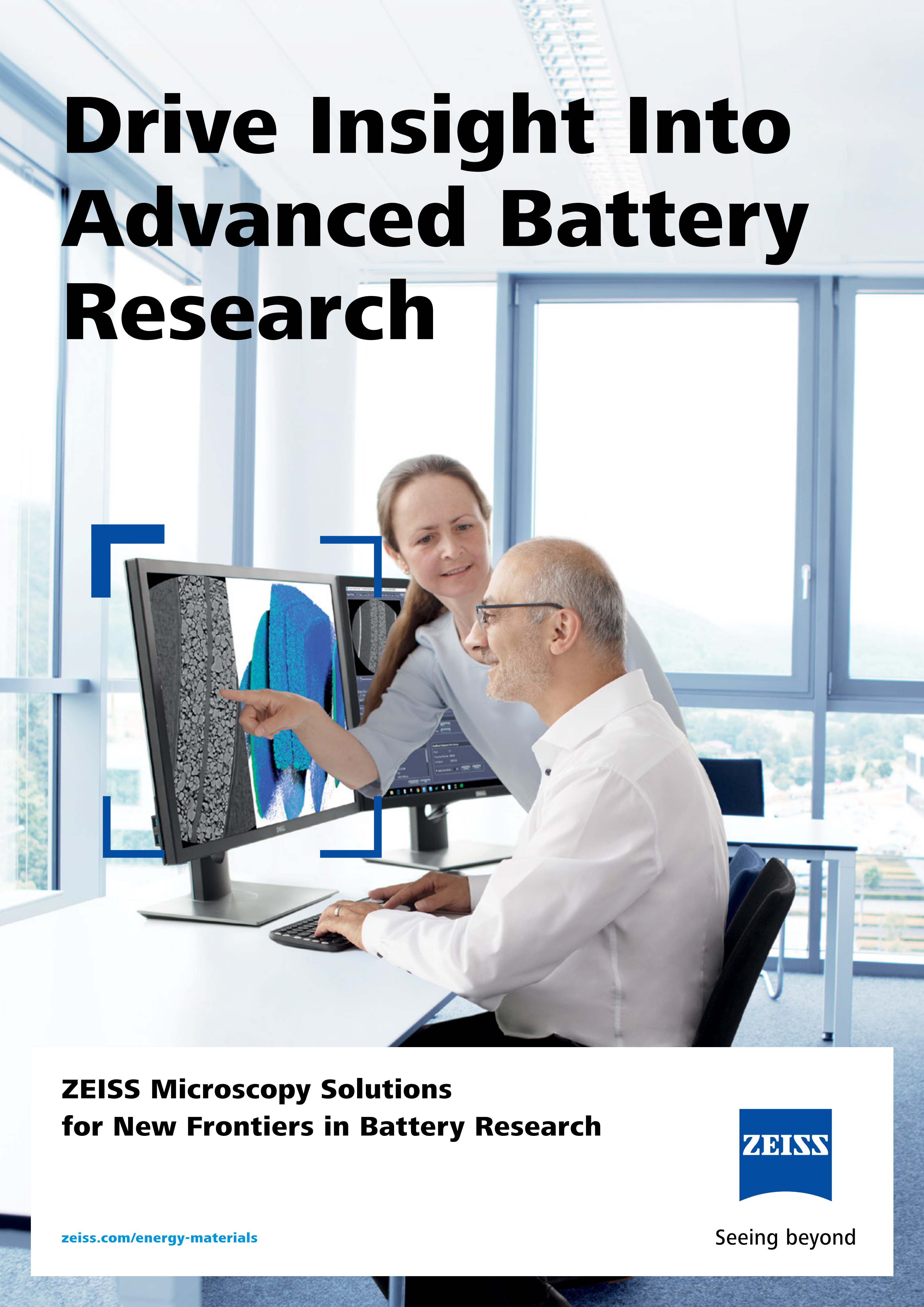
Drive Insight Into Advanced Battery Research



ZEISS Microscopy Solutions for New Frontiers in Battery Research

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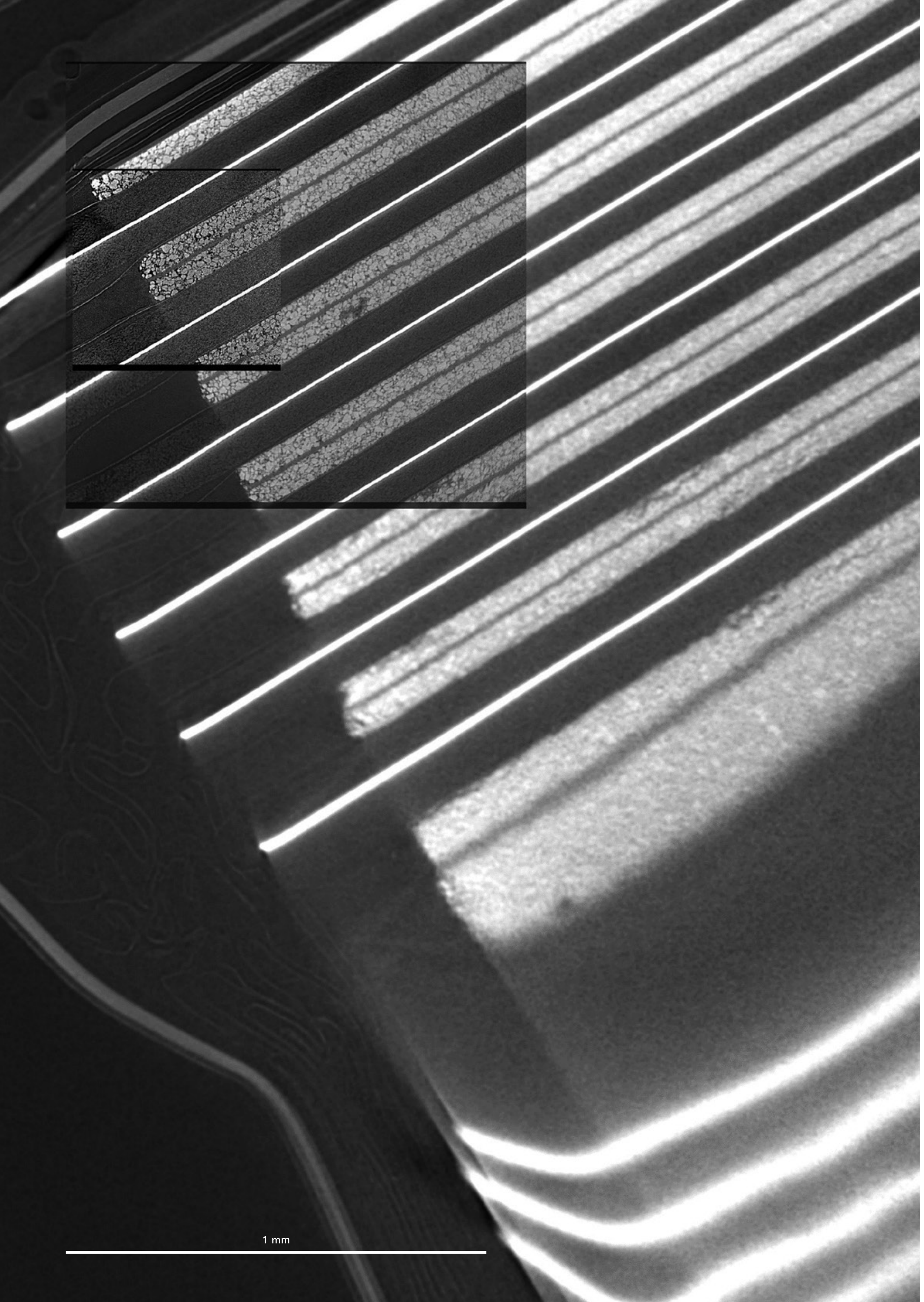
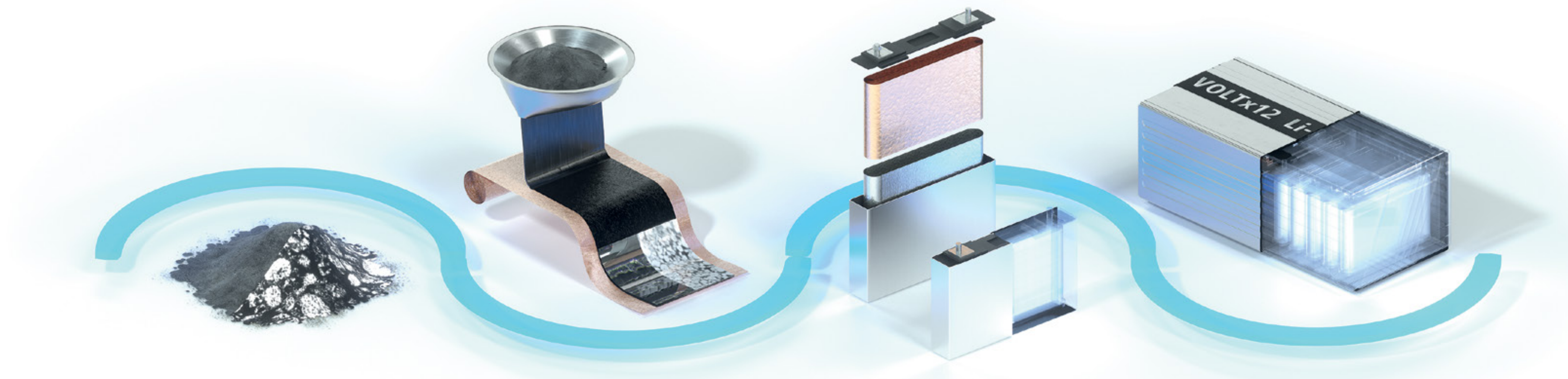
Seeing beyond



