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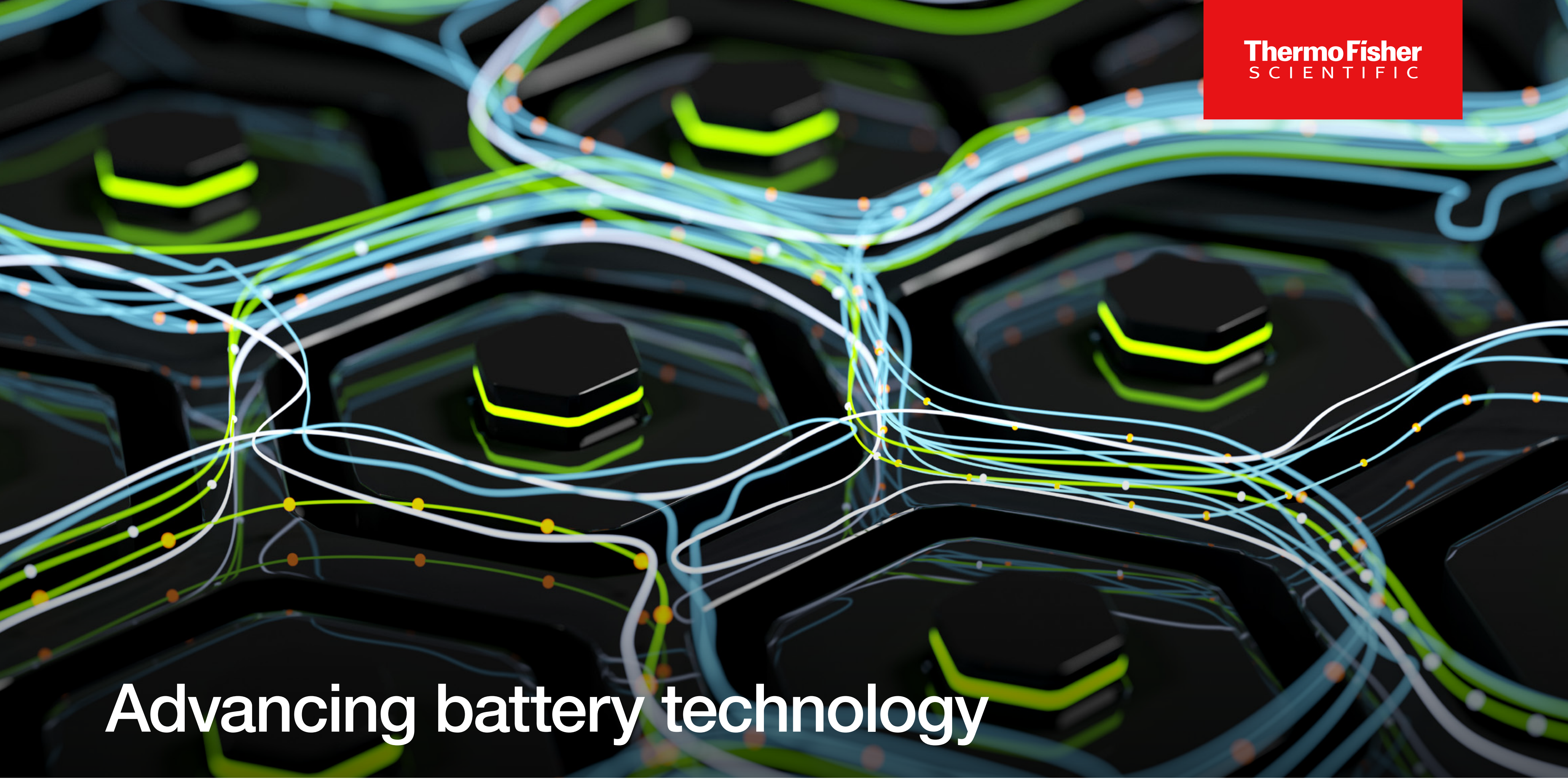

Advancing battery technology

Uncovering surface insights with X-ray photoelectron spectroscopy

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To reach carbon neutrality, we must first develop better battery technology to support energy storage, including power grid storage, electric transportation, and consumer electronics applications. The work requires a complete understanding the materials that make up a cell, which in turn requires a comprehensive array of analytical techniques. Surface analysis, particularly X-ray photoelectron spectroscopy (XPS), is one of the leading methods used to perform surface and interface characterization, and it is well-suited to the materials used in cell construction.

XPS and related surface analysis methods reveal the chemistry of the outer few atomic layers of a sample. XPS identifies and quantifies surface chemistry for inorganic or organic materials. For battery materials such as electrodes or separators, this is the region that is in contact with the electrolyte. How this interface develops over time is crucial to the performance of the device. XPS is used for research and development, materials screening, and failure analysis, often in concert with structural analysis methods such as scanning electron microscopy or other spectroscopic techniques such as Raman spectroscopy.

In this eBook, we introduce XPS and other important surface analysis techniques, describe the common workflows used to analyze battery materials, and highlight application examples to show how XPS technology can accelerate development of battery technology.

Intro to surface analysis

Every material has a surface layer, which can be up to three atomic layers thick, or about 1 nm, depending on the material.

Layers up to approximately 10 nm are considered ultra-thin films, and layers up to approximately 1-2 µm are thin films. The remainder of the solid is referred to as bulk material, as shown in Figure 1. This terminology is not definitive, however, and the distinction between the layer types can vary depending on the material and its application.

