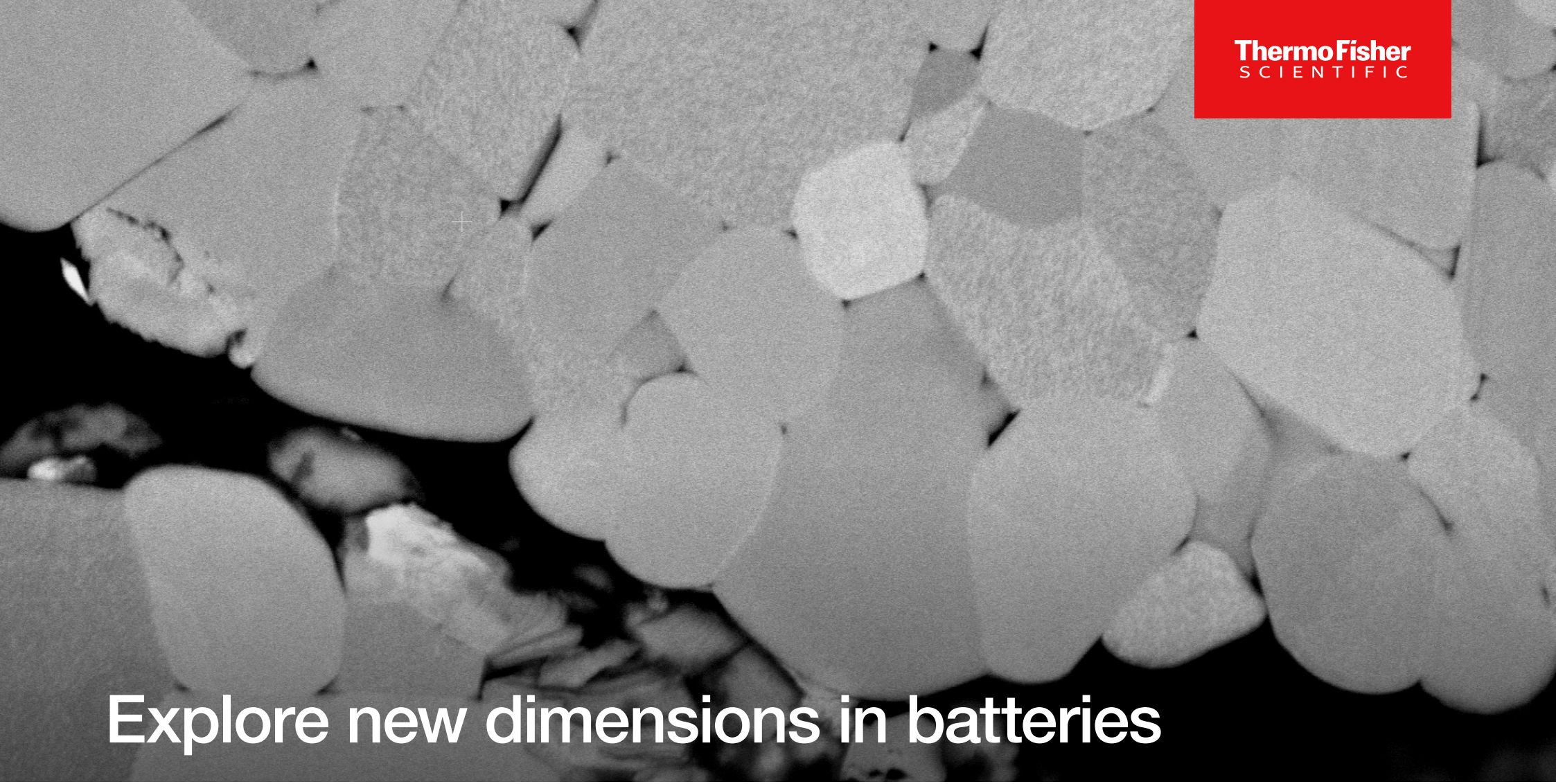

ThermoFisher SCIENTIFIC

Explore new dimensions in batteries

Advancing lithium battery research and development with DualBeam Technology

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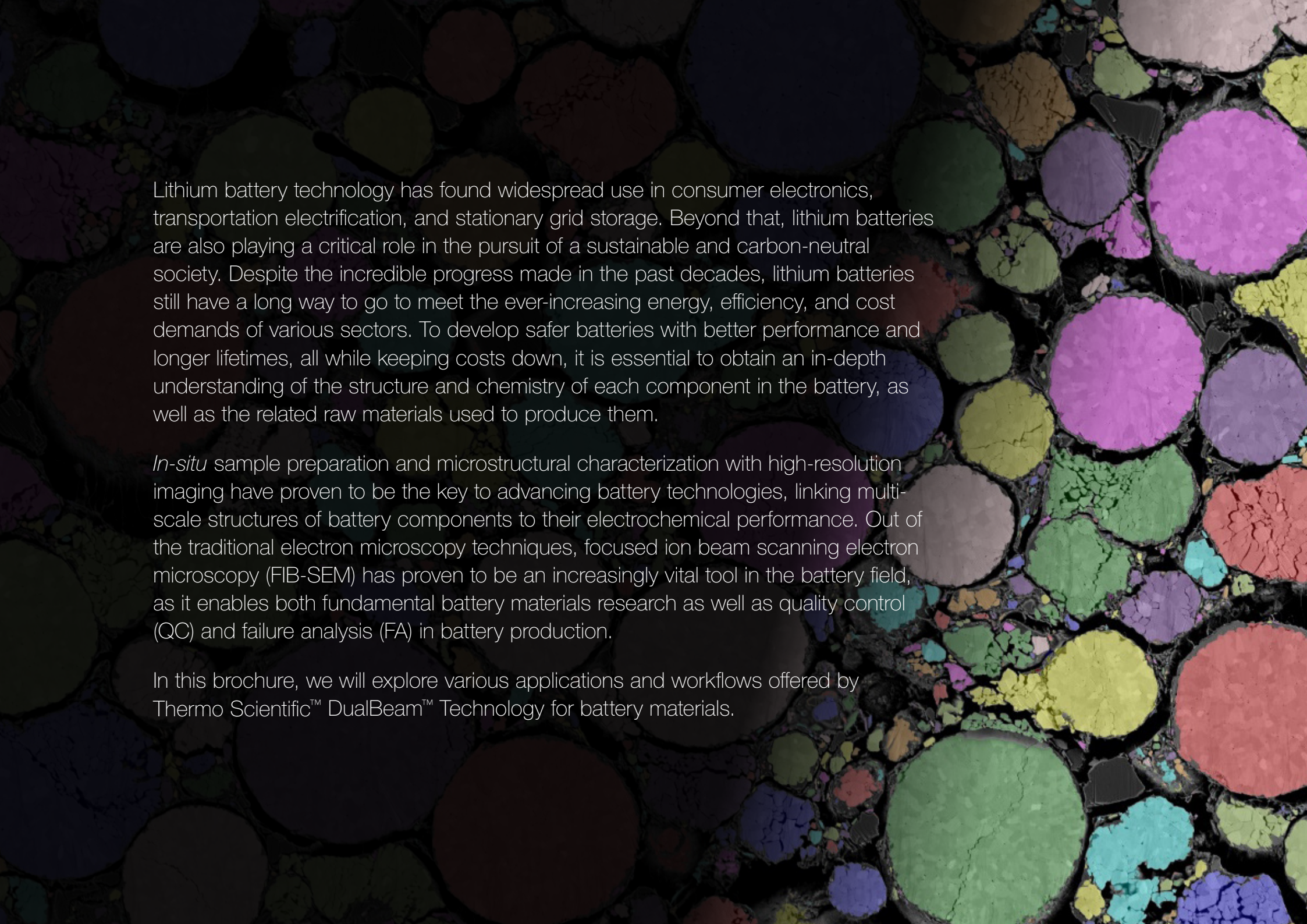


Lithium battery technology has found widespread use in consumer electronics, transportation electrification, and stationary grid storage. Beyond that, lithium batteries are also playing a critical role in the pursuit of a sustainable and carbon-neutral society. Despite the incredible progress made in the past decades, lithium batteries still have a long way to go to meet the ever-increasing energy, efficiency, and cost demands of various sectors. To develop safer batteries with better performance and longer lifetimes, all while keeping costs down, it is essential to obtain an in-depth understanding of the structure and chemistry of each component in the battery, as well as the related raw materials used to produce them.

In-situ sample preparation and microstructural characterization with high-resolution imaging have proven to be the key to advancing battery technologies, linking multi-scale structures of battery components to their electrochemical performance. Out of the traditional electron microscopy techniques, focused ion beam scanning electron microscopy (FIB-SEM) has proven to be an increasingly vital tool in the battery field, as it enables both fundamental battery materials research as well as quality control (QC) and failure analysis (FA) in battery production.

In this brochure, we will explore various applications and workflows offered by Thermo Scientific™ DualBeam™ Technology for battery materials.

Thermo Scientific DualBeam Technology

First commercialized by Thermo Fisher Scientific (formerly FEI) in 1992, DualBeam Technology has been widely used to characterize battery materials, and has provided novel methods for the visualization of micro- and macro-structures (from atomic, to electrode, to cell level) that cannot be accessed by other characterization techniques.

Fundamentally, DualBeam Technology integrates a SEM and FIB column together in a single instrument, oriented at a 52-degree angle (Figure 1A), with the FIB (for material milling and polishing) coinciding with the electron beam (for high-resolution imaging). This configuration can achieve in-situ and site-specific milling of samples together with simultaneous high-resolution imaging.

Figure 1B shows an SEM image of an $Li(Ni_xMn_yCo_{1-x-y})O_2$ (NMC) cathode cross-section milled by a Xe^+ plasma focused ion beam (PFIB). Thanks to advanced beam control and column designs, the resulting cross-section surface is smooth and artifact free. DualBeam Technology can be used to create such cross-sections anywhere on a bulk battery electrode or particle sample, and can be immediately followed by high-quality cross-sectional imaging with the SEM. Putting these two beams in one instrument opened many possibilities for materials characterization while also extending microanalysis to the third dimension (compared to traditional SEM).

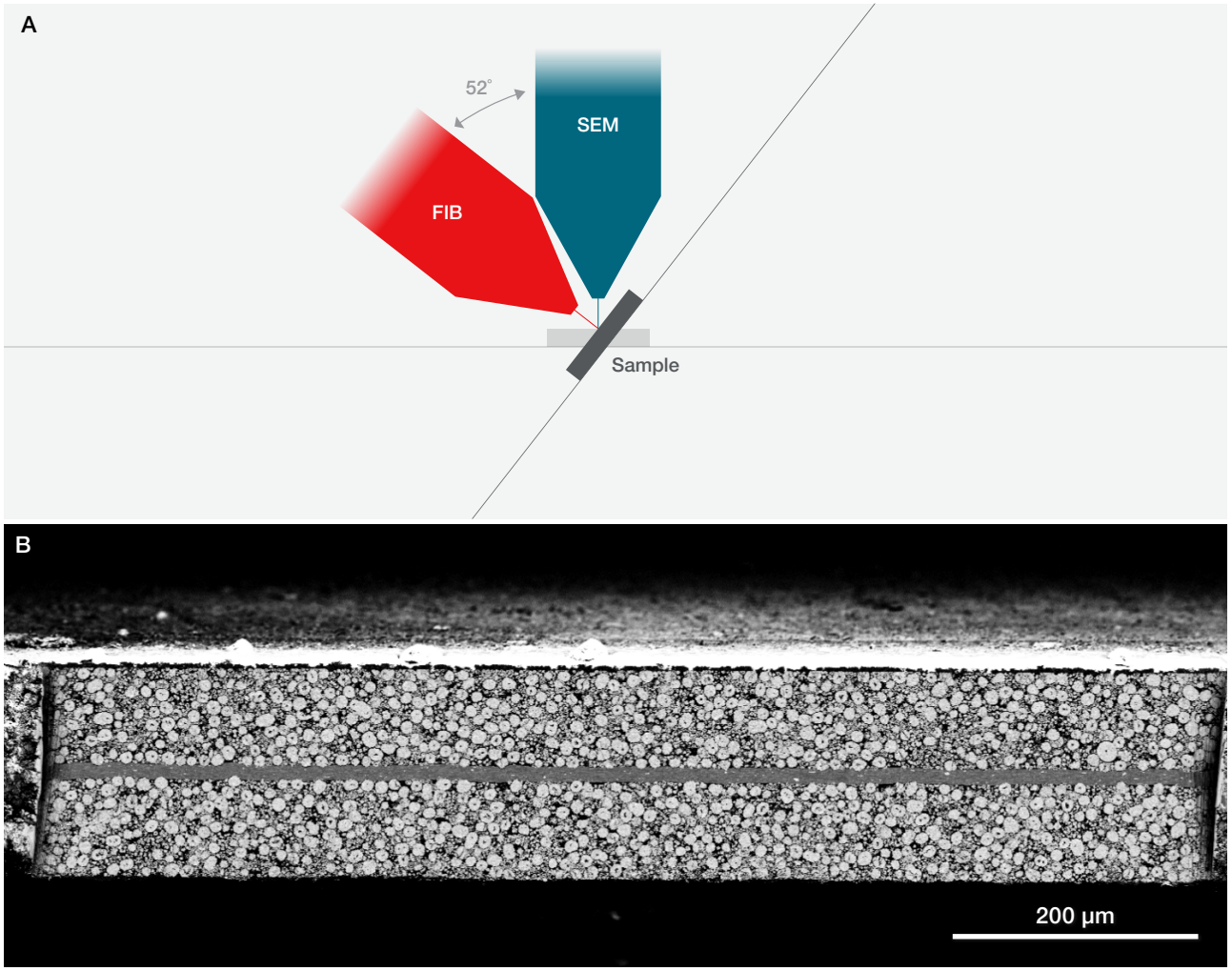


Figure 1. A) Graphical illustration of the DualBeam concept. B) 1,000-µm wide cross-section of an NMC cathode.

