers, no matter their size, whenever they buy bulk lithium hydroxide.

With this in mind, one of Thermo Fisher Scientific's clients asked whether it is possible to recognize both lithium hydroxide monohydrate and lithium carbonate with Raman analysis, and if so, do the spectra differ? And can the carbonates in the hydroxide be quantified and identified?

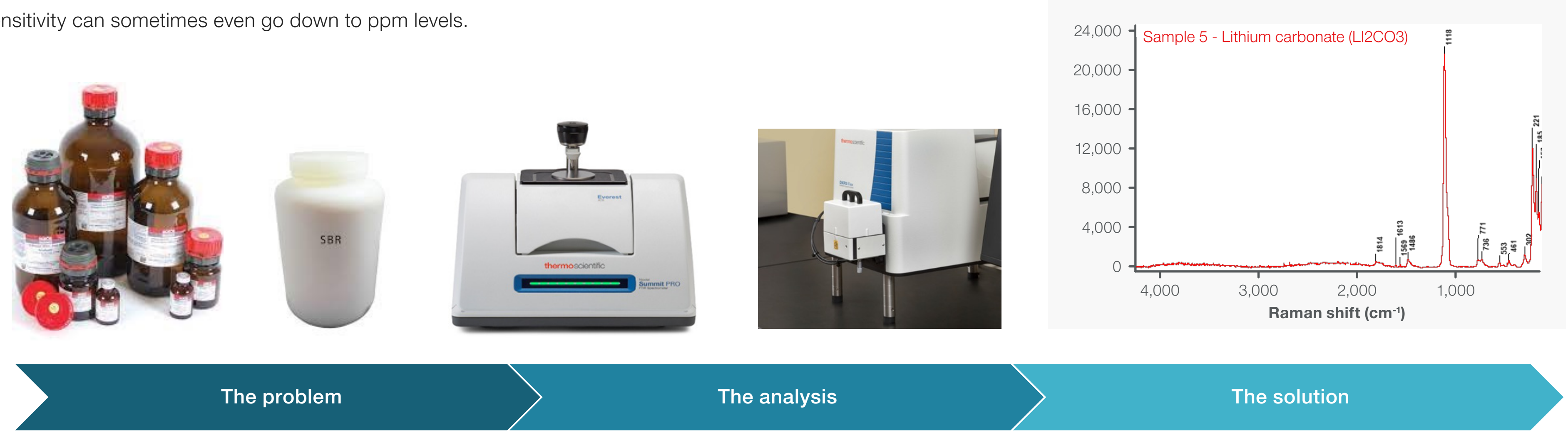


Figure 3d. Raman analysis can solve issues regarding assessment of moisture-sensitive compounds.

For this experiment, the Thermo Scientific™ DXR3 SmartRaman Spectrometer was employed. This instrument is very versatile and flexible and removes the need for complicated sample preparation. The sample can be measured however it is stored, be it in a polyethylene bag or different kinds of glass vials. There are some automation capabilities built into the analyzer, along with a fiber optic probe which can do *in-situ* measurements. While an individual sample spot of Raman analysis may be quite small, with the instrument's Variable Dynamic Point Sampling (VDPS), it is possible to analyze a larger area (for example, 5mm x 5mm) and thereby avoid any in-homogenization effect of a sample through averaging numerous data points over a larger area. The resultant spectrum provides trustworthy answers.

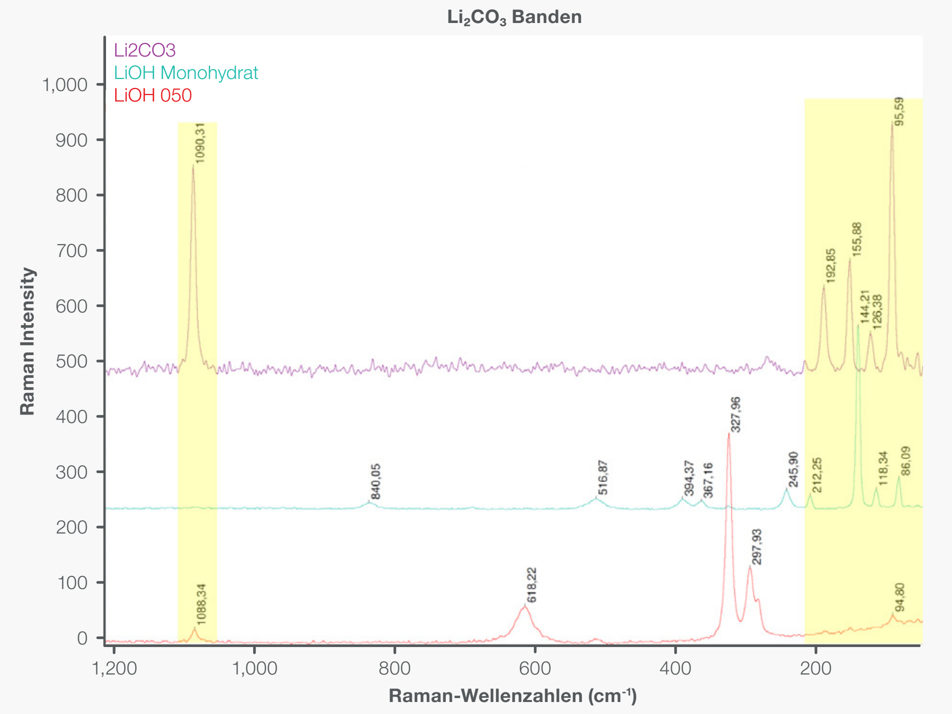


Figure 3e. Comparison of spectra of lithium carbonate, lithium hydroxide monohydrate, and lithium hydroxide 050.

Figure 3e shows the spectra of lithium carbonate, lithium hydroxide monohydrate, and lithium hydroxide 050, which is a battery grade material. The peaks shaded in yellow (located around 1090 cm^{-1} and below 200 cm^{-1}) depict the carbonate bands that are present. Notice that the spectrum of lithium hydroxide monohydrate (the green plot) does have some carbonates present as well, which is what the client wanted to see.

It was also asked, is it possible to see the differences between different forms of lithium hydroxide? The spectra in Figure 3f demonstrate that it is. When several battery-grade lithium hydroxide materials are compared, it is clear that some of them are ultrapure and some of them do have a varying quantity of lithium carbonate present. If multiple carbonate samples were to be analyzed, it would also be possible to see the differences between different grades of lithium carbonate.

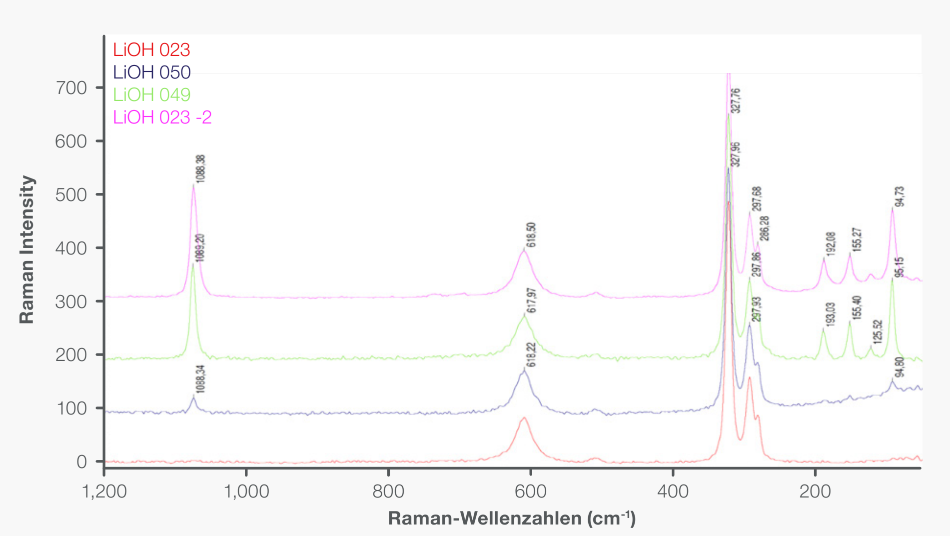
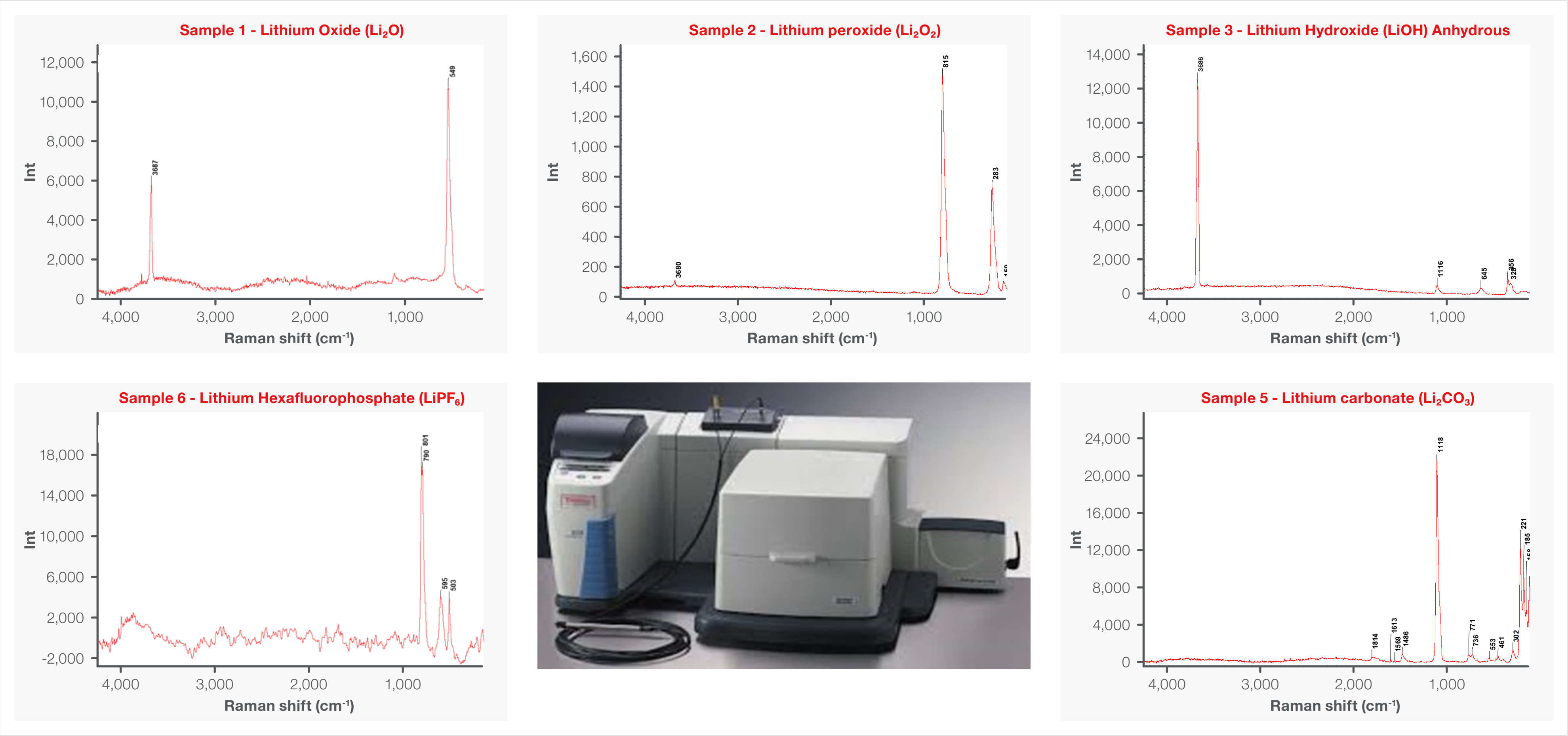


Figure 3f. The Raman spectra of four samples of battery-grade lithium hydroxide materials.

The various lithium compounds commonly found in the raw materials used for batteries each have their own distinct Raman signatures. These differences are demonstrated in Figure 3g, which shows several examples of lithium compounds. Materials such as lithium oxide, lithium peroxide, lithium hydroxide anhydrous, lithium carbonate, and lithium hexafluorophosphate all look quite distinct from one another.



Sample 1 - Lithium Oxide (Li_2O)

Sample 2 - Lithium peroxide (Li_2O_2)

Sample 3 - Lithium Hydroxide (LiOH) Anhydrous

Sample 6 - Lithium Hexafluorophosphate ($LiPF_6$)

Sample 5 - Lithium carbonate (Li_2CO_3)

Figure 3g. Spectra of (i) lithium oxide; (ii) lithium peroxide; (iii) lithium hydroxide; (iv) lithium hexafluorophosphate; (v) lithium carbonate.

Raman spectroscopy can be used for direct in-line measurements in battery manufacturing

Leveraging the versatile probe offerings and small footprint of the Thermo Scientific MarqMetrix All-In-One Process Raman Analyzer, integrating Raman measurements directly into your process is fast, easy, and reliable.

The MarqMetrix All-In-One Process Raman Analyzer has been proven to detect customary battery materials such as common electrolytes, anode material (graphite), and cathode materials (LCO, NMC, LMO). It has even shown the capability to monitor key process parameter changes in recycling workflows.

With the Thermo Scientific™ MarqMetrix™ Process BallProbe™ Sampling Optic, Raman measurements can be taken effectively in harsh conditions, offering an ideal solution for continuous monitoring.

Thermo Scientific MarqMetrix All-In-One Process Raman Analyzer.

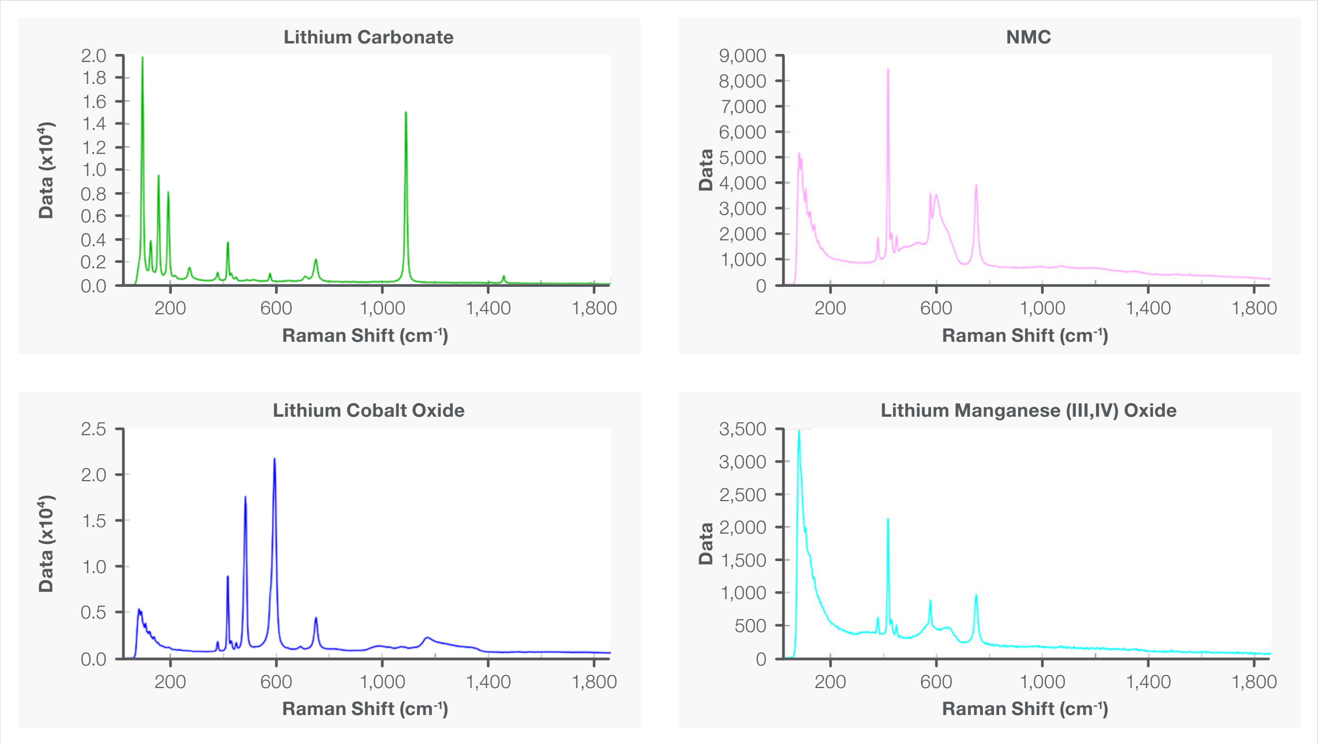


Figure 3h. Raman Spectrum of (i) Lithium Carbonate; (ii) Nickel Manganese Cobalt (NMC); (iii) Lithium Cobalt Oxide; & (iv) Manganese (III,IV) Oxide collected on the MM AIO.

Watch out for the water

Lithium-ion batteries should be virtually free of water because water reacts with the conducting salt $LiPF_6$ to form toxic hydrofluoric acid (HF). Traces of water can also negatively impact the electrochemical performance of the lithium-ion battery. This is especially the case for nickel-rich cathode materials where the Ni^{3+} ion, in the presence of water and CO_2, promotes the formation of lithium hydroxide and lithium carbonate.

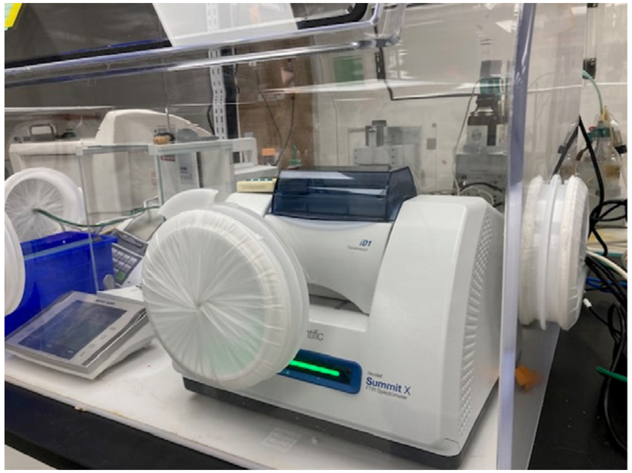


Figure 3i. A Nicolet Summit X FTIR Spectrometer inside a glovebox.