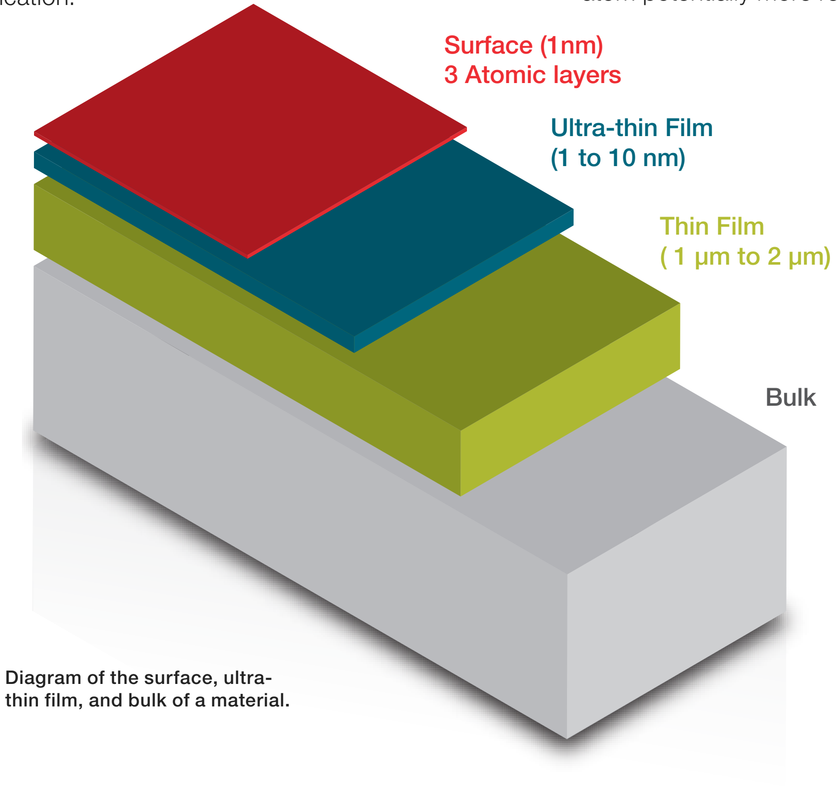


Figure 1: Diagram of the surface, ultra-thin film, thin film, and bulk of a material.

The surface represents a discontinuity between one phase and another, which means the physical and chemical properties of the surface can be different from those of the bulk material. While these differences predominantly affect the topmost atomic layer of the material, they can extend to the atoms in the near-surface, ultra-thin film region too.

In the bulk of the material, an atom is surrounded in a regular manner by atoms composing that material. Because a surface atom is not surrounded by atoms on all sides, it has bonding potential, which makes the surface atom potentially more reactive than atoms in the bulk.

What is XPS?

XPS can measure the elemental composition, empirical formula, chemical state, and electronic state of the elements within a material. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays and measuring the kinetic energy of the electrons that are emitted from the material being analyzed.

A photoelectron spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum due to atoms emitting electrons of a characteristic energy. The energies and intensities of the photoelectron peaks make it possible to identify and quantify all surface elements except hydrogen and helium.

Photoelectrons can travel only a few nanometers in matter before losing kinetic energy, which prevents their detection. This makes XPS very surface sensitive. The real strength of XPS, however, is to combine this surface selectivity with its ability to investigate the chemical bonding states of surface elements. If you measure the kinetic energy of the photoelectron peaks in finer detail, you see that, even for the same element, the peak energy may shift depending on the surface chemistry. This is known as the chemical shift. The ability to detect and quantify this shift is what makes XPS such a powerful analytical technique.

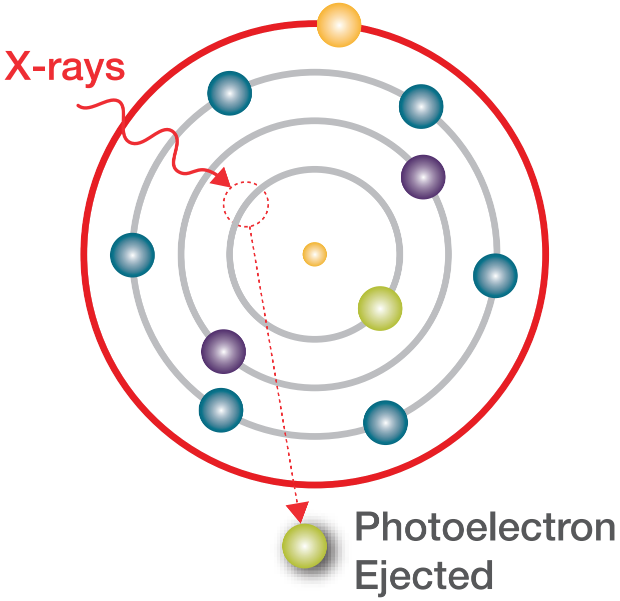
Basic XPS theory

The surface of a material is comprised of atoms of the various elements present. As shown in the diagram in Figure 2, the nucleus is surrounded by electrons at different orbitals. The energy each electron has within the orbital is referred to as the binding energy, which varies depending on the orbital's proximity to the nucleus. Energy is supplied when the surface is irradiated with X-rays. If the energy supplied is greater than the electron binding energy, the electron can leave the atom, which is known as an ionization event. These electrons are referred to as photoelectrons because they are the result of an interaction involving X-ray photons.

The spectrometer's analyzer counts the number of photoelectrons with a particular kinetic energy as it scans the energy range. The binding energy can then be calculated as follows: $BE = hv - KE$. Peaks correspond to electrons from a specific orbital in an element's atom, providing three important bits of information:

1. The peak indicates which element the photoelectron came from
2. The orbital, in conjunction with the element, mostly defines the binding energy
3. Shifts in the peak position indicate small changes in binding energy caused by the chemical environment

The example in Figure 3 shows spectra of three lithium compounds, illustrating the chemical shift as the chemistry changes from lithium metal to lithium oxide and lithium hydroxide. The area of each peak can be measured and used to directly calculate the amount of material present in the surface.



$BE = hv - KE$

Binding Energy = X-ray Photon Energy - Kinetic Energy of photoelectron

Element	Positive charge on nucleus (number of protons) is acting on the electron
Electronic configuration	Energy level that electron occupies
Chemical state	Influence of other elements bonded to atom varies the orbital energy level by small amounts

Figure 2: Schematic of the XPS process.

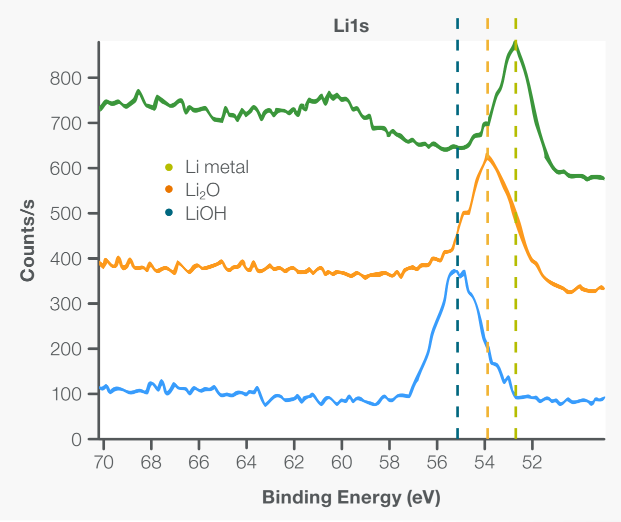


Figure 3: Representative spectra for lithium in different compounds.