Gallium FIB

Gallium FIB-SEM uses a liquid metal ion source (LMIS) to generate the milling beam. Ga+ has high current density at low beam currents, providing high-quality surface polishing. Its maximum milling current is ~100 nA, which makes it well-suited for targeting cross-sections that are <100 µm wide. (For example, $LiFePO_4$ cathodes or separators that have feature of interest <1 µm in size.)

Plasma FIB

PFIB uses an inductively coupled plasma (ICP) source to generate the milling beam from a variety of possible gas sources, most commonly xenon. Due to its source design, PFIB can maintain excellent beam shape at high current while still preserving a decent beam-current density at low beam currents. The maximum milling current for a PFIB can be 2,500 nA, 25x the maximum current of gallium FIB. Therefore, PFIB can easily access cross-sections as wide as several hundred micrometers, which is ideal for characterization of most NMC cathodes (at ~10 µm size). In addition to Xe+, the Thermo Scientific™ Helios Hydra™ DualBeam offers multiple ion species (xenon, argon, oxygen, and nitrogen) for milling. Different ions can offer unique benefits for distinct battery components. For example, graphite anodes, which were previous difficult to mill with Xe+, can be easily milled and polished with an Ar+ beam.

Laser PFIB technology

The Thermo Scientific™ Helios™ 5 Laser PFIB allows you to prepare millimeter-scale samples in order to access larger areas of interest. The femtosecond laser, attached to the specimen chamber, enables the highest throughput among the three technologies. The focus point of the laser coincides with both the SEM and FIB and can routinely open ~1-3 millimeter-wide cross-sections at good milling quality, which can be further polished with PFIB (areas up to 1-mm wide). This technology is best applied to large sample volume analysis, examining specimens such as graphite anodes, coin cells, or even pouch cells.

Figure 2. Thermo Scientific DualBeam instruments with different ion/milling sources.

In-situ 2D cross-sectioning and analysis with DualBeam Technology

One of the most straightforward ways to study battery microstructure is to create cross-sections and image them with SEM. Traditionally, cross-sectional studies have been performed with a combination of broad ion-beam (BIB) polishing and SEM imaging; the cross-section would be prepared in a dedicated broad ion beam polisher and then transferred into an SEM for cross-sectional imaging.

Compared to this BIB-SEM workflow, cross-sectioning with FIB-SEM offers several benefits. Instead of being limited to the edge of the bulk sample, DualBeam Technology can create site-specific cross-sections anywhere on the sample surface. This allows you to perform cross-sectional analysis at your area of interest with nanometer-scale accuracy. For example, a foreign particle or contaminant can be identified on an electrode with optical microscopy, and this image is then used to guide the FIB-SEM in locating the defect. SEM imaging and subsequent FIB cross-sectioning at the specific location can provide direct answers on the nature (and potentially even the origin) of defects.

Additionally, due to the structure of the DualBeam instrument, SEM imaging is always available during the whole process of cross-section milling; there is no need to transfer the sample for imaging.

You can even use the SEM to monitor the milling process live, which makes it much more straightforward and less time consuming to tune the milling process.

Another advantage of DualBeam Technology is the capability of polishing multiple sites/samples automatically with a range of available automation software. First, the multi-purpose sample stage of Thermo Scientific™ Scios™ and Helios DualBeams can carry up to 18 samples in one sample loading cycle. Automation software can then be used to define multiple cross-section sites on each of these samples and the cross-sectioning is performed automatically.

Figure 3 shows the capability of DualBeam instruments to study different types of battery samples, from well-established NMC and $LiFePO_4$ (LFP) cathodes to next-generation sodium and solid-state batteries. High-quality cross-sections can be routinely made despite the porous nature of battery electrodes. This is achieved through excellent beam control and automatic rocking mill polishing, which are incorporated throughout all Thermo Scientific DualBeam instruments.

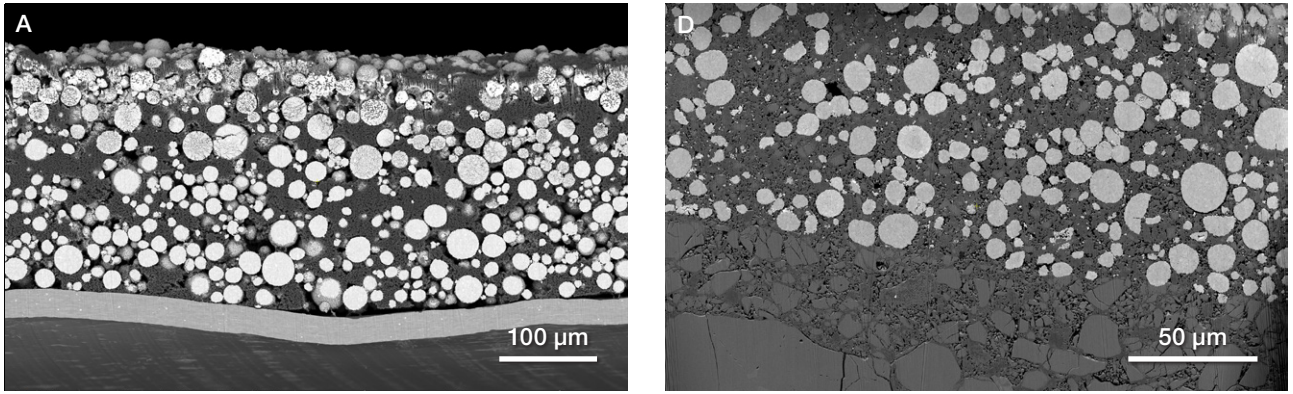


Figure 3. Various types of battery cathode cross-sections created and polished with DualBeam Technology. A) $Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O_2$. B) $LiFePO_4$. C) A sodium battery cathode. D) A solid-state cathode with a sulfited solid electrolyte.

Since battery electrodes have highly complex microstructures at multiple length scales, accurate characterization at these different scales is critical for a full understanding of any performance-structure relationships. High-quality FIB-SEM enables such analysis at the electrode level, as demonstrated on an NMC electrode in Figure 4.

A 600-µm wide cross-section through the whole electrode (Figure 4A) can be milled in 2 hours with a combination of high-current rough milling and subsequent automatic rocking polishing at lower beam currents.

High-resolution SEM imaging can be done immediately after a high-quality cross-section is prepared with FIB, and multiple detectors are available for imaging with different contrast mechanisms. Particle-level details, such as particle cracks and size distributions across the electrode, are accessible at a horizontal field width of 10–100 µm (Figure 4B). The ICD (in-column detector) is unique to the Helios DualBeam family and offers excellent materials contrast together with crystallographic channeling contrast, providing high-resolution information from individual grains (e.g., NMC particles) within a sample (Figure 4C). Nanometer-scale features such as the contact between conductive carbon and active material, or the nanopores within an NMC cathode, can instead be captured by the high-resolution imaging capability of the Thermo Scientific™ Elstar Electron Column in the Helios DualBeam series. Figure 4D shows a high-resolution image of an area where the carbon and binder domains (CBD) connect with an NMC particle. The cross-sectional analysis can be used to efficiently check electrode quality after manufacturing and can also play an important role in postmortem analysis.

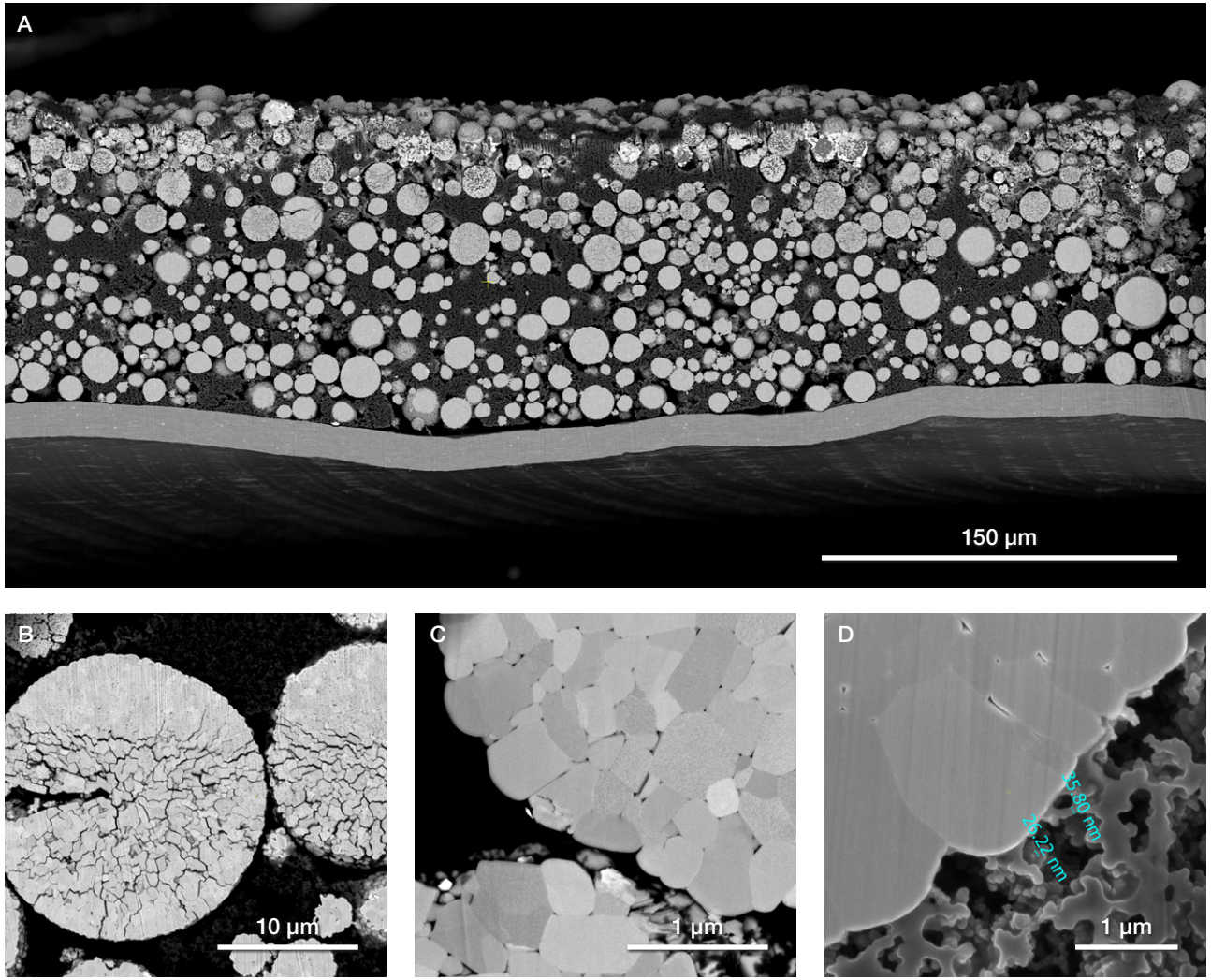


Figure 4. Multi-scale SEM images taken from a 600-µm wide cross-section milled with a Helios PFIB, clearly resolving features from millimeter to nanometer scale.

In addition to high-resolution SEM imaging, DualBeam instruments can obtain a range of analytical and quantitative insights from in-situ cross-sections, providing more in-depth information on battery-electrode structure-performance relationships. For example, the addition of an energy-dispersive X-ray spectroscopy (EDS) detector allows for easy identification of chemical distributions. As seen in Figure 5, the distribution of oxygen (NMC particle), fluorine (binder material), and aluminum (current collector) are clearly mapped with EDS. This technique can be used to routinely check the homogeneity and distribution of different ingredients in a battery electrode for failure analysis or quality/process control purposes.

Sometimes, imaging by itself can already provide quantifiable data. As shown in Figure 5E, Thermo Scientific™ Avizo™ 2D Software, combined with the excellent image contrast of a concentric backscattered (CBS) electron detector, can definitively segment individual NMC particles in an electrode cross-section. Quantitative data, such as particle-size or material-volume distributions across the electrode thickness, are readily available. With machine learning and scripting, it is even possible to create automated image analysis recipes to meet your specific analytical needs.