One way to mitigate the potential dangers from moisture is to work in a controlled environment like a glovebox. Gloveboxes can be purged with an inert gas like argon, and several models of Thermo Fisher Scientific spectrometers are compact enough to fit inside, like the Thermo Scientific™ Nicolet™ Summit™ X FTIR Spectrometer pictured in Figure 3i. Once the spectrometer is set up in the moisture-free compartment, the analytical process to use the ATR-FTIR is straightforward: prepare the sample, set the sample on top of ATR, and capture a spectrum. This can reveal information including hydration of the peaks (see Figure 3j) and different salt compositions. Raman spectroscopy is very sensitive to hydrated and anhydrous forms of polyatomic salts. Lithium salts and oxides have unique spectra and Raman spectroscopy can be utilized under controlled conditions like those in a glovebox to check the quality and contamination of battery materials such as lithium salts, electrolytes, or electrode slurries.

Key benefits of the Nicolet Summit X:

- Accurate identification of battery components
- Analysis of degradation mechanisms
- Quantification of additives and impurities

thermofisher.com/summit

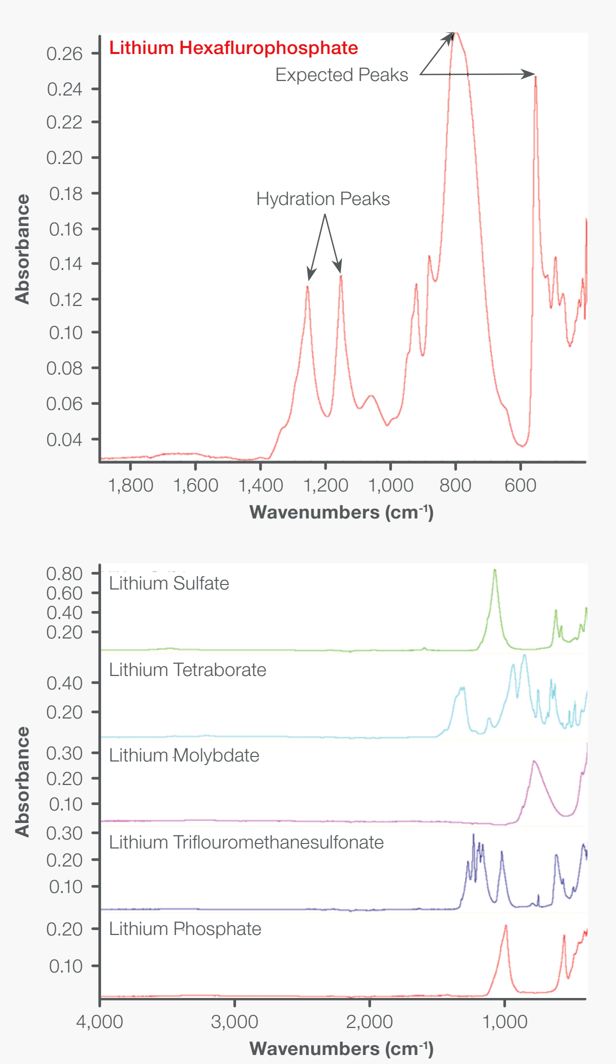


Figure 3j. Raman spectrum showing the presence of water in a lithium hexafluorophosphate sample (top). Comparison of spectra of various lithium salts (bottom).

Cost savings with spectroscopy

Ascertaining the suitability of materials is obviously important, but how that suitability is determined can have a large effect on cost and operational efficiency too. Traditionally, Karl Fischer titration has been the method of choice, but it has its own disadvantages. Karl Fisher uses solvents, and the typical cost of solvents and their disposal is equivalent to cost of a few NIR spectrometers per year. Karl Fisher takes 15 to 40 minutes per sample; it's not repetitive; it's also dependent upon a skilled operator. Meanwhile, an NIR spectrometer like the Thermo Scientific™ Antaris™ II FT-NIR Analyzer can qualify and quantify battery raw materials much more efficiently. An Antaris NIR system can determine chemical identity and moisture content from the same spectrum, allowing users to quickly ascertain the suitability of the materials before the dosing and mixing in-line or at-line. This is highlighted in the spectral images shown in Figure 3k. A typical near-infrared spectrum of some solvents clearly shows how the water band changes according to the concentration present in the samples.

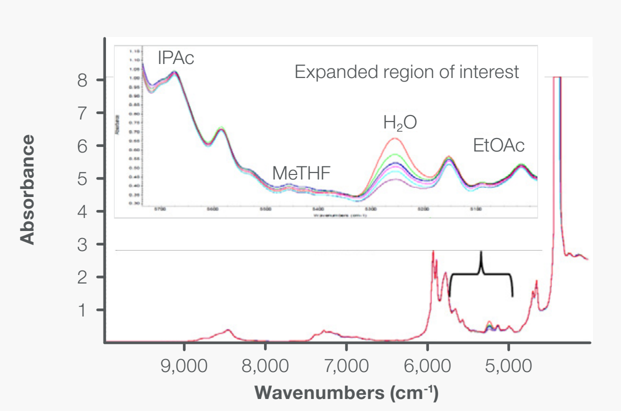


Figure 3k. Infrared spectra of common solvents used in battery production, with emphasis on the effect of the presence of water.

Battery slurry assessment with NIR

Battery slurry has many components: electrode material, carbon in multiple forms, polymers, binders, and solvent. All these interconnected materials play an important role in the quality of the electrode coatings, including aspects such as particle size, packing density, and porosity. In addition to those important factors, Zeta-potential can be also one of the very important factors which determines whether particles are pulled to aggregation. Particles with high Zeta-potential typically form aggregates. This leads to the non-uniformity in the electrode coating, and non-uniformity can be detrimental to battery performance. To evaluate the homogeneity of a slurry, or to take an in-line look at the purity of an electrolyte, or to measure moisture in electrolyte in the slurry, an in-line NIR technique is ideal solution.

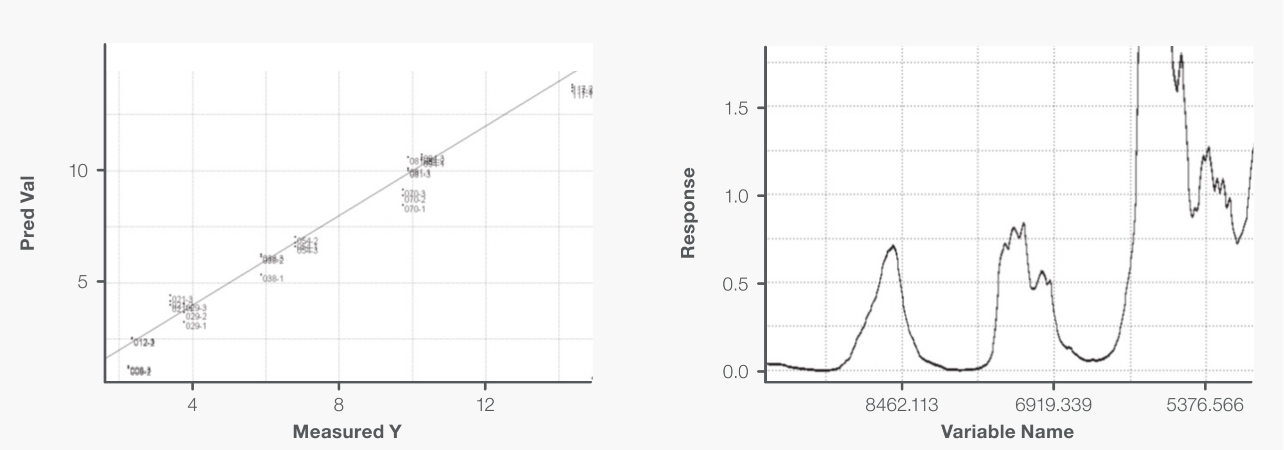


Figure 3m. Moisture measurement in an electrolyte using a calibration curve.

Figure 3m which shows an example of moisture measurement in an electrolyte in the range of 2 to 10 ppm. This analysis was performed on an Thermo Scientific™ Antaris™ MX FT-NIR Process Analyzer, the calibration of which is very easy. It requires ten qualified samples with known moisture values of electrolyte. After these are prepared, spectra are collected via the PLS method, and then the method is validated with five validation samples. After that, this method can be used in the future to predict all moisture values in the electrolyte. In the same way, the method could be based on PLS, or created especially for a given slurry.

Slurry coatings for anodes and cathodes contain a large percentage of solid particles of different chemicals, sizes and shapes, and they are highly viscous. Because of this, thorough mixing of slurries poses a major challenge in the battery manufacturing process. Evaluation of slurries is also difficult, since manufacturers mainly rely on physical tests to verify their homogeneity.

Vibrational spectroscopy tools like inline near-infrared (FT-NIR) Antaris II or (Raman) DXR3 Flex can help evaluate the homogenization because they can generate spectra as the slurry preparation process evolves and give a clear indication when the process is complete. This can take the guesswork out of the mixing process and ensure it is stopped at the right time before inducing overprocessing or excess shear on the slurry.

The purity of any recovered solvent NMP can also be continuously monitored using an Antaris MX system with a specific probe configuration or transmission cell. The process can be totally automated, it doesn't involve sampling or any wet chemistry, and it can verify that whatever amount of NMP is recovered and refined is again battery-grade material.

The techniques described in this section show how vibrational spectroscopy can be helpful to screen inorganic lithium salts without sample preparation. They can verify the hydration and crystallinity of the salts. They make it possible to accurately determine moisture levels in solvents, electrolytes, and anode and cathode materials. Infrared spectroscopy can help determine the degree of solvation in slurries and it can perform quick screening for impurities of lithium salts even in a glovebox setting. The benefits of Raman and near-infrared spectroscopy for quick assessment of battery materials are numerous and diverse.

Figure 3n. Antaris MX FT-NIR Process Analyzer.

Key benefits of the Antaris MX:

- Non distructive online monitoring
- High sampling rate to provide real time feedback.
- Simultaneous multi-point detection to enable more flexible process control sctrategy

thermofisher.com/antarismx

Graphene Use in Cathode Manufacturing

Graphene is a single-atom-thick layer of carbon atoms. It has many properties that make it attractive for use in batteries. Graphene's atoms are arranged in a hexagonal lattice, neatly bonded with sp^2 hybridization to form a coherent unit, as shown the top image in Figure 4a. *Graphite*, not to be confused with graphene, is comprised of the sp^2 bonded planar units stacked together, as shown in the lower image of Figure 4a. The properties of graphene and graphite are vastly different.

While graphene can be used in multiple components in batteries, this section of the eBook will focus on the use of graphene in cathode materials in lithium-ion batteries.

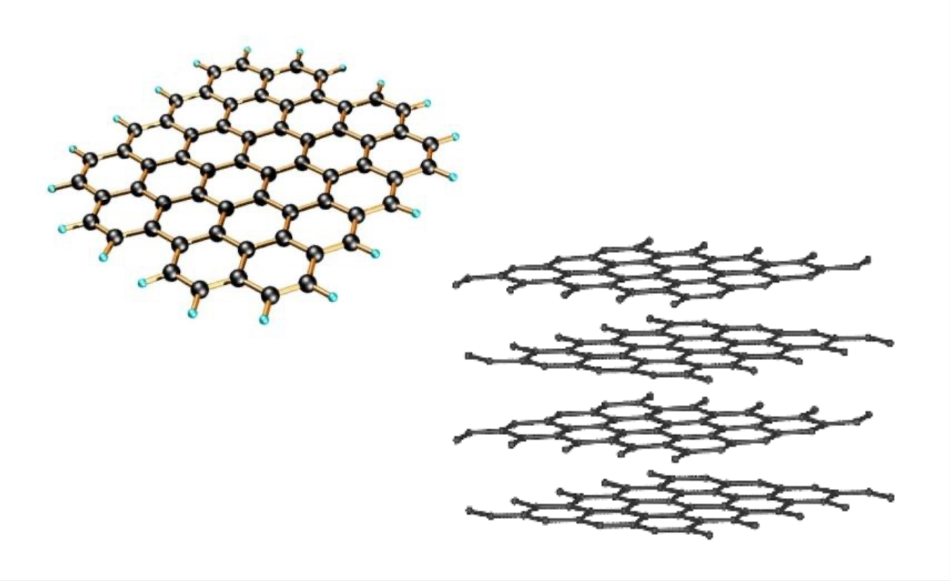


Figure 4a. Graphene (top) and graphite (bottom) are both allotropes of carbon.

Key attributes of graphene

Since it contains only a single layer of atoms, the thickness of graphene is just under 0.3 nanometers, or three angstroms. Graphene is 200 times stronger than steel by weight and 1000 times lighter than paper. It is also an excellent conductor of heat and electricity. Because of its structure and strong covalent bonds, it is impermeable to even small molecules. All these properties create huge potential for graphene to be used in everyday materials to make them lighter, stronger and better. During graphene manufacturing, processes can be put in place to create sp^3 bonds and other defects. Introduced "purposeful defects" can help tune the electrical, thermal, chemical and mechanical properties of graphene. However, this type of change may also happen in an uncontrolled manner with degradation over time, even with normal use.

Properties such as superior barrier capability, outstanding electrical conductivity, and excellent structural stability make graphene an ideal choice for use as battery components. Graphene can also be used as a superior conductive additive because of its higher surface-to-mass ratio than conventional conductive additives. This can lead to the development of batteries with higher energy density and ultra-long cycle lives.

The use of graphene can make batteries physically stronger while making them lighter. With its impermeable properties, it can inhibit corrosion of electrode materials while increasing the conductivity of electrodes. In addition, graphene's superior mechanical properties benefit electrode materials' stability, which leads to enhanced capability and cyclic stability. These qualities are especially needed for demanding batteries uses such as powering electric vehicles.

Graphene use in cathodes

Graphene is most often used in combination with other elements to form electrode materials. For example, graphene forms a 3D electron-conducting network in a lithium-ion battery's cathode material when it is properly mixed with lithium oxide compounds. As illustrated in Figure 4b below, graphene can be sandwiched between lithium oxide component layers.

Other ways of achieving higher conductivity are also possible: Particles of lithium oxide compounds can be wrapped or encapsulated by graphene; alternating layers of graphene and lithium oxide compounds can be formed; or graphene and particles of lithium oxide compounds can be mixed in different configurations as well.

Lithium compounds are used for the main material of cathodes, but incorporating graphene enhances the conductivity and increases the rate capability and cycle ability of the cathode material. This also increases the strength and reduces the corrosion, which can open up the ability to use a wider choice of electrode materials. For example, lithium iron phosphate (LFP) is known to have very low conductivity. Thus, by itself, LFP is not a good choice as a cathode material. However, when mixed with graphite, the material's conductivity is significantly enhanced. Since lithium iron phosphate is a low-cost material compared to more traditionally used lithium cobalt oxide, the incorporation of graphene leads to huge cost savings. In theory, with this property, many low-cost materials could be utilized to make effective cathodes.

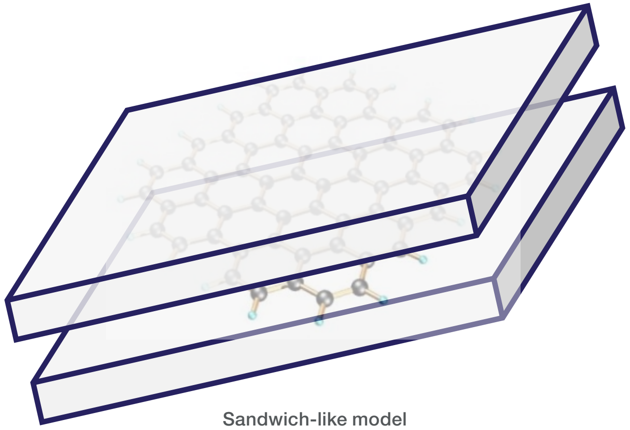


Figure 4b. A graphene layer sandwiched between two layers of lithium oxide.

Why isn't graphene widely used in lithium-ion batteries?

It is important to note that the use of graphene in lithium-ion batteries is mostly in research space and has not been widely commercialized.

This is because, as much as there are benefits of mixing graphene with cathode materials, improper mixing presents a huge disadvantage: Unsuitable mixes can impede lithium-ion migration, which will then reduce the capabilities of batteries. This can very easily happen because the graphene synthesis process is complicated. Creating perfect graphene, much less mass producing it in an industrial or commercial setting, is extremely difficult.

Creating large-sized graphene sheets without defects is a challenge. Applying appropriate addition methods, including understanding the need for the right additive is also challenging. When dealing with such thin materials, operating without impurities is not an easy task either, especially when even a very tiny amount of impurities can disrupt the properties. And while defects are almost inevitable, degradation with storage and use is also well known. With all these challenges, graphene manufacturing for use in batteries is very costly, and the manufacturing itself is not the only cost concern. Currently, the ability of graphene and graphene-mixed cathodes to withstand numerous charging/discharging cycles is far from ideal, so if these materials are to be utilized in batteries, the need for frequent replacement or repairs could add to the cost as well.

Raman spectroscopy uses for graphene

What kind of information can we get from Raman spectroscopy, or more specifically, what kind of information is relevant to graphene? Start by looking at the spectra of graphene and graphite, seen in Figure 4c. In Figure 4c, the top spectrum is graphene and bottom is graphite. At first glance, the two spectra look extremely similar. This is not too surprising, since graphite is predominantly stacked graphene. However, there are some notable differences between the spectra. Some of these differences can be seen with close examination of G band, which is the peak around 1580 cm^{-1}.

The differences are more pronounced in G' band (the "G-prime" band, also referred to as the "2D" band) in the vicinity of 2700 cm^{-1}. Note the relative intensities of G bands and the G' bands showing a clear difference between graphene and graphite.