Depth profiling

In addition to collecting information from the surface, depth profiling is important to many XPS applications, and analysis of battery materials is no exception. Depth profiling is an experimental method in which an ion beam is used to sequentially remove material from the surface, with spectral acquisition performed between etching cycles. This process makes it possible to create a chemical composition profile that shows changes in the sample from the surface into the bulk.

Monatomic ion sources, typically using Ar^+ as a projectile, have been used for decades to investigate changes in chemistry across the depth of a layered material or to clean inorganic surfaces. A monatomic ion source, however, has limitations when used on materials such as battery electrodes or polymer separators, where the energetic ions will damage the surface and change the chemistry of the analyte. It can particularly affect alkali metal ions, such as lithium, and polymeric materials such as the organic compounds used in binder or in separators.

New gas cluster ion sources overcome these limitations, enabling analysis of material classes previously inaccessible to XPS depth profiling. The key to minimizing the damage is reducing the energy going into the surface while maintaining enough to remove material. By making the projectile much heavier with a weakly bound cluster of gas atoms, it is possible to remove material while spreading the energy and the single charge across the whole cluster. This vastly decreases the “damage zone” on the remaining surface because there is significantly less energy imparted into the material by the cluster impact. It also delivers XPS spectra that accurately represent the real chemistry.

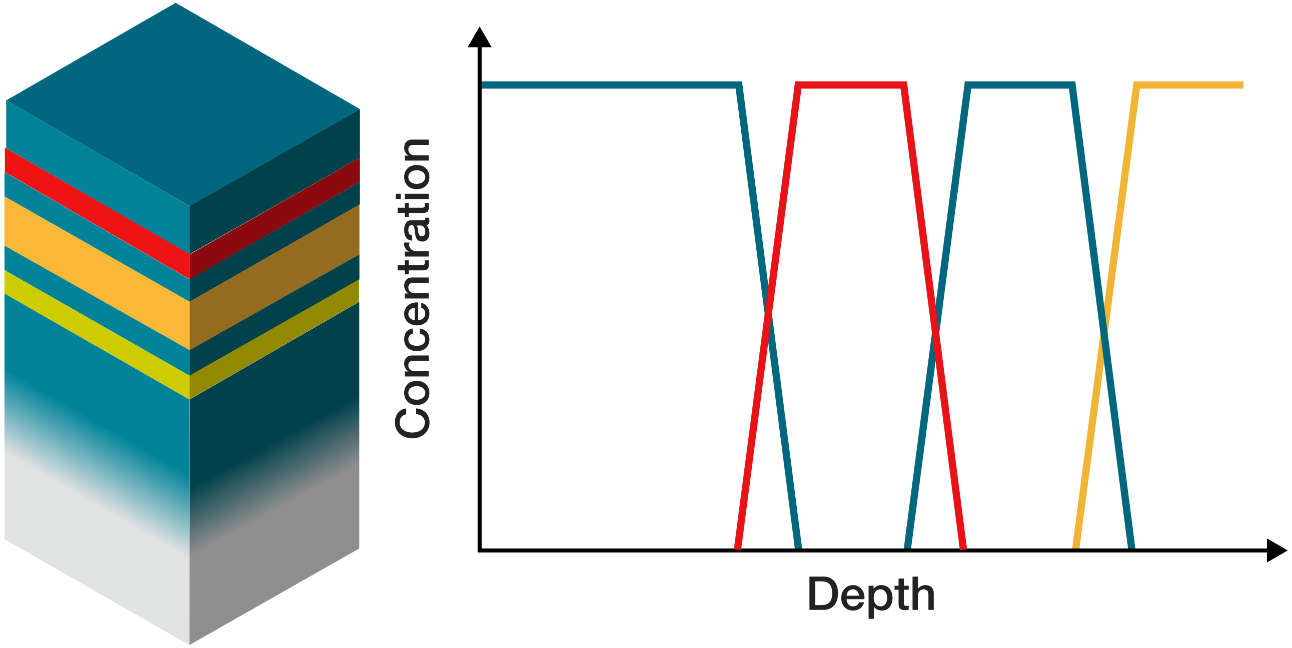


Figure 4: Depth profiling analysis via XPS.

Monatomic vs. cluster ions for depth profiling

Monatomic ions (Ar^+)	Cluster ions (Ar^+_n)
High energy per atom (200 eV—4 keV)	Low energy per atom (1 eV—100 eV)
High etch rate	Low etch rate for large clusters
Deep surface penetration	Minimal surface penetration
Can damage surface chemistry	Non-damaging to surface chemistry
Ideal for etching inorganic material	Large clusters ideal for etching organic material

The Thermo Scientific™ MAGCIS™ Dual Mode Ion Source operates in both monatomic and gas cluster modes, allowing depth profile analysis of the widest range of sample types.

XPS instruments

Modern lab instruments generally use a monochromated X-ray source, which delivers a narrow spread of X-ray photon energies and results in better resolution of the peaks in the spectrum.

The X-rays are usually Al K-alpha radiation generated by bombarding an aluminum target with electrons. The X-ray beam is monochromated using a quartz crystal, which has a lattice spacing suitable for Bragg diffraction of the desired photon energy. The crystal is generally shaped to refocus the X-ray beam to a point at the sample. Figure 5 shows the geometry of all the analytical components used in XPS, which have been carefully considered to optimize performance.

A low energy electron flood gun is essential for insulator analysis. This allows analysis of insulating samples by replacing the emitted photoelectrons and preventing positive charge buildup at the surface, which would distort the spectrum. Without the flood gun, it would be impossible to get good, high-resolution spectra of oxides, polymers, or composite materials.

The ion gun is used to gently remove material from the surface of the sample, either to remove contamination or to perform depth profiling. Generally, systems equipped with a monatomic ion source that bombards the surface with single ions. These types of ion beam can damage some sensitive samples, which is especially true of the materials in Li-ion batteries. This damage can be minimized by using gas cluster ion beams—large clusters of gas ranging from 75 to 2000 atoms—to bombard the surface. This approach is helpful in creating depth profiles of layered polymer systems, including polymer-based electrolyte materials for solid state batteries.