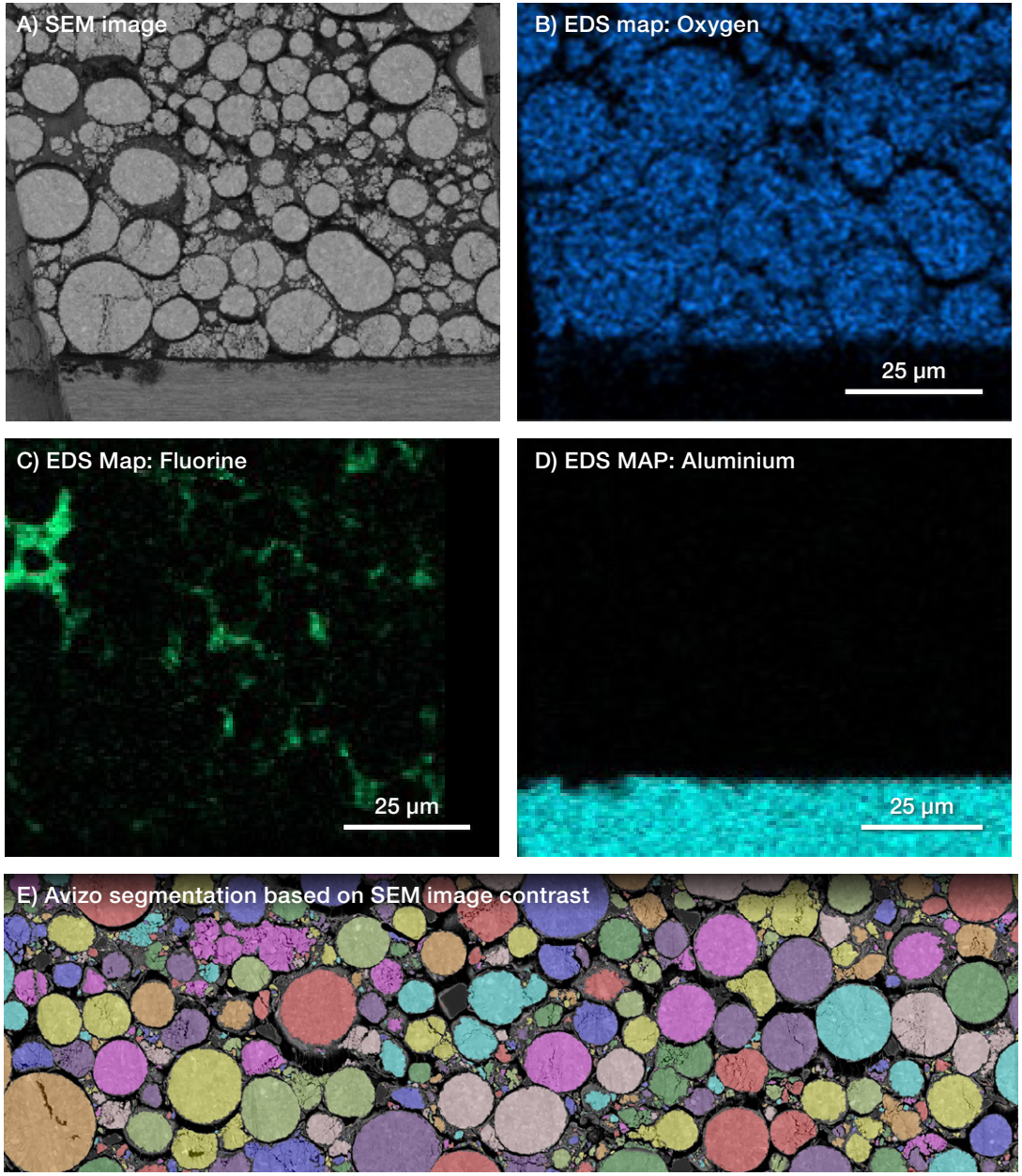


Figure 5. After *in situ* cross-sectioning (A), multiple analytical techniques can be applied to the sample, including elemental analysis with EDS mapping (B-D) or quantitative image analysis with Avizo 2D Image Processing Software, based on image contrast (E).

3D imaging and analysis of battery components with DualBeam Technology

In addition to its excellent cross-sectioning capabilities, DualBeam Technology also offers 3D imaging through the power of dedicated Thermo Scientific™ Auto Slice & View™ 5 Software. First, the coincidence geometry of the FIB and SEM is used to perform nanoscale serial cross-sectioning. After this, raw data is automatically collected with Auto Slice & View Software and a true 3D volume is reconstructed from the 2D images with Avizo Software (Figure 6).

When the DualBeam instrument is working in Slice & View mode, high-resolution SEM imaging is performed after each controlled FIB slice. The thickness of each polished slice can range from several to hundreds of nanometers with sub-nanometer accuracy and repeatability.
The whole slice (FIB cross-sectioning) and view (high-resolution SEM imaging) process is automatically repeated by Auto Slice & View Software.

A fully autonomous acquisition (typically performed overnight or over the weekend) produces hundreds or even thousands of image slices with a reliable and consistent slice thickness.

The resulting 3D volume, reconstructed with Avizo Software, reveals properties that are difficult or even impossible to investigate with 2D cross-sectioning (e.g., connectivity and tortuosity).

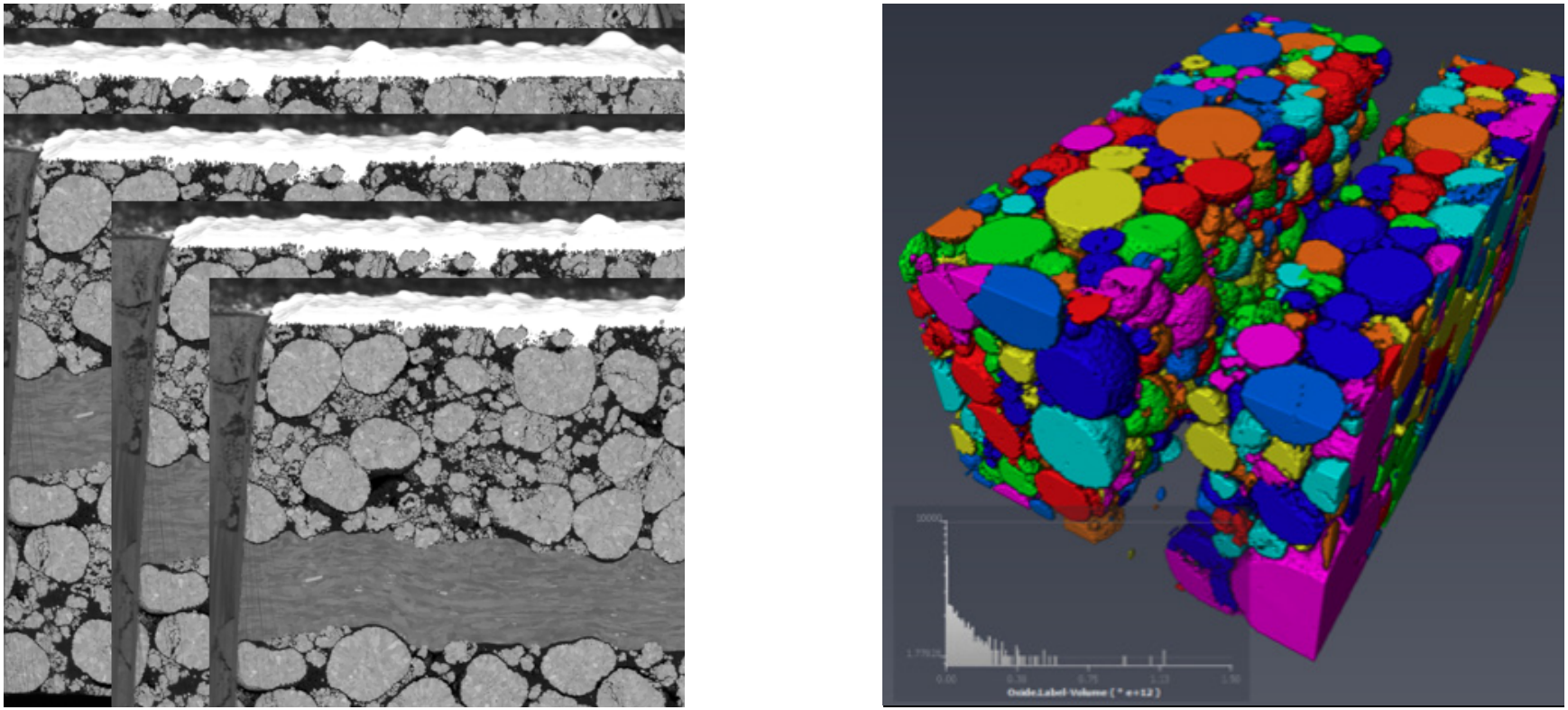


Figure 6. Illustration of the 3D analysis workflow using DualBeam Technology. Auto Slice & View Software was used for raw data collection followed by 3D reconstruction with Avizo Software.

Examples of the Auto Slice & View workflow

Figure 7 shows the Auto Slice & View analysis of a cycled NMC cathode from raw 2D data to the final reconstruction. The raw data (Figure 7A) shows microstructural features in the cathode sample, including cracks inside the NMC particle, the carbon and binder domain (CBD), as well as pores between the particles and the CBD.

Avizo Software is subsequently used to segment and quantify these features, as shown in Figure 7B. Differing image contrast is used to segment the NMC particles (red), cracks (green), carbon binder (dark blue), and pores (light blue). Following image segmentation, Avizo Software can also quantify these features. Notably, Figure 7A and 7B only show the data from an individual slice. The whole Slice & View dataset consists of hundreds of these images, cross-sectioned sequentially at a distance of 100 nm between slices. Avizo Software can analyze both the 2D images as well as the entire 3D reconstruction, quantifying the segmented features in 3D (Figure 7C).

Due to the high milling capability of PFIB, data from volumes as large as 106 μm^3 can be routinely and automatically collected through an overnight data acquisition. Such large volumes provide statistically significant data for microstructural studies.

Reconstruction and analysis with Avizo Software can visualize and quantify 3D features in the battery sample, including crack interconnectivity, pore space tortuosity, particle sizes, and volume fractions. This data can then be linked to the electrochemical properties of the sample, revealing the link between the microstructural evolution of a battery and its performance.

The connection between microstructural changes and performance loss is not only used for failure analysis; 3D volume data, reconstructed from real battery electrode samples, can serve as a 3D template that models the electrochemical processes in a battery. This information can be critical for optimizing the design of next generation batteries.

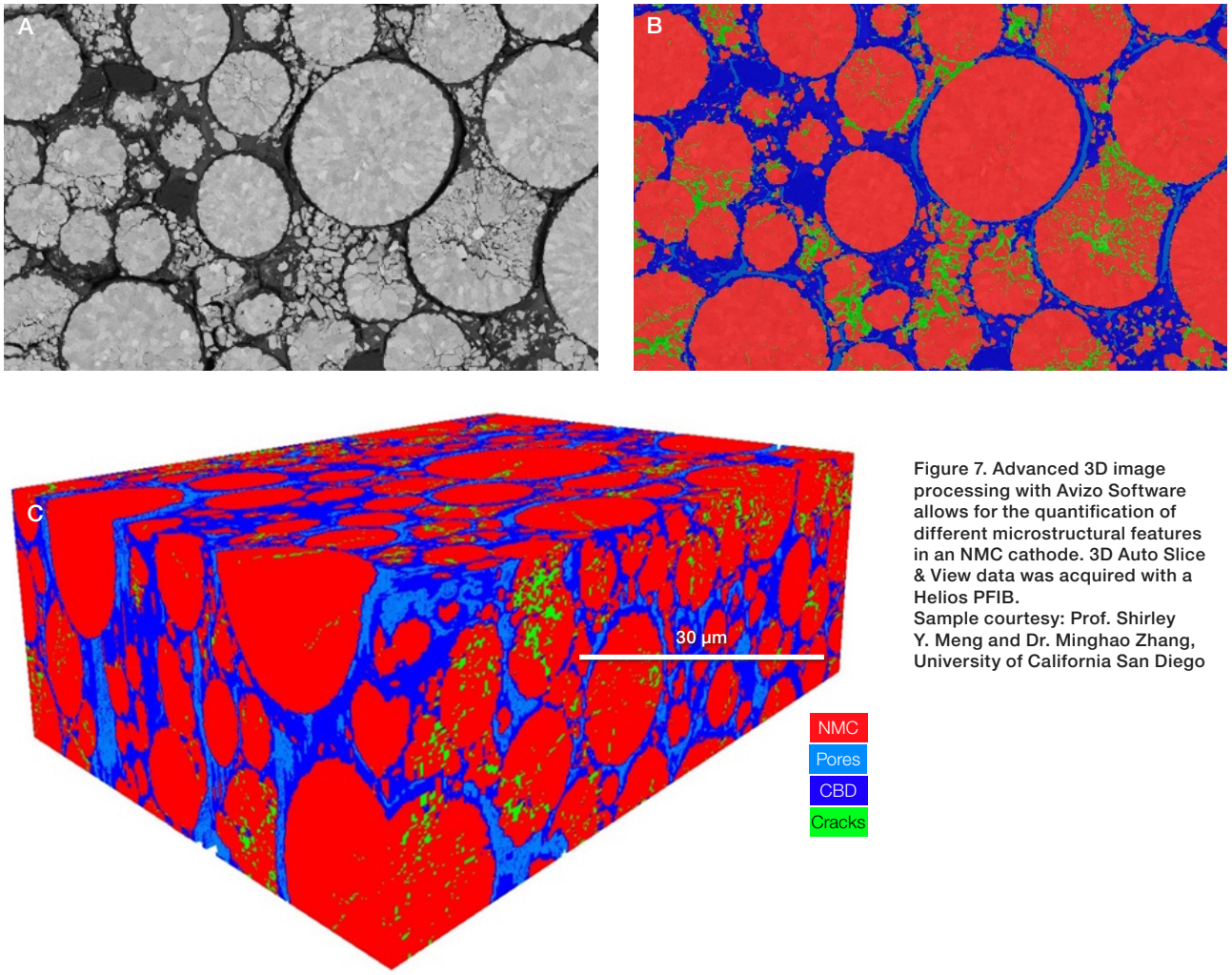


Figure 7. Advanced 3D image processing with Avizo Software allows for the quantification of different microstructural features in an NMC cathode. 3D Auto Slice & View data was acquired with a Helios PFIB.
Sample courtesy: Prof. Shirley Y. Meng and Dr. Minghao Zhang, University of California San Diego

The cathode example in Figure 7 shows that 3D analysis is possible using only SEM contrast. However, SEM does not always provide enough information to segment all present components. For example, binders and additives can be challenging to distinguish with SEM imaging alone.

3D EDS, in combination with SEM imaging, can be an effective method for studying different components in battery electrodes. Auto Slice & View Software can collect EDS data along with the SEM images, generating elemental maps from each slice that can be recombined into a 3D representation containing chemical information (Figure 8C,8F).

