Scanning electron microscopy for lithium battery research

Advanced imaging solutions for better batteries

thermo scientific

In the past decade, lithium battery technology has attracted significant attention thanks to its wide application for consumer electronics, transportation electrification, and stationary grid storage. It also plays a critical role in achieving a sustainable and carbon-neutral society. To date, although a lot of progress has been achieved in battery technology, current lithium battery technology is not sufficient to meet the rapidly increasing demand from society for better battery technology. To develop safer batteries with longer life and better energy and power performance, an in-depth understanding of the structure and chemistry of each component and related construction materials is essential.

Scanning electron microscopy (SEM) is an imaging and analysis technique for the characterization of the materials' structure and chemistry at the microscale and nanoscale. Currently, it is widely used as an effective characterization tool among battery materials and cell manufacturers during materials R&D, quality control, and failure analysis. The materials used to construct batteries are vastly different; for example, separator materials are electrically insulating and beam-sensitive, and Li-metal anode samples are electrically conductive and extremely air-sensitive. Scientists and engineers are facing a variety of challenges to accurately extract structure information on different battery samples. Therefore, it is important that the SEM manufacturers provide guidance to the battery field on sample handling and imaging strategies for battery characterization.

In this brochure, we will discuss different imaging solutions to resolve the challenges that battery scientists and engineers are facing in their daily life when characterizing battery materials via SEM.

Battery materials imaging: cathode-related materials

Cathode precursor morphology plays a critical role in the final structure of the cathode materials that impact the materials' performance. Therefore, analysis of the nanometer-scale features (e.g., primary particles) on the cathode precursor surface is essential.

Using the characterization of ($Ni_xMn_yCo_2(OH)_2$) particles as an example, as shown in Figure 1, higher acceleration voltage imaging at 5 KeV results in the fine structure information not being well captured on the particle surface due to the large interaction volume. Low-energy SEM imaging at 800 eV provides high data quality, where details of fine structure are clearly observed. Therefore, this imaging approach is an effective method to characterize the finely detailed surface structure on the battery materials. If the material is beam-sensitive, using low-energy imaging will minimize or eliminate any damage the SEM might induce.
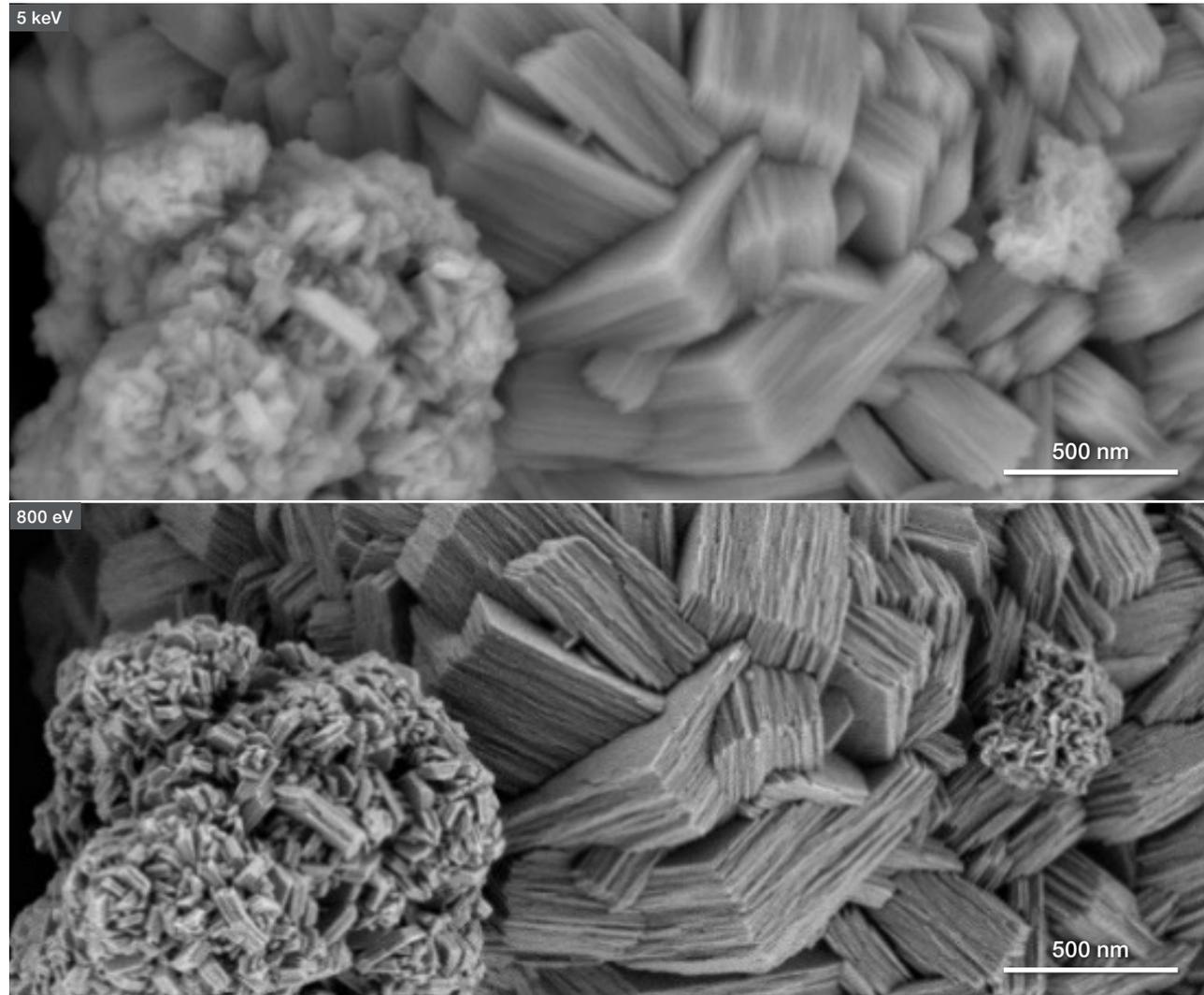
Figure 1: Imaging of the $Ni_xMn_yCo_2(OH)_2$ at 5 keV (top) versus 800 eV (bottom) using the Apreo SEM.

When characterizing such materials in the analytical lab of the battery production site, it is critical to have an imaging solution that provides superior image quality and high efficiency with a safe operation procedure, namely the capture of high-resolution images at long working distance. (e.g., a longer working distance is generally preferred for users of varying skill as it will minimize the risk sample and system damage). Thanks to the Thermo Scientific™ Apreo 2 SEM's unique Thermo Scientific Trinity™ In-Column Detection System, combing low-energy imaging with T1 in-lens backscatter detector, you can image battery materials with high resolution at a 10 mm working distance (shown in Figure 2).
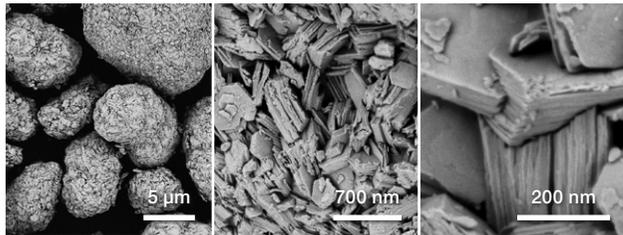
Figure 2: Low-energy imaging of $Ni_xMn_yCo_z(OH)_2$ at a 10 mm working distance with T1 detector from Apreo 2 SEM at different magnifications.