Content

Introduction



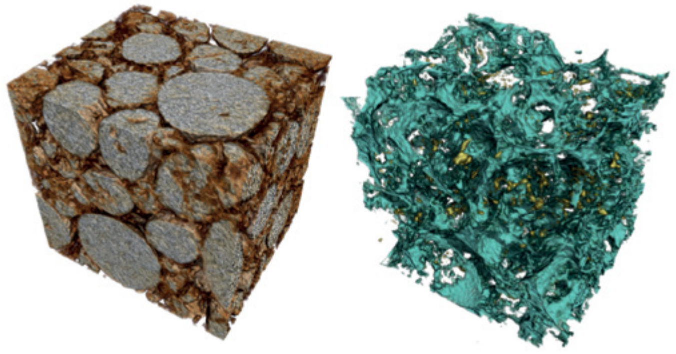


Figure 1: *Nanometer-scaled 3D X-ray microscopy images showing cathode particles from a commercial lithium ion battery (left) along with the corresponding pore network surrounding the particles (right).*

As the effects of climate change become increasingly obvious and dramatic, scientists face new challenges to develop materials and devices for clean, carbon-free energy production and storage. In this spirit, batteries are changing the face of transportation and hold the promise to revolutionize the electrical grid when combined with clean and renewable energy sources. However, to realize the full potential of this technology, major improvements must be made in device performance.

Device performance is intrinsically tied to microstructures across many orders of magnitude in length scale. To this end, researchers need a comprehensive understanding of not only these microstructures, but how they evolve as the device ages and how they change during operation. Since these devices operate in non-ambient conditions, *in situ* microstructural measurements play a key role in answering these questions. Read on to learn how ZEISS microscopy solutions work to accelerate the time to innovation in battery research and development.

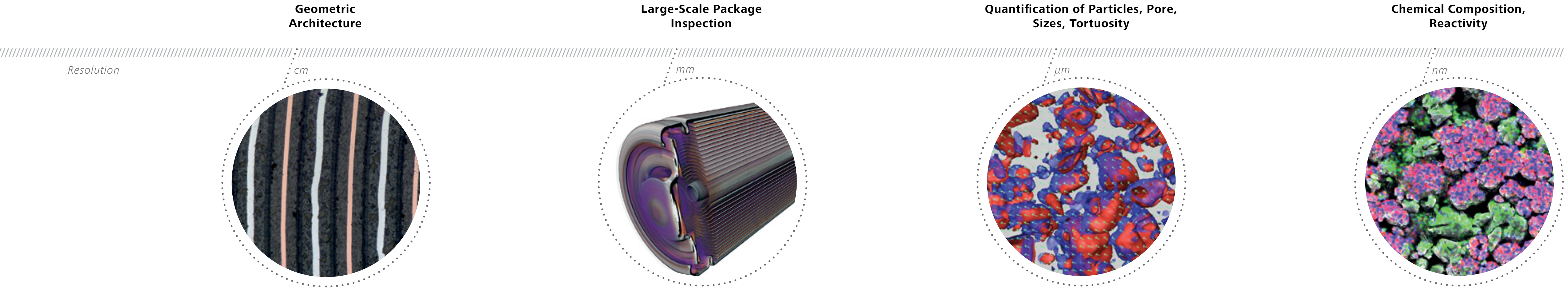
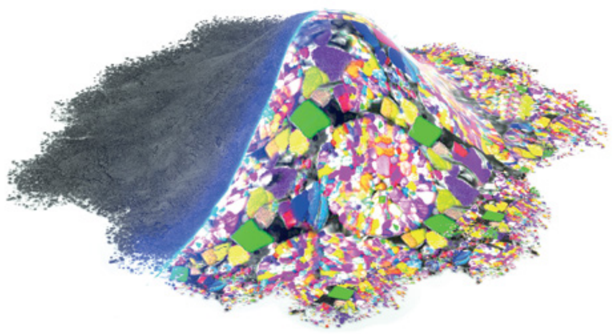


Figure 2: *Relevant features of batteries or their components spanning length scales from centimeters to nanometers characterized by multiple imaging and analytical techniques. From left to right, optical micrograph of a polished battery cross section, X-ray microscopy image of an intact battery cell, X-ray microscopy image of battery cathode particles, and scanning electron microscopy image overlaid with energy dispersive spectroscopy image of mixed chemistry battery cathode particles.*

Materials
Synthesis and Evaluation



To push the boundaries of performance, researchers are developing new materials with improved properties. Whether they store more lithium, demonstrate better stability with cycling, utilize cheaper or more abundant elements, or pave the way to completely new battery architectures, new materials have and will continue to advance battery performance into the future. Understanding the microstructures of these new materials and the role they play in device performance is critical in accelerating the development cycle.

Rigorous understanding helps researchers intelligently design new materials with targeted property improvements, shortening the time to discovery. Advanced microscopy methods can reveal the essential micro- and nanoscale structures that are needed to understand these new materials and give rapid feedback to researchers designing and synthesizing novel battery materials. Light, electron, and ion microscopy provides the resolution, contrast, and analytical modalities needed to provide insights into this critical area.

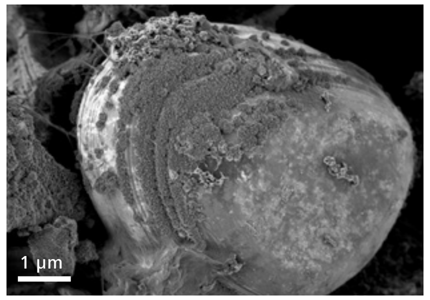


Figure 3: *Scanning electron micrograph of a $LiCoO_2$ battery cathode particle showing surface morphology, polymer binder, and conductive additives. Image collected with GeminiSEM at extremely low voltage (600 V) with an Inlens secondary electron detector. The particle can be seen to have a layer of white alumina – which is sometimes applied to increase the surface hardness of the cathode to reduce cracking and slow the aging process.*