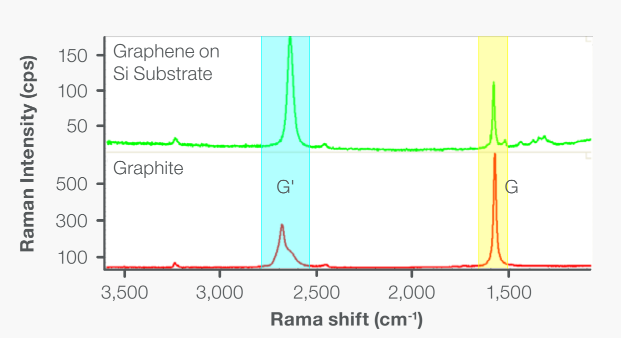
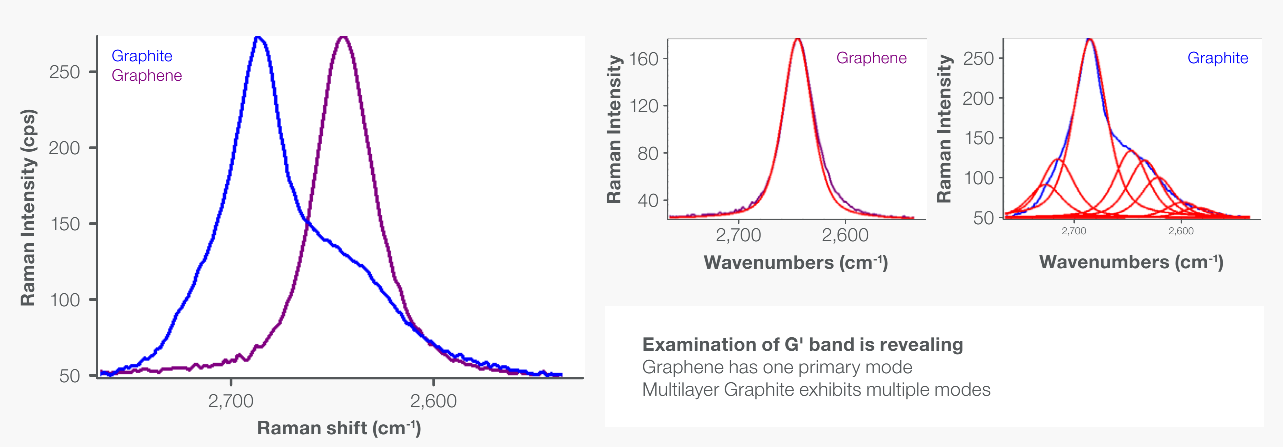


Figure 4c. Raman spectra of single-layer graphene vs multi-layer graphite.



Examination of G' band is revealing
Graphene has one primary mode
Multilayer Graphite exhibits multiple modes

Figure 4d. The G' band changes with the number of carbon layers present.

A closer look at the G' bands of graphene and graphite reveals a significant difference. Both the shape and the position of these bands are different, and both are telling. The peak shift in graphite is a result of interaction between stacked graphene layers, which have a tendency to shift the band to a higher frequency. The images in Figure 4d show curve fitting using Gaussian-Lawrencian Fit, which gives more resolution to these bands. The curve fit finds essentially the single band in the single-layer graphene spectrum, whereas in the graphite spectrum it reveals a number of underlying bands. This represents the different inter-layer interactions that occur at different depths within graphene. The G' band can be used to determine the thickness of a graphite sample, as discussed below.

The G band has been shown to have a rather straightforward peak position dependance on the number of layers present. Figure 4e shows the effect layer thickness has on the position of the G band. As a layer thickness increases, the band position shifts towards lower energy, representing a slight softening of the bonds as the thickness increases. In the reference image here, Wang and colleagues have shown that the position of the G band for the n layer of graphene is given by the equation [$\omega G = 1581.6 + 11/(1 + n1/6)$]. It should also be noted that the G band is quite sensitive to doping and even minor strain. This needs to be considered when attempting to use the band for determining layer thickness.

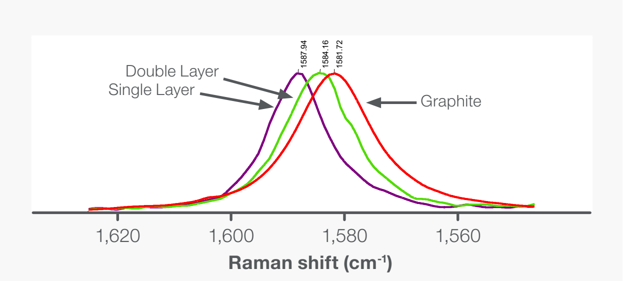


Figure 4e. The peak position shifts with the number of layers.

Another piece of information demonstrated by Raman spectra is that there is a linear increase in G band intensity with an increase in number of graphene layers. As you can see in Figure 4f, as the number of layers increases, the intensity of G band increases.

Figure 4g shows an alternative method for determining the number of graphene layers based upon the G' or 2D band. In contrast to the G band method, the G' band method depends not only on the band position but also on the band peaks. With enough graphene layer thickness, the spectra (notice the topmost plots in Figure 4g) display some rather dramatic peak shape differences, which can be seen as complex band splitting. The bands in this figure have been deconvoluted into their component peak contributions using a Voit peak fitting to better slow the splitting of this band. (The overall peak is in red; component peaks are shown in different colors underneath it.) The base splitting of the G' band from single-layer graphene to multilayer graphite arises due to the symmetry lowering that takes place with increasing layers in the sample. These distinct band shape differences allow G' band to be useful in determining the number of layers present in graphene samples.

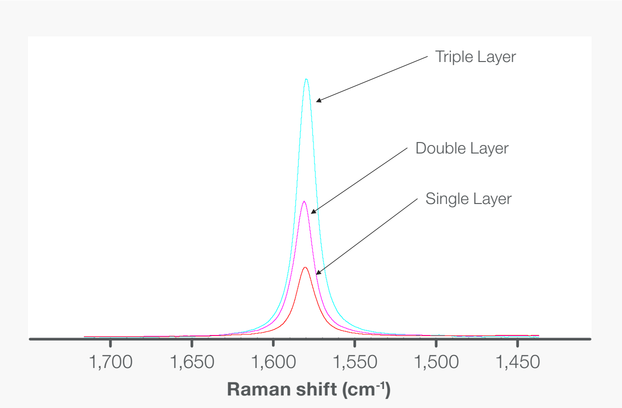


Figure 4f. The intensity of the G band increases with the number of layers.

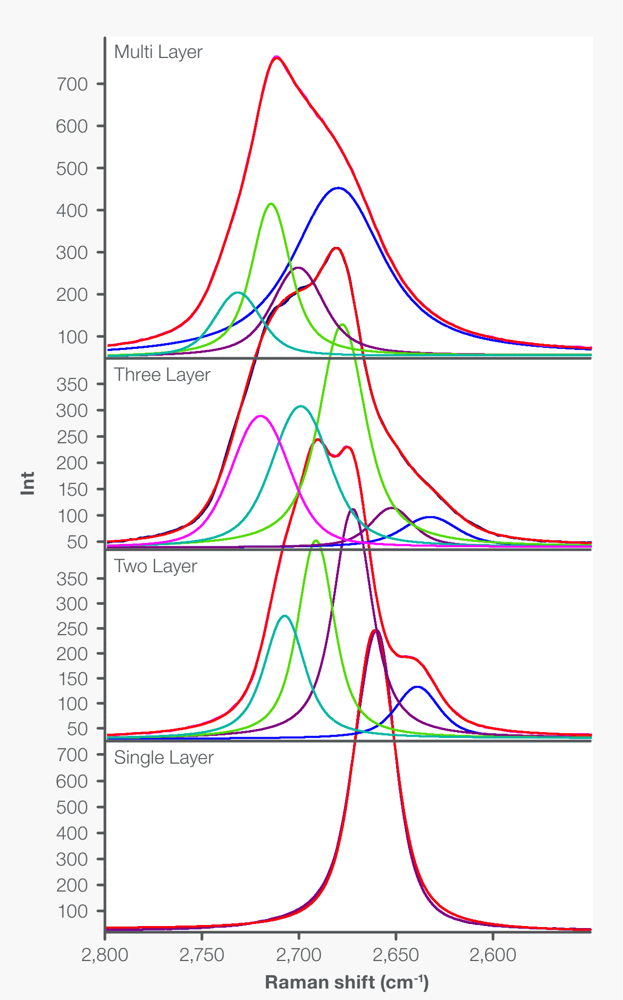


Figure 4g. The G prime band changes in both position and peak shape with increasing graphene layers.

Another important piece of information revealed by Raman spectroscopy is that single layer graphene can be identified by intensity ratio of the G' and G band; when the ratio of intensity of the G' or 2D band to the G band is two, the sample is a single layer of graphene.

Graphene is also very sensitive to environmental strain. In the example illustrated in Figure 4h, there are three situations analyzed: before, during, and after a strain is applied to a graphene sheet. A significant strain was induced on the sample by bending it. The middle plot shows the behavior of graphene when the strain is applied. Relative to the bottom (pre-strain) spectrum, the G and G' bands shift to lower frequency. This shift is completely reversible as can be seen in the top (post-strain) spectrum, which shows the G' and G bands returning to their previous relaxed position. (Note also that the other bands present in the graphene spectra are not affected by this strain.) This demonstrates yet another way in which Raman analysis can help perform characterization of graphene samples.

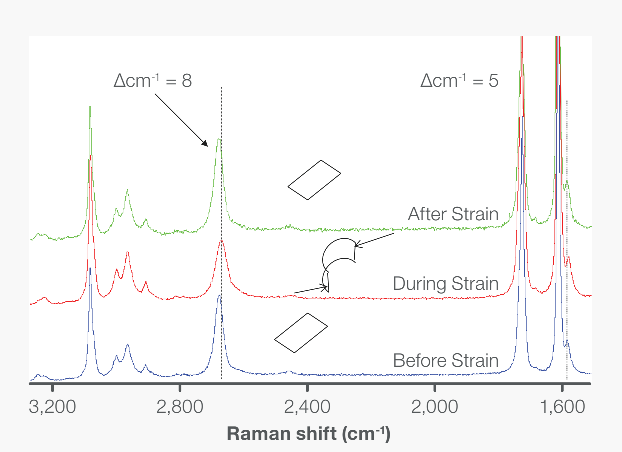


Figure 4h. The effect of strain on graphene is evident in Raman spectra.

Using Raman imaging for a wider view

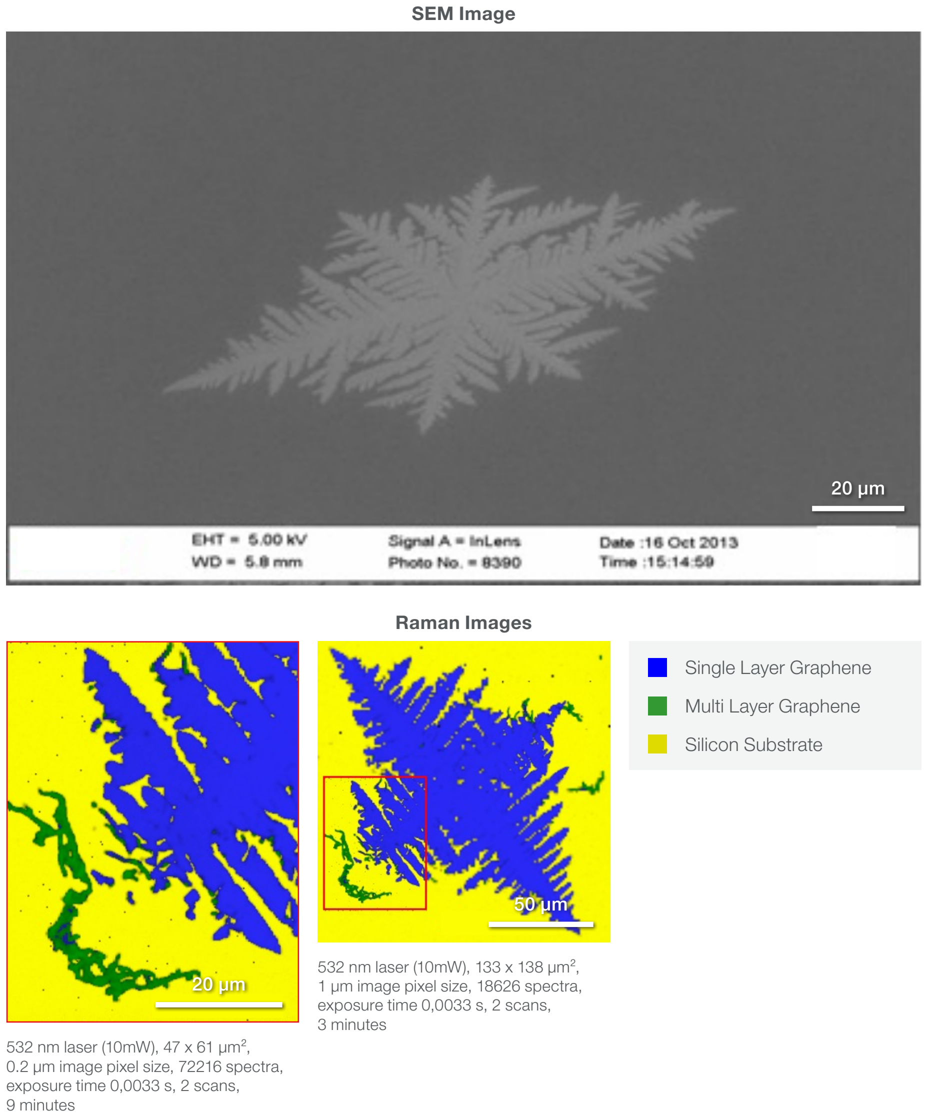
Raman spectroscopy is often used to analyze a localized point on a sample. However, in real world samples such as those used in batteries, it's essential to be able to view a larger area. A broader analysis allows for information such as shape, size, uniformity and defects to be clearly visualized. To get this type of information, Raman imaging serves as an excellent tool.

Raman imaging produces an image of the sample by applying a multivariate curve resolution, or MCR. To do this, thousands of individual points in a given area are analyzed as the sample is moved up/down or left/right relative to the incident light and the detector. These individual points are pieced together via MCR to map out a two-dimensional area. The resultant image reveals a wealth of information about the observed area.

In Figure 4i, a picture of a scanning electron microscope is shown next to Raman images. SEM is a much slower and more intricate (not to mention more costly) technique than Raman, but here the detailed SEM and Raman images showing dendritic growths of single-layer graphene can be seen and compared. In this case, the graphene was grown on a copper substrate, which acts as a catalyst for film growth, but it was transferred in a series of steps to a silicone surface. The fine dendritic growths are visible in both the SEM and Raman images, but in the Raman image, it is possible to see the discrete portions of the sample that are clearly single-layer graphene, and they are distinct from other portions of the sample that are multilayered graphene.

The various colors indicate different components in the sample. From these Raman images, we can surmise that they are more than likely the bits and pieces of melted down graphene that could have been a result of an inefficient transfer process.

These Raman images were generated without the need to input any information in regard to the location of expected peaks, peak intensities or ratios of peaks. The left bottom image in the figure is just a section of the sample (full image on the right) with Raman spectra collected at higher resolution, or more spectra per unit area.



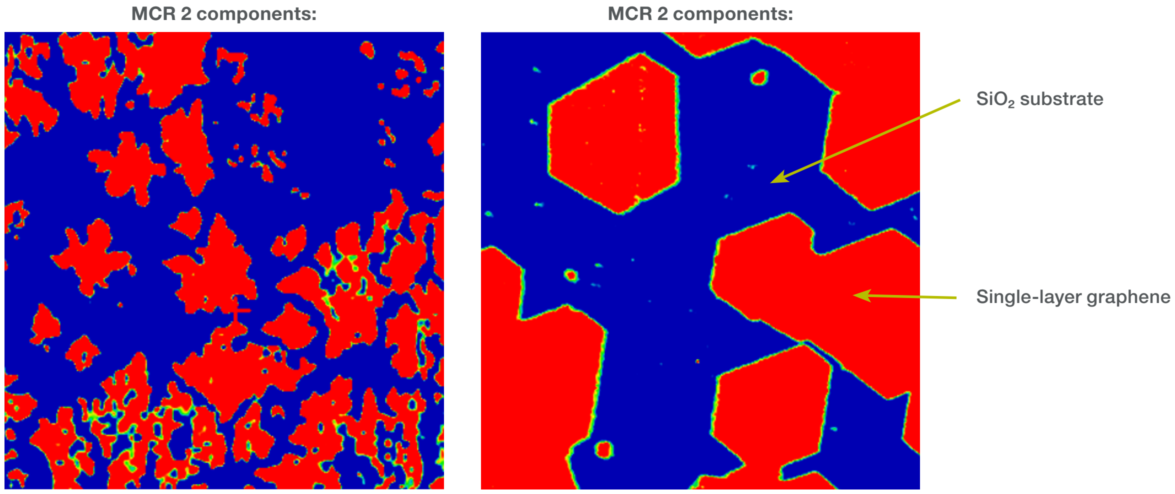
532 nm laser (10mW), 47 x 61 µm², 0.2 µm image pixel size, 72216 spectra, exposure time 0,0033 s, 2 scans, 9 minutes

532 nm laser (10mW), 133 x 138 µm², 1 µm image pixel size, 18626 spectra, exposure time 0,0033 s, 2 scans, 3 minutes

Figure 4i. Raman imaging can distinguish structural differences.

Another example of the value of Raman imaging is provided in Figure 4j, which shows examples of different types of graphene film growth at different resolutions. In this case, graphene that was grown faster, shown on left, displays non-uniform growth and much smaller domains. In the image of hexagonal growth on the right, we can see much larger red areas of single layer graphene and blue areas of silicon substrate. Both images show many small sites of single-layer graphene in red, while the blue color indicates the silicon substrate. These images are based on the ratio of the G' band to the G band of graphene. Note that the area of the left image showing the non-uniform growth (50 x 50 micron) is much smaller than that of the hexagonal growth sample on the right (175 x 175 micron). Some of the data collection parameters, including the number of spectra collected and total time needed to collect spectra, are also shown here. This is just for reference to show that higher resolution or larger area samples measurement incur longer data collection times. These parameters can and should be optimized according to each individual lab's needs.