In cathode materials development, one of the methods to enhance performance is to modify materials through surface coating. It is critical to characterize the surface coating properties to evaluate the effectiveness of the coating process and understand how it impacts the electrode's ultimate performance. However, it is challenging to characterize the coating via SEM imaging due to the small amount of coating materials on the cathode, which does not enable clear contrast. Figure 3 shows images of the $Li(Ni_xMn_yCo_z)O_2$ (NMC) with the Apreo 2 SEM via T1 backscattered electron (BSE) detector with and without an energy filter.
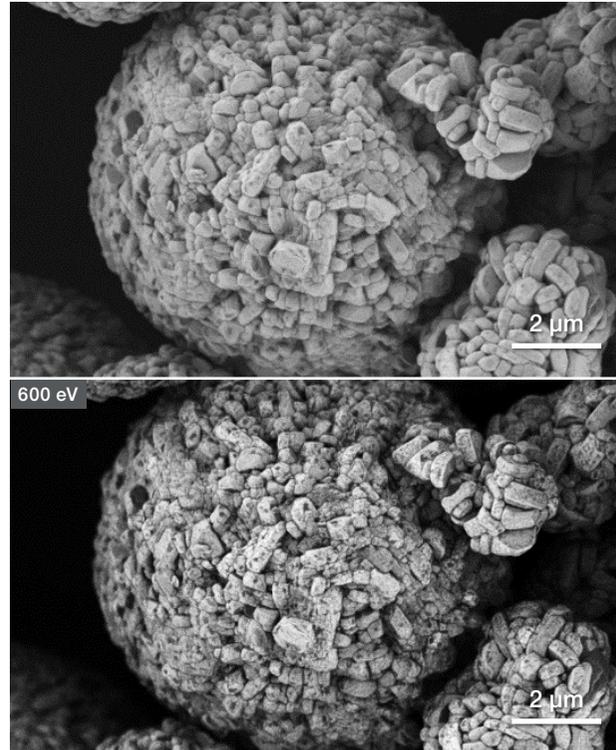
Figure 3: Imaging of the NMC particle surface by adjusting the energy filter of the compound lens to enable coating contrast; without energy filtering (top) versus 600 eV energy filtering (bottom).

The BSE image collected via the T1 detector shows a high-quality image to characterize the primary particle on the surface, while the coating is not clearly visible.

By employing the compound lens with an energy filter, more precise contrast is enabled by optimizing the imaging conditions, enabling the coating materials of the NMC cathode surface to be clearly seen.

Another important approach to advance cathode technology is to optimize the cathode synthesis process, which requires an in-depth understanding of the crystal growth process and mechanism. *Ex situ* imaging can provide structural evolution information at different synthesis conditions. However, there are always some uncertainties in the sample preparation process that impact the interpretation of the data. For example, in a heating experiment, the material's structure may have changed during the sample cooling process before characterization in the SEM. Therefore, *in situ* experiments are preferred to accurately capture the structural evolution process. Figure 4 shows an example of the monitoring of the solid-state reaction process between LiOH and $Ni_xMn_yCo_z(OH)_2$ via an *in situ* heating experiment within the Thermo Scientific Quattro ESEM on the *in situ* heating stage. The formation process of the $Li(Ni_xMn_yCo_z)O_2$ was monitored. Detailed morphology information of both reacting materials and their distribution at certain heating temperatures can provide guidance for optimization of the cathode synthesis process.

Figure 4: Monitoring of the structure evolution synthetic process of Li $(Ni_xMn_yCo_z)O_2$ between the LiOH and $Ni_xMn_yCo_z(OH)_2$ reaction at different temperatures.

Battery materials imaging: anode materials

When using SEM to characterize anode materials, such as graphite, silicon, and silicon oxide, the characterization needs are similar as for cathode, which requires nanoscale features imaged at the particle's surface, long working distance for safe operation, and coating property evaluation.

Using SiO_x development for anode materials as an example, the carbon coating is applied to the material to provide fast electron transport and rate kinetics. When evaluating the coating property on such materials, coating uniformity is a critical parameter to characterize. Figure 5 shows an approach to adjusting the accelerating voltage of the SEM to understand the coating uniformity on the SiO_x particle's surface. At 100 eV, the carbon coatings have full coverage on the SiO_x particles.

When accelerating voltage is increased, the increasing interaction volume results in differing elemental contrast, where some non-uniform coating, namely thinner carbon coverage area, starts to appear on the edge of the particle surface, which helps the researcher to evaluate the coating uniformity quality. This SEM imaging approach requires high-performance low-energy imaging to enable high image quality and clear contrast on such a thin coating layer for assessment.
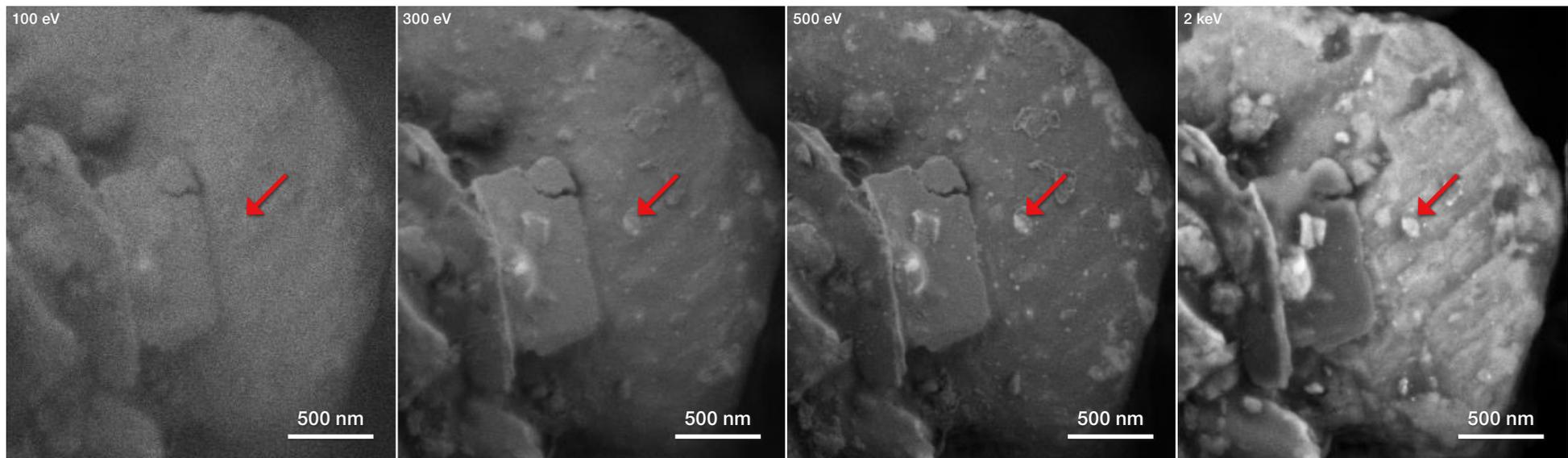
Figure 5: Adjusting the accelerating voltage from 100 eV to 2 keV to monitor the dark contrast (carbon coating) change on the SiO_x anode materials.

Battery materials imaging: separator
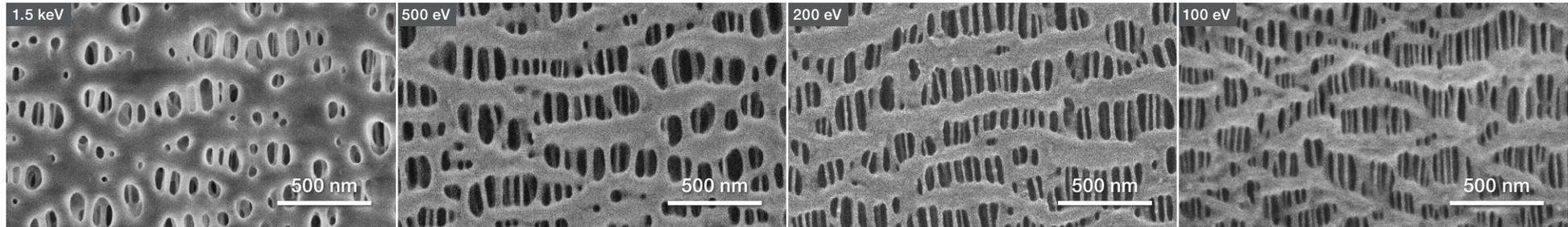
Figure 6: Imaging analysis of the dry processing separator sample with the Apreo 2 SEM. A lower landing energy enables less damage on the separator sample.