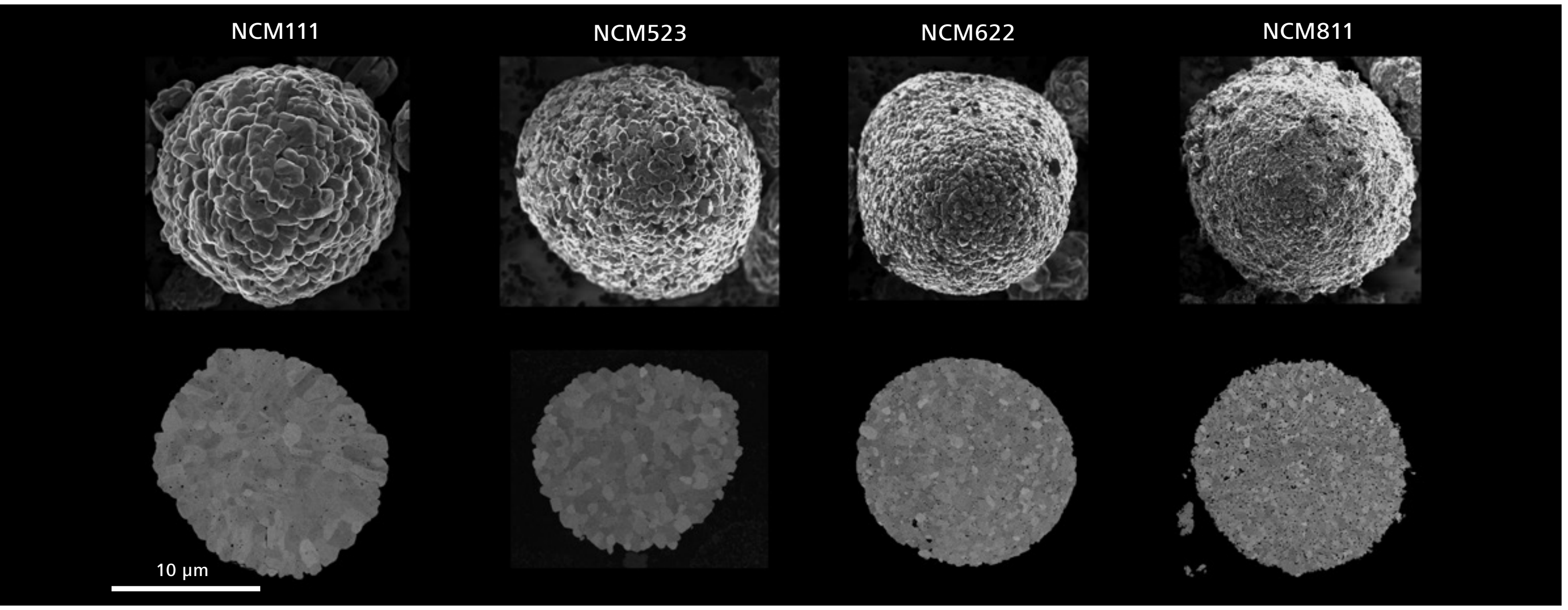
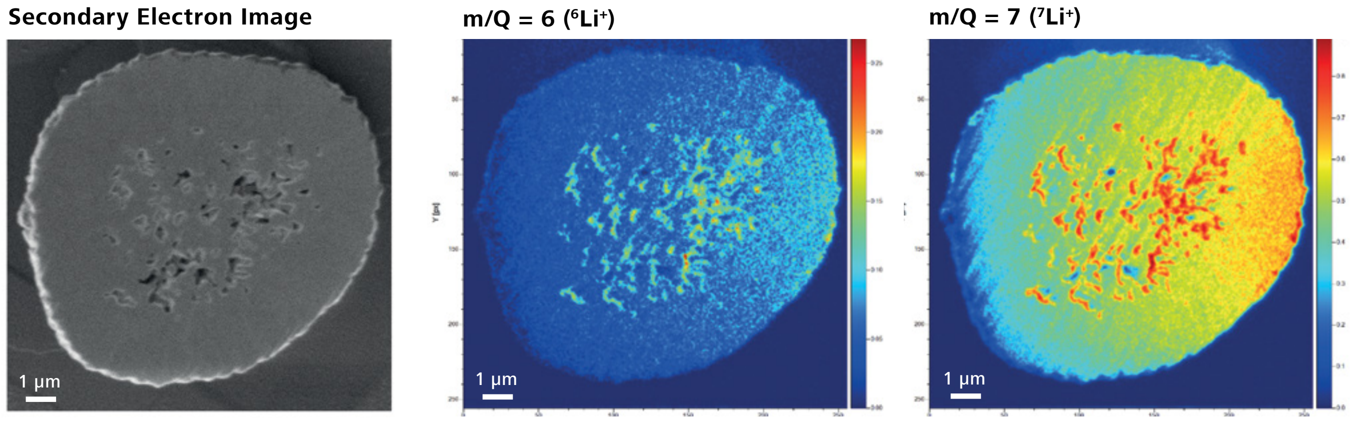


Figure 4: *Lithium Nickel Cobalt Manganese (NCM) cathode particles in ratios (111, 523, 622, 811) Ni:Co:Mn – nickel rich chemistries are cheaper, but far more challenging to manufacture with quality at scale. Excellent grain / channeling contrast can be seen from the EsB detector of the GeminiSEM.*



Secondary Electron Image | **m/Q = 6 ($^6Li^+$)** | **m/Q = 7 ($^7Li^+$)**

Figure 5: *Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging of lithium isotope distributions in a lithium nickel manganese cobalt oxide (NMC) cathode particle using a Crossbeam FIB-SEM instrument. ToF-SIMS can not only detect lithium in all its states in battery materials, but can also distinguish between different atomic isotopes of the element, helping researchers monitor possible isotopic effects of lithium transport in battery materials.*

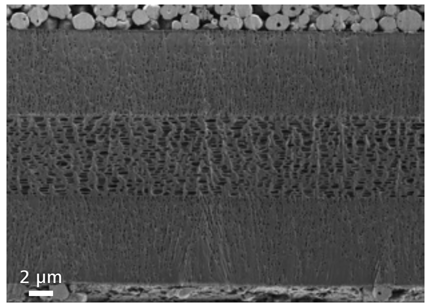


Figure 6: *Cross-section image of an uncoated polymer separator membrane from a lithium ion battery imaged with GeminiSEM at 500 V with the InLens SE detector. Sample was prepared using cryogenic argon-ion cross polishing to preserve the separator morphology prior to imaging. Delicate materials such as this separator must be imaged at low voltages to avoid damaging the intricate structure.*

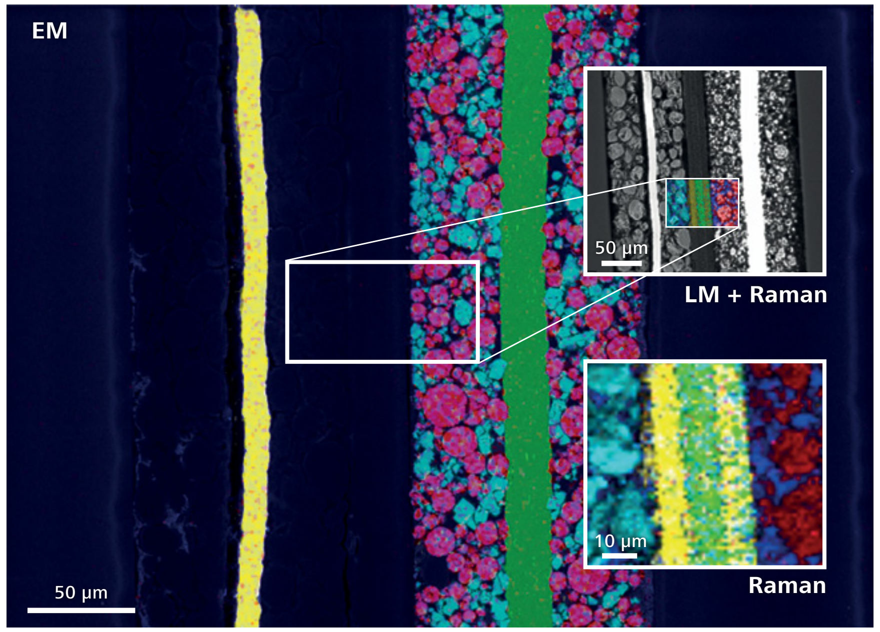


Figure 7: *SEM image with EDX mapping of a lithium-ion battery cross section where the colors correspond to copper (yellow), aluminum (green), NMC (pink), and LMO (light blue). Top inset shows a light microscopy image of the same region with a Raman overlay in the highlighted region. Lower inset shows Raman mapping in detail with 2 different polymers, polypropylene (PP) and polyethylene (PE), in the separator (yellow and green), graphite anode particles (light blue), cathode particles (red) and carbon binder (dark blue).*

Electrodes

Structure

As batteries are complex functional composites, understanding cell performance requires knowledge of how the arrangements of individual materials into electrode microstructures relates to ion movement and cell cycling.

Different electrode formulation processes may impact electrode microstructure and, ultimately, cell performance. Replacing existing materials with new ones may dramatically change the overall electrode microstructure, altering the charge and discharge properties.

ZEISS FE-SEM and FIB-SEM instruments provide suitable resolution and contrast to characterize electrode-level microstructures rapidly and successfully.

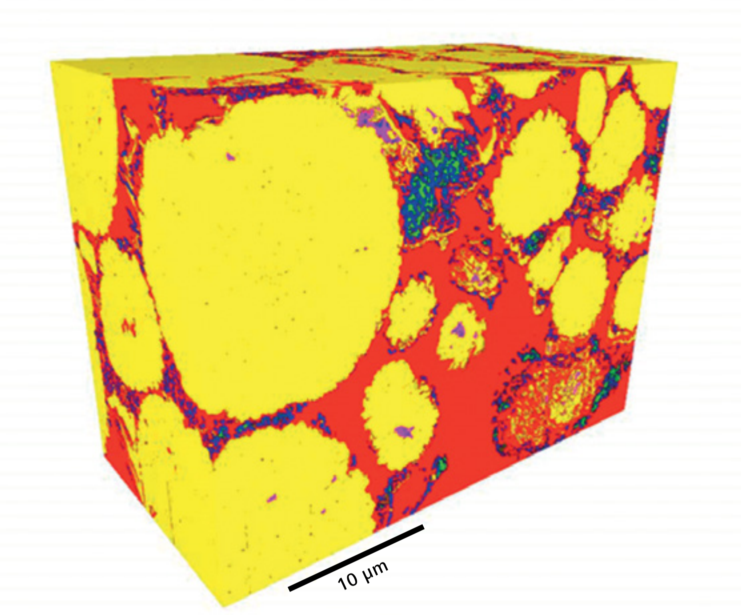


Figure 8: *3D rendering of a segmented FIB-SEM tomography data set of a NMC battery cathode. In the volume pictured the colors correspond to the following features: Yellow – NMC particles; Magenta – interior pores and cracks in the NMC particles; Blue – carbon binder; Green – pores contained within the carbon binder; Red – bulk porosity in the electrode. Data collected on Crossbeam FIB-SEM using Atlas 3D.*