The spectra and images shown in this section were presented to show that Raman spectroscopy and imaging are very powerful to evaluate graphene for a variety of applications, including to help produce higher quality components for batteries. Although graphene manufacturing and analysis is currently mostly limited to research, Raman could also conceivably be used for checking the quality of graphene film in a quality assurance role when graphene is mass produced.



50 x 50 µm surface area
10,000 spectra
Acquisition parameters: 100 Hz (10 ms/spectrum)
~16.7 minute collect time

175 x 175 µm surface area
122,000 spectra
0.5 µm pixel size
Acquisition parameters: 100 Hz, 10 scans
~3.4 collect time

Figure 4j. Raman imaging reveals differences resulting from fast, non-uniform growth (left) compared to slower, more uniform growth with larger domains of single-layer graphene (right).

Key benefits of the DXR3xi microscope:

- Visually driven image acquisition
- A microscopy-first approach to spectroscopy analysis
- Information in real time

thermofisher.com/dxr3xi

Thermo Scientific DXR3xi Raman Imaging Microscope.

TGA-IR Hyphenation and Gas Analysis

There is a need in both battery manufacturing and battery-related research to be able to quickly analyze battery components as well as complete cell chemistries, and to understand the failure mechanisms and unwanted reactions that might occur. FTIR spectroscopy is extremely well-suited to meet this need. Furthermore, coupling FTIR with the thermogravimetric analysis generates a wealth of information to help analyze the thermal stability of these materials. When FTIR spectroscopy is coupled with thermogravimetric analysis, a complete de-formulation analysis of battery materials can be obtained.

FTIR spectroscopy connects the structure of materials with function and the composition of the material—how those atoms and molecules are put together and how that informs what those materials can do. With relatively easy to almost no sample preparation, FTIR can rapidly screen materials and identify what that material is, know how much of it there is, what form is present. This can be done on a wide range of sample types; almost any kind of material you can think of, and at any point in the process, can be analyzed with FTIR spectroscopy. As it regards batteries, FTIR can be applied at all stages, from the incoming raw materials to the research and development process all the way to failure analysis.

The information in a vibrational spectrum is rich, and contains a great deal of information that can be extremely useful. (Refer to Section 1 of this eBook for a synopsis.) The presence of vibrational modes and their peak positions tell about the molecular structure; when compared against libraries of spectra or standards, a material can be identified quickly. Peak intensities can give information about how much of a given material is present, making it possible to do quantitative studies with the right calibrations. Additional information in peak shape or the shift of those peaks is can provide important information about the physical and chemical properties of the material under study.

Coupling the data from the vibrational spectrum with a technique called thermogravimetric analysis can generate even more detailed information and useful insights, as we shall describe here.

In TGA-IR spectroscopy, a thermogravimetric analyzer is linked to an FTIR spectrometer fitted with a gas cell. The material to be analyzed is placed into a sample pan which hangs on a highly precise balance. This is the “gravimetric” portion of TGA. The sample is then heated, and changes in mass are recorded as a function of temperature; this is the “thermo” portion.

With the sample in the furnace, a controlled ramping of temperature is performed while the balance continuously measures the change in mass. (Different experimental methods may be developed to adjust temperatures or other parameters as needed.) This process generates quantitative information, specifically about how much of the materials that make up the original sample remain upon heating or decomposition. TGA analysis can be done on its own, or it may be coupled with another analytical technique to create a hyphenated method.

For TGA-IR, any gases that are produced in the TGA experiment can be transferred to a gas cell in a coupled FTIR spectrometer. (See the diagram in Figure 5a.) The gases can then be analyzed via spectroscopy to identify what materials are being evolved from the sample. When the FTIR data are aligned with the mass changes curves and the thermal data from the TGA telling the temperatures at which those materials were evolved, it is possible to build a complete picture of the de-formulation and the original composition of the material that was being analyzed.

TGA-IR can be applied to a wide range of materials and de-formulation or failure analysis questions. The technique can be used to determine the composition of an unknown material, or to diagnose what is different about the composition of a part that might not be working as expected. Often this gets applied to polymers, plastics, or rubber, but it can be applied in several other avenues—one of those being battery electrodes.

TGA-IR instrumentation

To perform TGA-IR experiments, the TGA instrument must be connected to either the Nicolet Apex or the Nicolet iS50 FTIR Spectrometer. A transfer line is then connected from the exhaust port of the furnace on the TGA to the inlet of the gas cell on the FTIR. Beyond this, Thermo Scientific's OMNIC software with Mercury TGA analysis makes data analysis from both the TGA and the FTIR spectroscopy very simple, and in doing so provides a complete picture.

OMNIC Software for TGA-IR analysis

Figure 5b shows a snapshot of what the output of a TGA-IR analysis can look like, with a plot of TGA peaks adjacent to the FTIR spectrum of the same sample. The data displayed here come from a model compound, calcium oxalate monohydrate. When a sample of this is placed into the TGA and the temperature is ramped up to 900 °C, the material decomposes. It breaks down into carbon monoxide, carbon dioxide, and water, which are evolved over the course of this experiment. With OMNIC software, on the FTIR side it produces what is called a Gram-Schmidt profile.

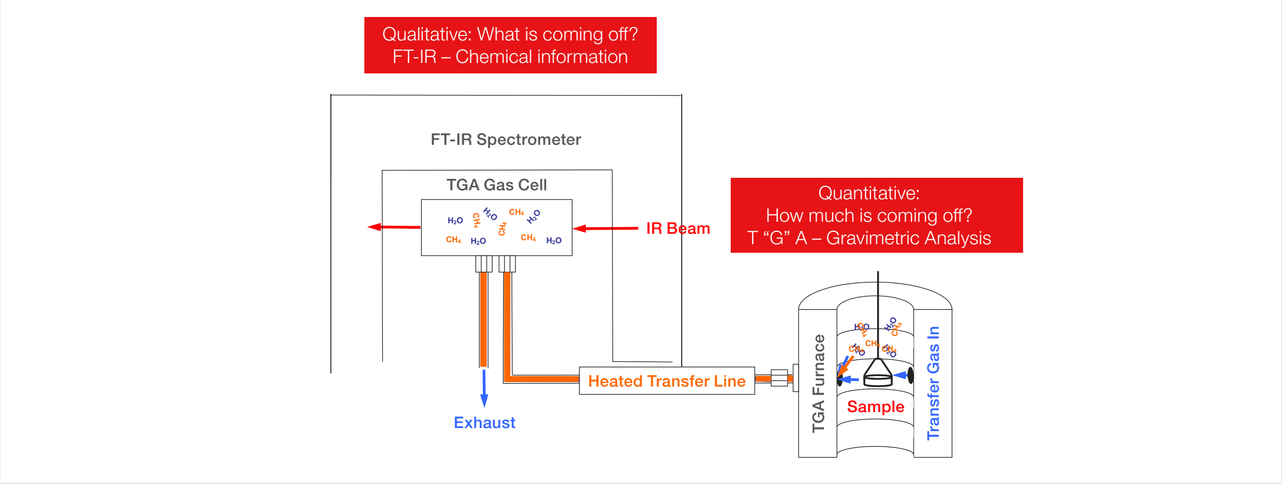


Figure 5a. Diagram of TGA-IR connectivity and functions.

TGA-IR Applications

- Reverse Engineering
- Failure Analysis
- Polymers
- Epoxies/Resins/Adhesives
- Entrained solvents
- Breakdown products
- Textiles/Paper products

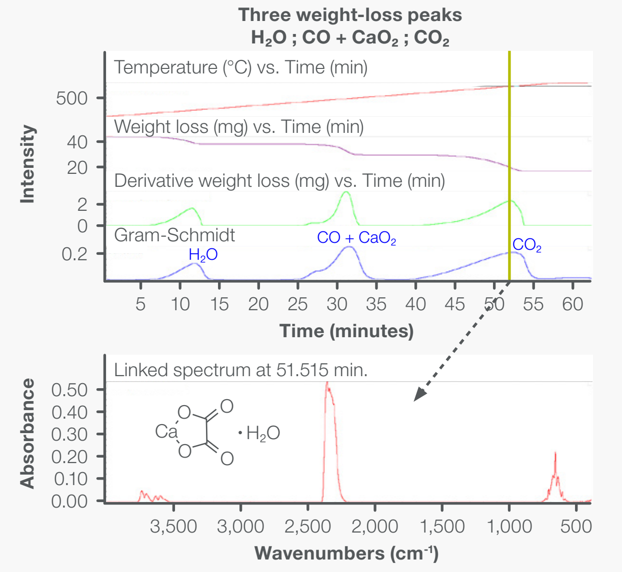


Figure 5b. TGA-IR analysis of calcium oxalate monohydrate shows spectra with three weight loss peaks.

The peaks in a Gram-Schmidt profile directly correlate with the steps in the TGA weight-loss curve, and effectively show the change in the IR absorbance relative to the initial state. Each peak in this profile is produced when a new material is measured by the spectrometer. In this layout, it becomes apparent how these peaks correlate directly with the derivative weight loss curve from the TGA. The purple curve shows the weight loss over the course of the TGA portion of the experiment. The software can be directed to look at the point when the first amount material is evolved, and then the second or the third event, and at any of those points in this time trace the software can extract out the infrared spectrum. When done throughout the entire time trace, all of those events can be analyzed to identify what is present.

Figure 5c contains another example showing what OMNIC software can do. With a single click, the software will analyze the data, pick apart that overall Gram-Schmidt profile, and produces separate plots of the components that evolved over the course of the experiment. In addition, the library spectra are provided for each of those materials, and the composite spectrum of all those components can be presented as it is at the top right of the figure.

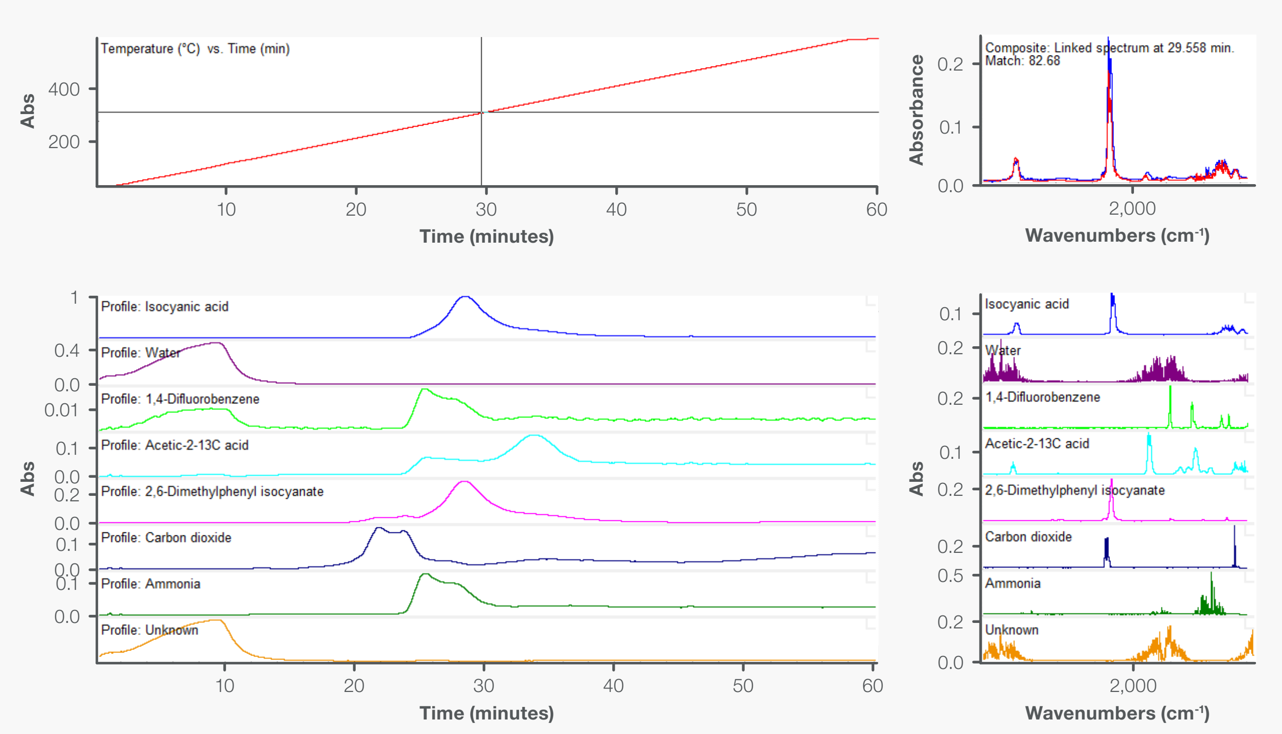


Figure 5c. Example results from OMNIC software for a TGA-IR analysis.

Case study: TGA-IR use for failure analysis of cathode material

One of the chief challenges in being able to move beyond the current limitations of lithium-ion batteries lies in finding a cathode material that does not exhibit capacity fade. A high capacity cathode material that will maintain its capacity over several charging and discharging cycles is absolutely essential for constructing an effective battery.

In the example that follows, a group was researching a battery of a type called a lithium metal polymer battery. Lithium metal was used as an anode, the electrolyte was a polymer, and then a high capacity vanadium oxide composite material was being investigated for the cathode. While the vanadium oxide composite is theoretically a very promising material, it unfortunately exhibits high capacity fade. The research group used TGA-IR with a Thermo Scientific Nicolet FTIR spectrometer to uncover the reaction mechanism, in order to determine the events that were happening to limit the capacity of this vanadium oxide cathode. Presented here is merely an overview of the story that emphasize the usefulness of vibration spectroscopy, showing how a research group used TGA-IR to uncover the failure mechanisms in a new battery cathode material. (The work described herein was originally published in the ACS Journal of Applied Materials and Interfaces; for the complete paper with full data, please refer to that publication.)

To summarize the problem, the research group noticed that when they analyzed the whole cathode composite material via TGA-IR, there were new products being formed. These unexpected products indicated some side reactions were happening at the elevated temperatures where these batteries were being used.

And so, since TGA is the perfect technique to probe the thermal stability of these materials, the group systematically undertook a TGA-IR analysis to identify what reactions were actually happening, and to determine which parts of this cathode material were involved in this pathogenic side reaction that was destroying the cathode performance.

The group subjected the cathode composite to TGA-IR analysis and found that at elevated temperatures, an unexpected component appeared. The spectra in Figure 5d show the complete picture of the experimental data that OMNIC software can provide, and this imagery was helpful in deducing the exact nature of the problem. The three dimensional plot in Figure 5d (top) shows the infrared wavelengths plotted against the time for that experiment, with a third axis revealing how the intensity changed over time as well. The appearance of unexpected peaks that were readily identifiable at 150 °C (see Figure 5d (bottom), red plot) showed even more strongly at 180 °C (Figure 5d (bottom), green plot). All this evidence indicated that there was an unwanted chemical reaction occurring within the cathode at the targeted temperatures of use.

In Figure 5d (bottom), the infrared wavelengths at three different temperatures are plotted, illuminating the evolution of various gases as the temperature changed. A comparison of the spectrum acquired from the cathode composite at 180 °C to a library of known spectra revealed that an unwanted product of 1,4-dioxane was being evolved. (See Figure 5e.)

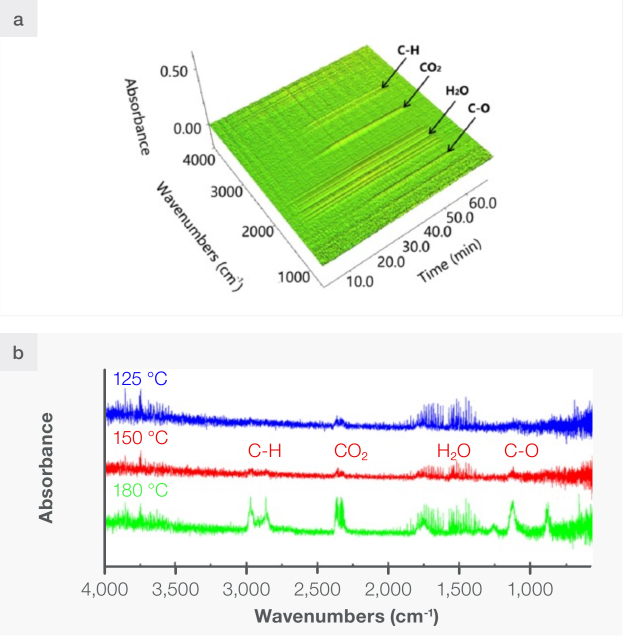


Figure 5d. (top) *in situ* 3D plot of IR spectra at 180 °C; (bottom) comparison of individual spectra from V_6O_{13}-based cathode composites at 125, 150, and 180 °C.

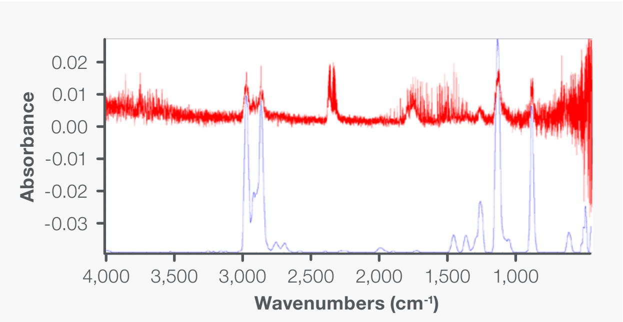


Figure 5e. Comparison of TGA-IR spectrum of gas phase of V_6O_{13}-based cathode composites (red) at 180 °C, and 1,4-dioxane (blue). Source: ACS Appl. Mater. Interfaces 2018, 10, 19667-29674.