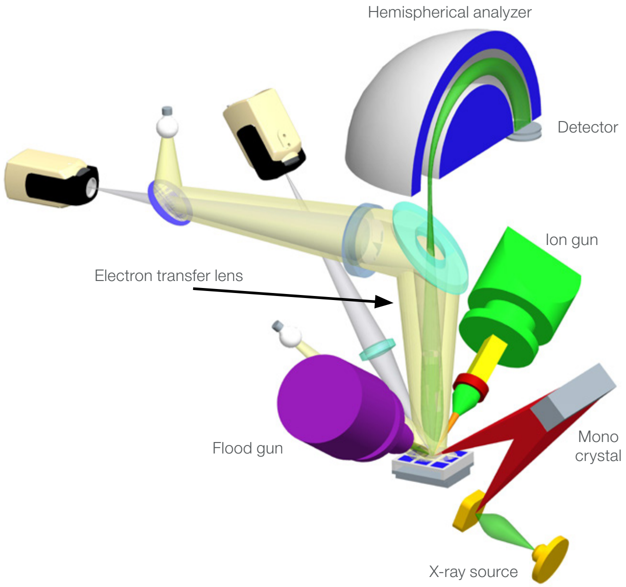


Figure 5: The internal geometry of the analytical components in the Thermo Scientific™ Nexsa™ G2 XPS System.

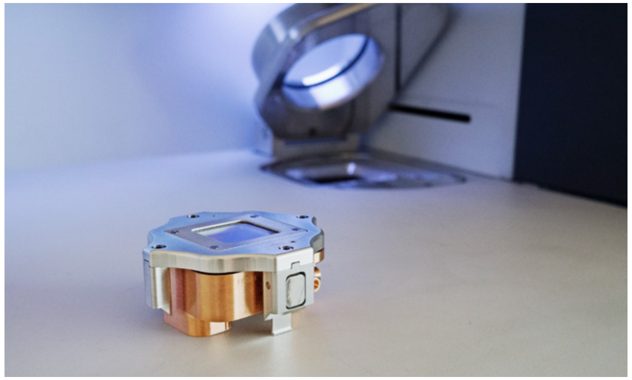


Figure 6: Vacuum transfer module for Thermo Scientific XPS Systems.

Vacuum sample transfer solution

Battery materials like lithium metal and sulfide solid electrolyte are very sensitive to air and moisture. They must be introduced into the XPS system without air exposure for accurate analysis. To do this, the samples are first loaded into a vacuum transfer module (VTM) in a glove box and then transported to the XPS system under vacuum. As the VTM is held together by air pressure, it automatically opens during the pump-down cycle, automatically completing the sample transfer process. Transferring samples under vacuum minimizes chemical changes in the lithium compounds within the electrode, ensuring that the data is representative of the sample.

Why use XPS to study battery materials?

The surface chemistry of a battery is crucial because the composition and behavior of molecules and ions at the surface directly influences the performance, efficiency, and lifespan of the battery.

For example, the solid electrolyte interface (SEI) layer, which forms on the surface of the electrode and is composed of reactants between electrolyte and electrode, can stabilize the electrode and help transport Li-ions. Because of this, the chemical composition of the SEI plays a crucial role in battery performance.

XPS, which specializes in investigating the surface chemistry of materials, delivers proven performance for SEI analysis and can be used to effectively analyze battery materials for a variety of reasons.

XPS benefits

- Because XPS is surface selective, it can focus on the surfaces of components (e.g., surface coating on active materials) used to construct a cell, which are critical to performance
- XPS can detect and quantify all elements except hydrogen, which means that determining the presence and concentration of lithium is possible without special detectors
- XPS can determine the chemistry of both organic and inorganic materials (e.g., the SEI layer), which makes it ideal for analyzing the complex mix of compounds used within a battery
- XPS is performed inside a vacuum system, so there is no chance of air exposure during the analysis; samples can be easily transferred into instruments from air-free environments through sample transfer vessels, such as the Thermo Scientific™ K-Alpha and Nexsa™ G2 Vacuum Transfer Module or the Thermo Scientific™ CleanConnect™ Sample Transfer System, or by having a glove box attached to the entry-lock door
- Ion sources can remove material from the surface to extend analysis into the bulk of the sample
- Further capabilities for in-situ sample biasing, sample heating and cooling, or other analytical methods such as Raman spectroscopy can also be added to create a comprehensive analytical solution for battery material or cell analysis

Application examples

XPS has proven to be an important part of the entire battery research and development process, supporting analysis of everything from raw materials to samples of finished products.

The examples here highlight just a few experiments in which the technique helped create better batteries.

Technique	Application example
General spectra analysis	Surface composition analysis of cycled electrode
Depth profiling	Elemental profile analysis of the solid-state electrolyte
XPS imaging	Interface analysis of solid-state battery
In-situ heating	SEI decomposition process analysis
CISA workflow	Binder composition and structure analysis

Example 1: Surface composition analysis of a cycled electrode

During the electrochemical cycling process of a battery, an SEI layer that is tens of nanometers thick forms, which protects the electrode surface and facilitates ion transport. Because this layer is critically correlated with battery performance, understanding the structure and chemistry information of the interface is crucial and of significant interest. In this example, XPS was used to study the surface chemistry differences between two samples: one from a pristine, unused cathode and another from a cathode that had been through several charge and discharge cycles and held in a charged state.

Figure 7 shows the variation in NMC components of the two samples, excluding oxygen and carbon. While the relative intensities of nickel, manganese, and cobalt are similar between the two, the used cathode contains about 40% less lithium. This is to be expected in a sample from the charged cathode.

The survey spectra show a significant amount of residue from the binder, which was made of a mixture of fluorine- and oxygen-containing polymers, on the surface of the unused cathode sample. This provides insight into the status of the binder on the unused cathode, which impacts the performance of the electrode by impeding ion transport.