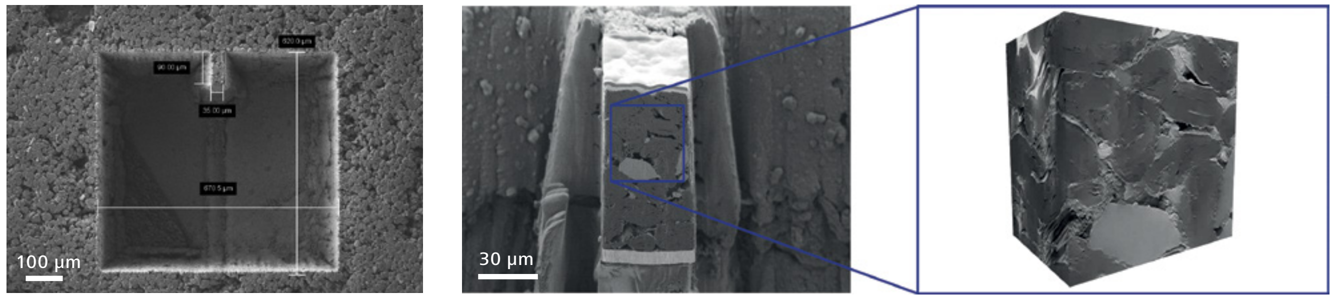


Figure 9: *(Left) Laser milled trench and material "nose" to provide access for FIB-SEM tomography of the mixed graphite + silicon anode material. The trench measures over 600 µm across, approximately 100 µm deep, and was fabricated with a total laser milling time of 54 seconds. (Middle) Close-up SEM image of the material after FIB-milling to prepare for tomography acquisition. (Right) 3D rendering of the final FIB-SEM tomography volume. Sample fabricated and imaged on Crossbeam laser.*

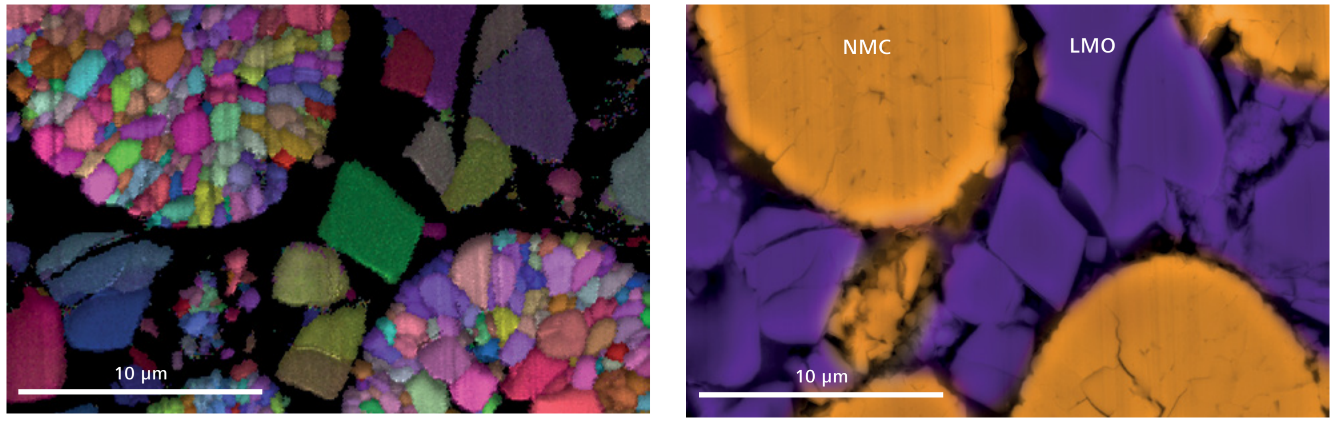


Figure 10: *(Left) EBSD map of a mixed NMC / LMO cathode material after pseudo symmetry cleanup and additional grain dilation clean-up, showing the crystallographic orientations of the grains and sub-grains for each type of particle. (Right) EDS phase map of the two different phases showing the clear distinction between NMC and LMO particles.*

Computational materials modeling is emerging as a key method for accelerating the battery and material development cycle. In this framework, battery architectures and materials can be altered, designed, and tested using a "digital twin" to explore large areas of parameter space that would be impractical experimentally. Critically, many essential structural characteristics like porosity can only be fully understood in 3D.

ZEISS FIB-SEM instruments with Atlas 3D or ZEISS Xradia X-ray microscopes are examples of solutions that provide true and accurate 3D imaging. They do so with the isotropic voxels needed to reliably measure properties like tortuosity, pore size distributions, and pore connectivity across many different length scales, and provide input to advanced transport and diffusion modeling.

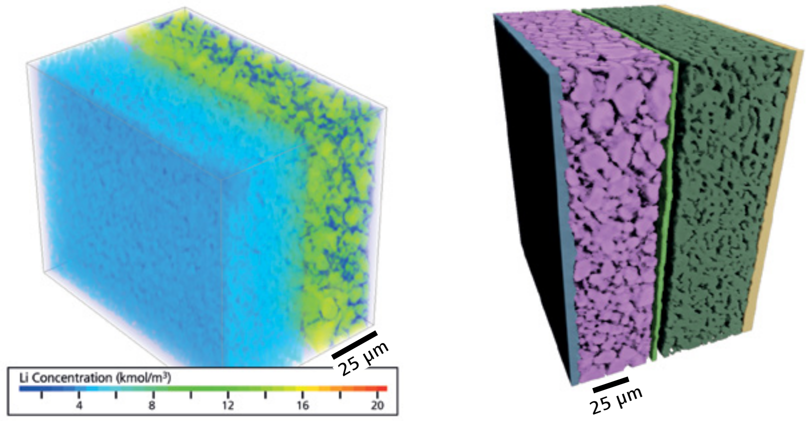


Figure 11: *Modeling charging and transport phenomena in batteries and battery materials requires accurate microstructural input to the modeling software. 3D microscopy solutions like FIB-SEM tomography and X-ray microscopy can deliver accurate, high resolution 3D images of battery materials to modeling packages. (Right) Segmented phases from an X-ray microscopy scan of an intact commercial pouch cell battery. Blue – cathode current collector; Magenta – cathode particles; Light Green – polymer separator membrane; Dark Green – graphite anode particles; Tan – anode current collector. Imaged on Xradia 620 Versa. (Left) – Simulated lithium concentrations obtained with battery analysis module of GeoDict (Math2Market GmbH) in a battery cell using the segmented XRM data as geometric input.*

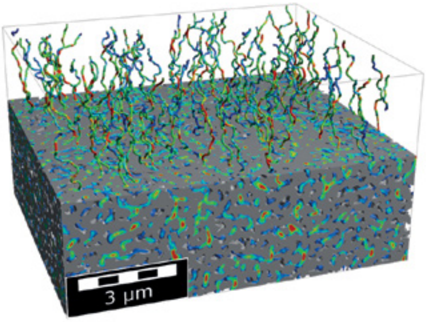
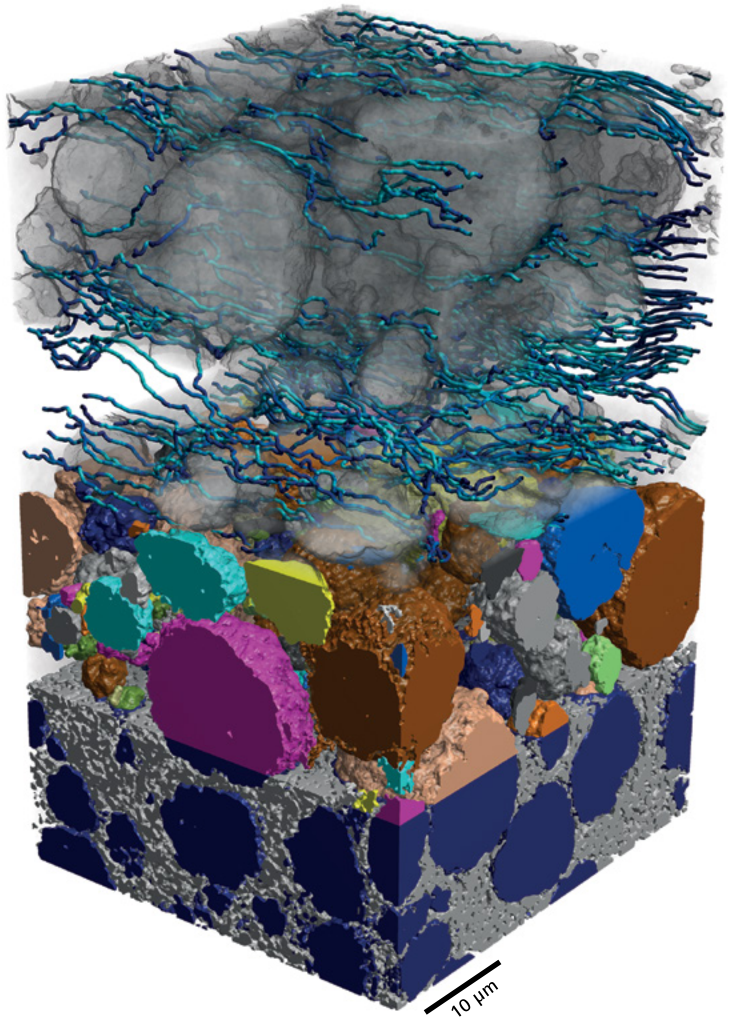