To figure out which components were involved in this reaction, the group performed some control experiments on the pure starting materials. In Figure 5f are the TGA weight loss curves for the individual starting materials over the course of various temperature ranges (0 to 500 °C for carbon, 0 to 200 °C for V_6O_{13}, and so on). These four key parts of the composite mixture—the carbon, the vanadium oxide, the polymer binder and the lithium—all exhibit basically negligible weight change.

The vanadium oxide has a slightly higher weight change than the others, but this is due to a known phenomenon and is well understood. That means this TGA data acquired on the pure starting materials show that these components, each on their own, are thermally stable across the temperature range of interest.

The next step was to start to put these different materials together into two-component mixtures, and then perform the TGA-IR analysis again to determine which of these combinations is producing the observed reaction from the composite.

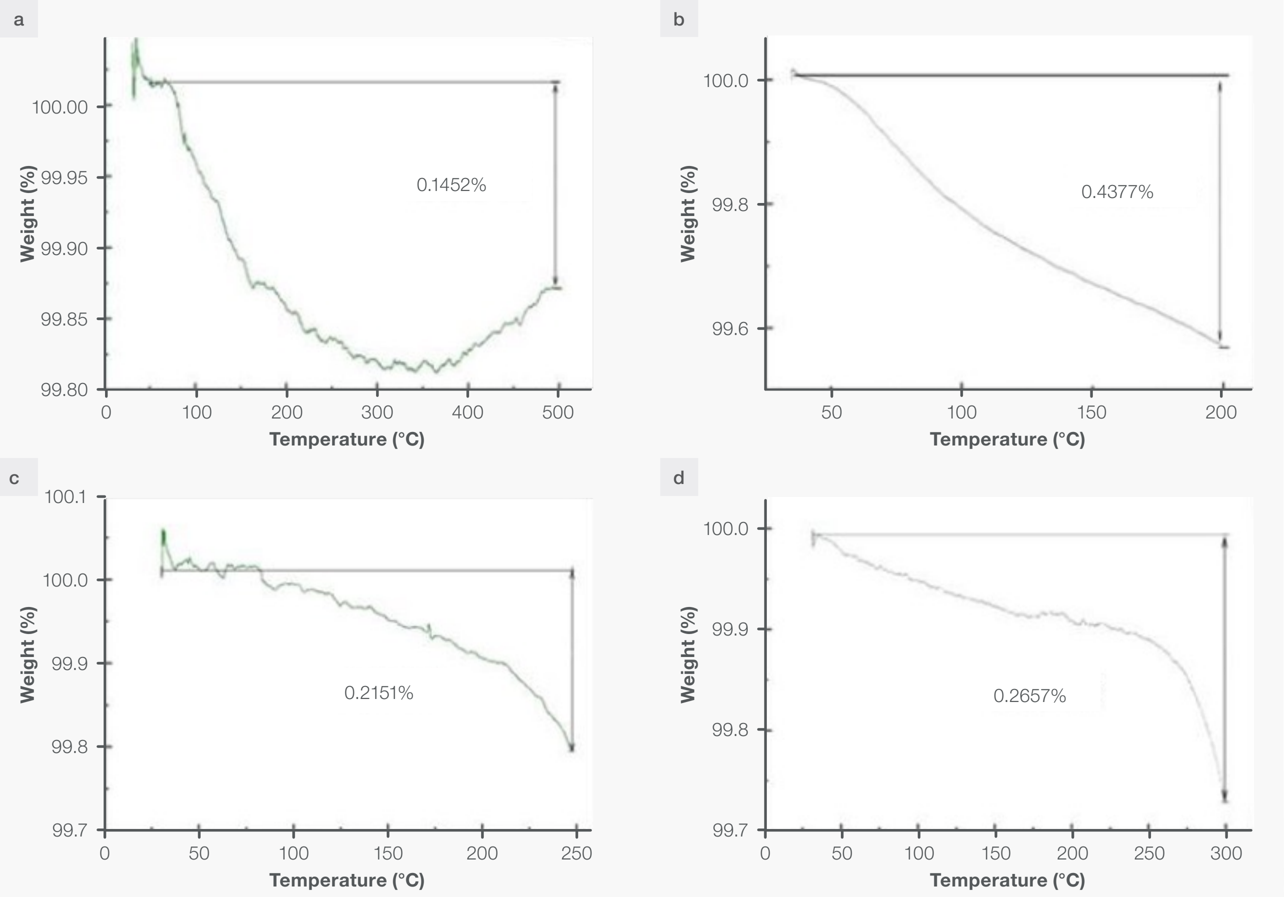


Figure 5f. TGA-IR spectra of pure starting materials used to synthesize cathode. (a) carbon; (b)V_6O_{13}; (c) polymer binder; (d) Li imide. Source: ACS Appl. Mater. Interfaces 2018, 10, 19667-29674.

It was found that the vanadium oxide, when mixed with the polymer binder, produced data that looked nearly identical to the composite data. Just those two ingredients on their own looked to be producing the dioxane material. Figure 5g shows the infrared spectrum from the original cathode, while Figure 5h shows the infrared spectrum at one of the temperatures for just this polymer binder mixed with the vanadium oxide on its own. The agreement between the TGA-IR data is striking. Thus, it was determined that a reaction between the polymer binder and the vanadium oxide is one of the chief unwanted developments that's happening at elevated temperatures to reduce the capacity of the electrode.

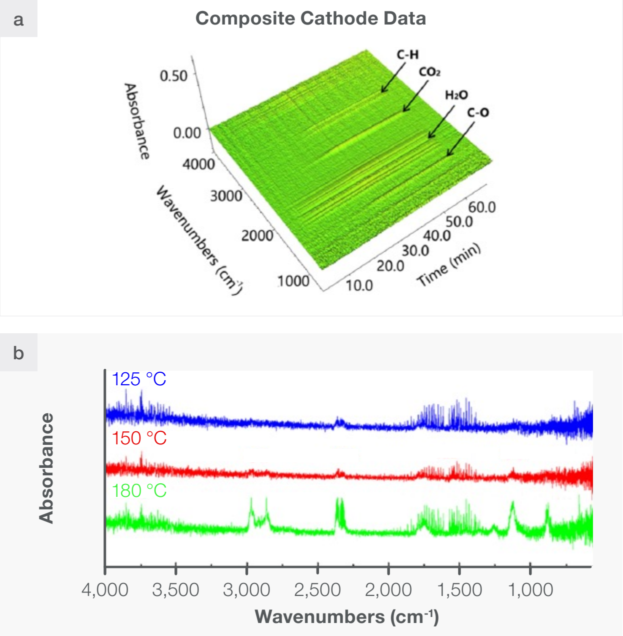


Figure 5g. (top) *In situ* three dimensional (3D) image of IR spectra at 180 °C; (bottom) comparison of individual spectra of the TGA exhaust gas from V_6O_{13}-based cathode composites heated at target temperatures of 125, 150, and 180 °C.

This incident demonstrates that TGA-IR can be used to not only identify what reaction is occurring, but also to determine the temperature at which it starts to happen. The technique can also be used to identify if another side reaction is occurring. Consider this further experiment with the same vanadium oxide composite.

Figure 5i shows the weight loss curves of the polymer binder/vanadium oxide mixture at different temperatures. The data indicate that this reaction between the polymer binder and the vanadium oxide begins to happen about 140 °C. But beyond this, the group wanted to be sure that the carbon dioxide evolving from this reaction was due to the carbon in the electrode and not carbon dioxide from the atmosphere.

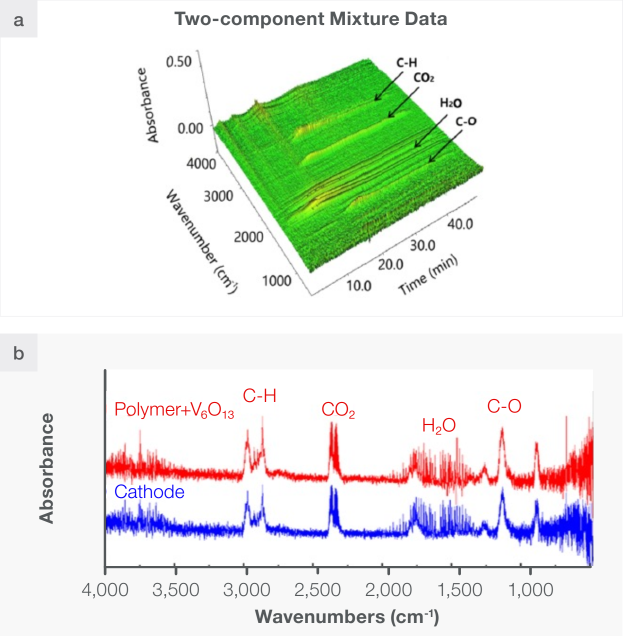


Figure 5h. (top) *In situ* three dimensional (3D) image of IR spectra at 180 °C of the TGA exhaust gases of mixture of V_6O_{13} and polymer binder; (bottom) a comparison of the *in situ* individual spectra of TGA exhaust gas from a mixture of V_6O_{13} and polymer binder a cathode composite.

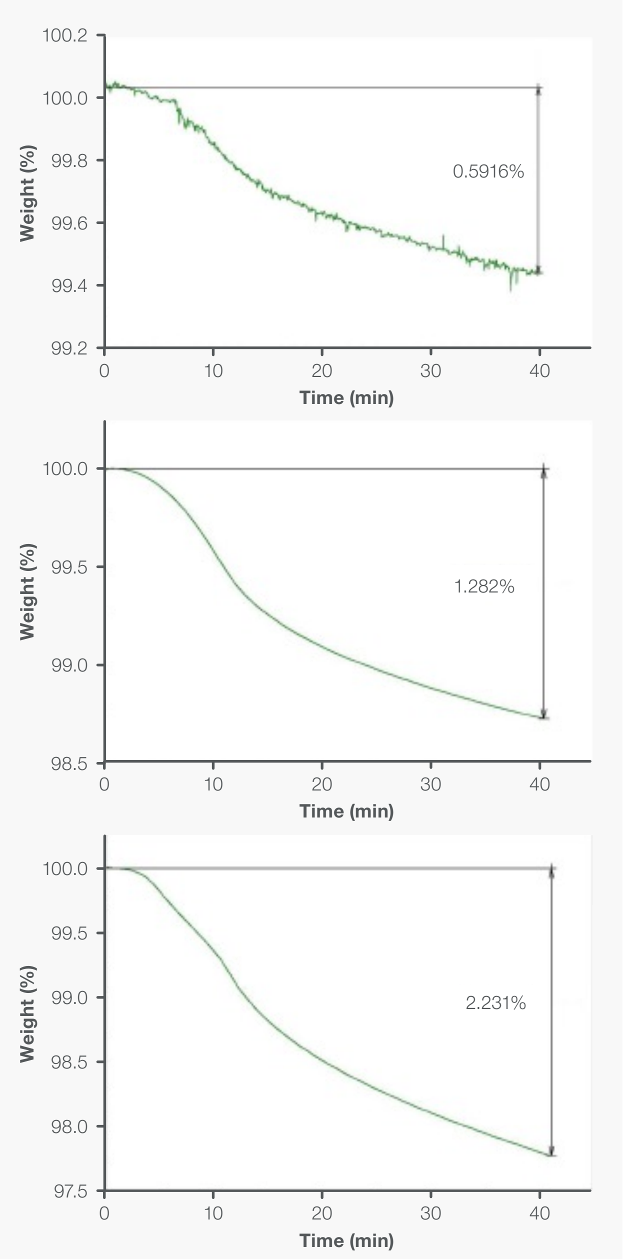


Figure 5i. TGA profiles of mixtures of polymer binder and V_6O_{13} carried out at various target temperatures of (top) 135 (middle) 140 and (bottom) 150 °C.

This brings to light another desirable feature of gas phase spectroscopy: isotopic sensitivity. Exploiting this feature, the group ran a control experiment with carbon-13 in the electrode material to verify that the CO_2 peak detected in the TGA-IR data was from the carbon material in the electrode and not from the atmosphere. The peak shift that occurred when using carbon-13, which would not have occurred if the source of carbon for the side reaction was atmospheric, indicated that the electrode material was indeed the source of the side reaction.

Coupling the power of these two techniques, thermogravimetric analysis and FTIR spectroscopy, allows for a rich understanding of this full reaction mechanism. With this hyphenated technique of TGA-IR, it is possible to probe aspects of thermal stability, to identify decomposition products, and even to know which reactions will happen at what temperature. This allows researchers be able to identify contaminants or to determine the original composition of a material that might have been unknown. As demonstrated in the experiments described here, TGA-IR can even help perform failure analysis and identify degradation mechanisms in battery materials.

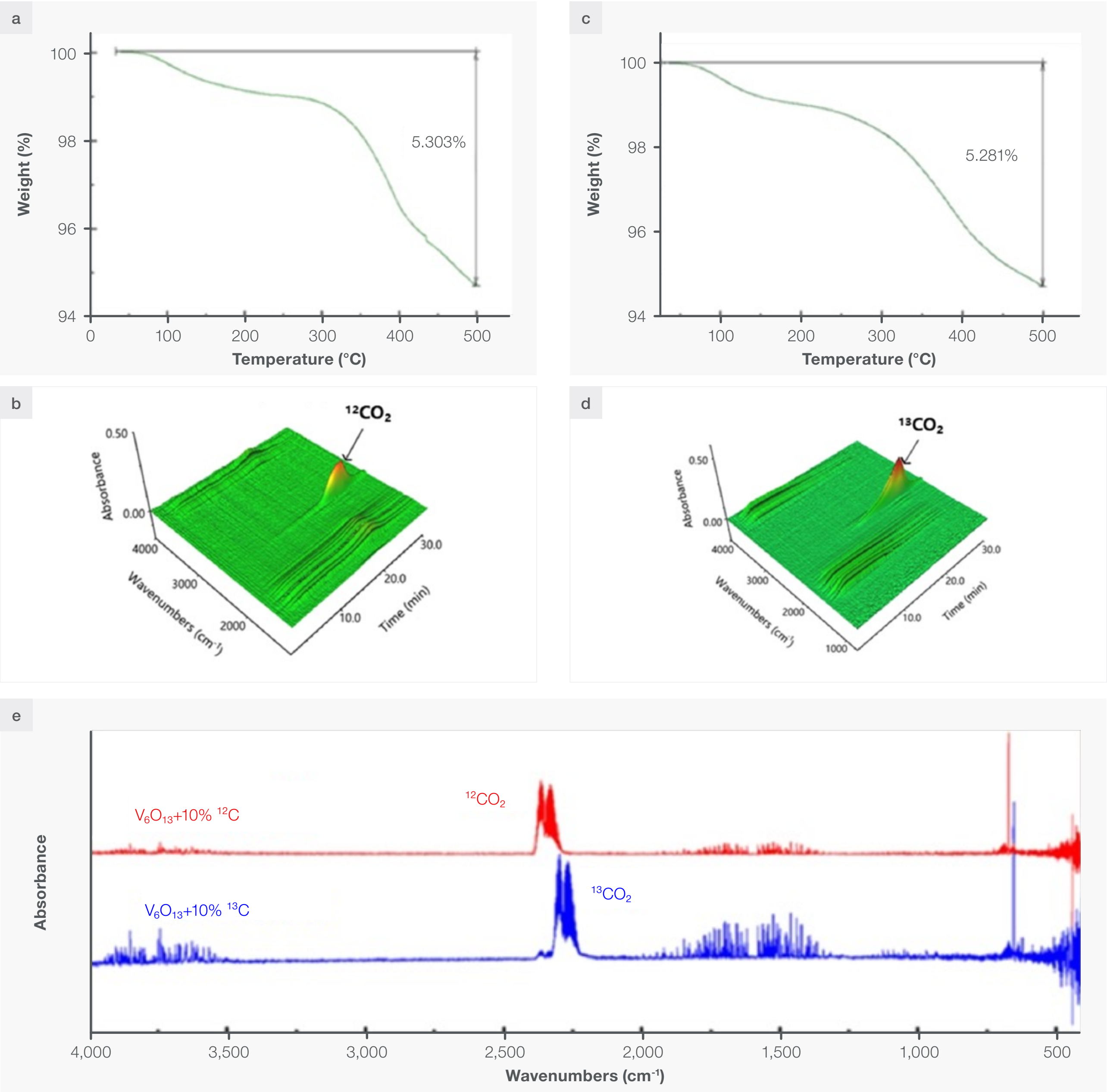


Figure 5j. Carbon-13 isotopes were used to confirm that the carbon source was the electrode and not ambient air. Source: ACS Appl. Mater. Interfaces 2018, 10, 19667-29674.

Analysis of gas emissions from Li-ion battery failures

Research is ongoing to find the right chemistry for lithium-ion batteries that can satisfy demands for charge density, stability, and safety. With increasing demand for energy density in each battery package, the issue of safety becomes a major concern. if the battery package is damaged or breaks down, the quickly released energy can lead to catastrophic results.

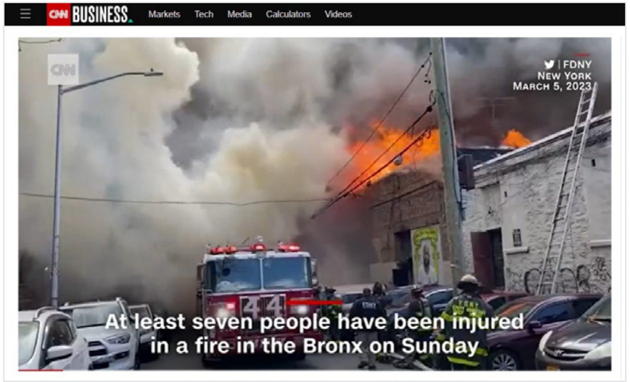
Three ways a battery breaks down

Researchers classify the causes of a thermal breakdown of a battery into three causes: overheating, overvoltage, or mechanical damage.