Read the app note

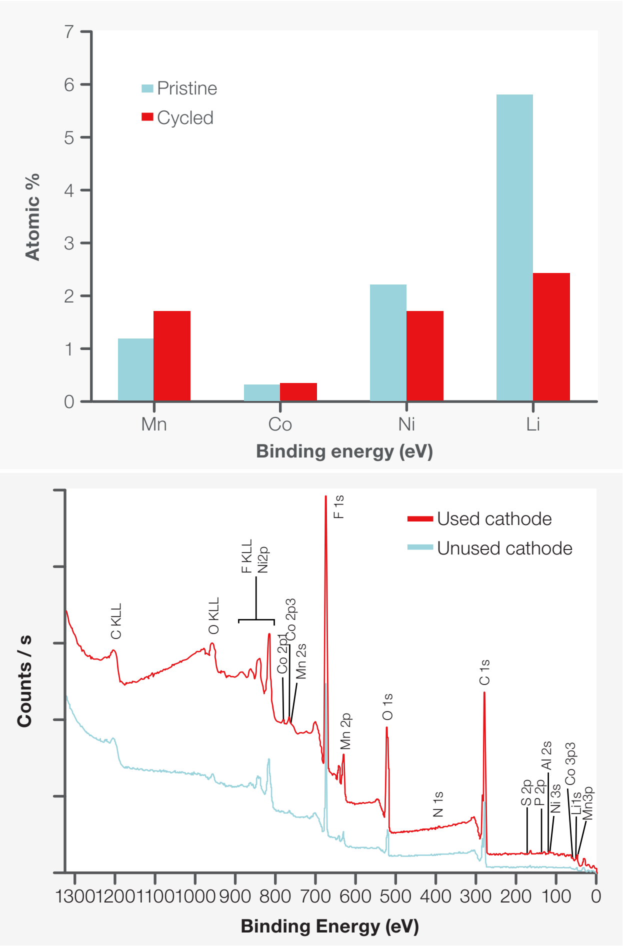


Figure 7: Composition variation for NMC components and survey spectra from pristine (blue) and cycled (red) cathode samples.

Example 2: Elemental profile analysis of a solid-state electrolyte

A solid-state battery is an advanced energy storage device that replaces the traditional liquid or gel-like electrolyte found in conventional batteries with a solid electrolyte material. These batteries are gaining significant attention and research interest due to their potential to revolutionize the energy storage industry.

One of the critical components that ensures the performance of solid-state batteries is the solid electrolyte, as they are inherently more stable and less prone to thermal runaway events. Lithium phosphorus oxynitride (LiPON) possesses several highly beneficial material properties, making it one of the frontier electrolyte material options for solid-state batteries. Its ionic conductivity is relatively high—up to 10^{-6} S cm^{-1}—while the parasitic electronic conductivity is very low, the electrochemical stability window is rather high, and the material is stable even against a metallic Li anode.

To further improve the performance of LiPON, it's critical to understand the elemental and chemical composition throughout the film. In this example, depth profiling via ion sputtering was used to analyze the LiPON to understand the elemental distribution across the film. Both monatomic profiling and Ar cluster profiling can provide the elemental distribution of the LiPON film (Figure 8). However, monatomic profiling tends to damage the very chemistry of the sample by pushing the Li to the boundary of the Si substrate. Small Ar clusters, on the other hand, minimize the sample damage and show the correct elemental distribution. This indicates that when handling a beam-sensitive battery sample, using a strategy like Ar clustering avoids sample damage and delivers accurate results.

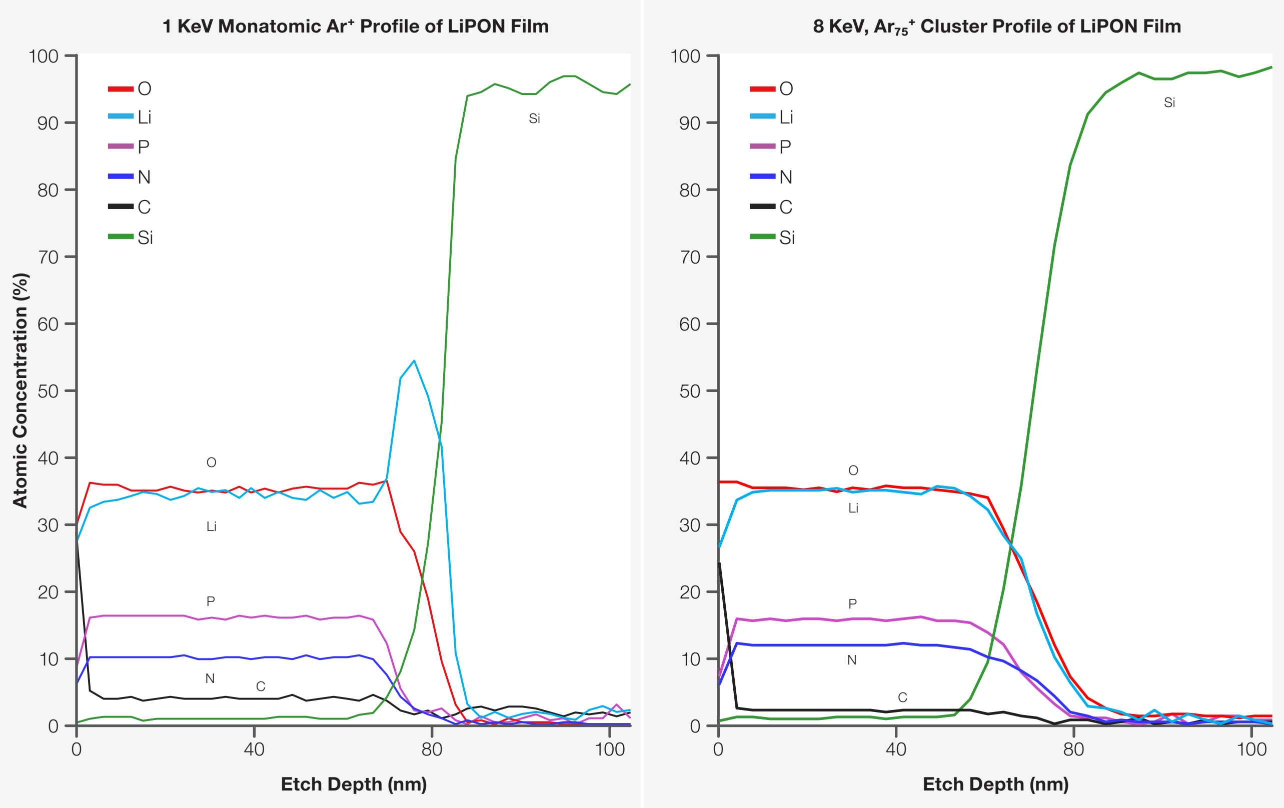


Figure 8: Comparison of depth profiling analysis of the LiPON solid-state electrolyte via monatomic ion profiling with an Ar$^+$ cluster ion source.