Figure 12: *3D X-ray nanotomography imaging and digital material simulation to map diffusion behaviors in an NMC lithium ion battery cathode (right) and polymer separator membrane (above). Images collected using Xradia 810 Ultra nanoscale X-ray microscope. Data analyzed using the battery analysis module of GeoDict by Math2Market, GmbH.*



Electrodes

Degradation

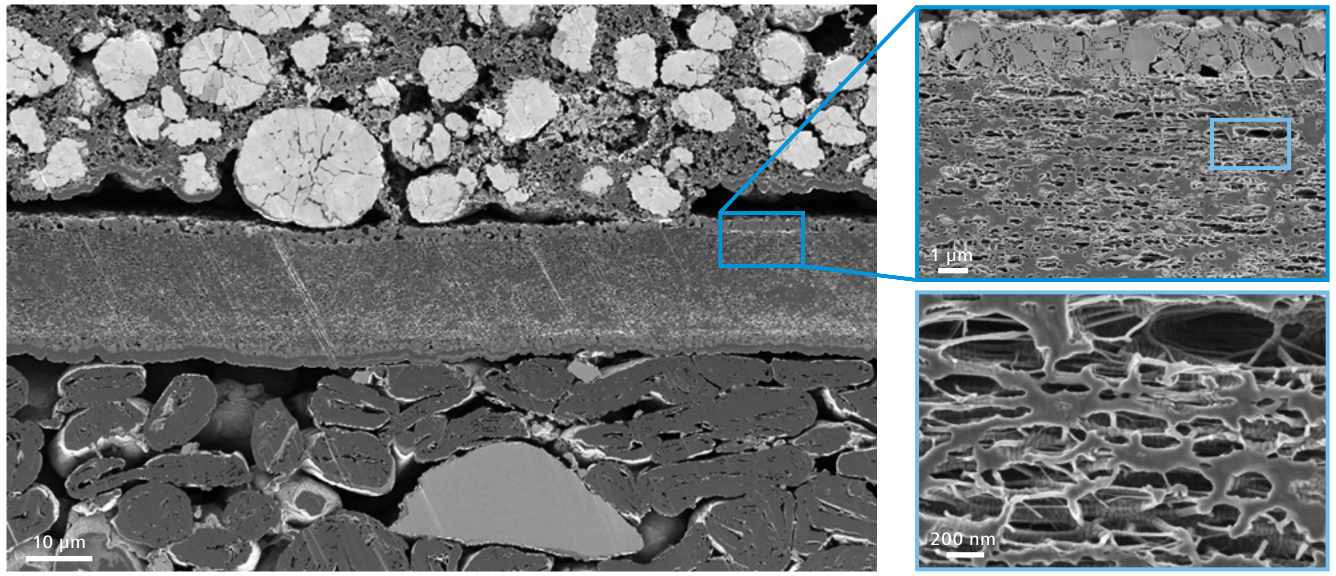


Figure 13: *Cryogenic argon ion polishing and air-free sample transfer enables observation of fine microstructures in battery electrodes in their native state using FE-SEM imaging. (Left) Cross-section of an aged lithium-ion battery electrode stack containing NMC cathode particles + carbon binder (top), a ceramic coated polymer separator membrane (middle), and a graphite + silicon anode (bottom). The images at right show successively higher magnification images of the delicate polymer separator membrane with the microstructure left intact due to the low kV imaging conditions. Imaged with ZEISS GeminiSEM, 1 kV, Inlens SE detector.*

Sensitive, reactive, delicate materials like those used in battery construction require careful sample preparation approaches to ensure accurate and representative imaging and analysis. Air-free handling in an inert gas glovebox and air-free transfer modules keep reactive surfaces from being contaminated and corroded.

Cryogenic temperatures during cutting and polishing steps minimize sample damage and ensure the images obtained represent the true microstructure of the materials and electrodes they comprise. Meanwhile, FE-SEM imaging with Gemini optics ensures maximum information and contrast on carefully prepared sample surfaces, even at the low electron energy settings needed to preserve delicate material structures and reveal hidden contrasts. Additionally, cryogenic FE-SEM imaging and FIB-SEM tomography provide detailed 2D and 3D information while ensuring minimal sample damage and alteration due to imaging and ion milling.

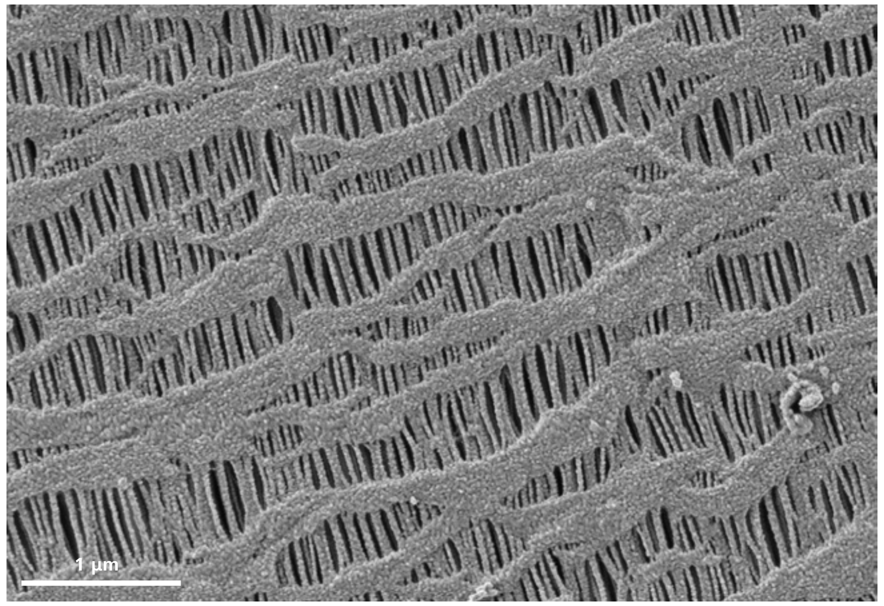


Figure 14: *Polypropylene separator foil imaged at cryogenic temperature, -160°C. At room temperature the sample is very sensitive to electron beam irradiation, so its structure is heavily modified by the imaging beam. At ultra-low temperatures, the structure is much more robust and can be observed for several minutes without damage with a ZEISS FE-SEM and a cryo stage.*

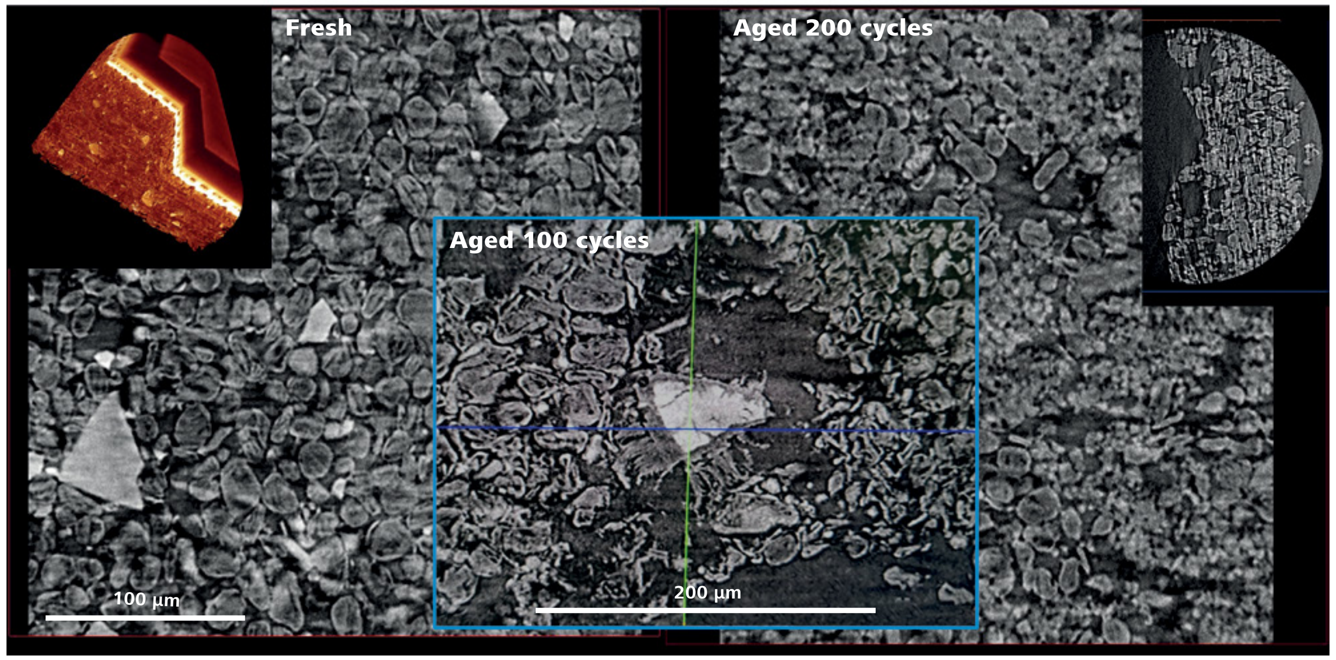


Figure 15: *X-ray microscopy images of a mixed graphite + silicon anode material in pouch cell batteries after different numbers of charge / discharge cycles. Clean, fully intact silicon particles (brighter phase) can be seen mixed with the rounder graphite particles (darker phase) in the fresh battery. In the 100 cycles aged battery the silicon particles can be seen to grow secondary phases that rapidly expand and push the graphite particles away. In the 200 cycles aged battery the silicon particles have been completely pulverized into smaller particles dispersed amongst the graphite.*

As batteries age over charge / discharge cycles, capacity and other performance indicators can fade. Microstructural changes to electrode architectures and the materials that they consist of play a key role in driving battery performance degradation with cycling. Understanding the mechanisms involved in these degradation phenomena is key in designing the next generation of battery materials and architectures that last longer, charge faster, and store more energy.