Overheating – In the normal course of battery operation, the chemical reactions that occur inside the sealed battery pouch are exothermic. If a battery becomes too warm, these reaction can reach a high enough temperature that can, under some circumstances, cause the chemical components to break down. Once something starts to break down, the reaction cascades and spreads very quickly, releasing even more energy. This chemical breakdown happens incredibly fast, and all those reactions generate so much heat that they can turn a liquid into a gas. The pressure builds up dramatically within the sealed pouch until it ruptures.

Overvoltage – The high power density at a battery's electrodes can initiate reactions going on at the electrode surface. For example, at the anode, the growth of dendrites (long narrow fingers of metallic growth that sprout off the electrode) cause short circuits or generate or electronic sparks. In such a case, the sparks or unplanned voltage path can generate enough energy to set off the electrolyte solution.

Mechanical failure or rupture – If an electric car gets in a car crash and some aspect of the collision fractures the battery casing, the interior components of the battery can be exposed to the atmosphere. Since electrolyte compounds are all highly reactive with moisture, once that battery package is broken open, any moisture in the air will start a series of very fast cascading chemical reactions. As with the other failure methods, once the components start to react, the whole breakdown process goes very, very quickly, generating a dangerous amount of heat and off-gases.



At least seven people have been injured in a fire in the Bronx on Sunday

Figure 6a. A scooter's Li-ion failed batteries caused a fire in a building where it was kept.

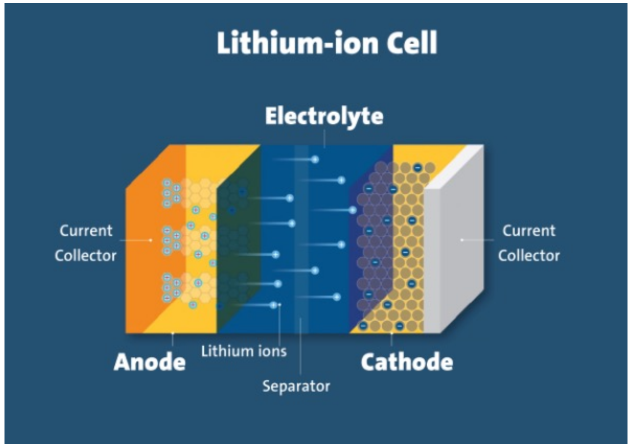


Figure 6b. Schematic of a basic lithium-ion battery.

Products of electrolyte breakdown

A major focus of research regarding safety innovations is the battery electrolyte, which is the solution that carries the charge between the two electrodes. Some common breakdown mechanisms of battery electrolytes are shown in Figure 6c. The top component of this list, the lithium hexafluorophosphate electrolyte itself, can break down due to thermal excitation or by exposure to water. As the listed reactions show, this is a potential source of hydrogen fluoride gas, which is highly reactive and extremely toxic.

The majority of gas emissions are due to the products of combustion, which include carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4). Also, different carbonate solutions like the solvents dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) or ethylene carbonate (DEC) generate a variety of breakdown products in the form of lighter carbon compounds. The products can include ethene or ethane ("C2 compounds") or propene or propane ("C3 compounds"). These small fragments of lighter hydrocarbons are generated when the original carbonate compound breaks apart. Many other compounds might be formed as well, like aromatics or other fragments of the original carbonates, but these smaller C2 and C3 compounds are the major components seen during chemical breakdowns.

$$LiPF_6 \rightarrow LiF + PF_5$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF$$

Figure 6c. When lithium hexafluorophosphate breaks down into its components, those components are reactive towards water and will produce toxic HF gas.

Gases evolved from lithium-ion battery breakdowns under different thermal/charge states can provide insight into breakdown mechanisms, as will be discussed below.

Using FTIR to identify battery gas components

As mentioned in Section 1, FTIR measures chemical vibrations and rotations, generating a unique "fingerprint" for each chemical. The specific energies where each chemical absorbs infrared light is a result of the distinctive combination of atoms put together into a molecule, and this analysis works across a broad spectral ranges.

The five different components depicted in Figure 6d clearly possess their own unique spectral shapes and regions where they absorb. When measured at high spectral resolution to obtain a large number of data points (plotted here on the x-axis), FTIR generates not just one band for each compound, but a broad range or an envelope of spectra. The spectrum for methane, shown in green, has a whole range of different vibrational and rotational patterns that we can use.

Water is often involved in combustion or explosions or gassing. This means water (purple plot) is something that must always be taken into account as a potential spectral interference. The blue plot at the top is sulfur dioxide, and it is obvious that there is heavy overlap with the water bands. While a portion of the methane plot also overlaps with the water and sulfur dioxide plots, the broad range of FTIR allows the clear identification of other methane bands without interference.

The high spectral resolution and the unique spectral shapes generated by FTIR analysis allow users to analyze chemicals even with heavy spectral overlap. With strong bands and weak bands, a single gas can be identified and measured in a single measurement, even with other components present. Sensitivity ranges from low parts-per-million levels up through percent levels of other components, even when they are all in the same sample. This ability to measure multiple components all at once in a single spectrum is a key advantage of FTIR.

It should be noted that diatomic molecules like oxygen or nitrogen, and noble gases like argon, are all invisible to FTIR. These species do not develop a dipole moment during their vibration and thus are impossible to measure using infrared analysis.

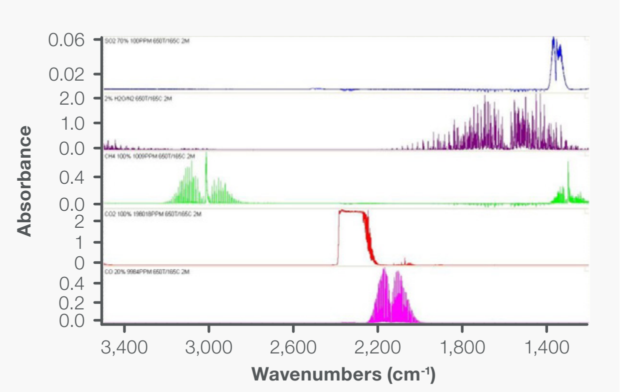


Figure 6d. FTIR analysis provides unique spectral shapes for different species. From top to bottom: sulfur dioxide, water, methane, carbon dioxide, and carbon monoxide.

Measuring components despite interference

A pair of high-resolution spectra are shown in Figure 6e. In red on the bottom is a carbon monoxide spectrum from a calibration standard, while a spectrum from a combustion sample is in blue on top. The CO bands are clearly present in the sample spectrum, but so are other bands from different compounds present. To the left side is evidence of carbon dioxide, and some water bands are interfering as well.

If a simple peak height or peak area measurement were applied here, interfering spectra could cause trouble—it would be impossible to know whether the sample of interest (CO) or spectral interference was being measured. But with the wide spectral range provided by FTIR, some special algorithms can be used to overcome this issue. Specifically, the Classic Least Squares algorithm, or CLS, can assess all the different bands present and then perform a peak shape or a curve fit analysis to match the calibration standard and the sample. This makes it possible to measure specific components even with heavy spectral interference.

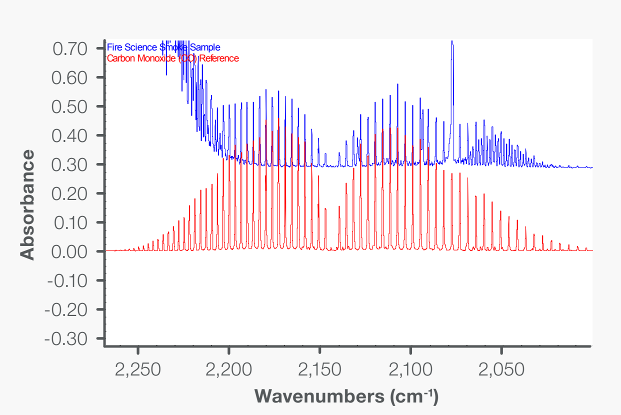


Figure 6e. Overlay of spectrum from CO calibration standard (red, lower) with spectrum of CO from a combustion reaction (blue, upper).

Identifying multiple gas products in a battery breakdown

This example shows the FTIR spectroscopic analysis of an actual thermal overload of a lithium ion battery. The spectrum of the overall gas emissions is depicted in red at the top of the image in Figure 6f. It is a very complex spectrum with many different bands. Yet with the proper algorithms and calibration references, it is possible to identify the presence of multiple components within the sample.

Multiple reference spectra are shown in different colors below the spectrum of the overall sample, allowing for points of comparison. (The complex spectrum for water, in dark blue, has been moved towards the bottom to make visualization of the other components easier.) In purple is methane; the methane bands partially overlap with another large component at around 2900 cm^{-1}. However, the bands can still be identified at a slightly higher wavenumber range, near 3100 cm^{-1}.

The presence of carbon monoxide (green, with bands prominent at ~2100 cm^{-1}), carbon dioxide (maroon, with a large peak at ~2300 cm^{-1}), and ethene (also in green, with bands at <1000 cm^{-1}) can be verified in the sample.

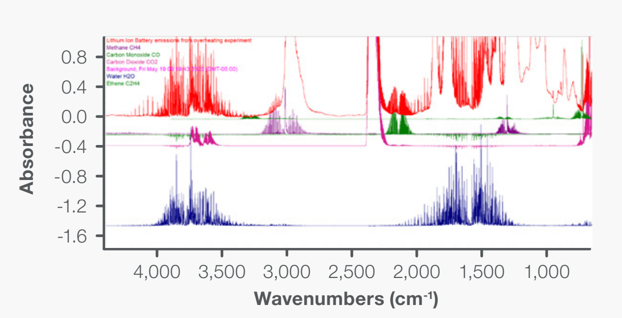


Figure 6f. Spectrum of the gases emitted thermal overload of a battery (red) compared to spectra of various calibration standards of the carbon-based component gases.

Figure 6g shows another set of spectra from the same overheated battery, with a few more calibration components. In pink is hydrogen fluoride, which is probably the gas of most interest regarding electrolyte breakdown. While there are some water bands on top of it, the HF bands can be clearly seen where they stick up. Also included are different carbonate solutions, with partial breakdowns or non-broke down solvent bands. There are several different carbonate-related peaks mapped here; this matrix could be more complex or simpler depending on what compounds comprise the electrolyte solution.

All these components of interest were able to quantified in this single FTIR analysis. The large amount of water was also taken into account when performing the analysis.

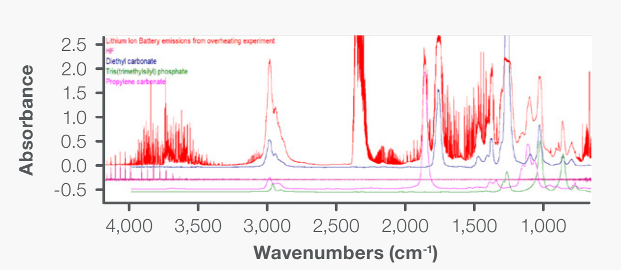


Figure 6g. Spectrum of the same thermal overloaded battery as in Figure 6f, but with overlays of reference spectra for HF and carbonate breakdown products.

Gas levels relative to battery charge state

In this example, hydrogen fluoride emissions were generated from an electrolyte breakdown that was initiated by the application of a propane torch to the battery. The concentrated flame caused the battery to overheat and thus break down. The bottom graph in Figure 6h shows the hydrogen fluoride released across several different experiments. The different colors of plotted lines indicate different charge states of the tested battery. It is quite noticeable in the lower plot that the breakdown patterns and reaction kinetics differ depending on the charge state of the battery. Meanwhile, the upper image shows plots of the heat release rates that were measured coming off the torched batteries. As with the HF levels, the amount of heat released was greater when the battery was more fully charged.

This information came from one of a series of papers by a Swedish research group that, together with Chalmers University Institute and the Swedish Institute of Research or RISE, released several studies regarding FTIR measurements. (This particular paper was published in the journal *Nature*. Anyone who is interested in more about the use of FTIR to measure HF and other components is recommended to investigate some of those papers.) One significant accomplishment of this group was the development of calibrations for some of the intermediate components that form during the breakdown of lithium hexafluoride phosphate. It is very difficult to obtain a calibration reference for these intermediate chemicals because they are so reactive; it's not really possible to go buy a cylinder of a reactive intermediate from a specialty gas supplier. However, the Swedish group was able to measure those intermediates and add those to their calibration method.

Analytical instrumentation and method

Sampling for FTIR is actually quite simple. Basically, a sample line is hooked up, the sample is pulled through, and the gas flows through the pipe into the instrument. That's all there is to it.

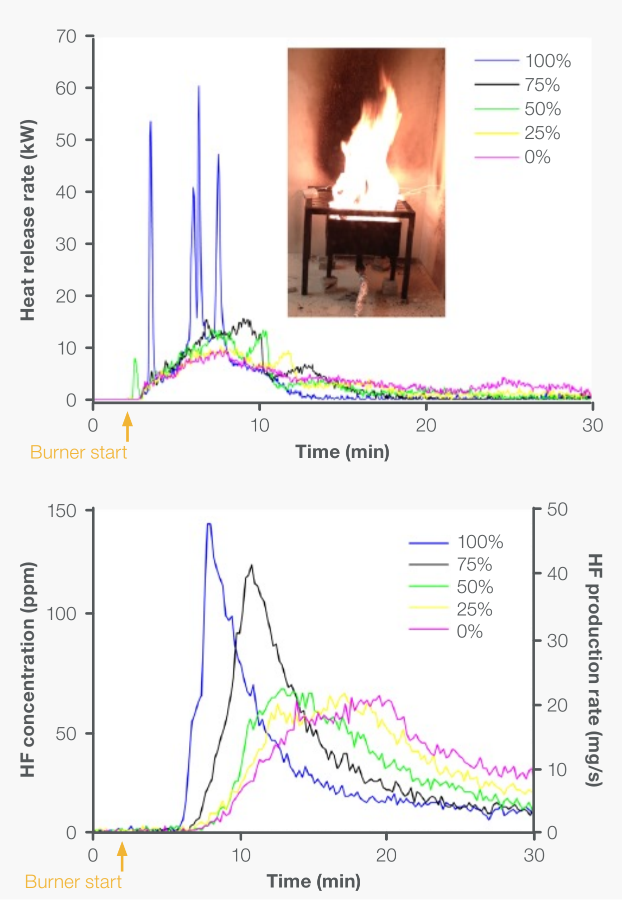


Figure 6h. Plot of heat release rate (top) vs concentration of HF released (bottom) at different battery charge levels, for a battery undergoing thermal breakdown due to a propane torch. Warning: Batteries should NOT be heated with a propane torch.

The Thermo Scientific™ Antaris™ IGS Gas Analyzer is illustrated in Figure 6i. The industrial gas system is shown the upper image, with the associated gas cell at the bottom of the image. The IGS includes a sampling controller, some heater controllers, flow meters, and a vacuum pump behind to pull the sample through. Those items merely control the gas flow through the gas cell. The sample is held elsewhere, wherever the compromised battery actually ruptures and burns. The key aspect of analysis is to control the temperature and pressure as the gas flows through the gas cell.

Figure 6i. Antaris industrial gas system.

Temperature must stay elevated in order to ensure all samples remain in the gas phase. No moisture or any of the components should condense out; this would change the chemistry of the reaction and it could even cause some corrosion or problems with the gas. For these reasons, the Antaris IGS has heated lines, often with a soot filter or a particle filter in front to prevent any particulates from entering the heated line or the gas cell. A vacuum pump creates suction to pull the sample through. The system's internal pressure is monitored to keep it constant as the sample passes through; this assures constant sample density, which is necessary for accurate and reproducible sampling. Thus, the Antaris IGS provides simple, continuous measurements via FTIR without the need for sample extraction or the preparation of derivatives.

OMNIC Software capabilities

In practice, many people want to measure how lithium-ion battery chemical reactions or the kinetics of the reaction lead to changes in concentration over time. OMNIC software can actually measure the different components quantitatively and display them in a plot, as show on the top section of Figure 6f. Three different components, HF, formaldehyde, and carbon monoxide, are in the sample. Time is plotted on the x-axis, while measures of the change in of the concentration in the gas in ppm is on the y-axis. This allows users to see what happens as the reaction develops. Different chemical components can be tracked simultaneously.