As seen in Figure 8, EDS maps from each cross-section show the distribution of silicon (SiO particles), oxygen (CMC), fluorine (PVDF), and carbon (graphite). The 3D reconstruction of the EDS data provides the spatial distribution of the CMC additive and its relationship with the SiO particle distribution. This 3D EDS capability is a powerful addition to conventional Auto Slice & View analysis and enables the study of chemical distributions in batteries with unprecedented accuracy.

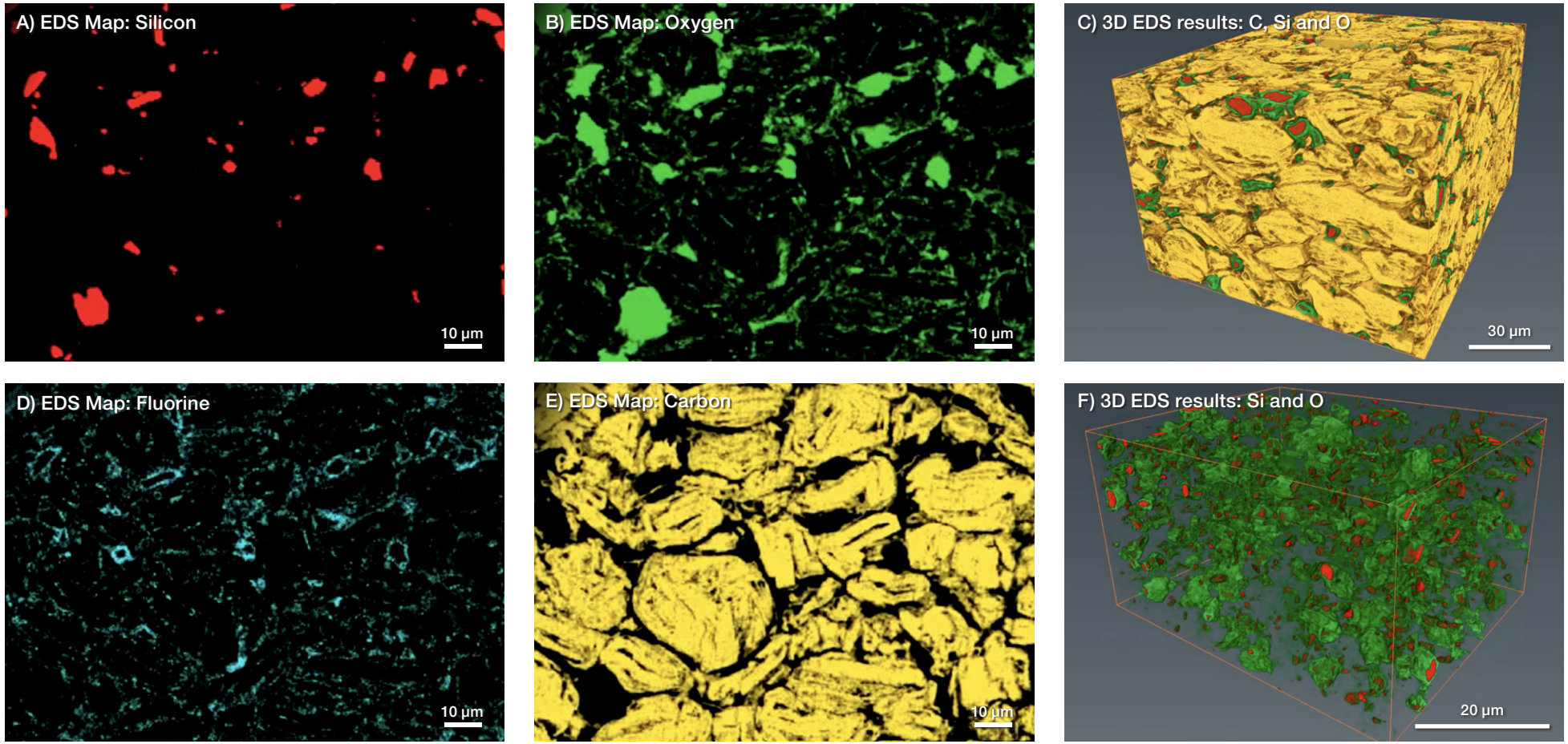


Figure 8. 3D EDS results showing the spatial distribution of CMC, PVDF additives and SiO particles in a graphite anode.

TEM sample preparation of battery materials

Another key application of DualBeam Technology is sample preparation for TEM (transmission electron microscopy). TEM, and its associated techniques such as STEM (scanning transmission electron microscopy), enable microstructural studies at atomic resolution, and require electron-transparent samples (typically thinner than 100 nm). Understanding battery material behavior at the atomic level is critical for revealing microstructure-performance relationships and advancing battery development. For example, this approach can be used to characterize the structure and composition of solid-state interface (SEI) layers, which are a crucial component that impacts battery cyclability.

The precision milling and in-situ lift-out capabilities of DualBeam instruments have enabled the development of optimized TEM sample preparation workflows. First, a small chunk of the bulk material (e.g. a cathode particle) is milled; a Thermo Scientific™ EasyLift™ Nanomanipulator is then used to lift out the chunk in-situ onto a TEM grid. The FIB is then used again to thin the chunk down to sub-100-nm thickness.

Until recently, TEM sample preparation has been a complicated process requiring a skilled operator. (The manual process of TEM lamella preparation consists of 37 key steps.) Continuous optimization and development of both software and hardware have led to the creation of Thermo Scientific™ AutoTEM™ Software to address this challenge. AutoTEM Software automates TEM lamella sample preparation and is designed to work with all Thermo Scientific DualBeam instruments.

With the recent release of AutoTEM 5 Software, all 37 steps of lamella preparation are now reduced to 3 manual steps:

1. Defining a location on the bulk sample (e.g. an electrode) where a TEM lamella is needed
2. Indicating where on the TEM grid the chunk lamella will be attached/transported to
3. Setting the desired thickness of the lamella in nanometers

After these steps, simply pressing “run” in the user interface will allow AutoTEM 5 Software to take control of the FIB-SEM, automatically performing all the steps necessary to make a TEM lamella.

Figure 9 demonstrates the AutoTEM 5 Software process on an NMC cathode. Critically, automated TEM lamella preparation does not stop at a single lamella. As shown in Figure 9, AutoTEM 5 Software can make multiple lamellae from multiple sites on the same bulk sample, or from multiple bulk samples. In the overview image (Figure 9D), 9 lamellae were created automatically and are ready for lift out.

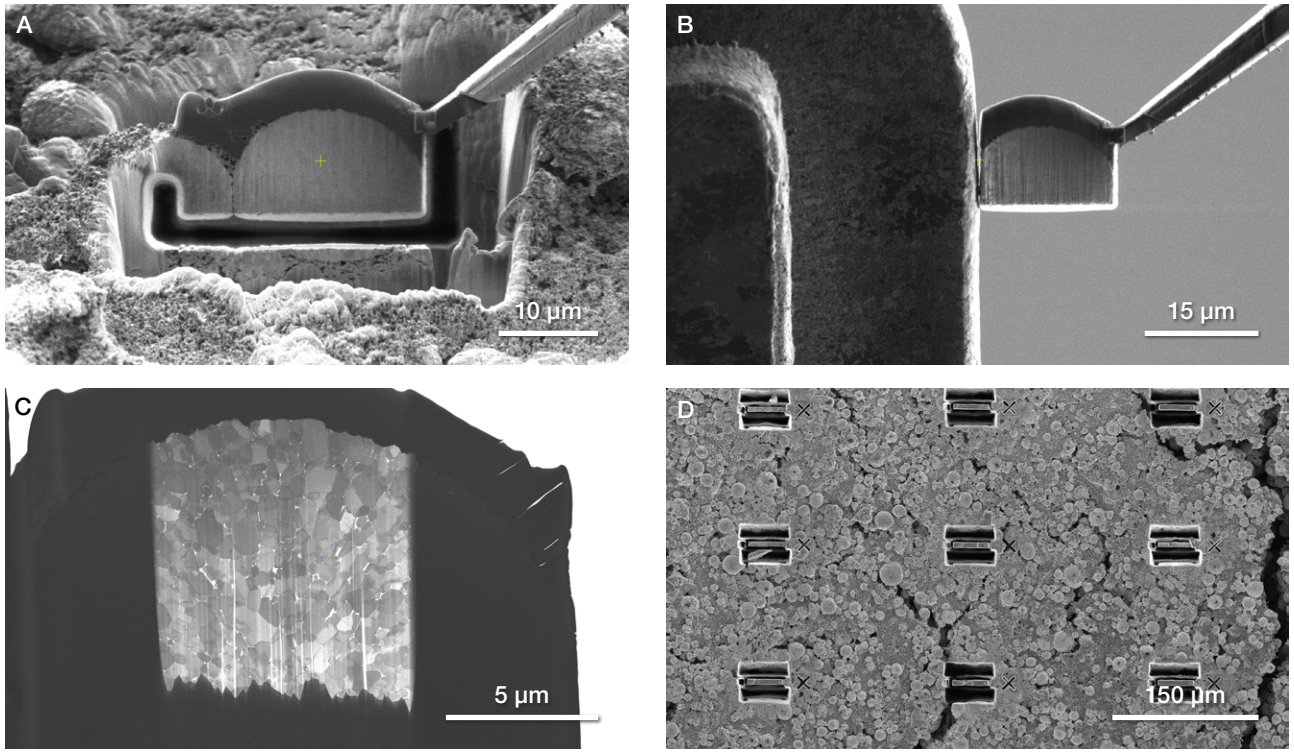
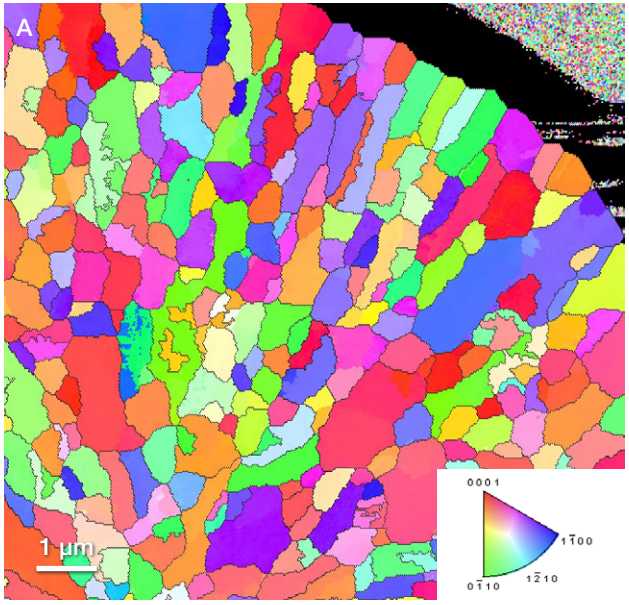


Figure 9. Automated TEM sample preparation from an NMC cathode with AutoTEM 5 Software. A) The lamella is prepared and is ready for lift out with the EasyLift Nanomanipulator. B) Automatic transfer to a TEM grid. C) Finally, the lamella is automatically thinned to electron transparency. D) Multiple lamella can be created from the bulk during the same workflow.

Once a lamella is successfully made, it is not only ready for atomic-resolution imaging and analysis with TEM, but can also be used with a range of ultra-high-resolution transmission imaging techniques inside the DualBeam instrument; Figure 10 provides two examples. In Figure 10A, individual grains of an NMC particle has been clearly indexed with the transmission Kikuchi diffraction (TKD) technique, showing crystallographic information within a single particle. In Figure 10B, a single grain of a multi-grain NMC particle is imaged; nanoscale features such as dislocation distribution can be reliably imaged without needing to transfer the sample to a separate TEM.

Overall, AutoTEM 5 Software has significantly lowered the technical barrier associated with traditional FIB-SEM preparation of TEM samples. 37 manual steps have been reduced down to three, making lamella preparation highly accessible.