ZEISS FE-SEM and FIB-SEM instruments provide powerful platforms for understanding the microstructural and chemical changes involved in these processes. In addition, ZEISS X-ray microscopes allow for *in situ* monitoring of electrode degradation over many cycles without the need to open the cell.

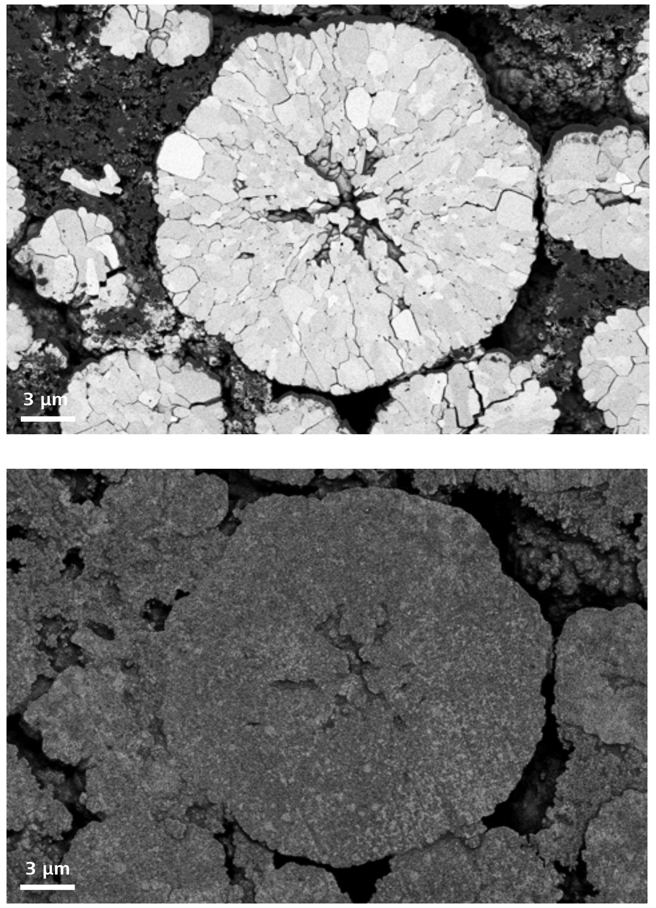
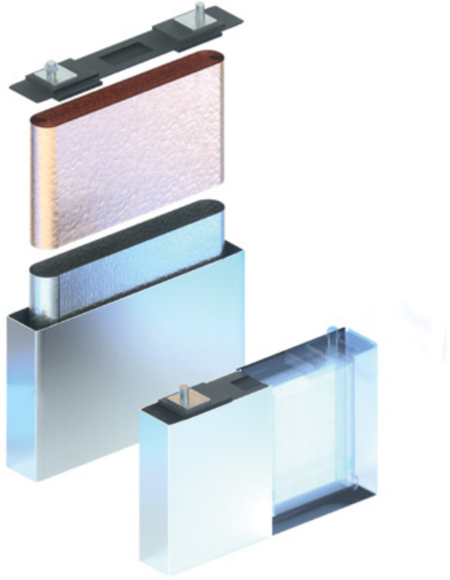


Figure 16: *(Top) FE-SEM image of a polished NMC cathode particle in a lithium-ion battery electrode after air-free sample handling. (Bottom) The same particle surface after exposure to air. Details of the microstructure are obscured and the microstructure has been altered.*

Cells

Assembly and Degradation



At the device level, understanding component arrangements and how they change with cycling is key to understanding how cells perform. Imaging inside intact batteries is difficult due to the closed nature of these devices and the air-free handling requirements for many of the constituent materials.

ZEISS X-ray microscopy with Resolution at a Distance (RaaD) allows you to uniquely view microstructures inside complete battery cells with industry-leading resolution and contrast without cutting them open. See layers, particle distributions, foreign particle inclusions, and inactive components as they exist in functioning cells – whether production cells (such as 18650 or 21700 cylindrical cells) or research scale cells (such as pouch and coin cell geometries).

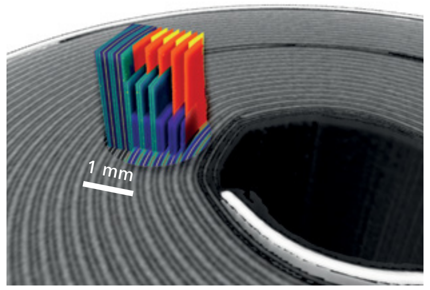


Figure 17: *Overview (black and white background) and interior region of interest (colorized central region) X-ray microscopy images from a commercial 18650 cylindrical cell lithium-ion battery. Defects in the layers can be inspected and visualized in the high resolution images which were collected at 1.0 µm / voxel.*

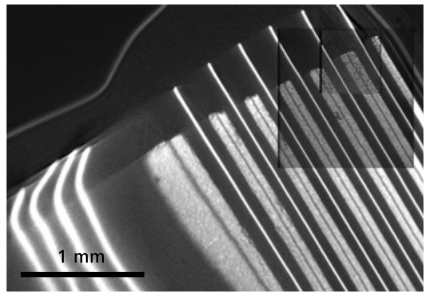


Figure 18: *2D slices from 3D X-ray microscopy images of a commercial smartwatch pouch cell battery showing successively higher magnifications of interior regions of the battery. At lower magnifications the battery electrodes and structural components can be seen and measured, including low contrast materials like the polymer separator membrane. At the higher magnifications the individual particles of the anode and cathode electrodes can be resolved, as well as defects in the electrodes.*

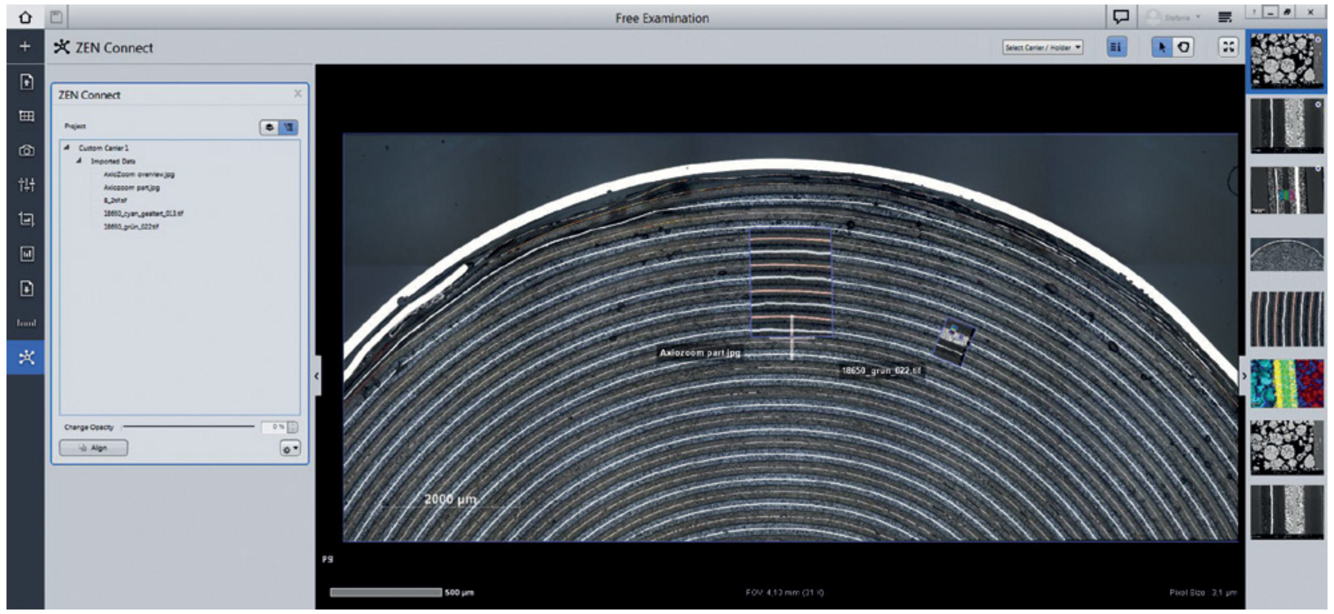


Figure 19: *Images of a sectioned commercial 18650 lithium-ion battery from light, electron, and Raman microscopy registered and collocated in ZEN Connect for multiscale inspection and analysis.*