As one of the major components in batteries, the separator plays a key role in preventing physical contact between electrodes and enabling ion transport.

SEM provides microstructural information like porosity, pore morphology, and contaminants distribution of the separator at the nanoscale to help assess the separator quality and performance. However, due to the intrinsically poor thermal conductivity, electronic conductivity, and beam sensitivity of the separator, characterization of the separator sample without damage is challenging. Figure 6 shows a study of the accelerating voltage effects on separator imaging. At a 1.5 keV acceleration voltage, clear beam damage effects are observed on the separator, where the polymer shows melting and distortion of the pore shapes. Such structural information provides incorrect structure-property-performance interpretation.

Decreasing the voltage to 100 eV significantly minimizes the beam damage and maintains pore structure and polymer features. In addition, detectors with nanosecond response rates are also critical to secure quality data collection before sample damage. This study indicates the importance of the imaging condition optimization in battery materials characterization. For separator characterization, low-energy imaging and a high-speed detector are essential to obtain high-quality SEM data for structural analysis.

Once the SEM image of the separator sample is collected, important structural characteristics related to pores and polymers can be obtained via quantitative analysis of the SEM data. Figure 7 demonstrates the process of using Thermo Scientific Avizo2D Software to analyze the pore structure of a wet-processing separator sample. The pore size distribution is achieved to enable a quantitative understanding of the separator property.
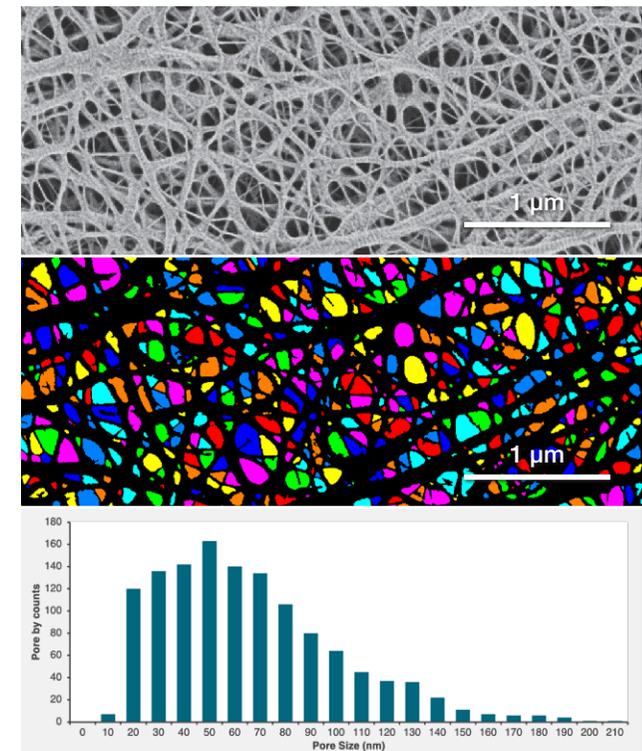
Figure 7: 2D pore size distribution analysis on the wet-processing separator sample via a preset workflow from Avizo2D Software.
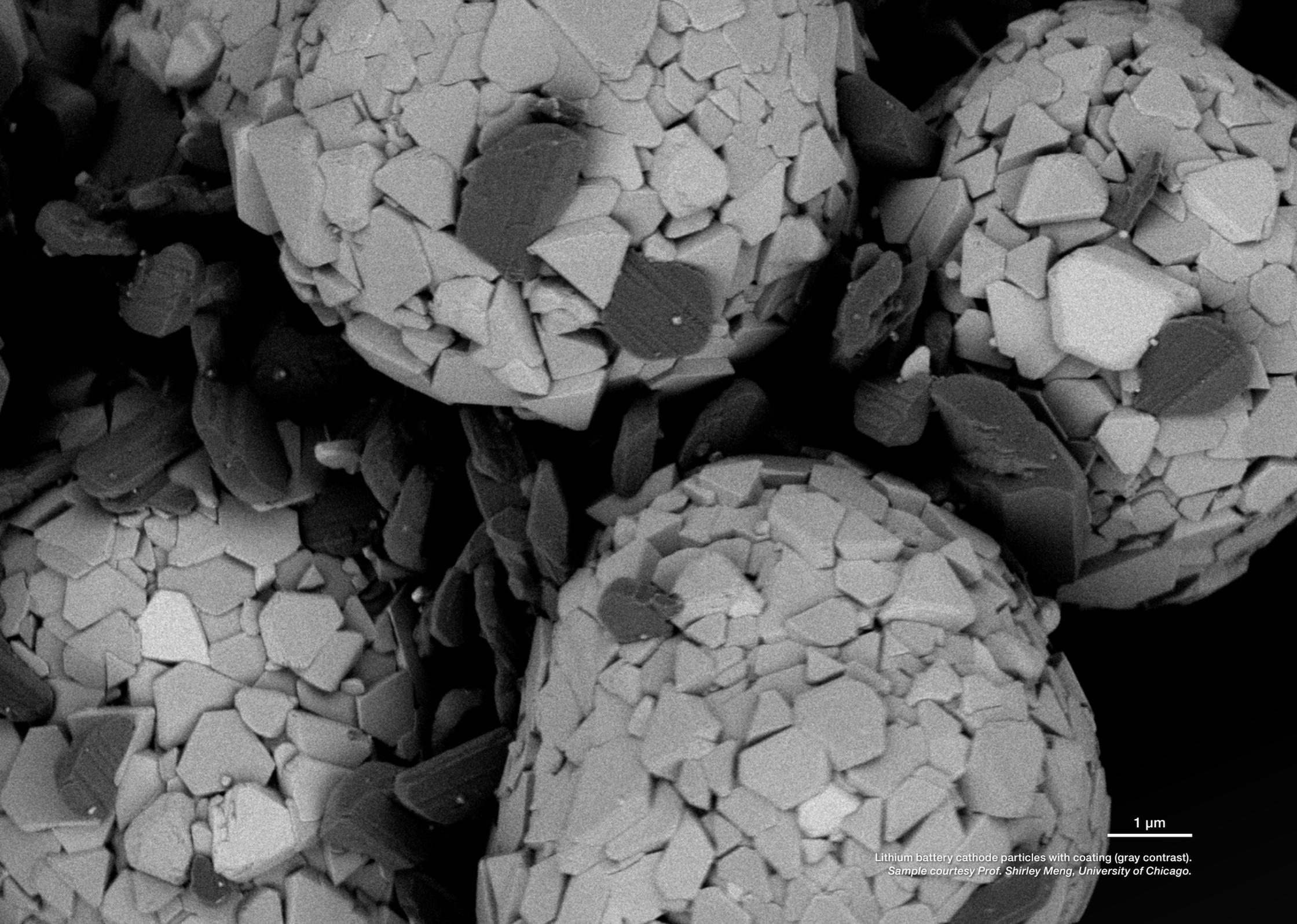
1 µm

Lithium battery cathode particles with coating (gray contrast).
Sample courtesy Prof. Shirley Meng, University of Chicago.

Battery electrode imaging

Battery electrodes, including anodes and cathodes, are the other two important components needed to construct a battery.

In general, the battery electrode consists of active materials, a binder, and conductive carbon. Understanding how different phases are distributed to construct an electrode facilitates the structure-performance correlation analysis between the electrode and final cell performance.