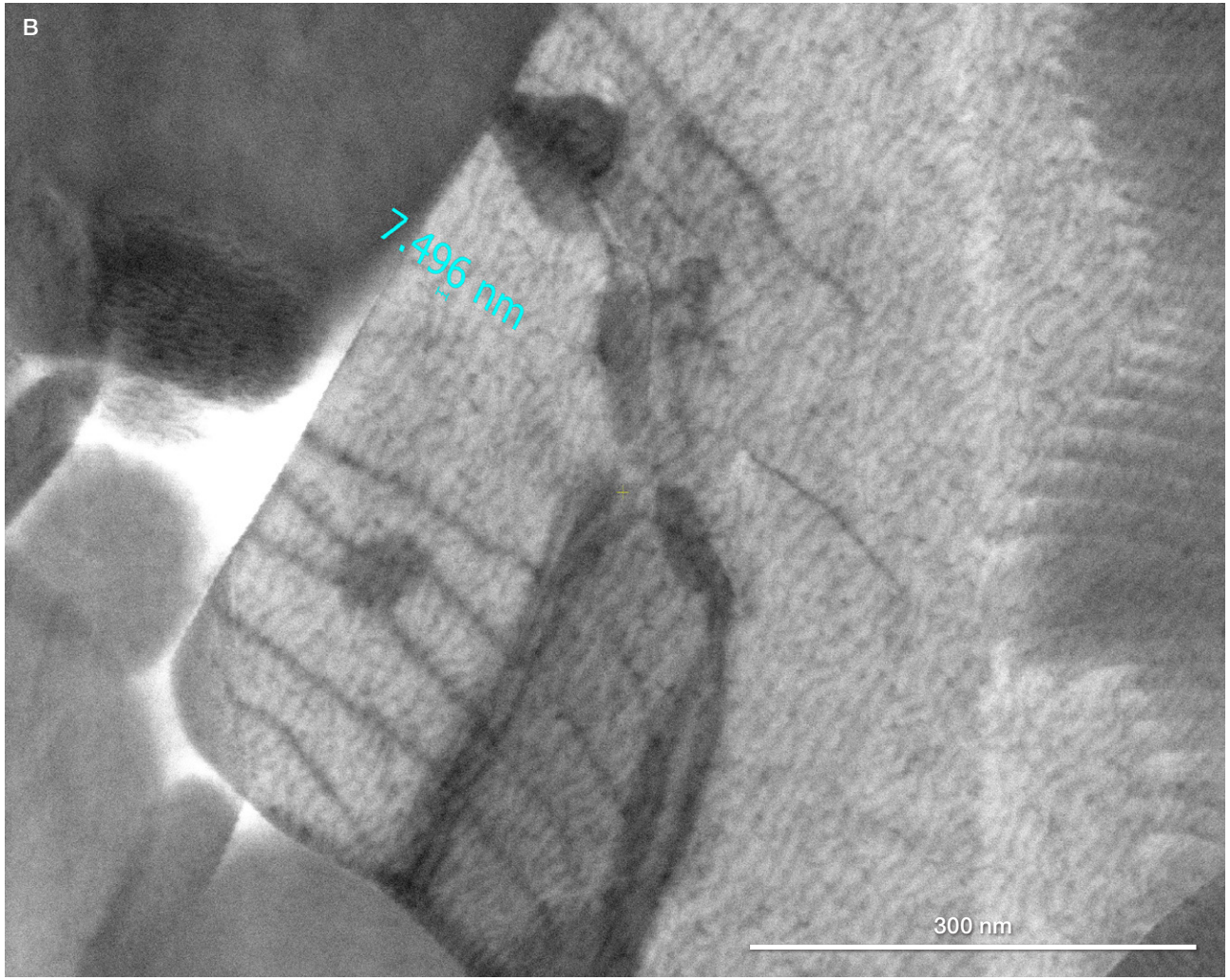


Figure 10. A) Transmission Kikuchi diffraction map shows the grain orientation of each individual sub-micron grain in an NMC cathode. B) High-resolution STEM imaging of a TEM lamella prepared from an NMC cathode.

Emerging DualBeam techniques for the study of battery materials

Large-area, site-specific automated surface polishing

FIB-SEM can effectively prepare 2D cross-sections of battery materials; however, in some cases, high-quality 2D information is also required from larger surface areas in order to reveal correlations between battery structure and performance. For example, it is well known that crack formation in active particles can either occur during calendaring or battery cycling, and correlates with cell performance. Analyzing these cracks across large areas, at different depths and with relevant statistics, can be extremely valuable for battery performance optimization.

PFIB-SEM enables fast access to large cross-sections that are hundreds of microns wide and deep, allowing for the collection of multimodal information at nanometer resolution. It provides both milling and imaging at the same location, so regions of interest can be located with high accuracy. Specifically, mounting of the battery sample at the center of the stage rotation axis allows for automatic PFIB-SEM spin milling (Figure 11). The PFIB is positioned at a glancing angle of 0.5–1.0 degrees relative to the sample surface, and the stage can be moved to several stationary positions at which the ion beam mills the sample. The result is a high-quality, large-surface-area section of the electrode.

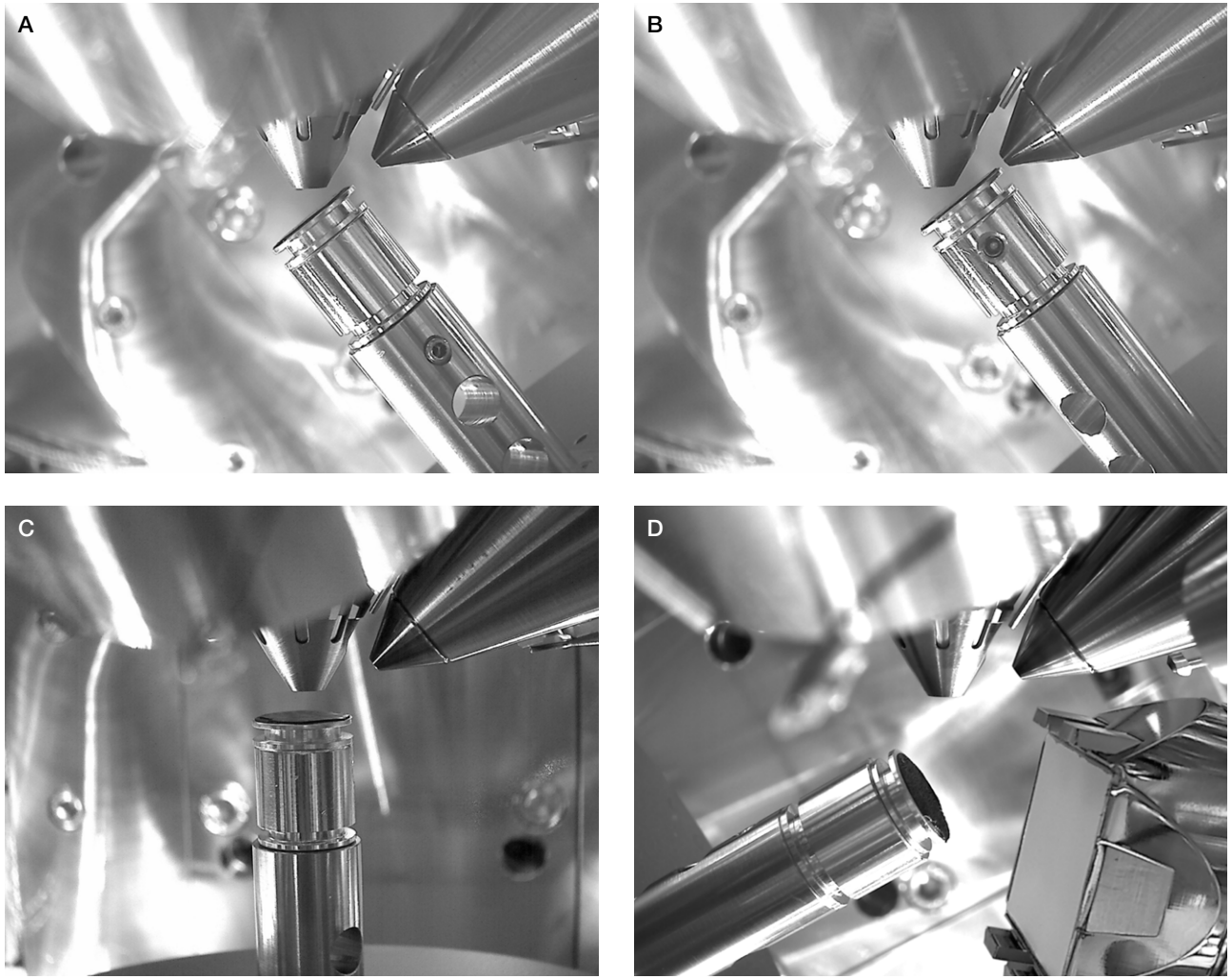


Figure 11. PFIB spin milling set-up for large-area sample preparation. Stage A) on-axis and B) off-axis compucentric rotation. C) SEM/EDS and D) EBSD data collection geometries.

The PFIB-SEM spin milling technique can be applied to the anode, cathode, or used to track structural evolution during polishing. Figure 12 shows the polishing of an NMC cathode and a graphite anode with the Helios Hydra DualBeam.

The spin milling technique enabled large-area polishing while also providing information at different depths, depending on the number of spins of the stage.

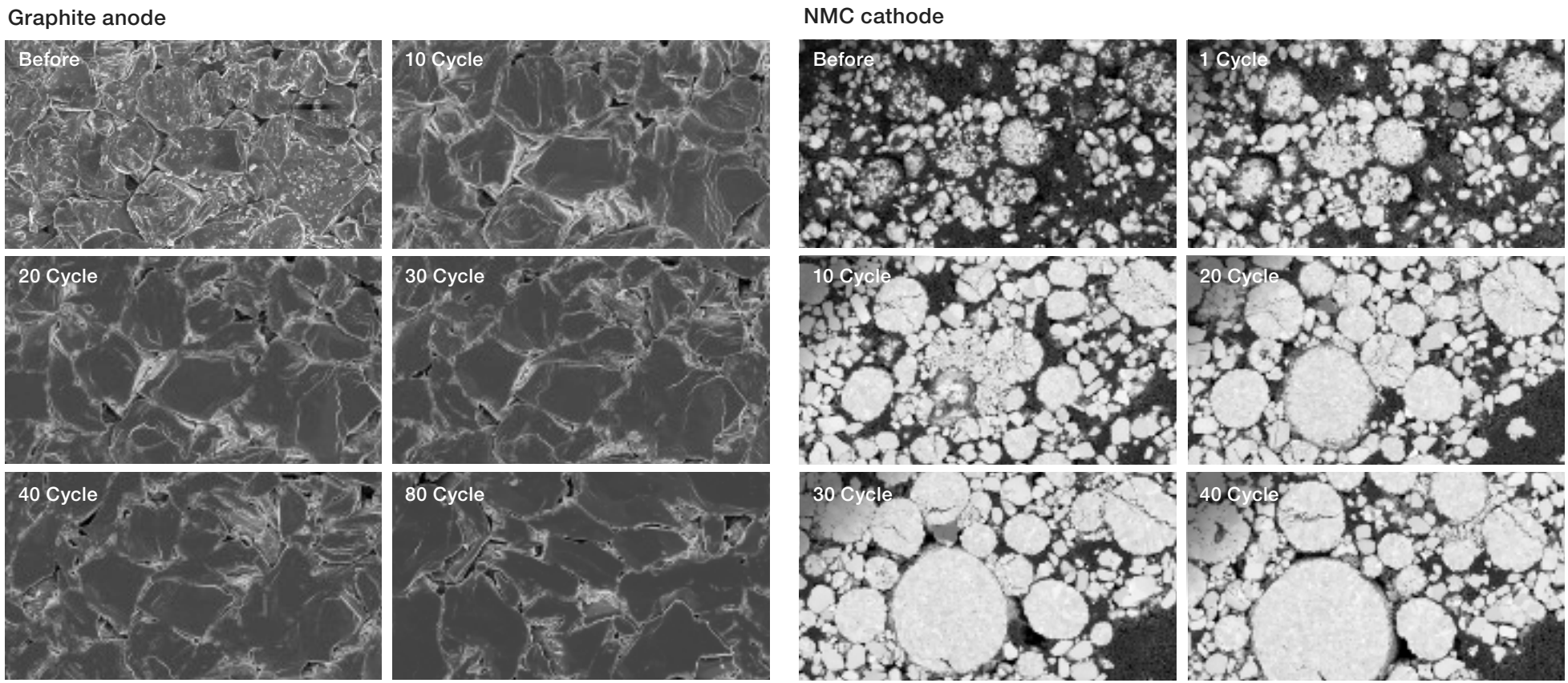


Figure 12. Spin milling analysis of a graphite anode and NMC cathode at various depths. Numbers indicate how many stage spins have been used to polish the sample.

Inert Gas Sample Transfer workflow

One of the biggest challenges in the electron microscopy of battery materials is the risk of contamination and damage during sample handling and transfer. This can be the result of air, moisture, or beam sensitivity associated with various battery components (e.g. Li metals, SEI layers, solid electrolytes, charged electrodes, etc.).

For atomic-resolution analysis, preserving sample integrity is particularly challenging, as the process involves sample transfer and handling between multiple different instruments; from glovebox, to FIB-SEM, to TEM. The Thermo Scientific IGST Workflow is specifically designed for reliable and repeatable characterization of air, moisture, and/or beam-sensitive battery materials.

The IGST Workflow protects both the bulk sample and the prepared lamella against air and moisture contamination by maintaining an inert argon atmosphere with the Thermo Scientific™ CleanConnect™ Sample Transfer System, which moves the sample in an inert-gas sample-transfer holder between the glovebox and the instruments. Additionally, if the sample is vulnerable to beam-damage, cryogenic temperature characterization can be incorporated into the workflow.

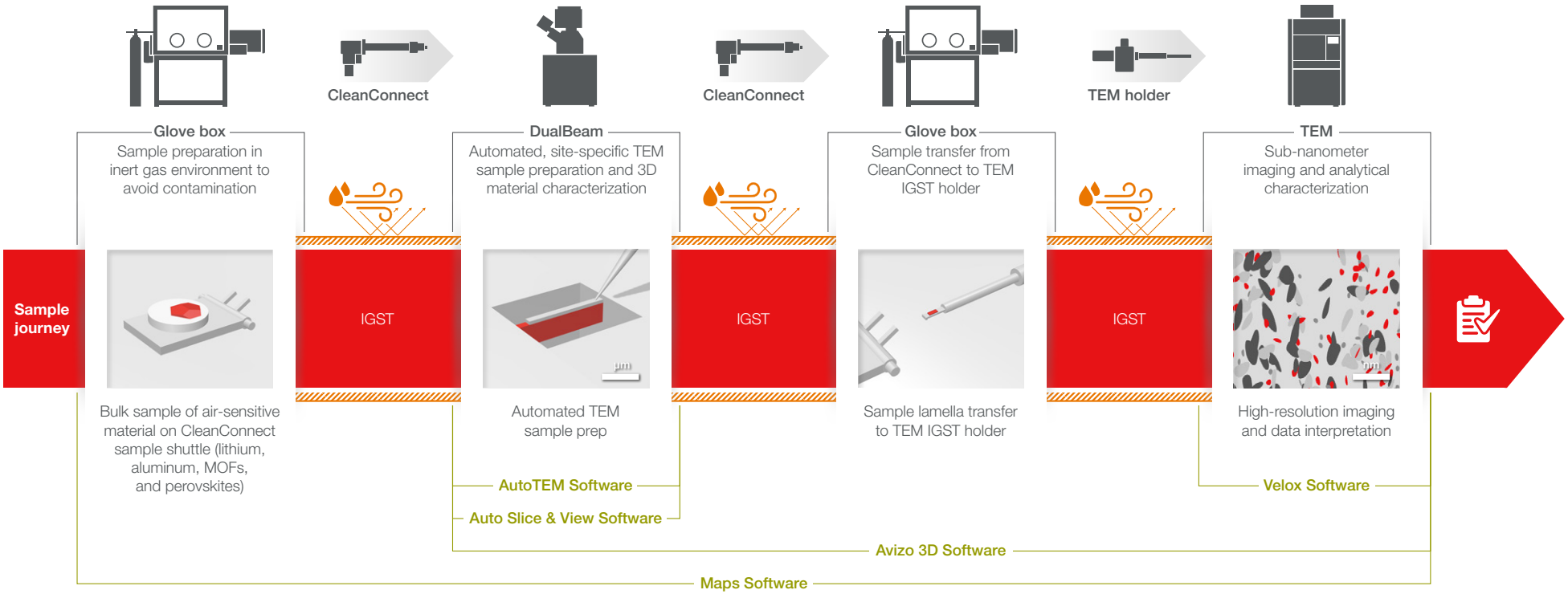


Figure 13. Inert gas workflow for nanoscale analysis, containing Thermo Scientific DualBeam and TEM systems.