Application Highlight

4D Study of Silicon Anode – Volumetric Changes in a Coin Cell Battery Using X-ray Microscopy

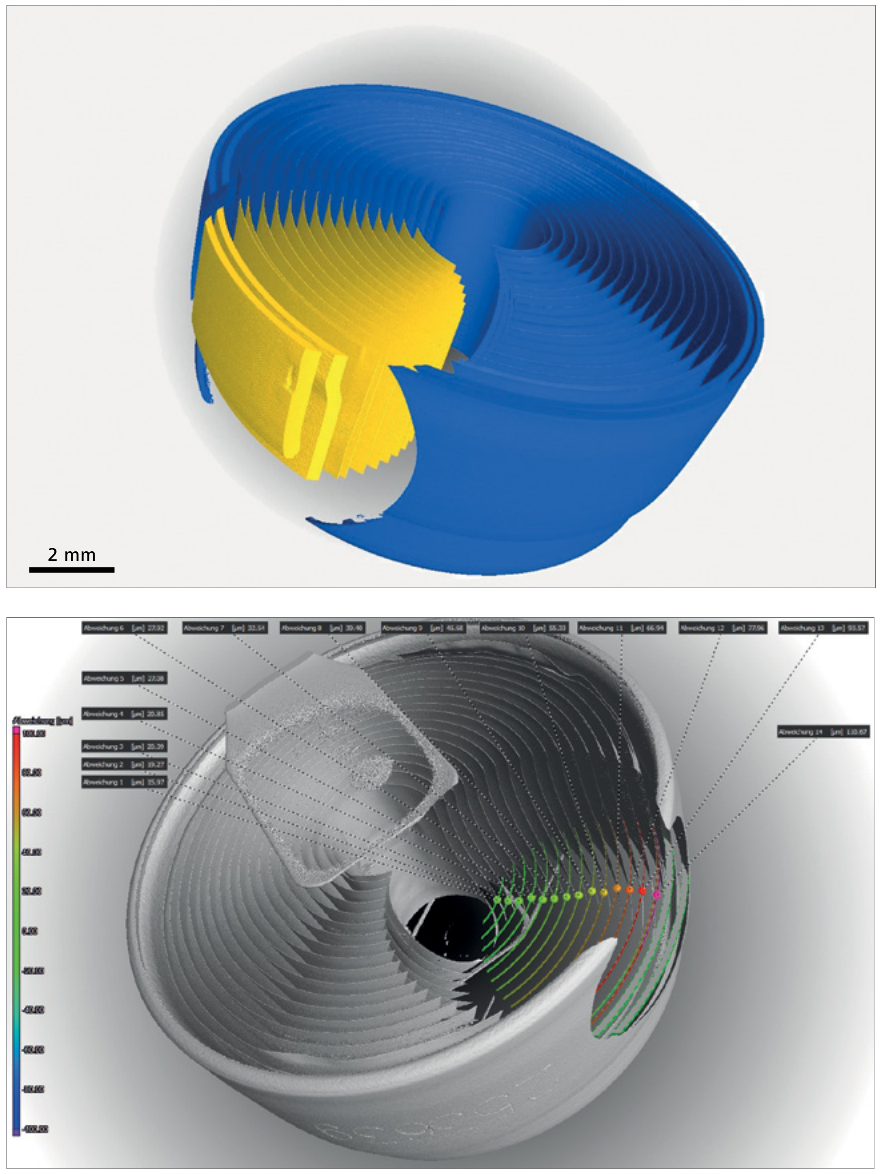


Figure 20: *Investigation of changes in LIB volume with ZEISS Xradia Versa. Top: Volume rendering of FFOV (Full Field of View) and ROI scans. Bottom: Displacement map of a VARTA CoinPower® CP1254 coin cell battery, modified to have silicon as the active material in the anode, after the initial charge state. The highest displacements are shown in red and occur near the exterior of the battery.*

Capacity is a key area of battery development and its outcome influences everyone's daily life. In the past, most research efforts have focused on the electrochemical side. However, as the chemistry and geometry of batteries change, more emphasis is dedicated to understanding microstructural changes beyond electrochemistry.

Stresses created inside the battery are key factors in enabling you to quantify the microstructural changes and monitor the repeatability of charge and discharge cycles. They lead to material damage, premature aging, and irreversibility. Also, novel electrode materials such as silicon anodes can boost capacity up to 10 times over traditional graphite anodes, but simultaneously present unique challenges to the microstructure due to large amounts of swelling upon charging.

Benefit from being able to observe complex processes in native environments using XRM. Reveal the position and arrangement of internal features using *in situ* kits in ZEISS X-ray microscopes, for example when investigating commercial coin cell batteries containing silicon anodes. Image the battery in different states of charge and generate displacement maps to reveal stress concentrations. This allows you to design systems to accommodate these new materials and their unique properties.

Correlative Workflows
Bridging Length Scales to Reveal New Insights

As batteries are constructed from components with important length scales spanning multiple orders of magnitude, understanding microstructures across many size ranges and contrast mechanisms is key to developing a comprehensive understanding of how microstructure affects material properties and battery performance. Correlative workflows allow the investigation of important properties like porosity, particle connections, and other microstructural features across length scales.

Non-destructive X-ray microscopy plays a unique role in these correlative workflows, guiding further investigations with detailed 3D maps of internal material microstructures. New capabilities such as femtosecond laser processing integrated with FIB-SEM instruments open paradigm-shifting routes to microstructural investigations.

Integrated laser milling in a dedicated chamber enables targeting regions of interest and rapidly accessing deeply buried features for nanoscale investigations with FIB-SEM while keeping the main instrument chamber clean for precision analytics including 3D EDS, 3D EBSD, tomography and ToF-SIMS.

Connected, correlative software environments allow the linkage of 3D data across instruments and length scales and enable the seamless visualization and interpretation of multiscale, multimodal data sets from multiple sources.