Figure 8 shows two different detectors in the Apreo 2 SEM used to study the SiO_x graphite anode. The T1 in-lens backscatter detector provides imaging contrast based on compositional information, where the SiO_x particles appear white and the graphite particles appear gray. The distribution of different particles within the electrode is immediately seen via backscattered imaging. The T2 detector collects more topographic information of the particles within the electrode.

In some cases, both topographic and compositional information are important for electrode structure characterization, which is beneficial when all data is compiled in one image. Figure 9 shows an approach for mixing the signals of electrode composition and topography from different detectors to form one image. The Everhart–Thornley detector (ETD) and T2 detector provide the topographic information collected from secondary electrons, and T1 provides compositional related contrast from backscattered electrons. Within the Thermo Scientific SEM user interface, you can generate data by mixing signals from different detectors with different ratios to optimize the structural information for performance analysis. In this case, the green and red colors indicate the distribution of the carbon/binder domain and $LiCoO_2$ materials, and the nanoscale topographic information of each type of material is also visible.

Figure 8: Studying the SiO_x/graphite anode via the T1 and T2 detectors to determine the composition distribution of SiO_x and graphite particles (top) and also topography information (bottom).
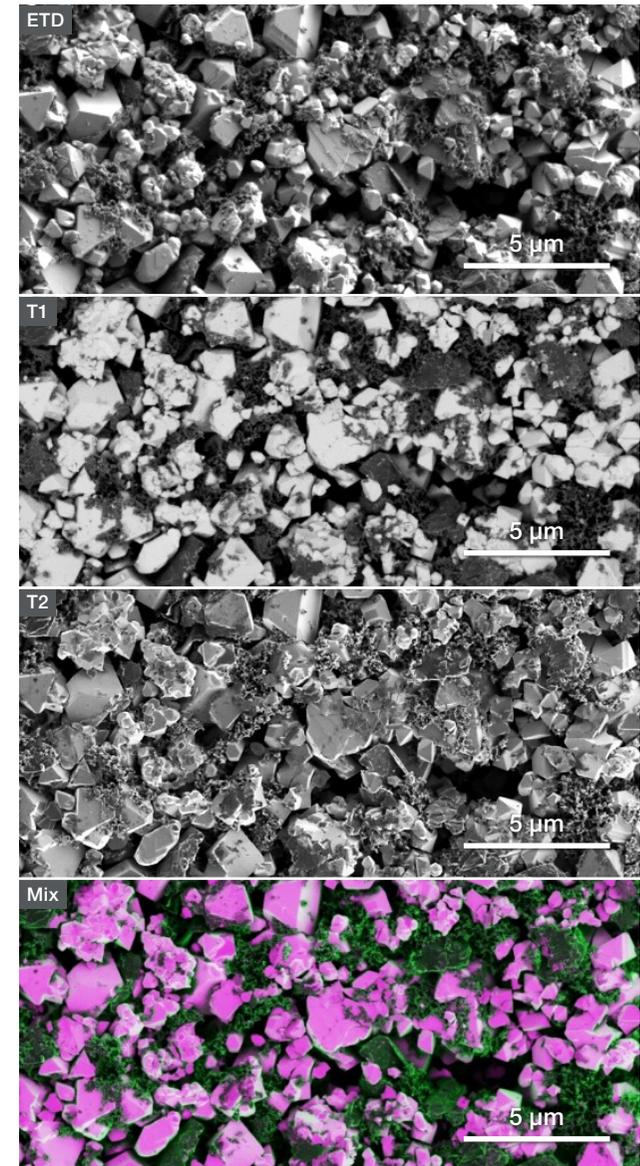
Figure 9: Simultaneous imaging of the electrode with multiple detectors. The signals from the T1 (BSE) and ETD (SE) detectors were mixed to learn both $LiCoO_2$ (pink) and carbon/binder (green) morphology and distribution on $LiCoO_2$ cathode.

Although binder distribution within the electrode is one of the key structural characteristics that impacts the quality and performance of the electrode, it is challenging to gain such information from routine analytical characterization techniques. X-ray diffraction can confirm the binder composition within the electrode, but the location information will be missing. Raman microspectroscopy can easily differentiate materials' differences, but the resolution will be limited.

When using SEM to study the binder distribution, as shown in Figure 10, the traditional BSE imaging provides good contrast between active materials ($LiCoO_2$, appears as gray contrast) and carbon binder domain (appears as dark contrast). There is no imaging contrast between conductive carbon and binder in the electrode because both materials are composed of elements with similar atomic numbers. Additional analysis is needed to further differentiate binder and conductive carbon. Taking advantage of the electrical property differences between carbon and binder within the electrode, the T3 detector from the Apreo 2 SEM's unique Trinity in-column detection system can effectively collect the low-energy secondary electrons, which show very bright contrast, generated from the binder. In this sample, the binder is mostly located in the bottom of the sample, which is not uniformly distributed within the electrode that did not meet the quality requirement.
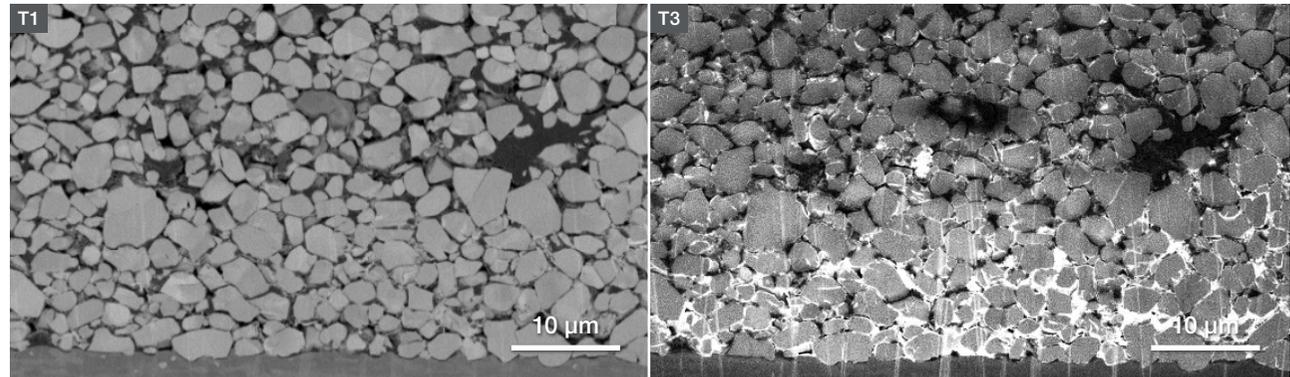
Figure 10: Imaging analysis of the $LiCoO_2$ cross-section via T1 (left, BSE signal) and T3 (right, low-energy SE signal) to study the binder distribution (white contrast) within the electrode.

Another approach to understanding the distribution of different materials is to characterize materials' distribution by tracking the unique element associated with each material via energy dispersive X-ray spectroscopy (EDS). Because carbon and binder are normally a thin layer coated on the surface of the active material, standard EDS at high energy (e.g., 10–20 KeV) has large volume interaction, which penetrates through the thin carbon/binder layer and gains a lot of signals from the active materials beyond.