Gas Sample Conditioning Example

Gas flow diagram showing sample conditioning before entering the spectrometer

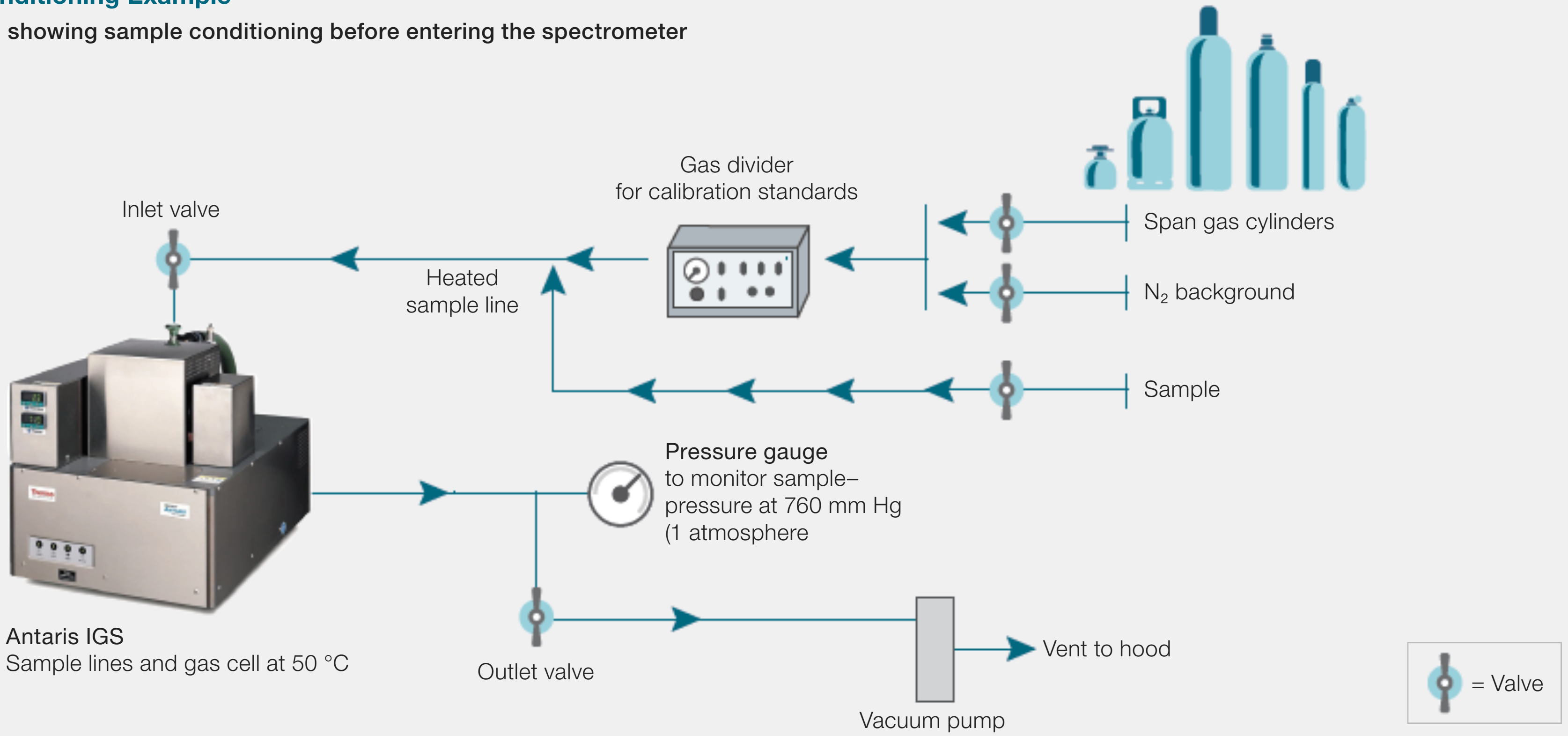


Figure 6j. Diagram of the sample flow for FTIR gas analysis.

The lower portion of Figure 6k shows the overall infrared spectrum. It is notably complex. A lot of water is present, as are methane and other hydrocarbons, with carbon dioxide and carbon monoxide mixed in too. As in the previous example, the calibration references can be matched up, even with heavy interferences like these, to generate good quality spectral results despite this complex concentration.

In addition to the display of concentration versus time, each one of these data points is saved and can be exported. Every time the system measures, the output data can be saved onto a connected local computer as a text file that can be easily opened into Excel. With this information, a concentration versus time spreadsheet is available, and it goes into a computer buffer which can be accessed by an external software program. Say, for example, a lab was running a calorimeter or other piece of equipment that recorded temperature or flow rate. The data from that acquisition system could be merged with the FTIR data in real time to create a composite information file that might deliver unexpected insights.

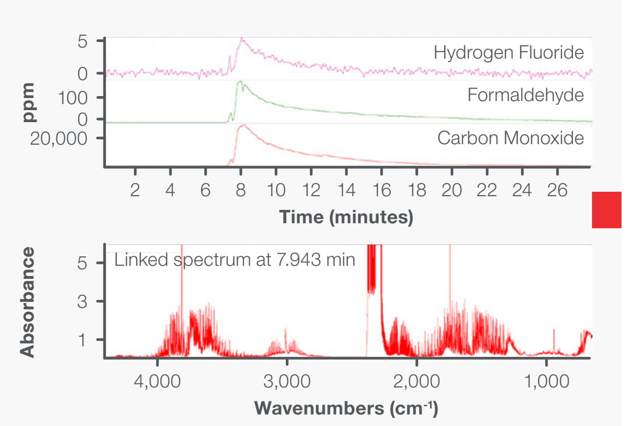


Figure 6k. A plot of sample concentration data over time. Resolution 1 sec. Infrared spectrum on the bottom.

Resources available from Thermo Fisher Scientific

Thermo Fisher Scientific offers turnkey calibration options where all calibration references are provided and all the absorbance bands and spectral interferences have been predefined. The system typically employed for this application uses a gas cell of 200 milliliters and a volume with an effective path length of two meters. This size cell allows quantification to range down to low parts-per-million concentrations and up to percent levels for some of the major components. Flowing the gas through a 200-mL cell, typically at a couple of liters per minute, means that the gas exchanges through the gas cell at a pace (on the order of 5 seconds) that permits measurement of a transient event. The sampling rate records data as quickly as one sample per second as the gas flows through the cell, generating real-time plots like those shown above in Figure 6k.

Along with a turnkey solution for calibrations regarding the most common chemicals, Thermo Fisher Scientific also enables users to adapt or add reference standards and to alter the quantitative method as needed to perform unique experiments. If diethyl carbonate is not used, the system can be directed not to waste processing time trying to quantify it. If some new electrolyte compounds or solvents are present, those can be incorporated into the method so quantitative results for those can be obtained.

To summarize, key advantages of FTIR analysis include the ability to measure multiple components in a single measurement, even when the sample mixture contains hydrogen fluoride gas and other hazardous electrolyte breakdown components. The analysis can be performed in real-time online with simple basic sampling requirements. Using an Antaris IGS Gas Analyzer, the temperature, pressure, and flow rate of gas through the cell can be controlled. The gases can be measured continuously, which enables monitoring of the reaction kinetics as they happen. With OMNIC Software, spectral data can be displayed, analyzed, and exported. Thermo Fisher Scientific provides various spectral libraries to help identify unknowns, plus the ability to add components to a method and actually fine tune or adjust calibrations for specific desired chemistries.

Features of the Antaris IGS Gas Analyzer with OMNIC Software:

- MCT Detector enables second-by-second sampling rate
- Display of up to 6 control charts during sampling
- Real-time analysis of 25+ components
- Time vs concentration results saved as a *.txt file
    - Importable into Excel spreadsheet
    - Support for real-time integration into external software

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Identification of polymer coatings and gases during lithium-ion battery recycling

No single analytical technique can provide comprehensive identification or quantification of recycled battery components. Various material characterization techniques may be used to focus on specific aspects of the process: XRF and XRD are well suited to elemental analysis; ICP-OES is used for looking at solvents; microscopy can be helpful for contamination detection; GC-MS and IR spectroscopy may be employed to evaluate the gases emitted during recycling.

The focus here will be on infrared technology and its usefulness in the recycling space. Infrared technology has long been used in recycling, especially for polymer recycling. Infrared spectrum acquisition is very easy, consisting of taking a type of sample (solid, liquid, or gas as well, using a gas cell), placing the sample in a spectrometer, and clicking “go” on the instrument. The resultant spectrum is delivered in a matter of seconds. With many different accessories now available, it is possible to measure many different types of samples.

There are several reasons to use vibrational spectroscopy to check the type of battery before it is dismantled, but one main reason is to learn which specific recycling process might apply. Much can be determined based on different types of fibers, polymers, the battery casing and so on. FTIR spectroscopy and microscopy are ideal for this. Meanwhile, Raman analysis can provide key insights regarding graphite-based materials like electrodes. These specific applications will be discussed in more detail below.

Battery recycling processes

When dealing with basic battery cell structure and the processes that are involved in recycling, there are generally two types of processes that are used: a pyrometallurgical process or a hydrometallurgical process.

The pyrometallurgical process is based on using thermal treatment of a battery to change its chemical structure and transform it into its various constituent parts like black mass, reduced metals, and so on. The other type of process, hydrometallurgical, is created by implementing a chemical treatment such as the use of acid or a basic type of leaching.

Regardless of the type of process, the functional identification of the materials prior to processing and the subsequent functional identification of the component parts, like black mass, metals, separators, solvents and electrolytes, are both required. In addition to these materials, toxic and hazardous gases may be released during either pyrometallurgical or hydrometallurgical processes, and these toxic and hazardous gases can help identify the battery type. Depending on the battery chemistry used, a specific gas or gases will be released. Information regarding the de-formulation of the battery or indications of moisture can also be determined when testing those off-gases.

Solids, liquids, or gases can be analyzed directly using attenuated total reflectance infrared spectroscopy, or ATR-FTIR. For some particular aspects of battery recycling, such as determining what form of carbon is present in the electrode, Raman microscopy is better suited. And if certain specific analyses are required—for example, if looking at a paint coating on a metal film—then there are different types of accessories available to make such analyses easy.

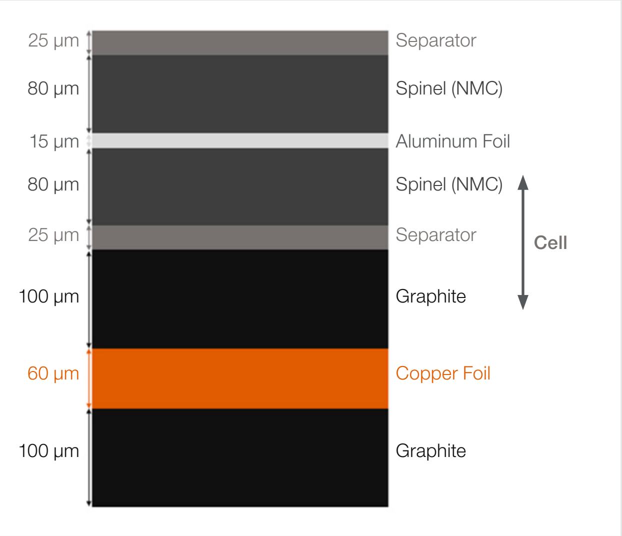


Figure 7a. Diagram of basic battery cell structure. For recycling purposes, these parts need to be identified quickly.

Figure 7b. Acquiring an FTIR spectrum requires little sample prep with the Thermo Scientific Nicolet Apex FTIR Spectrometer.

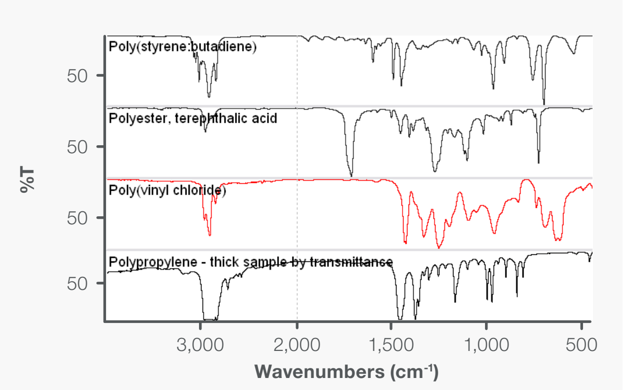


Figure 7c. FTIR quickly illuminates the differences between polymers.

Raman spectroscopy for enhancing efficiency and yield in hydrometallurgical processes

A prominent battery recycling company based in the U.S. has harnessed the capabilities of multiple Raman spectroscopy systems for its hydrometallurgical platform. By focusing on the efficient recovery of essential elements such as cobalt (Co), lithium (Li), and manganese (Mn) from the cathode active materials (CAMs) of expired or used lithium-ion batteries, the company has realized significant advancements in their recycling processes. For the transformation analysis of various CAMs, including lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC), lithium manganese oxide (LMO), lithium nickel cobalt aluminum oxide (NCA), lithium iron phosphate (LFP), and nickel metal hybrid (NiMH), the company utilized the Thermo Scientific MarqMetrix Process BallProbe™ Sampling Optic. This rugged tool was selected for its ability to operate effectively in harsh conditions, offering an ideal solution for continuous monitoring. Multiple models within the same device were deployed to cater to different chemical species, simplifying the analysis process.

Applications extended beyond recycling, as the Raman spectroscopy systems provided rapid online metrology for both anode and cathode materials. Precise measurements of polymers, graphite, nickel, manganese and cobalt materials further highlighted the versatility of the technology across battery-related domains.

FTIR spectroscopy for identification of battery components

The first application to highlight here is the identification or qualification of polymers. Different types of polymers are used in battery manufacturing. A polymer could make up a coating polymer in the casing of the battery, or one could be used as a main part of the battery in the form of a separator. Depending on the need, a battery separator could be porous, or it could be coated with ceramic or different functional coatings.

In order to identify this, the polymer can be directly mounted on an ATR attachment, and an analysis run with the press of a button. Results of molecules' vibrational interaction with infrared light can show clearly the difference between different types of aliphatic and aromatic polymers. It can also indicate different functional groups that might be present, like esters and amides. The technique allows users to differentiate between very similar polymers, with very small differences, such as high density polyethylene versus low density polyethylene. It can also differentiate the polymers based on their morphology, i.e., amorphous versus crystalline structure. Figure 7c makes clear the differences in the spectra for compounds that are as compositionally similar as poly(styrene:butadiene), polyester, poly(vinyl chloride), and polypropylene.

Macropolymer analysis

A macropolymer of a size around 10 microns or larger can be easily placed on an ATR attachment for analysis. Figure 7d shows an example of this. It pictures the spectrum of a polymer separator, acquired using a routine ATR-FTIR system. Through the acquired spectrum, it is possible to determine exactly what the polymer type is. In this example, the main polymer with the wavenumber bands at 2915 cm^{-1}, 1472 cm^{-1}, and so on, corresponds to polyethylene. Meanwhile, other bands like those at 1409 cm^{-1} and 1072 cm^{-1} index to polyvinyl fluoride. Still other absorption bands indicate the presence of hexafluorophosphate or some residual carbon.

The technique just described is very useful when dealing with a simple polymer with only a couple layers, and the sample could be reversed to have a look at both layers. However, a multilayer separator film is like that shown in Figure 7e has different materials in the different layers. In this example, the first layer is of nylon, which is just 10 microns across. The second one is urethane, 5 microns thick. A third is aluminum of width just 37 microns and the fourth layer is 30-micron-thick polypropylene. (Note that aluminum cannot seen by infrared; it is a pure element and does not have a covalent bonds, and therefore cannot be seen by any vibrational spectroscopic technique. Verification of the presence of Al requires the use of XRF.) To separate these two different layers of polymers, determine the thickness of the layers and establish what type of recycling processes we need to use, a routine application of FTIR microscopy is done. In this way the different compositional layers of the polymer can be clearly determined. The spectra of the various layers are shown in the lower right potion of Figure 7e.

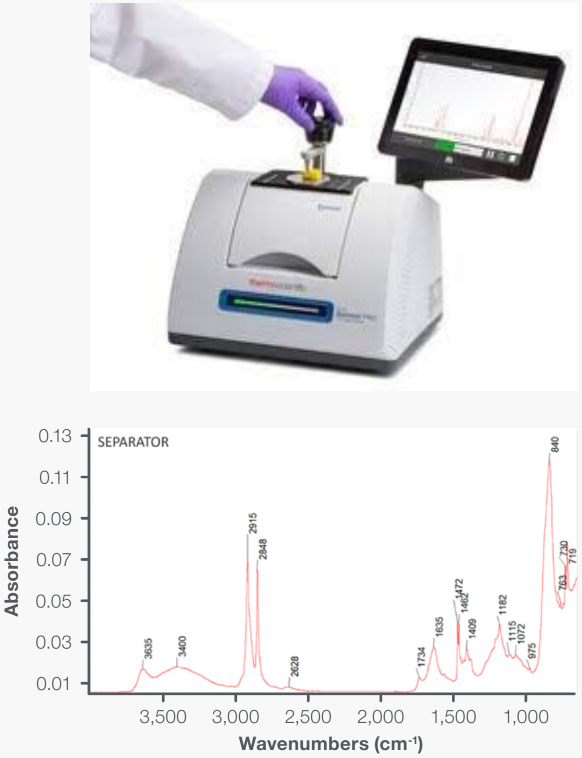


Figure 7d. Analysis of simple polymer by FTIR.

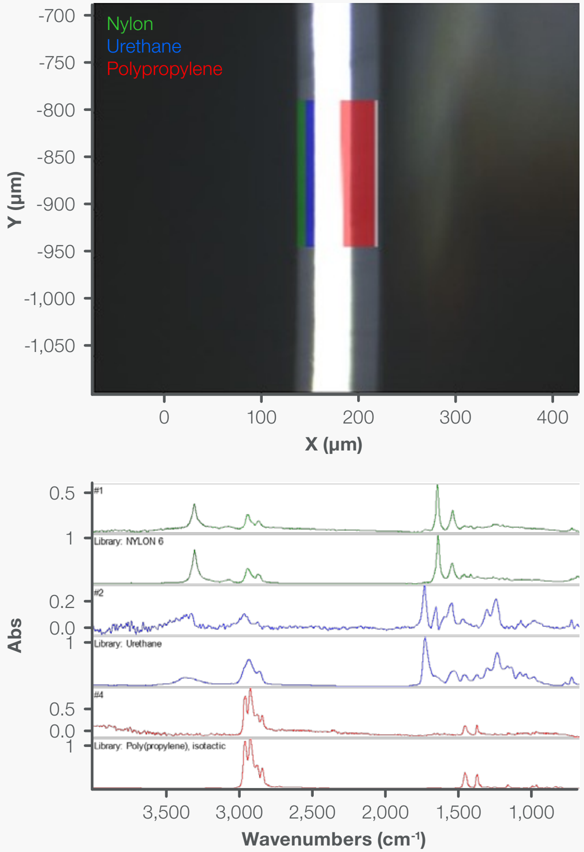


Figure 7e. Multi-layer polymer analysis can be performed.

Identifying polymer separator degradation

FTIR analysis can reveal if a separator polymer has been degrading as the battery is going through recycling. If a separator film degrades, it could result in the presence of unknown compounds which potentially may be hazardous. In this example, illustrated in Figure 7f, a video still image (upper right) shows the separator as a darker brown strip down the center of the picture. To the upper left is a chemical image which shows the fine structures associated with the separator itself. But the dividing line down the middle in red reveals degradation; it has fragments and gaps. In comparison, the green shows less degradation. The spectra at the bottom show the carbonyl band (from carboxylic acid) for each section of the sample, making apparent the degradation of the separator polymer despite the video image looking more or less intact.