Example 3: Interface analysis of solid-state battery

Within a battery, poor affinity of the lithium-electrolyte interface and uncontrollable growth of lithium dendrite on lithium anodes can degrade battery performance. To prevent this, it's important to understand not only the electrolyte and its interface but also the properties of the solid-state electrolyte.

In this experiment, researchers sought to address that challenge by modifying the interface with an Li_2S additive to create a stable interface in all-solid-state lithium metal batteries. To understand the interface, the researchers needed to visualize the evolutions of the interface to understand the chemical component that can stabilize the interfaces. They also needed to understand how various chemical constituents were distributed in the interface.

Using XPS, they identified and quantified the chemical information across the interface and during cycling. The SnapMap in Figure 9 shows the layered structure at the interface with elemental information that confirms the improved interface due to formation of abundant LiF nanocrystals at the Li/PEO interface when introduced with Li_2S as an additive.

Reference: Adv. Mater. 2020, 2000223 (https://doi.org/10.1002 adma.202000223)

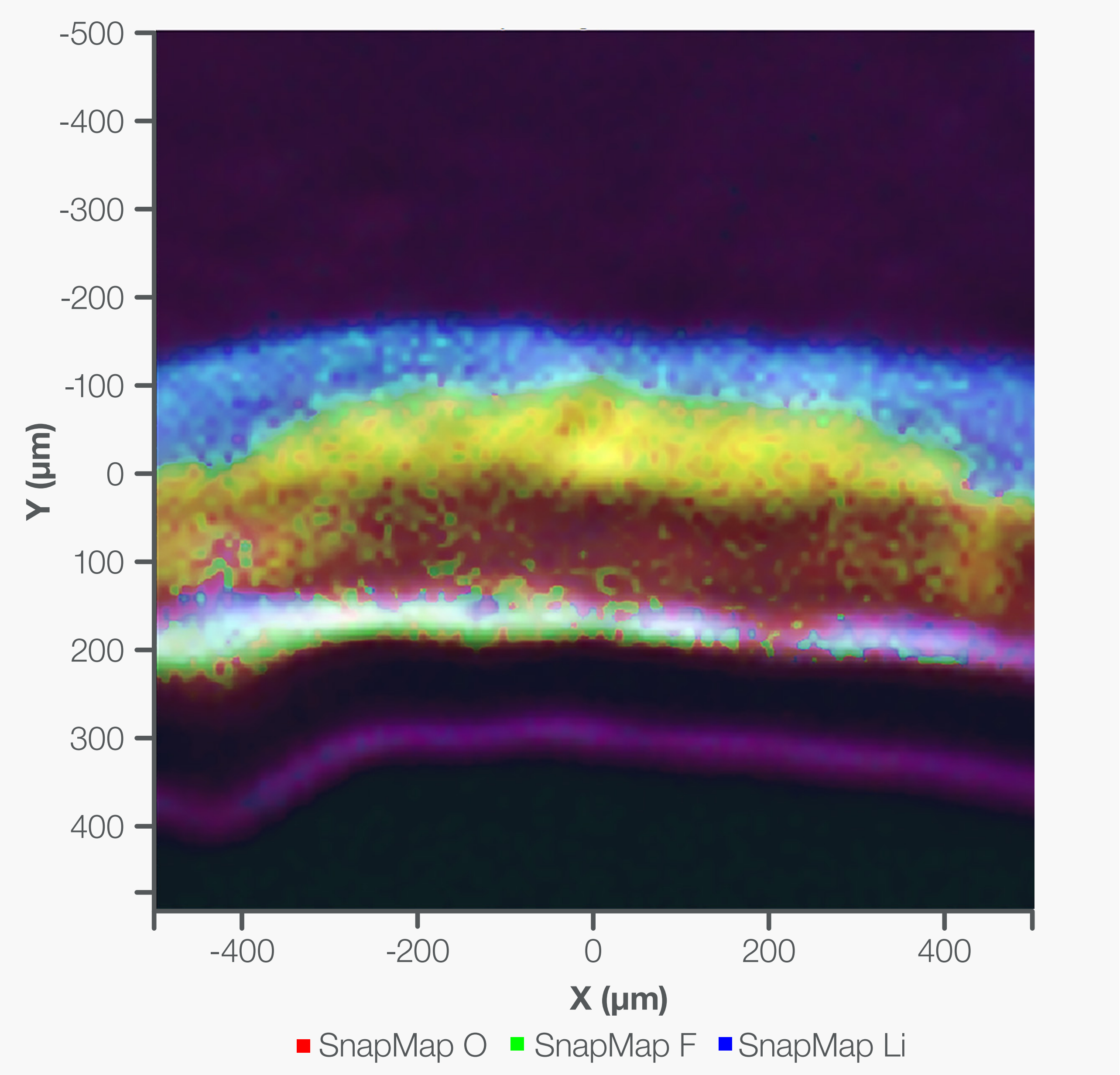


Figure 9: SnapMap analysis of the interface between Li-metal and PEO electrolyte.

Example 4: SEI decomposition process analysis

It is extremely important to understand the inherent thermal stability of the SEI layer, as it plays a significant role in regulating interfacial ion transfer and can have an impact on battery safety. It can thermally decompose easily, releasing heat and generating gas, which can result in thermal runaway and catastrophic failure of the battery. In this example, in-situ heating XPS experiments and ex-situ gas chromatography (GC) were combined to investigate the SEI's thermal decomposition process to determine the evolution of its composition with increasing temperature.

The decomposition process was studied from 25°C to 300°C using the Thermo Scientific™ ESCALAB 250 Xi X-Ray Photoelectron Spectroscopy Microprobe with an in-situ heating module. The SEI formed in the conventional carbonated electrolyte showed poor thermal stability, starting to decompose at temperatures lower than 50°C. Figure 10 shows the XPS spectra of the Li, F, and C at different temperatures. As the temperature increased, a significant amount of chemical bonds broke down into organic species and $Li_xPO_yF_z$, generating more inorganics such as Li_2O, LiF, and Li_2CO_3. The GC results further revealed that the organic component of SEI decomposed and released various flammable gases, including hydrogen (H_2), carbon monoxide (CO), and ethylene (C_2H_4). The decomposition rate of SEI was found to be almost linear with rising temperature. Prolonging the heating time or increasing the heating temperature exacerbated the SEI decomposition.