In this case, low-energy EDS analysis is required. Figure 11 was acquired using Thermo Scientific ChemiSEM™ Technology on an Apreo 2 SEM to perform real-time EDS analysis to study the distribution of different materials in a battery cathode at 2 KeV. The Ni and Mn distribution provides the distribution of the active materials, while the F indicates the location of the binder material distribution on top of the porous carbon materials shown in SEM in grayscale.
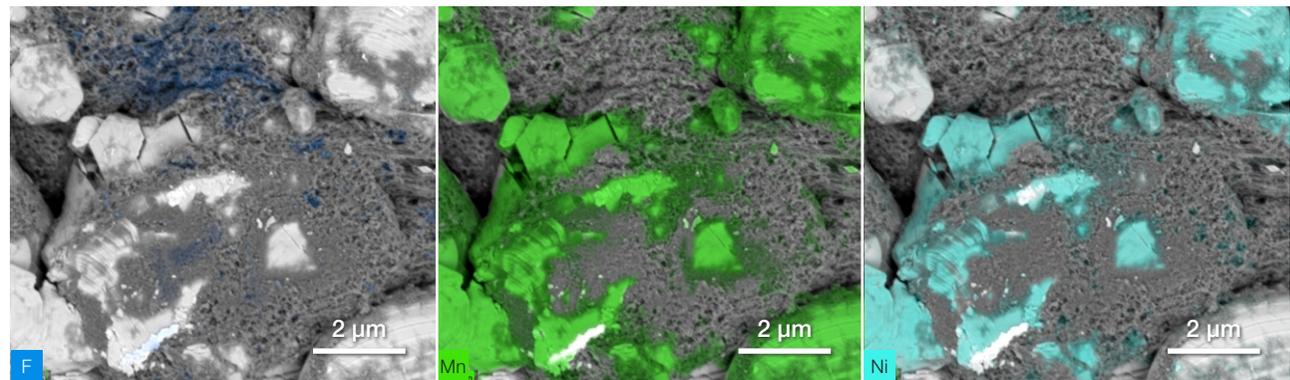
Figure 11: Study of the materials' distribution of a Li-ion battery cathode via ChemiSEM Technology at 2 keV.

One of the key benefits of ChemiSEM Technology is its high efficiency of data collection and analysis by integrating the SEM imaging and EDS workflow together. Figure 12 shows an example of using live EDS to identify the contaminants within the electrode on a Thermo Scientific Axia ChemiSEM. The large-scale overview of the sample, with quantitative elemental mapping data included, took 15 minutes to scan an area of 750 µm x 370 µm, where the area of interest that has contaminants was quickly identified. Using such an image as a reference, you can simply click on the point of interest to perform further detailed analysis. In this example, elements such as Al are considered as contaminants. In the current $LiCoO_2$ cathode, they may have been introduced via the raw materials synthesis sintering process. This process significantly decreases time-to-data for such a contaminant analysis process.

In addition to qualitative image analysis on structure, quantification on the battery electrode structure provides a more in-depth understanding of electrode structure-performance correlations. For example, when analyzing the battery electrode structure via a cross-sectional view, structural characteristics such as volume fraction, particle size, and particle cracking are critical for analysis. However, the quantitative extraction of those structural parameters requires complex image processing and analysis steps by an experienced scientist. Figure 13 shows an example of using Avizo2D Software to transfer the NMC cathode image to data. The preset workflow in Avizo2D Software allows for a four-phase (grains, pore, cracks, carbon and binder domain) detection and quantification of the cathode cross-section without the need for the user to be an image processing expert.
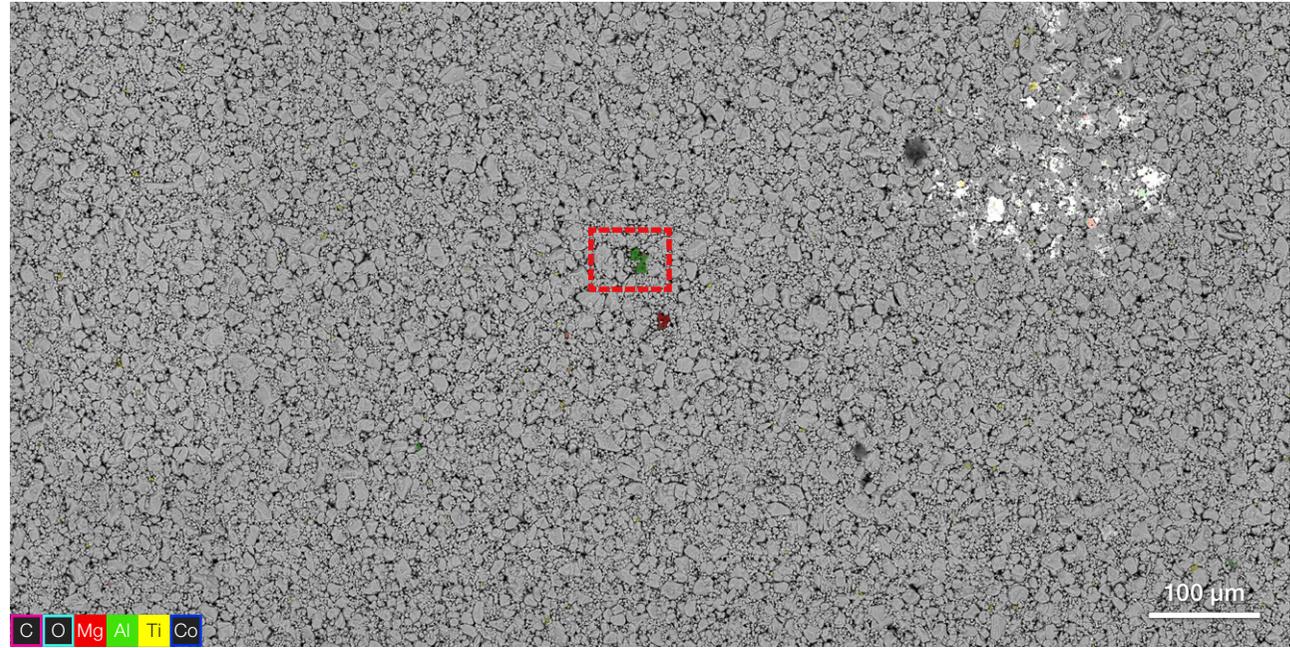
Figure 12: Large-scale contaminants analysis on $LiCoO_2$ cathode via Axia ChemiSEM. The red rectangle highlight the area of interest with potential contaminates.