Bulk lithium was tested in order to demonstrate the effectiveness of this workflow. Lithium metal was selected because it is a key component of next generation batteries, but is not just extremely air sensitive, but also sensitive to both electron and ion beams.

Using the CleanConnect System, a bulk Li-metal piece was successfully transferred from a glovebox to a Helios 5 Hydra DualBeam without signs of surface oxidation (Figure 14A). Next, the entire TEM lamella preparation process was carried out at cryogenic temperature (-178°C) due to lithium's sensitivity to beam damage. Bulk milling, lift out, attachment to the TEM grid, and final thinning were performed with a Thermo Scientific cryo-stage and cryo-EasyLift Nanomanipulator. To minimize ion beam damage to the final lamella, all ion milling was carried out with argon PFIB. The prepared lamella was then transferred to a Thermo Scientific™ Talos™ F200X TEM for final analysis (Figure 14B).

The importance of the IGST Workflow was further investigated by mimicking a conventional workflow with a short air exposure (Figure 15). The STEM bright-field images clearly show that the IGST workflow protects the lamella, with even a short air exposure completely changing the nature of the sample, which produces misleading results.

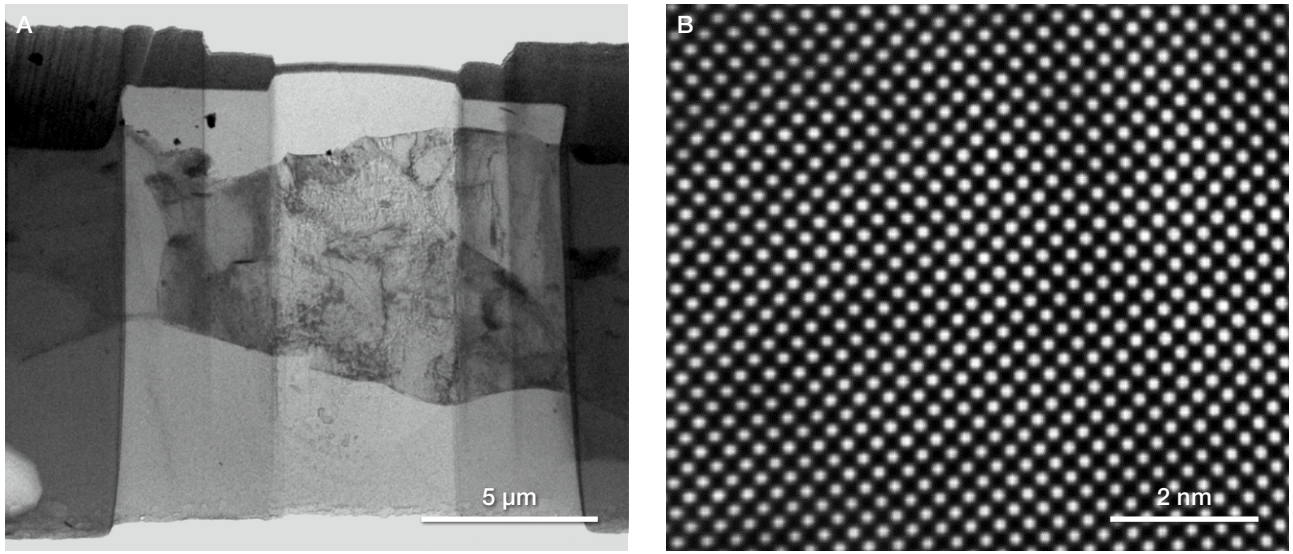


Figure 14. A) Li metal lamella with IGST workflow and B) Atomic-resolution TEM imaging of Li-metal atom columns. The IGST Workflow allowed the lithium metal lamella to stay crystalline with minimal signs of surface oxidation.

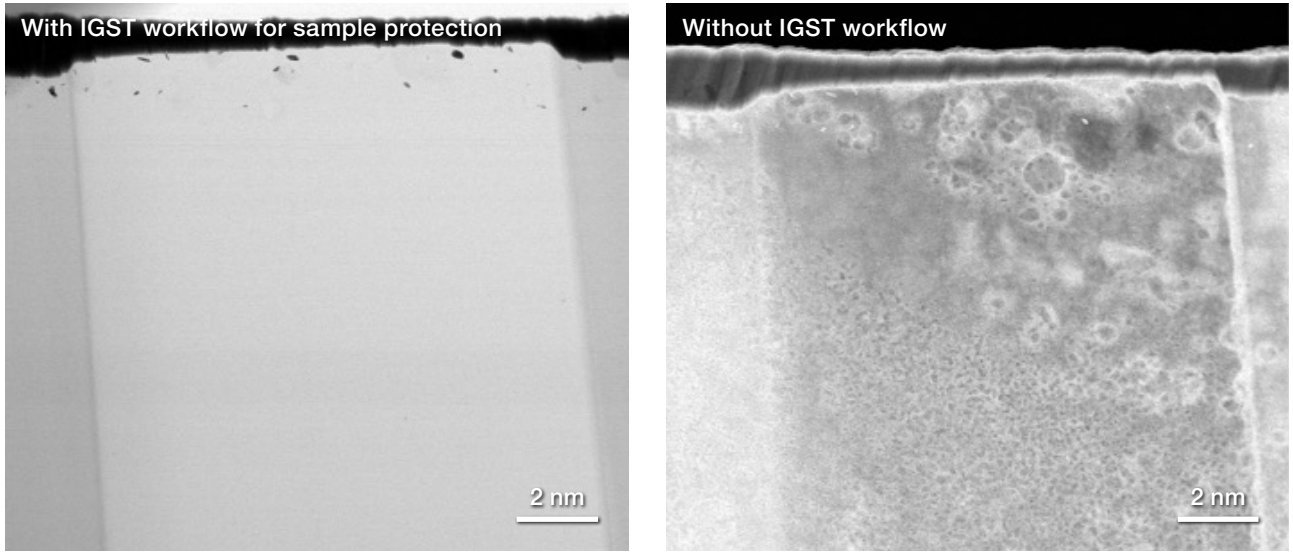


Figure 15. Li-metal lamella before and after 15 seconds of exposure in air.

The effect of short air exposure on a Li-metal lamella was further investigated with electron energy-loss spectroscopy (EELS) in TEM. Before air exposure, the lamella was predominately lithium (Figure 16A and 16C). After 15 seconds of exposure (Figure 16B and 16D), the lamella reacted with the oxygen, water vapor, and CO_2 in the air, resulting in significant amounts of oxygen (lithium oxide) and carbon (lithium carbonate) contamination.

The above results plainly demonstrate the capability and necessity of the IGST Workflow for the analysis of sensitive samples. Beyond that, this workflow also has the potential to address a number of pressing issues in battery research. For instance, the IGST Workflow can be used for the high-resolution characterization of SEI layer evolution along with post-mortem analysis, all while preserving the sample in its original state.

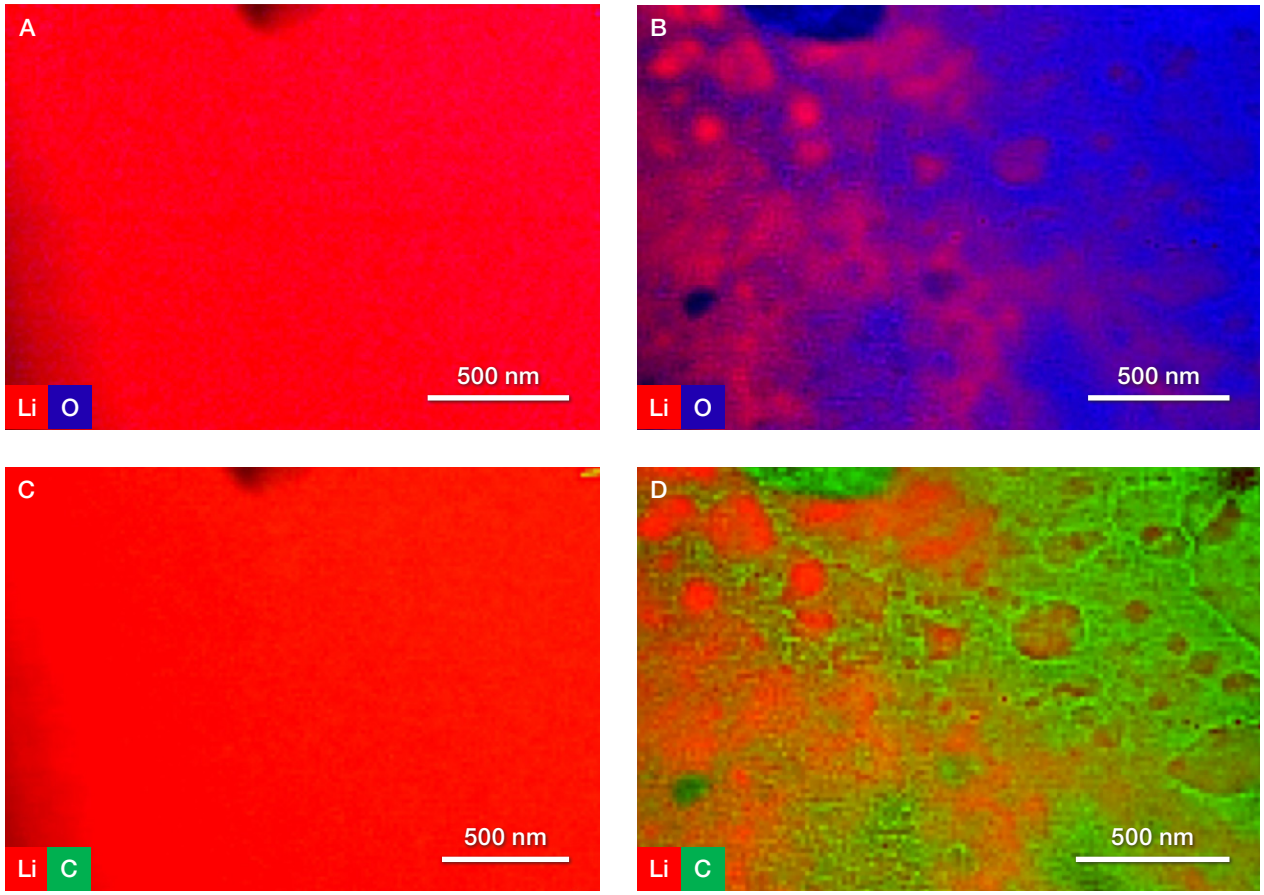


Figure 16. EELS quantification results showing a Li-metal lamella before and after 15 seconds of air exposure.

With IGST workflow for sample protection			
Element	Shell	Signal (Counts)	Comp. (at.%)
Li	K	6.768032e+11	94±4
C	K	5.9267e+09	2.98±0.14
O	K	9.3609e+08	2.92±0.14

Without IGST workflow (15s air exposure)			
Element	Shell	Signal (Counts)	Comp. (at.%)
Li	K	7.20142e+10	41.6±1.2
C	K	1.83907e+10	22.0±0.6
O	K	9.61318e+09	36.4±1.1

Cryogenic FIB

As discussed in the IGST Workflow, beam damage can have a significant impact on sample integrity. For instance, polymer separator films, polymer-based solid electrolytes, and binder materials are all highly beam sensitive, mainly due to their poor thermal conductivity, which causes them to quickly deform during FIB milling. Figure 17A shows an example of a ceramic-coated polymer separator film milled with FIB at room temperature. The cross-sectional image shows that the film shrinks and is structurally damaged by the FIB milling process due to the accumulated heat.

To avoid this damage, a specially designed Thermo Scientific sample stage is used to maintain the sample at cryogenic temperatures, reducing FIB-induced heating effects and maintaining the sample in its original state. Once attached to the main sample stage, the cryogenic sample stage circulates dry nitrogen gas (cooled with liquid nitrogen) inside the stage. This method allows for rapid cooling and warming while minimizing vibrations during cooling. The sample can reach -180°C from room temperature in less than 30 minutes of active cooling.

As seen in Figure 17B, lowering the sample temperature to -80°C kept the polymeric separator film stable under FIB milling. There are no signs of shrinkage, and both the porous structure of the film and the interface between the ceramic coating and the separator are well preserved. This is vital for the observation of true sample morphology, which connects the microstructural evolution of battery components to their electrochemical performance.