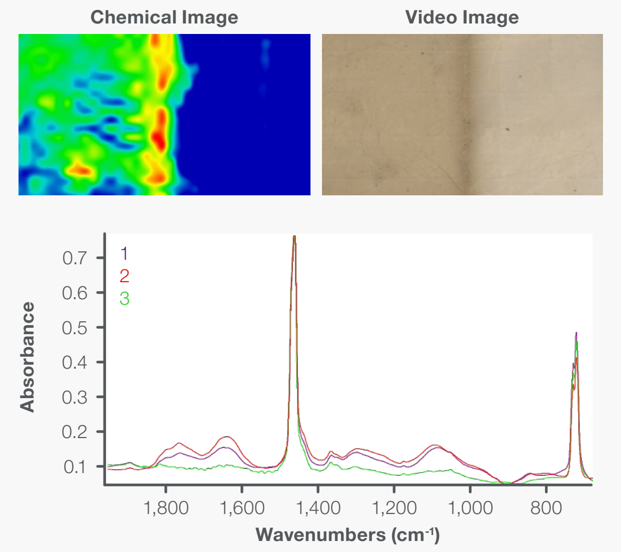


Figure 7f. Degradation shows up as different colors in the Raman map, while the correlation to the video image is clear.

Applications of vibrational microscopy

Apart from polymer samples, separators, and casings, there are several other applications of vibrational microscopy. For example, when the graphite-rich material known as black mass has been extracted, and when polymer separator has been extracted and refined for subsequent use in the new battery, there is a need to check them for contamination. Infrared microscopy and Raman microscopy and imaging can help detect different particles, making it possible to count them and look at their shape, and determine if those particles are the desired materials of if they are contaminants.

When recycling, there could be contamination introduced during the processing, in the form of fragments of other materials left over from earlier processing. The system could have different types of fibers in it, or maybe some polymer particles are present. There may even be some oxides present as well. All of these can be easily identified using vibrational microscopy. In both FTIR and Raman microscopy, instruments have dedicated workflows to do this.

Here is an example of how the process works using such a dedicated workflow. First a mosaic of the particles is acquired. (See Figure 7g.) Then the particles are counted and depending on the sizes of the particles, the number of identified particles can be increased or decreased. If those particles size 5 micron and above are wanted, or perhaps particles between five and ten microns, a choice can be made to see just those particles. Once those particles are selected, the FTIR spectra are acquired for each of particle fitting those criteria. The particles are then identified using algorithms. Identifications can be made based on library comparisons: there exist sets of general fiber libraries; groups of general microparticle plastics libraries; or dedicated libraries that might have for example different types of graphene that are of specific interest. The algorithm can determine exactly what the particle type is, perform a percentage match with respect to correlation to the reference spectrum, measure the area of the particle, and even assess the morphology or the shape of the particle.

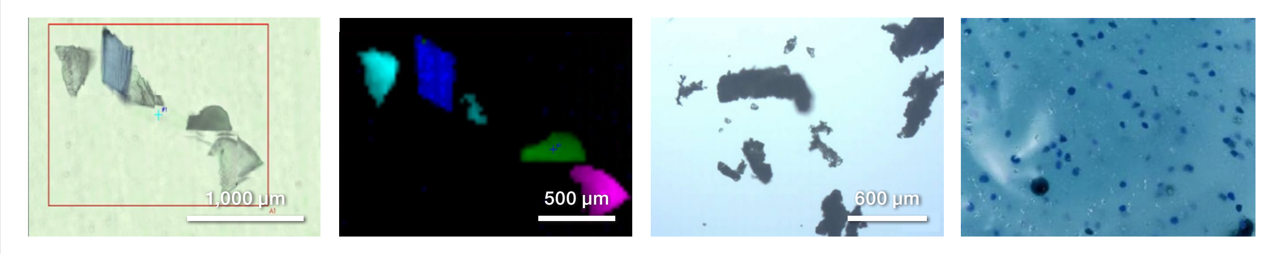


Figure 7g. FTIR microscopy shows shall variations and can be used to check for contamination.

Application of Raman microscopy

Shown in Figure 7h is data from an analysis of a cross-section of a carbon-based cathode. The analysis looks at different types of carbon films. The images show maps of different particle points on a sample set in a Raman microscope. The Raman spectra was acquired at each point, with data points then arranged into a composite image via software. The colored maps reveal the relative abundance of the two different types of carbons, amorphous and crystalline ("hard") carbon, at different places in the carbon film. The amorphous carbon section shows up as mostly blue, while the hard carbon image is dominated by red areas.

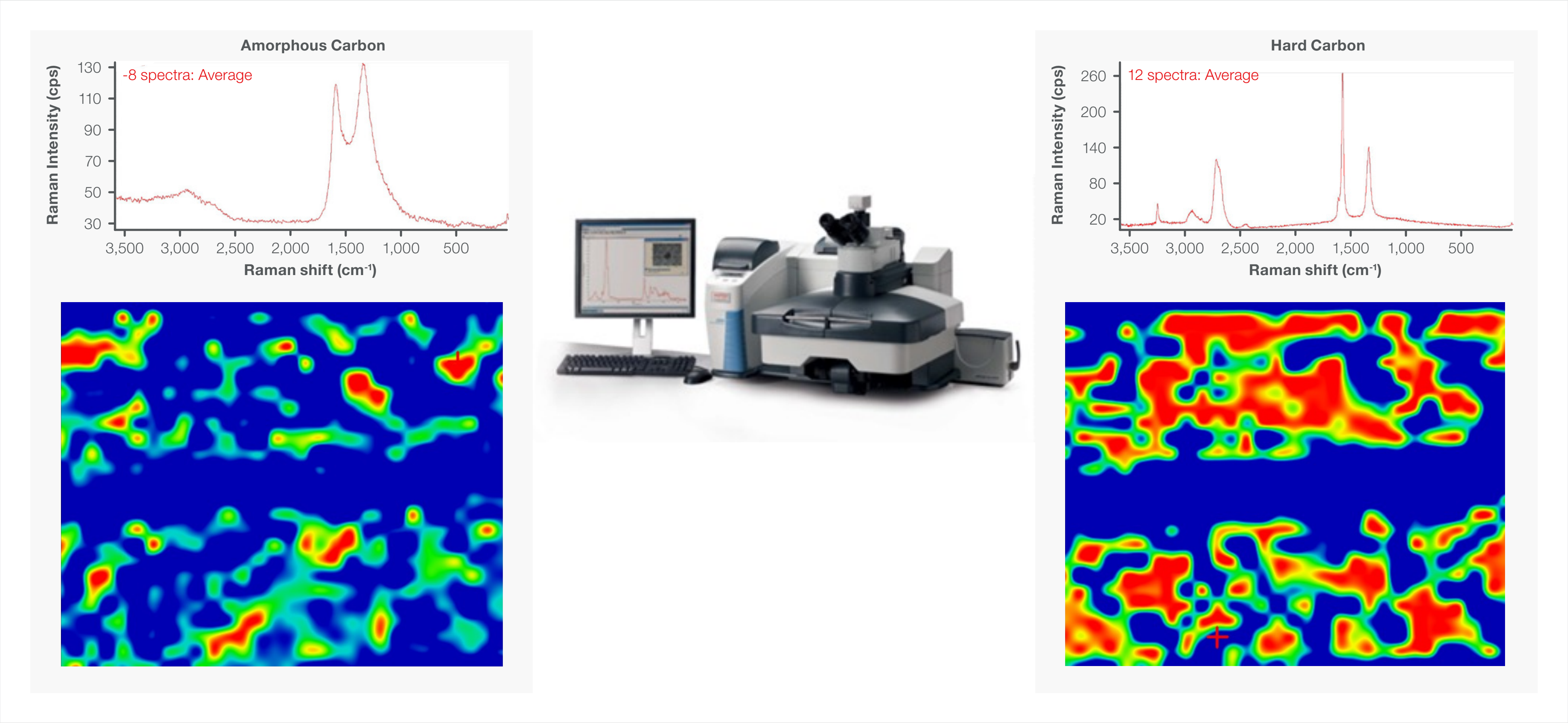
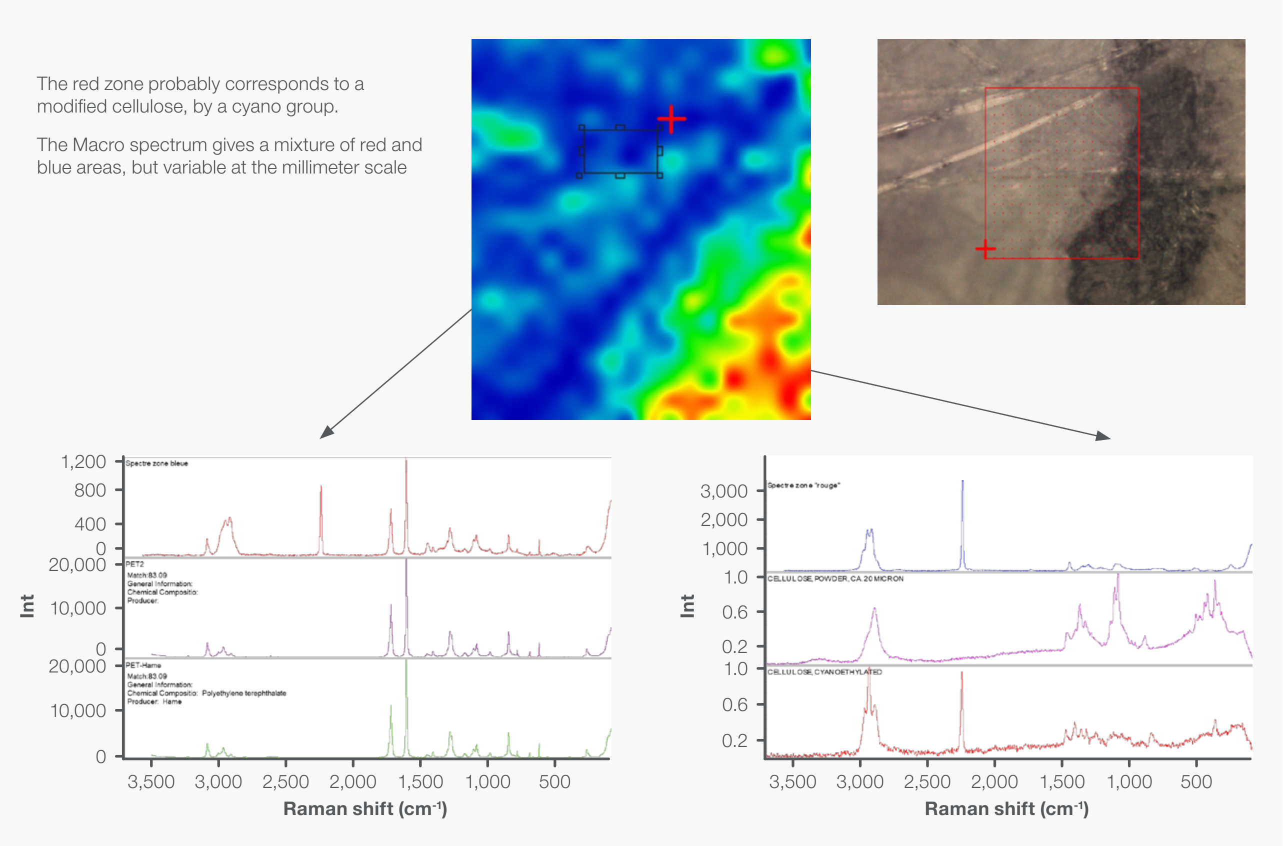


Figure 7h. Raman spectra and maps of amorphous (left) vs hard carbon (right) and Thermo Scientific DXR3 Raman Microscope (center).

Apart from infrared microscopy imaging, polymer separator evaluation can also be performed using Raman. In this case, the separator was first evaluated to see what type of separator it is (it is a PET/cellulose separator), and also to see if the separator sample is homogeneous enough for use. The area mapped was 180 by 150 microns, with 360 data collection points used to build the chemical image of this separator. In the Raman map (see Figure 7i), the red section indicates how the separator is modified by a cyano group.

A typical separator is just cellulose/PET, but this image shows cellulose and activated cyano-cellulose. The blue areas correspond to how the separator should be, when it is composed of the full fabric created by PET and cellulose. The degradation due to the cyano group can be clearly seen in the map in red, which matches up with the darker area in the photo image of the separator on the right. Just like the FTIR microscopy example above, Raman microscopy imaging can clearly show the degradation of the separator as well.



The red zone probably corresponds to a modified cellulose, by a cyano group.

The Macro spectrum gives a mixture of red and blue areas, but variable at the millimeter scale

Figure 7i. The Raman spectra and map both provide information about how a separator has undergone degradation.

Gas identification with combined GC-MS and FTIR

Gas generation is a byproduct of electrochemical and chemical reactions inside the battery that can occur when the battery is either operational or in storage, or even randomly when the battery is subject to thermal degradation or mechanical destruction such as shredding. Gas generation is typically increased due to ambient temperature, discharge current, and so on.

The common gas species that are generated from the lithium-ion batteries are often toxic: CO, HF, SO_2, NO_2, and HCl. These are typical gases that are generated not only during manufacturing but also during the recycling process. All these generated gases have to be identified, for safety and other reasons. Using GC-MS combined with FTIR can not only measure the types of gases being evolved, the technique can also help determine the isomeric compounds being released—components of some gases which cannot be detected by GC-MS.

For example, battery-swelling gases can be determined using a Thermo Scientific™ ISQ 7610 - ISQ 7610 GC-MS Configurator coupled with a Thermo Scientific Nicolet iS50 FTIR Spectrometer. The unique advantage of a setup such as this is, with a single click, both diatomic and isomeric components of a mixture of gases can be evaluated.

Gas identification with hyphenated TGA-IR

Another approach that can be taken by such labs is to use a TGA-IR module combined thermal gravimetric analysis / FTIR combined module, or TGA-IR module, to analyze gas produced during recycling. Please refer to Section 5 of this eBook for more detail on TGA-IR.

The TGA-IR analysis provides two-dimensional data which includes the measure of change over time. At different times, the different evolved gases which are related to the battery's composition are assessed. Using this information, the purity of the sample can be clearly determined. This is a standard application that is used in polymer recycling to determine the type of polymer and the evolved gases during the recycling process.

The other thing that TGA-IR can enable, by using vapor phase infrared spectra that are generated with the technique, is the determination of the components involved in the creation of such a sample. In a multi-component spectrum generated by a combination of four components, straightforward software processing can isolate the individual spectra and identify each of the four components that comprise the main spectrum. The high-resolution infrared spectrum would be able to distinguish between, for example, water, trimethyl amine, carbonyl sulfide, and 2-methyl-2-butanol. Knowing that those are the components of the gas mixture would help to identify the starting materials they came from—in this case, the profile of isocyanic acid corresponds to such a spectrum in an FTIR.

Deformulation analysis

Evolved gas analysis is important not just during mechanical recycling of batteries. There is also a need to look at the deformulation of the battery to be able to specifically treat that evolved gas and make sure that workers are protected. In such a setting where harmful gases might be evolved, gases like nitrogen are fed into the area first so that there is no explosion during the recycling of the battery. With this nitrogen stream set up, the evolved gases get filtered first, then passed through FTIR, and finally passed through a specific air treatment unit which can absorb different types of harmful gas.

In such a system with a continuous gas evolution process, there is a need for continuous gas evaluation. Continuous gas evaluation of the battery can be achieved by the Antaris IGS Gas Analyzer with Fire Science calibration. Multiple gas species can be evaluated down to low parts per million. This is a turnkey solution ready to use with calibration, certified calibrations, especially for fire science of the battery.

Figure 7j. The Thermo Scientific Antaris IGS Gas Analyzer with Fire Science calibration can provide continuous evaluation of gases evolved during de-formulation from battery recycling, measuring multiple gas species in a single measurement.

The Antaris IGS system provides a unique advantage because multiple gas species can be measured in 15 seconds. The system is cost effective because it does not require testing all the components one by one. In spectroscopy, multiple systems with multiple lasers would be needed. Using this technique, it is possible to measure a range of gases not limited to the usual products of combustion like carbon dioxide and carbon monoxide. It can evaluate powerful gases like hydrogen fluoride, hydrogen cyanide, acrolein, and also gases that are related to different electrolytes due of the presence of carbonates. (See the chart below of a list of smoke toxicity gases.) The system can be calibrated according to a customer need, and it comes complete, such that it can go online in rapid time. The complete IGS gas analyzer system includes the sampling system which can be heated to different temperatures, fully heated sampling lines, different gas cells such as a 2-meter zinc selenide window with 200 milliliter volume. Certified traceable fire science calibration standards are included too.

Smoke Toxicity Gases

Compound	Formula
Carbon dioxide	CO_2
Carbon monoxide	CO
Hydrogen fluoride	HF
Hydrogen chloride	HCl
Hydrogen bromide	HBr
Hydrogen cyanide	HCN
Sulfur dioxide	SO_2
Nitrogen monoxide	NO
Nitrogen dioxide	NO_2
Hydrocarbons	C1 – C4
Formaldehyde	CH_2O
Acrolein	C_3H_4O

Additional resources

This eBook is adapted from the Battery Value Chain Webinar Series with content presented by Dr. Lena Woodis, Jay Roberts, Sudhir Dahal, and Shailesh Karavadra.

To view these on-demand presentations in full, please visit **thermofisher.com/battery-webinar-series**

MarqMetrix All-In-One Process Raman Analyzer

Real-time analysis and rapid results

The Thermo Scientific MarqMetrix All-In-One Process Raman Analyzer is a cutting-edge solution that is easy to install and use. This advanced analyzer utilizes Raman spectroscopy to provide real-time analysis and rapid results in seconds, empowering users to optimize the recycling process of essential battery elements such as lithium, manganese, cobalt, and more. With its rich compositional information, quantitative and linear response, non-destructive nature, and ability to measure all sample types, this analyzer offers battery customers an invaluable tool for enhancing efficiency, reducing waste, and lowering costs in their recycling operations.

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