Other structural characteristics such as size distribution and cracking density can also be obtained for electrode structure evaluation.
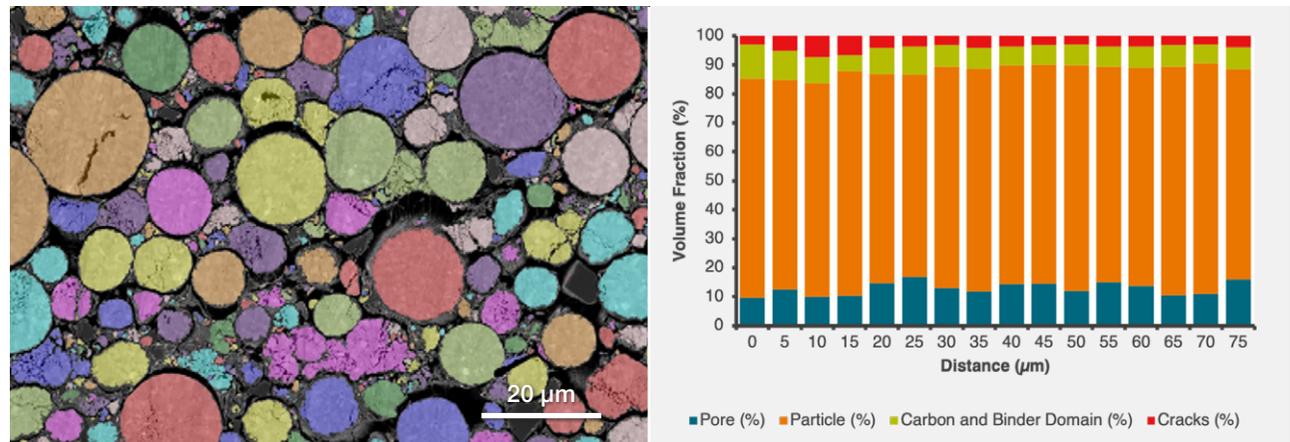
Figure 13: Phase fraction analysis on an NMC cathode along the calendaring direction via Avizo2D Software.
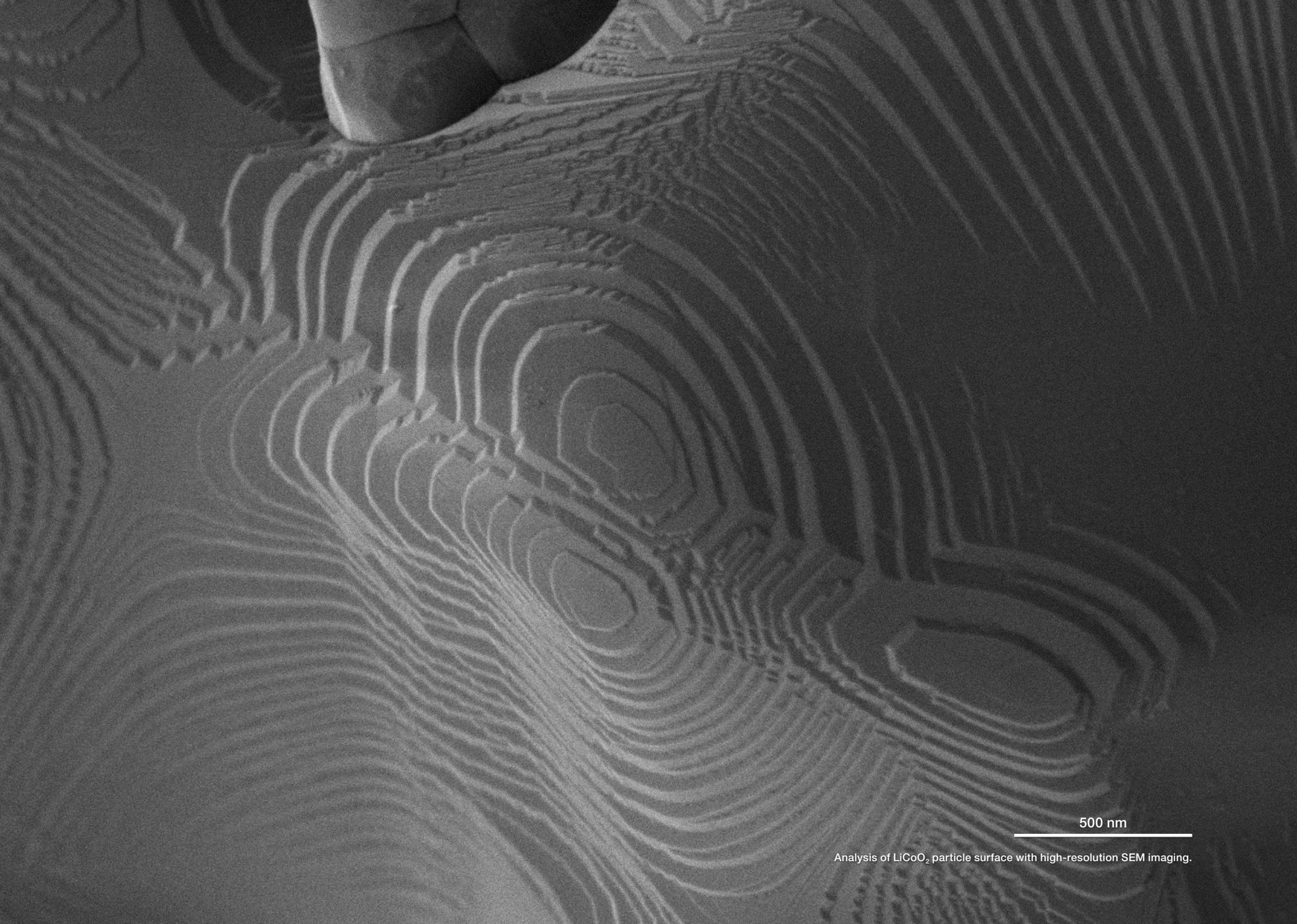
500 nm

Analysis of LiCoO$_2$ particle surface with high-resolution SEM imaging.
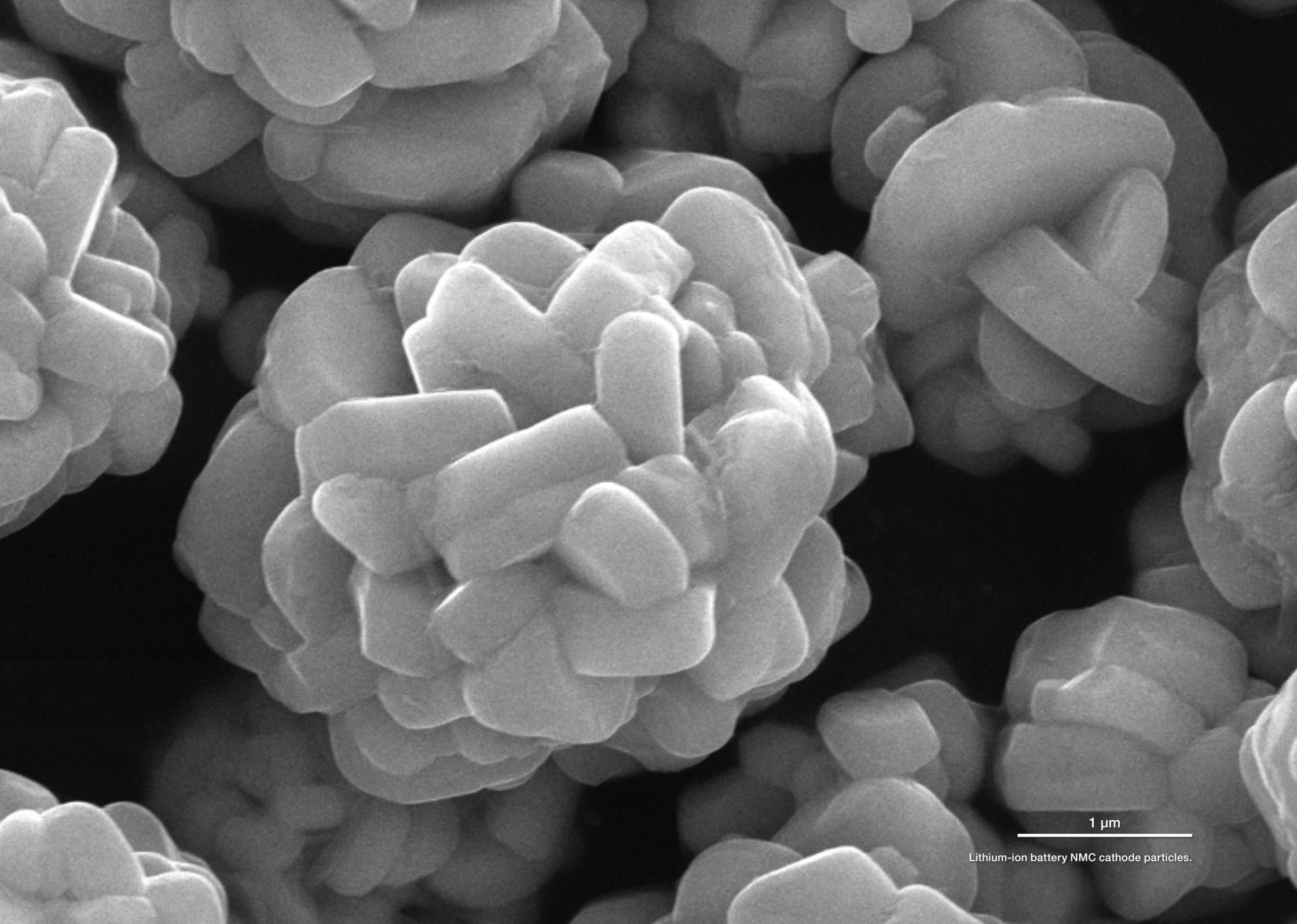
Lithium-ion battery NMC cathode particles.