The SEI's inherent thermal stability and its underlying relationship with the thermal runaway of LIBs could provide valuable insights into enhancing the safety of LIBs by reducing the organic components to create an inorganics-rich SEI.

[Read the journal publication](https://doi.org/10.1002/smll.202208239)

Reference: Small. 2023, 2208239 (https://doi.org/10.1002/smll.202208239)

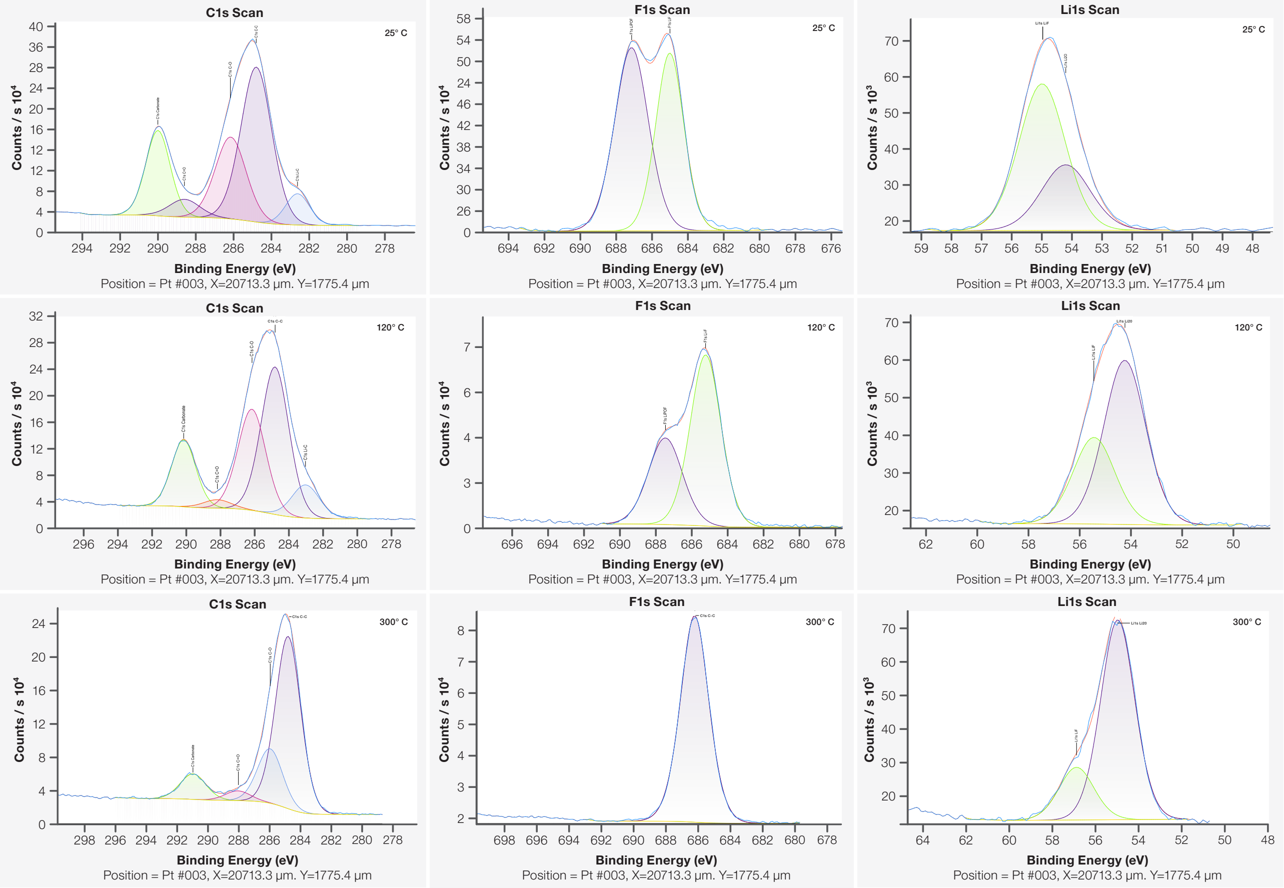


Figure 10: The XPS spectra of Li, F, and C at different temperatures during an in-situ heating experiment.

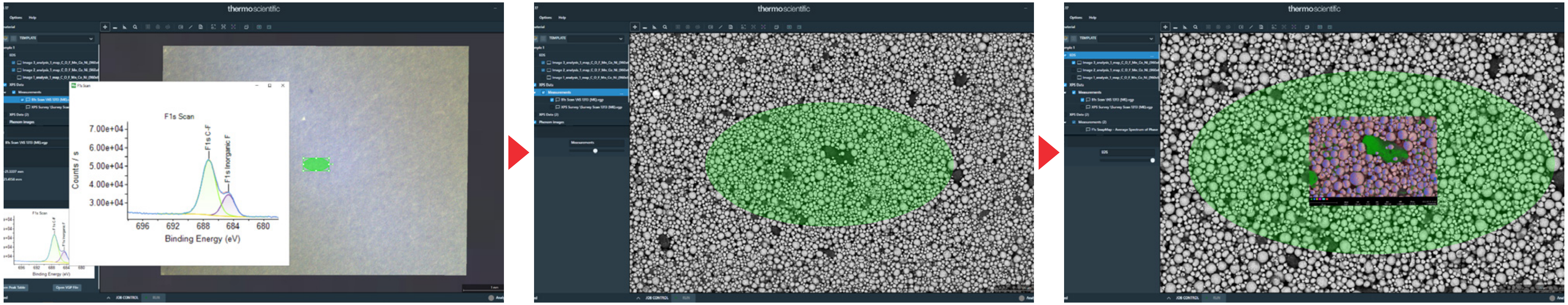
Example 5: Binder composition and structure analysis

By combining XPS with scanning electron microscopy (SEM) analysis, you can now accurately add chemical information from XPS to high-resolution structural information from the microscope. The combination of an SEM with an XPS instrument results in more robust data to analyze, increasing overall understanding of your research sample. Consequently, you can validate your data and get credible information to solve problems faster and ultimately design better materials.

Using the Thermo Scientific Correlative Imaging and Surface Analysis (CISA) Workflow, you can use and export images with stage coordinates from XPS to SEM or SEM to XPS to easily target an exact point of interest in the sample when transfering between systems. This also makes it easy to align datasets, ensuring that the data from each system was collected at the same position for greater accuracy.