Cryo-FIB also has applications in many other areas of advanced battery development. This includes the analysis of any temperature-sensitive materials, such as previously discussed lithium metals (due to their low melting point), as well as certain components in SEI or CEI layers. Cryo-FIB is likely to find more applications in battery analysis and development as novel, sensitive materials become more prevalent.

Thanks to recent instrument developments, it is now possible to have a ToF-SIMS detector installed directly on a DualBeam instrument for low-atomic-number elemental analysis. The FIB/PFIB can be used as the excitation ion source for the ToF-SIMS, allowing SIMS mapping/depth profiling to be routinely performed with DualBeam Technology.

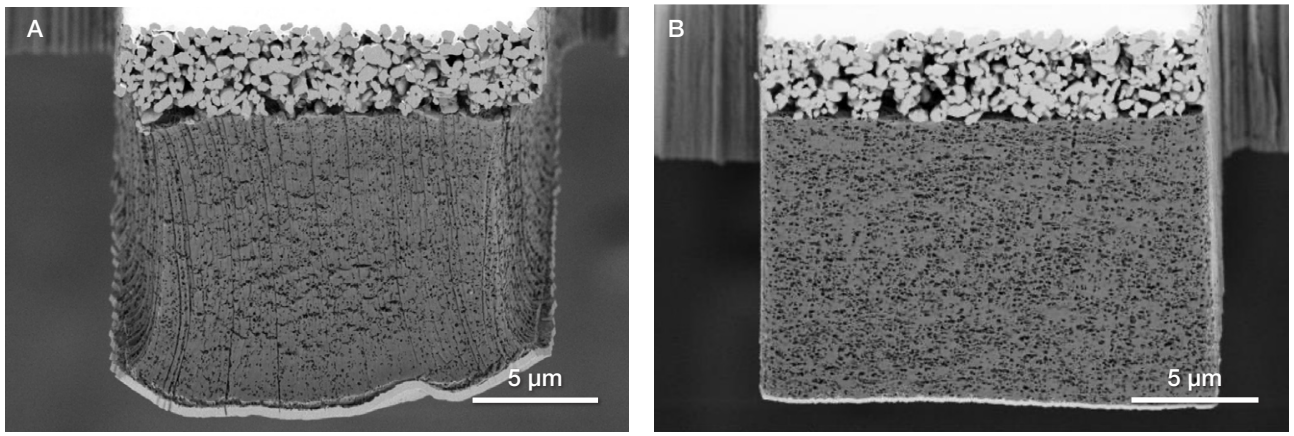


Figure 17. FIB cross-section of a cathode/separator film at (A) room temperature and (B) -80°C.

ToF-SIMS for light element detection

Although EDS has been widely used for element characterization within electron microscopes, one of its challenges is the analysis of low-atomic-number elements such as carbon, oxygen, lithium, and fluorine. These elements are highly prevalent in battery research, and dedicated time-of-flight secondary ion mass spectrometry (ToF-SIMS) is often used for such analysis instead.

As with dedicated ToF-SIMS tools, the ToF-SIMS detector in a DualBeam instrument can operate in positive or negative ion mode. Despite being highly challenging for traditional EDS analysis, ToF-SIMS was able to produce a $7Li^+$ positive-ion map from an NMC cathode sample (Figure 18A). FIB-based ToF-SIMS is able to easily characterize/visualize the lithium distribution with excellent spatial resolution. Detecting fluorine, particularly in the presence of manganese (i.e., in NMC particles) can be difficult with traditional EDS due to their peak overlaps. The negative fluorine ion map can, however, be easily generated with ToF-SIMS. Figure 18B shows the $19F^-$ negative-ion map of the NMC cathode, clearly revealing the binder (PVDF) distribution.

Combining SEM imaging, FIB processing, and ToF-SIMS detection in one instrument unlocks some unique applications. For example, the FIB can be used to prepare a site-specific cross-section, followed by high-resolution SEM imaging and EDS mapping. ToF-SIMS can then be used for elemental mapping of the same sample cross-section. The SIMS, EDS, and SEM results can be correlated, producing a robust understanding of the chemical/elemental distribution.

Correlative imaging analysis with µCT and laser-PFIB

So far, the focus has been on gallium and plasma FIB, which correspond to maximum milling scales of ~50 to 500 µm, respectively. Recently, Thermo Fisher Scientific has introduced a new DualBeam system equipped with femtosecond laser, which coincides with the FIB and SEM, further extending the instrument's milling capability to 1,500–2,000 µm (1.5–2.0 mm). This scale makes it possible to correlate results with non-destructive techniques, such as micro-computed tomography (µCT).

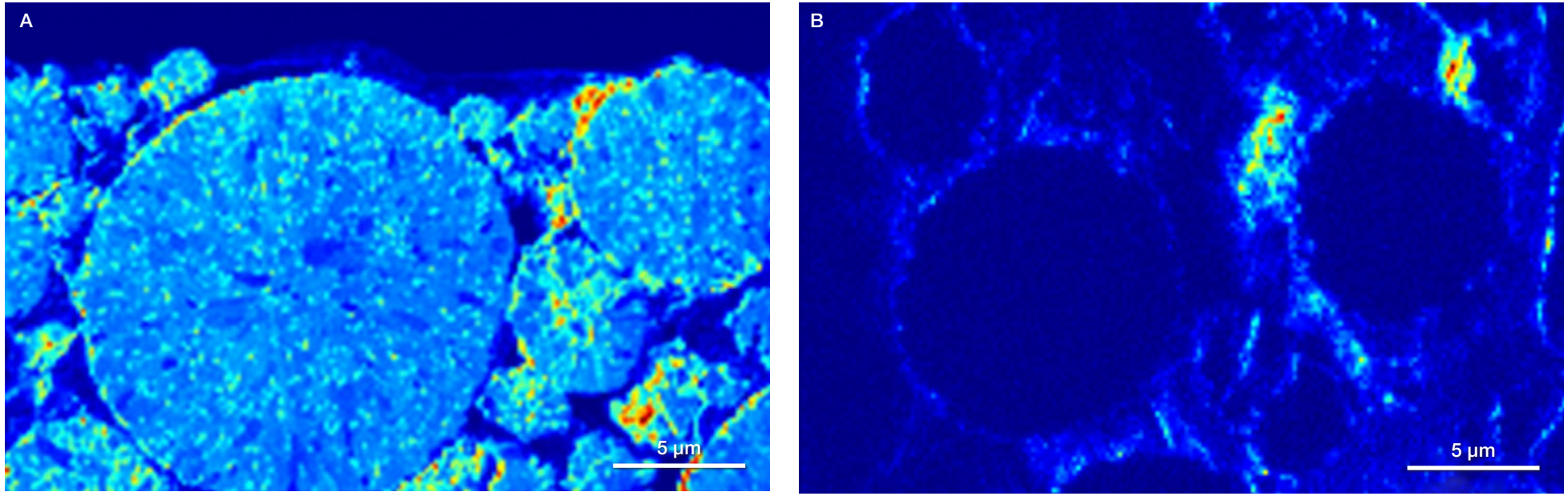


Figure 18. FIB-based ToF-SIMS maps of an NMC cathode cross-section. A) $7Li^+$ map showing lithium distribution. B) $19F^-$ map showing fluorine distribution in the binder.

Figure 19 shows an example of a workflow connecting µCT to laser PFIB. A µCT scan of a “jelly roll” pouch cell indicated a defect inside the battery (Figure 19A and 19B). CT data alone cannot determine the exact type and chemical composition of this defect. Additionally, it was about 1.5 mm below the top surface of the battery, putting it beyond the reach of either gallium or plasma FIB milling. However, it is well within the capability of laser ablation. The guidance of the non-destructive CT data was used to orient the sample and aim the laser to cut a cross-section right on the CT-identified defect.

The resulting laser-milled cross-section is shown in Figure 19C. A PFIB fine polish of the cross-section was followed by high-resolution SEM imaging, all without the need to break vacuum. A total of 15 electrode layers were milled through in only 30 minutes of laser ablation, and the defect was found on the 11th layer below the surface.

Further identification of the defect was carried out with SEM imaging and EDS elemental mapping. As shown in Figure 20, high-resolution SEM images of the defect show that it is a strand of cathode particles mixed into the graphite anode. Further EDS analysis confirms that the particles are rich in nickel, manganese, and cobalt, further confirming the defect’s identity. This indicates there is likely a cross-contamination issue in the cell manufacturing site, which needs to be addressed in order to improve the quality of the battery cell.

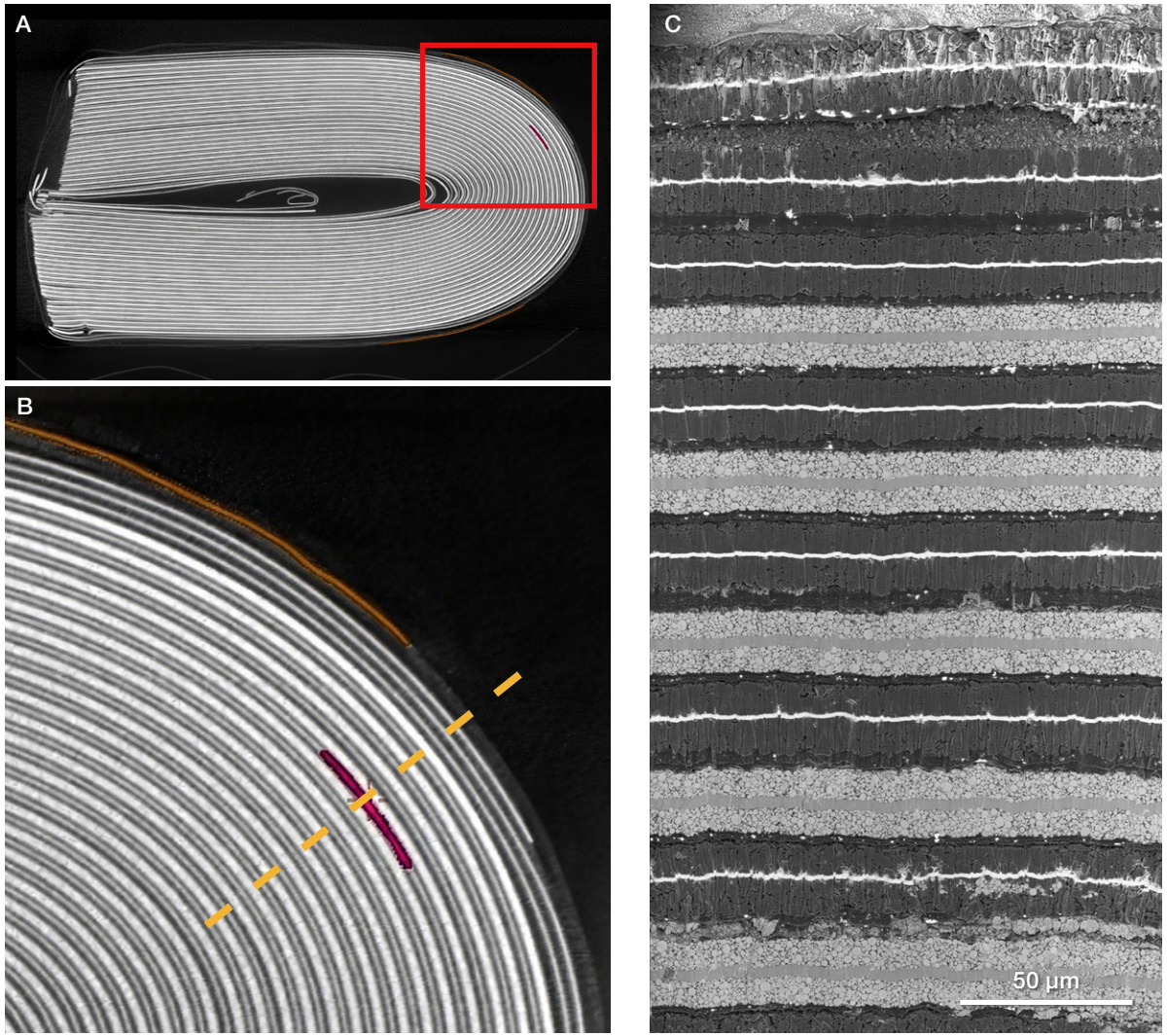
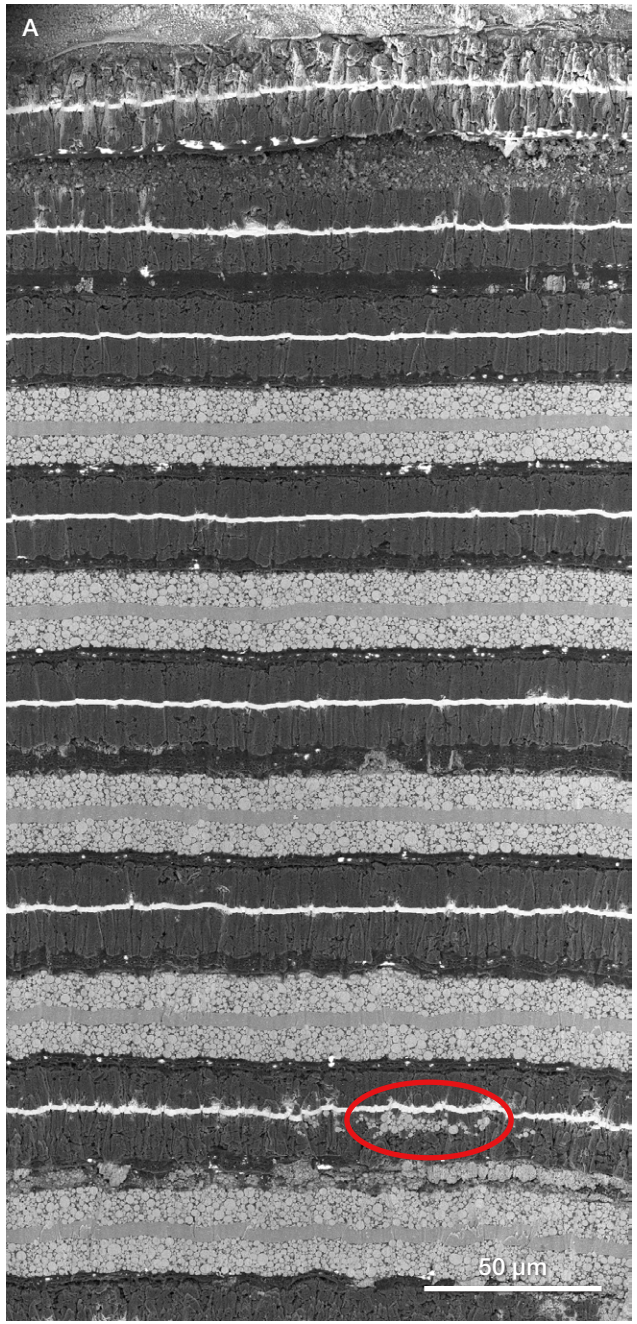


Figure 19. A) Overview image of the CT scan showing the location of the defect in the jelly roll battery. B) Defect (highlighted in red) identified with µCT, superimposed with a projected laser-cross-section plane (yellow dotted line). C) Laser-milled cross-section along the projected plane.