Preparing battery materials for imaging

Scientists, researchers, and engineers need pristine samples to accurately observe and characterize their materials or parts.

While DualBeam FIB-SEMs offer a site-specific method to prepare cross-sections with excellent cut-face quality, they can't accommodate cross-sectional areas larger than 500 µm wide, which often don't require site specificity.

- A dedicated ion beam polisher, on the other hand, can help create a high-quality sample surface for imaging without any surface contamination. These systems use a broad beam of ions to smooth the surface of a sample and remove any surface contamination or defects. There are several reasons why you might want to ion polish a sample for SEM characterization: •Reduced charging—Ion polishing can help reduce charging of the sample during imaging, which can be a problem when studying insulating materials or samples with low electrical conductivity.

- High resolution—By removing surface contaminants and defects, ion polishing helps you improve the resolution of SEM images and see smaller features on the sample surface.

- Surface analysis—Ion polishing can also be used to prepare samples for surface analysis techniques such as energy-dispersive X-ray spectroscopy (EDS) or X-ray photoelectron spectroscopy (XPS), which provide information about the chemical composition of the sample surface.

The Thermo Scientific™ CleanMill™ Broad Ion Beam System is a complete ion beam polishing solution that enables optimal SEM imaging and analysis of a variety of samples, including beam- and air-sensitive materials. It features a wide accelerating voltage from 0.1 kV to 16 kV that delivers everything from ultra-fine polishing to rapid milling.

With CleanConnect compatibility, the CleanMill System seamlessly integrates with the Thermo Scientific Inert Gas Sample Transfer Workflow, allowing you to prepare and image high-quality sample surfaces while completely protecting sample integrity.
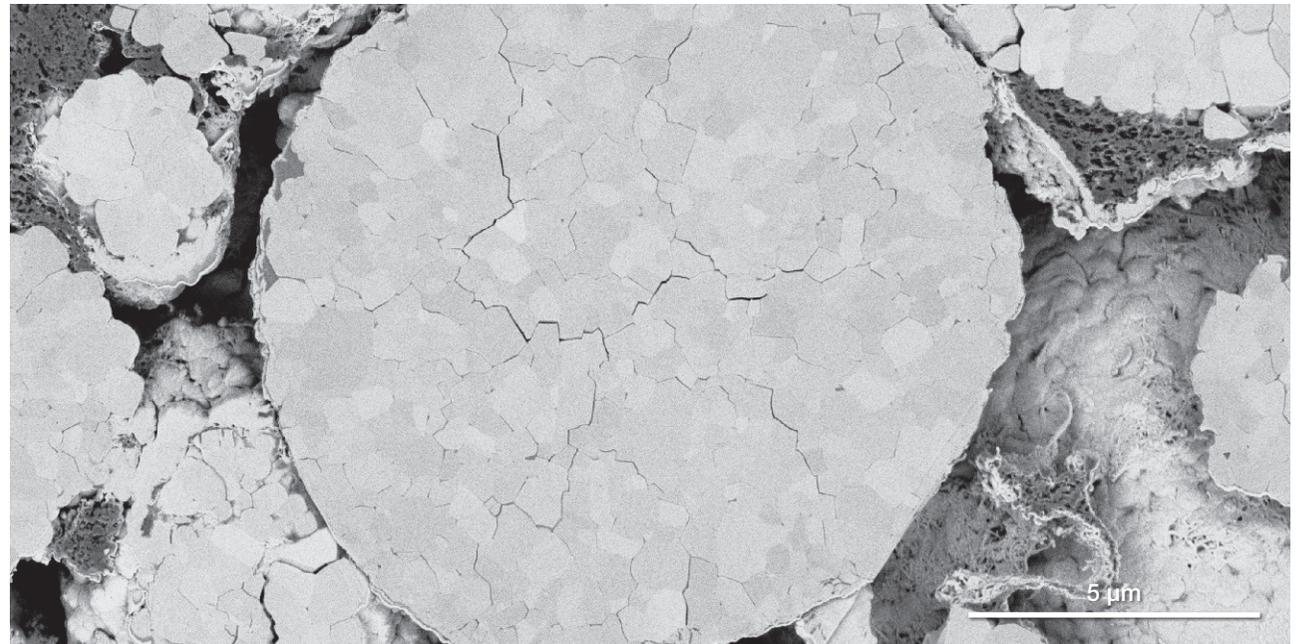
NMC cathode polished with the CleanMill System using 16 kV Ar+ ions with subsequent imaging on a Thermo Scientific™ Apreo™ 2 SEM using 2 keV in BSE mode.

Solutions to protect sample integrity

When you are performing SEM characterization on the battery materials, sample handling during the transfer process is important because some key battery samples, such as lithium metal, sulfide-based solid electrolytes, charged electrodes, etc., are sensitive to humidity and oxygen in the air.

If the sample is contaminated during the transfer process from glove box to the microscope, the characterization results will be incorrect. To secure the sample integrity for all floor-standing SEMs, Thermo Fisher Scientific engineers developed an inert gas transfer solution, the Thermo Scientific CleanConnect™ Sample Transfer System, which provides inert gas sample protection when transferring the sample between SEM and glove box. Figure 14 shows the 3D schematic of the CleanConnect System and how it is attached to the microscope. By using commercial lithium foil as a testing sample, the comparison of the glove box-stored sample, CleanConnect System-stored sample, and the air-exposed sample was performed. The CleanConnect System-stored sample sample does not show observable contamination on the sample surface, clearly demonstrating its capability for sample integrity protection that enables the battery sample to be characterized in its native state (shown in Figure 15).
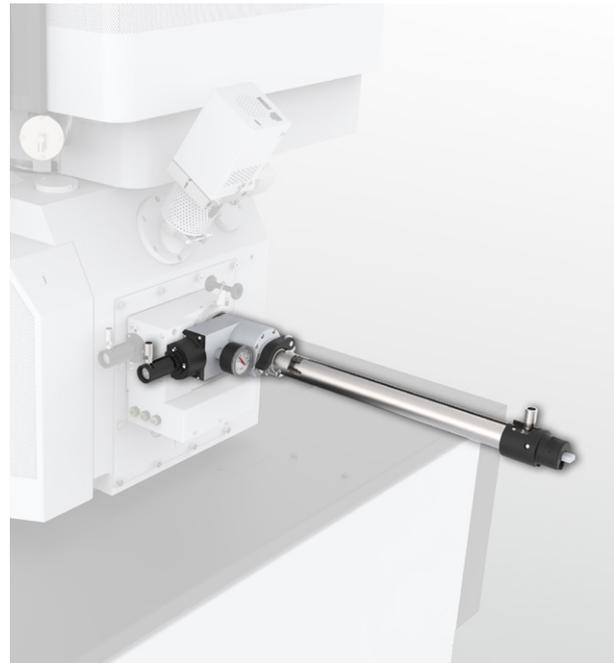
Figure 14: CleanConnect Sample Transfer System.

As transferred from glove box	Stored in CleanConnect for 30 minutes	Expose to air for 2 minutes
2 µm	2 µm	2 µm
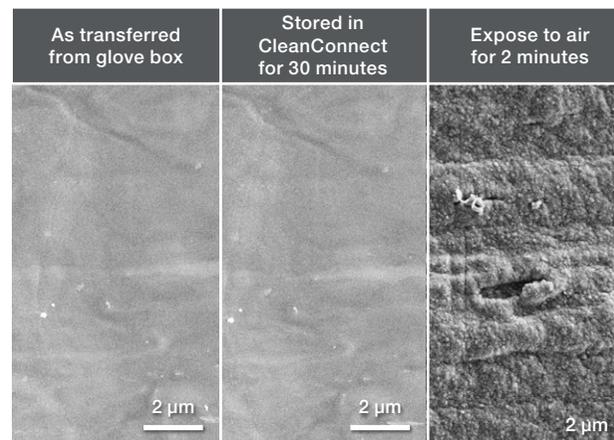
Figure 15: Performance of CleanConnect System on transferal of lithium metal sample.