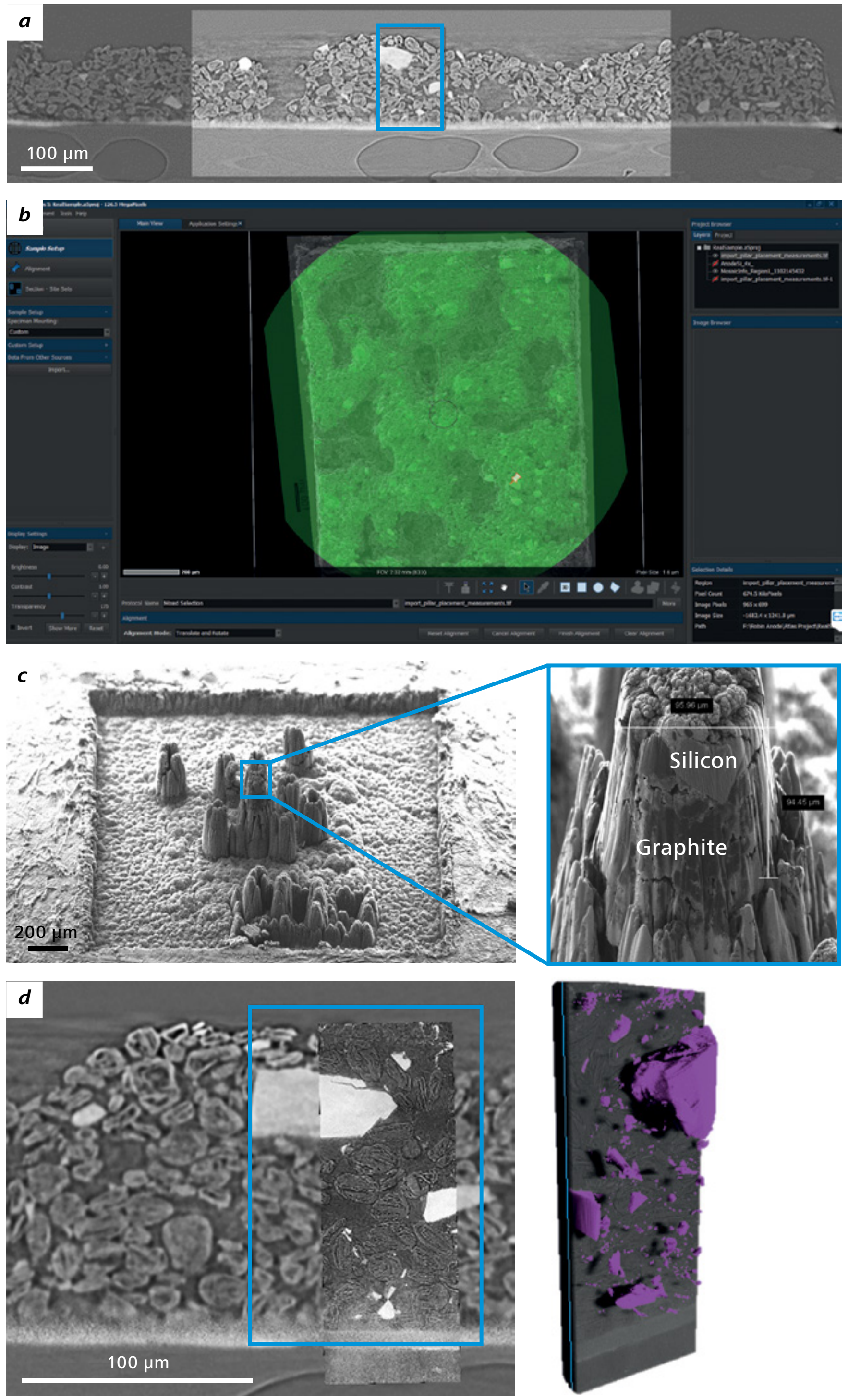
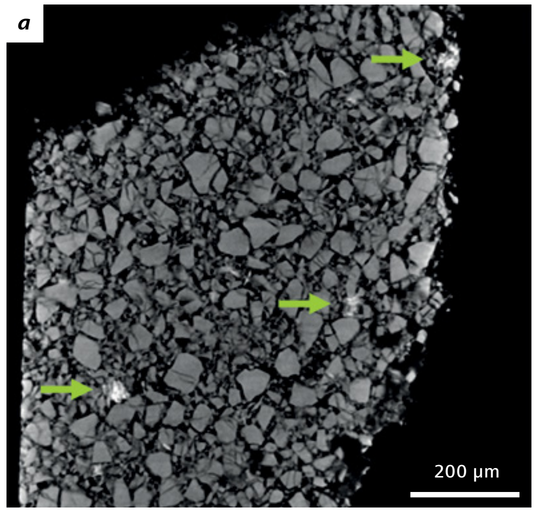
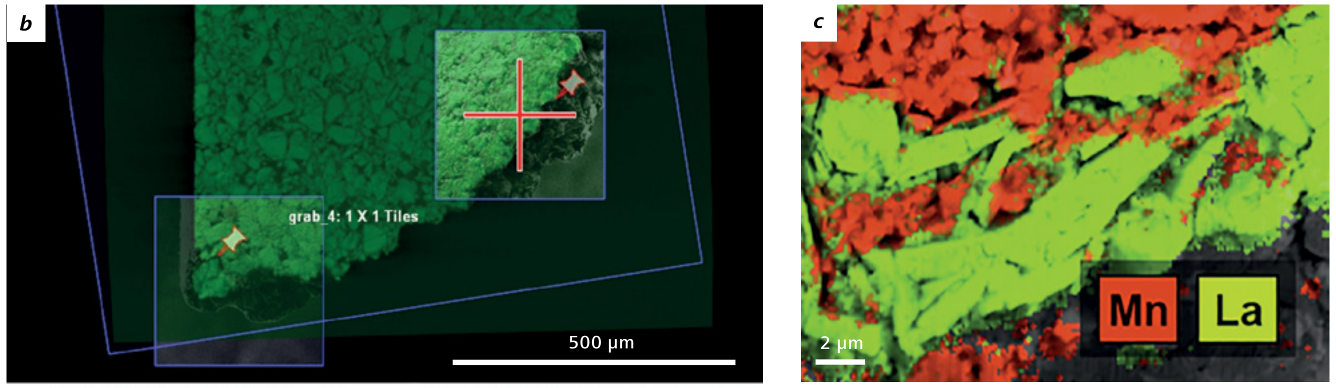


Figure 21: Correlative workflow to investigate microstructural details around buried silicon particles in a mixed graphite + silicon lithium-ion battery anode material. a) micron-scale 3D X-ray microscopy reveals overall microstructure of the anode material and the location of buried silicon particles at multiple resolutions. Selected silicon particles to target for further higher resolution 3D imaging are marked with the blue box. b) The Atlas 5 interface is used to register XRM data and LaserFIB FIB-SEM instrument views and select a region (circle in central area) for fs-laser ablation to produce a pillar for nanoscale X-ray microscopy with results shown in c). d) Nanoscale X-ray microscopy in Zernike phase contrast of the prepared pillar reveals details of the silicon and graphite particle connections as well as the locations of smaller silicon particles not seen at lower resolutions.

Foreign inclusion particles can be detrimental to electrode performance and indicate problems in supply chains or material handling streams during battery and electrode production. However, these particles are often buried beneath the surface, invisible to traditional SEM surface imaging.

ZEISS X-ray microscopy can reveal sub-surface details non-destructively and with high spatial resolution. Correlative software platforms like Atlas 5 can guide further investigation with FIB-SEM for nanoscale imaging and chemical analysis, zeroing in on the needed information quickly and efficiently.





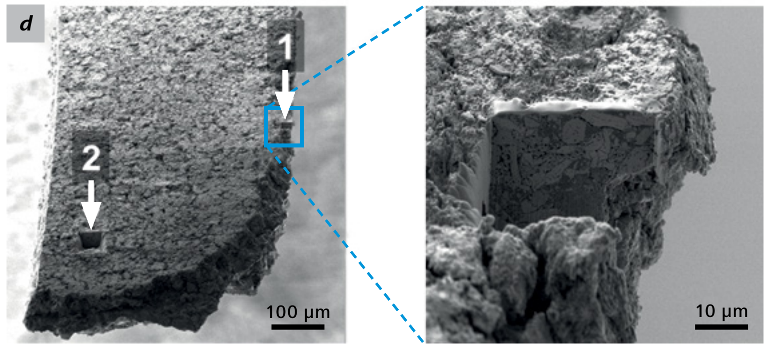


Figure 22: 3D correlation is used to identify and interrogate subsurface regions of interest. Anomalous particles inside a battery electrode were identified by X-ray microscopy a), which was used as a navigational aid b) to directly guide FIB-SEM milling and imaging c) to specific subsurface volumes d) along with EDX analysis.

Microscopy Solutions
Customize Your Success

ZEISS offers microscopy solutions for a large range of applications with excellent light, electron, and X-ray microscopes and various imaging systems. From 2D and 3D inspection capabilities to advanced analytical techniques, ZEISS can provide customized solutions to support the increasing demand for microstructural analysis of energy materials including batteries and their associated components with solutions such as:

ZEISS LSM 900 for Materials

ZEISS LSM 900 for Materials, the confocal laser scanning microscope (CLSM) from ZEISS, is the instrument you will need for materials analysis. Characterize 3D microstructure surface topography in your lab or multi-user facility. ZEISS LSM 900 for Materials enables precise, three-dimensional imaging and analyses of nanomaterials, metals, polymers, and semiconductors.

ZEISS GeminiSEM

ZEISS GeminiSEM stands for effortless imaging with sub-nanometer resolution. Innovations in electron optics and chamber design let you benefit from better image quality, usability and flexibility. Take sub-nanometer images below 1 kV without an immersion lens.

ZEISS Crossbeam laser

Your FIB-SEM for high throughput 3D analysis and sample preparation. Combine imaging and analytical performance of a high resolution field emission scanning electron microscope (FE-SEM) with the processing ability of a next-generation focused ion beam (FIB). Access deeply buried structures and benefit from rapid material ablation with the fs-laser.

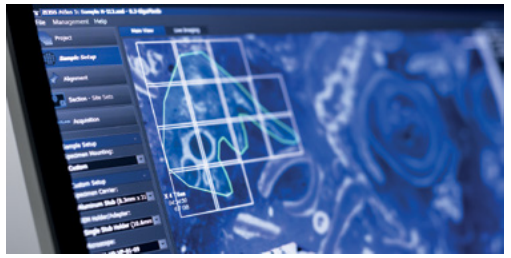
ZEISS Xradia Versa

The 3D X-ray Microscope for faster sub-micron imaging of intact samples. Building on industry-leading resolution and contrast, ZEISS Xradia 610 and 620 Versa expand the boundaries of your non-destructive sub-micron scale imaging.

ZEISS Xradia Ultra

Nanoscale X-ray imaging to explore at the speed of science. Imagine if you had synchrotron capabilities in your own lab. With the ZEISS Xradia Ultra family, you have 3D non-destructive X-ray microscopes (XRM) at hand that deliver nanoscale resolution with synchrotron-like quality.

ZEISS Atlas 5



Master your multi-scale challenge and create comprehensive multi-scale, multi-modal images in a sample-centric correlative environment. Atlas 5 is the powerful yet intuitive solution that extends the capacity of your ZEISS scanning electron microscopes (SEM) and focused ion beam SEMs (FIB-SEM). Efficiently navigate and correlate images from any source, e.g. light and X-ray microscopes.

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