The electrodes of a Li-ion cell are typically comprised of compressed active materials held together by a binder material. Using both SEM and XPS to see how the material changes with cycling is common. However, ensuring that the same areas are being analyzed can be challenging. In this example, the electrode was transferred on the same sample mount between the Thermo Scientific™ Nexsa™ G2 XPS System and the SEM.

The sample was analyzed first with XPS to determine fluorine chemical states. While both inorganic fluoride and organic fluorine chemistries were detected, the exact locations of the compounds could not be seen by XPS mapping. Once transferred into the SEM, it was possible to see the grain structure of the powder and identify regions where accumulations of the binder were present. Combining the chemical information from XPS and the structural information from SEM provided more insights on the status of the binder and its impact on battery performance than either technique could alone.



XPS analysis points with associated data.

SEM image added as layer.

EDS analysis in the SEM.

Figure 11: Analysis of the battery electrode using the CISA workflow.

Thermo Scientific XPS portfolio

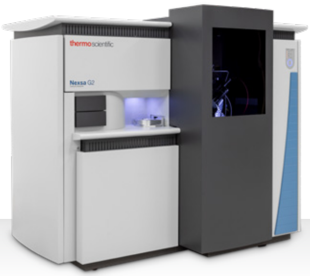
With the rapid evolution of battery technologies, understanding the chemical composition and surface properties of electrode materials is paramount for enhancing battery performance and durability.

The advanced XPS solutions developed at Thermo Fisher Scientific provide techniques that enable researchers, scientists, and engineers to advance battery research and development, ranging from exploring fundamental electrochemical processes to optimizing battery designs for next-generation battery development.

K-Alpha XPS System

- Routine operation
- Large-scale imaging
- Depth profiling

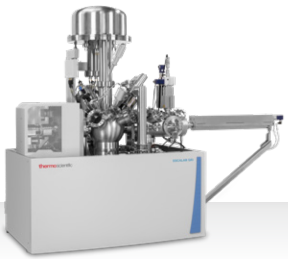
View instrument



Nexsa G2 XPS System

- XPS-ISS-UPS-REELS
- Raman integration
- Inert sample transfer
- Imaging and depth profiling
- Cluster ion source
- Four-point sample bias
- Sample heating

View instrument



ESCALAB QXi XPS Microprobe

- XPS-ISS-UPS-REELS
- AES-IPES
- Inert sample transfer
- Imaging and depth profiling
- Cluster ion source
- Sample heating and cooling

View instrument

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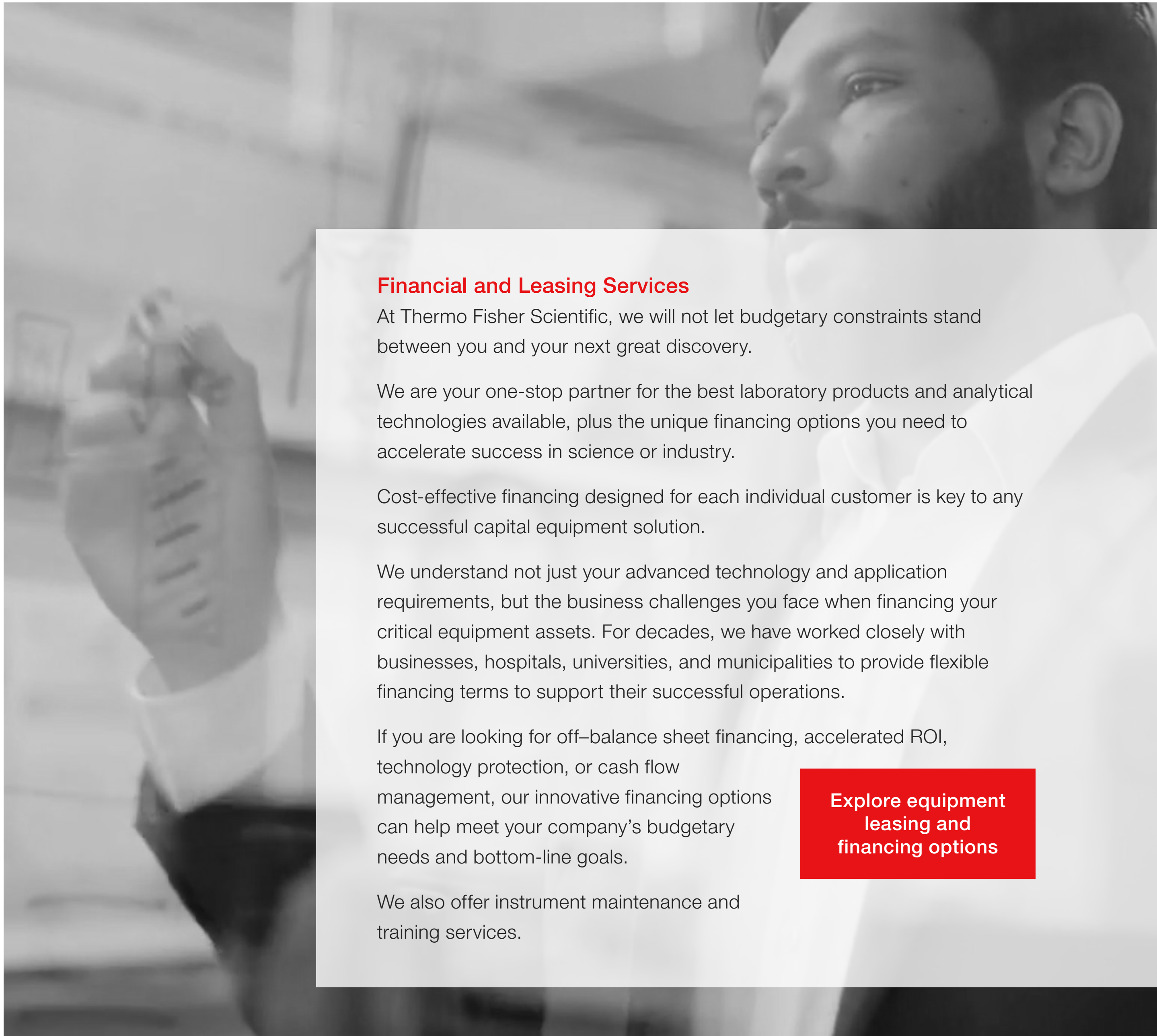

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