Additionally, Thermo Fisher Scientific has developed an argon-compatible desktop SEM to enable characterization of air-sensitive samples inside the glove box. As shown in Figure 16, the Thermo Scientific Phenom™ XL G2 Argon-Compatible Desktop SEM inside of a glove box enables both sample preparation and SEM/EDX analysis to be performed in the same glove box. This solution increases the sample imaging analysis throughput by skipping the sample transfer process outside of the glove box.
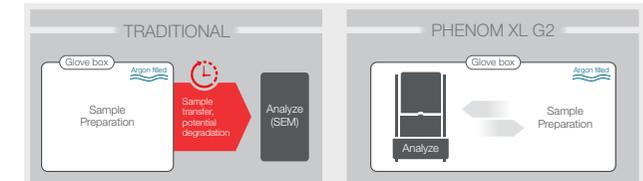
Figure 16: Comparison of traditional process versus the Phenom XL G2 Desktop SEM, showing time efficiency and sample preservation.

Automated SEM-EDS workflow for impurity analysis

During the battery production process, impurities are always introduced.

Impurities such as Fe, Cr, Zn, and Cu particles in the battery's raw materials have significant impact on the electrochemical performance and material stability and can even cause internal shorts with severe battery safety issues. As a standard QC process, ICP-OES is widely used in the industry to evaluate how much of those elements are within the materials during the manufacturing process. However, ICP-OES will not be able to provide information such as size and composition of the impurities. This structural information is important to identify the contaminant source in the materials production environment to help optimize the manufacturing process. As a complementary analytical solution, the Thermo Scientific Phenom ParticleX Battery Desktop SEM provides an automated SEM-EDS workflow that can identify the impurities in the battery materials.

Figure 17 shows both an example of the identification of the impurity in the NMC powders and the final data table with composition and size information, which can be generated after the test. Such a fully automated workflow provides a process to identify impurities in the battery raw materials with high throughput.

F Al S Fe Ba W Au C O Mn Co Ni
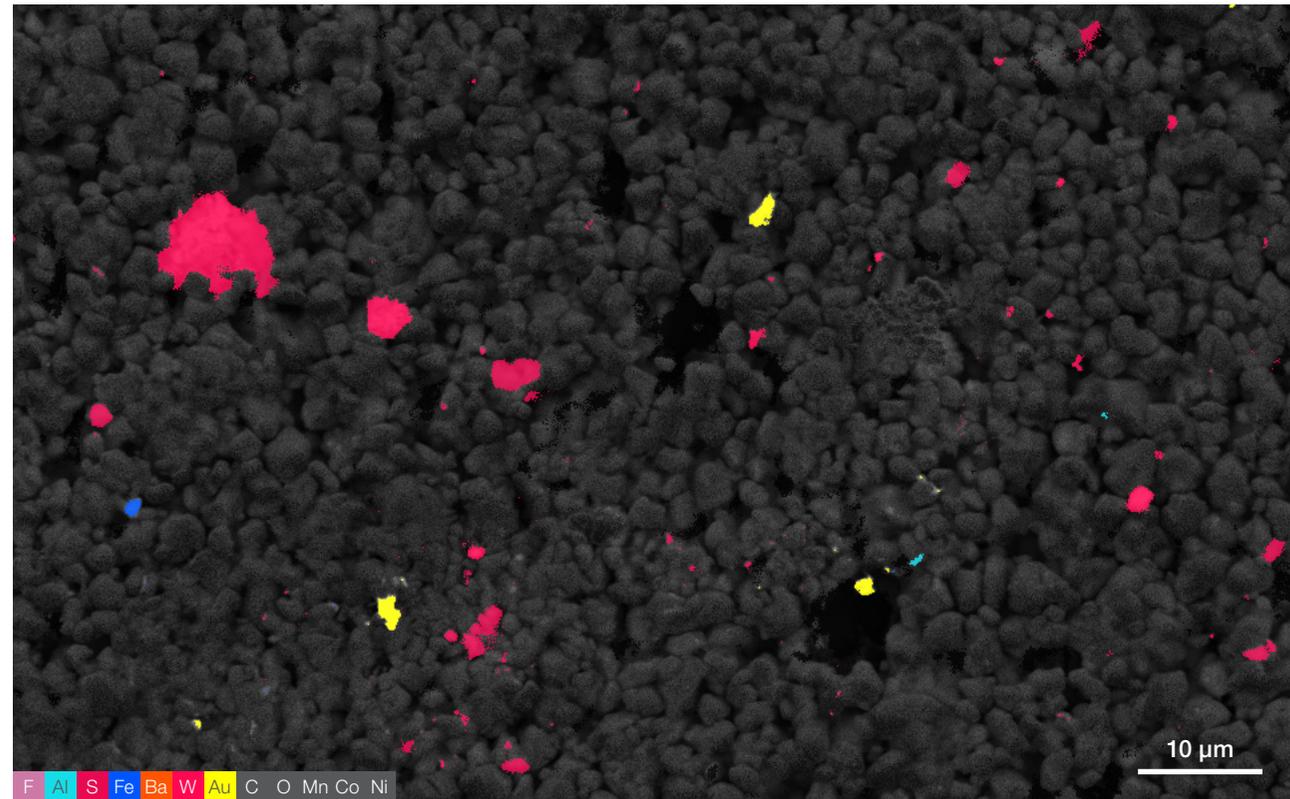
Size class		A	B	C	D	E	F	G
Size range (µm)	Total	5 ≤ X < 15	15 ≤ X < 25	25 ≤ X < 50	50 ≤ X < 100	100 ≤ X < 150	150 ≤ X < 200	200 ≤ X < 400
Iron	1		1					
Aluminium	443	256	167	19	1			
Other	272	123	115	32	2			
Salts	8	1	6	1				
NMC	99,286	37,745	43,173	17,398	960	8	1	1
Total counts	100,010	38,125	43,462	17,450	963	8	1	1

Figure 17: Identified particle contamination in NMC powders. Custom reports and classification table generated by Phenom ParticleX Battery Desktop SEM users.

About Thermo Fisher Scientific

We are the world leader in serving science. Our mission is to enable our customers to make the world healthier, cleaner and safer.

Step ahead. Step beyond. Duration 1.33

Our innovative solutions for 3D electron microscopy, spectroscopy, and microanalysis help materials science researchers advance their sample characterization to gain deeper insight into materials using the latest advances in analytical instruments. Our multiscale, multimodal solutions provide the additive manufacturing industry with imaging and characterization of powders and parts at nano- to atomic-level resolution.

Our TEMs, DualBeam™ FIB/SEMs, and comprehensive portfolio of SEMs, combined with software suites, take customers from questions to usable data by combining high-resolution imaging with physical, chemical, elemental, mechanical, and electrical analysis across scales and modes—through the broadest sample types.

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We also offer instrument maintenance and training services.

Thermo Scientific SEM portfolio

Phenom Pharos Desktop SEM
Phenom XL G2 Desktop SEM
Phenom P-Series Desktop SEM
Phenom ParticleX-Series Desktop SEM
Axia ChemiSEM
Prisma E SEM
Quattro ESEM
Apreo 2 SEM
Verios 5 SEM

SEM plays an instrumental role in lithium battery R&D and production. Thanks to the advanced SEM imaging techniques developed at Thermo Fisher Scientific, these solutions can meet a wide variety of needs in the battery industry, ranging from high-resolution imaging and *in situ* analysis to structural quantification and automated contamination analysis.

Our instruments and software can help you solve your SEM imaging challenges and also help you characterize the structure of your materials in their native state to develop better batteries.

Learn more at **thermofisher.com/battery-research**

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