Laser PFIB is not limited to correlative µCT, and can be used for a number of other applications. For example, the laser can be used to mill through both the shell and the interior electrodes of a closed coin cell. This allows you to directly observe the morphology and interfaces between the electrodes. It is an exciting time for laser PFIB as an emerging technology, and its capabilities/applications in battery research are continuing to be explored.

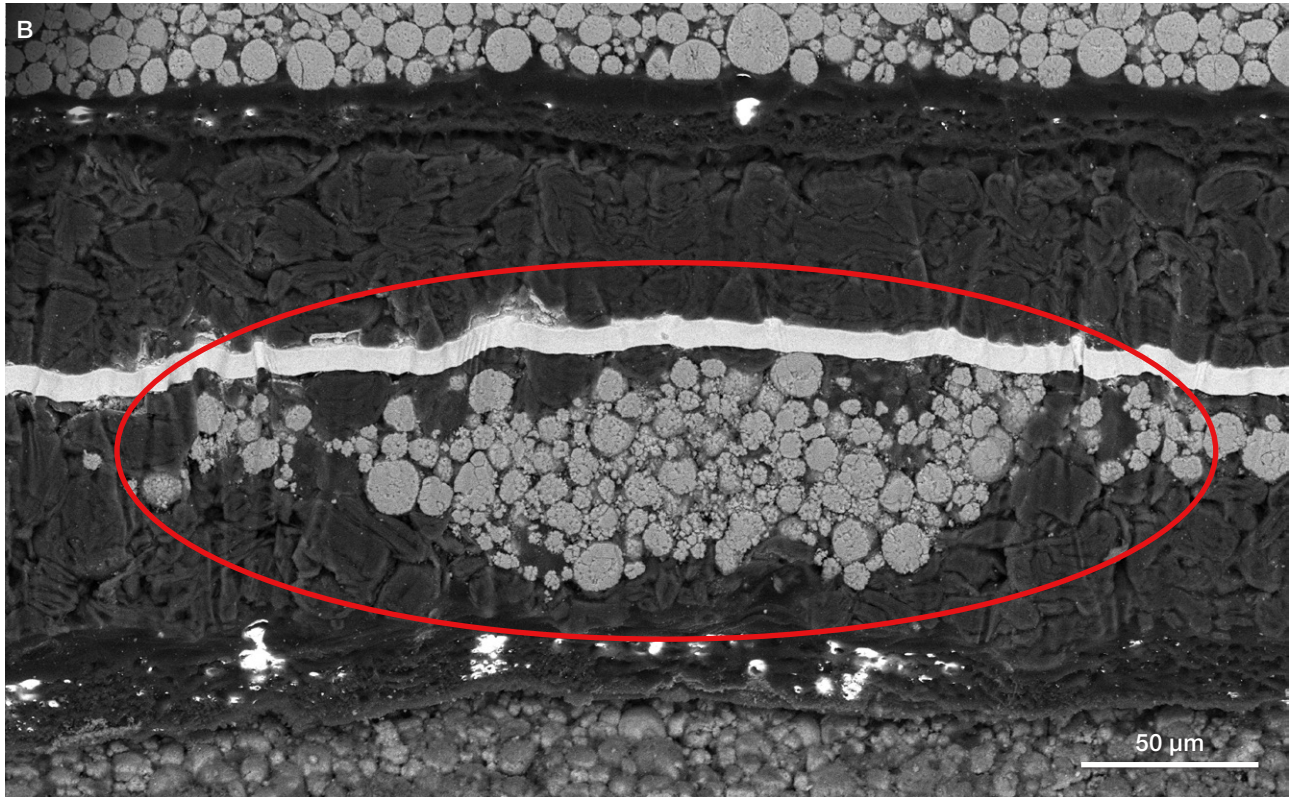


Figure 20. A) Overview of a large laser-milled cross-section showing a defect at the 11th layer of the battery cell. B) Close-up SEM image showing the morphology of the defect.

Summary

DualBeam Technology plays a key role in the research, development, and production of lithium batteries. With dedicated hardware and software solutions developed by Thermo Fisher Scientific, DualBeam instruments can meet a wide range of applications like standard cross-sectioning, 3D characterization, and TEM sample preparation. We have also enabled advanced characterization techniques on the DualBeam, such as IGST, cryo-FIB, ToF-SIMS, and femotosecond-laser milling. These techniques and workflows are indispensable for battery innovation in both academic and industrial environments, offering new dimensions for battery research.

Thermo Scientific DualBeam portfolio

Scios 2

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Helios 5 CX

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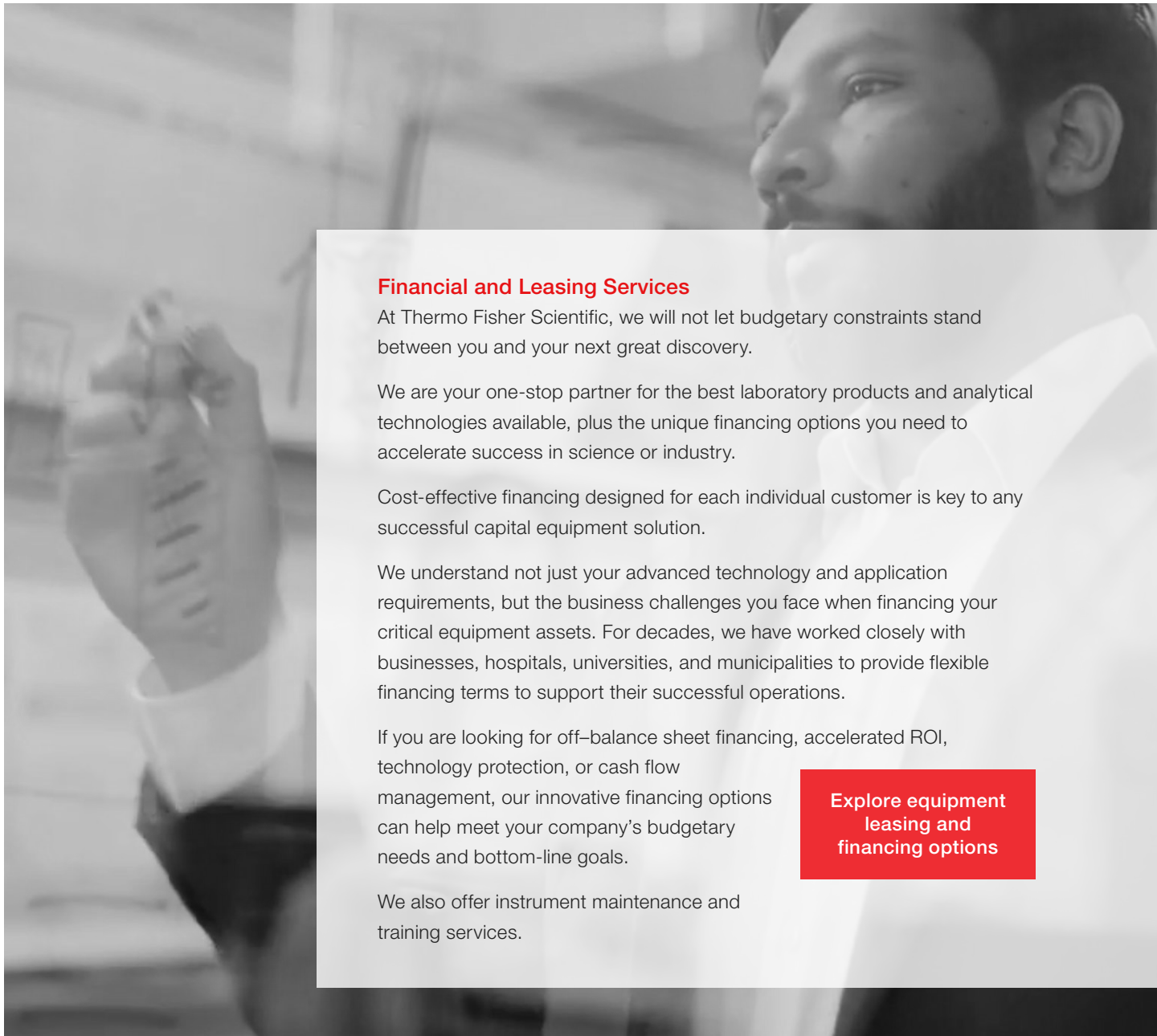

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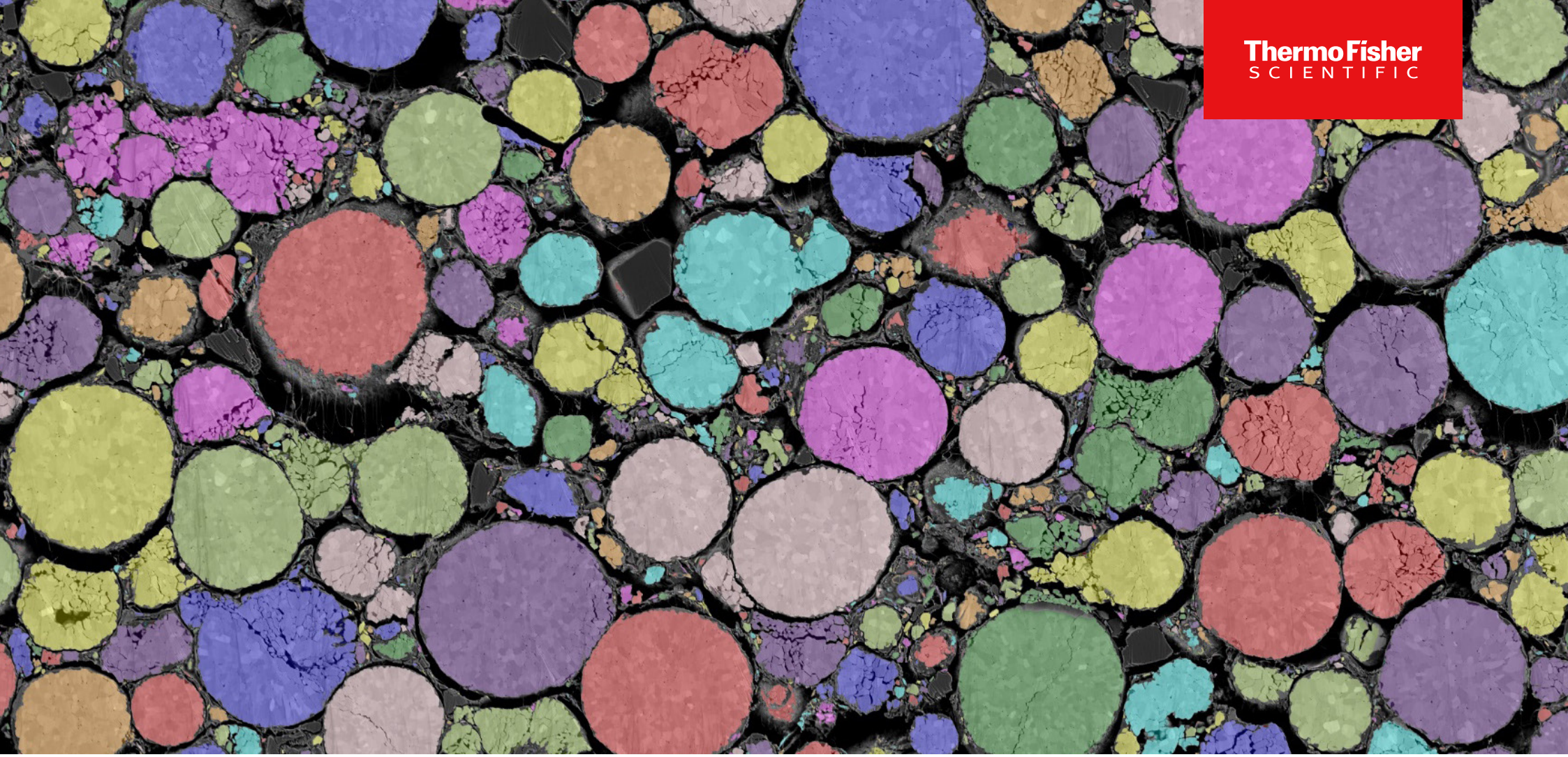

After cross-sectioning, multiple analytical techniques can be applied to a sample, including quantitative image analysis with Avizo 2D Image Processing Software, based on image contrast.

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

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