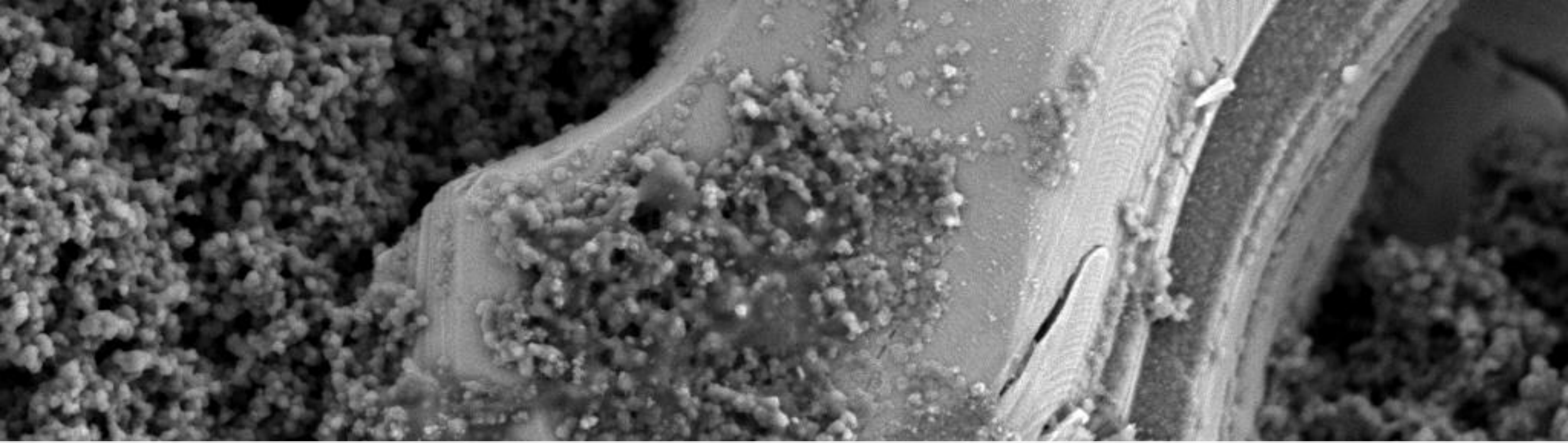


3D Imaging Techniques for Li-ion Battery Research

- NASA Aerospace Battery Workshop

Zhao Liu, Materials & Structural Analysis Division
Nov 2019

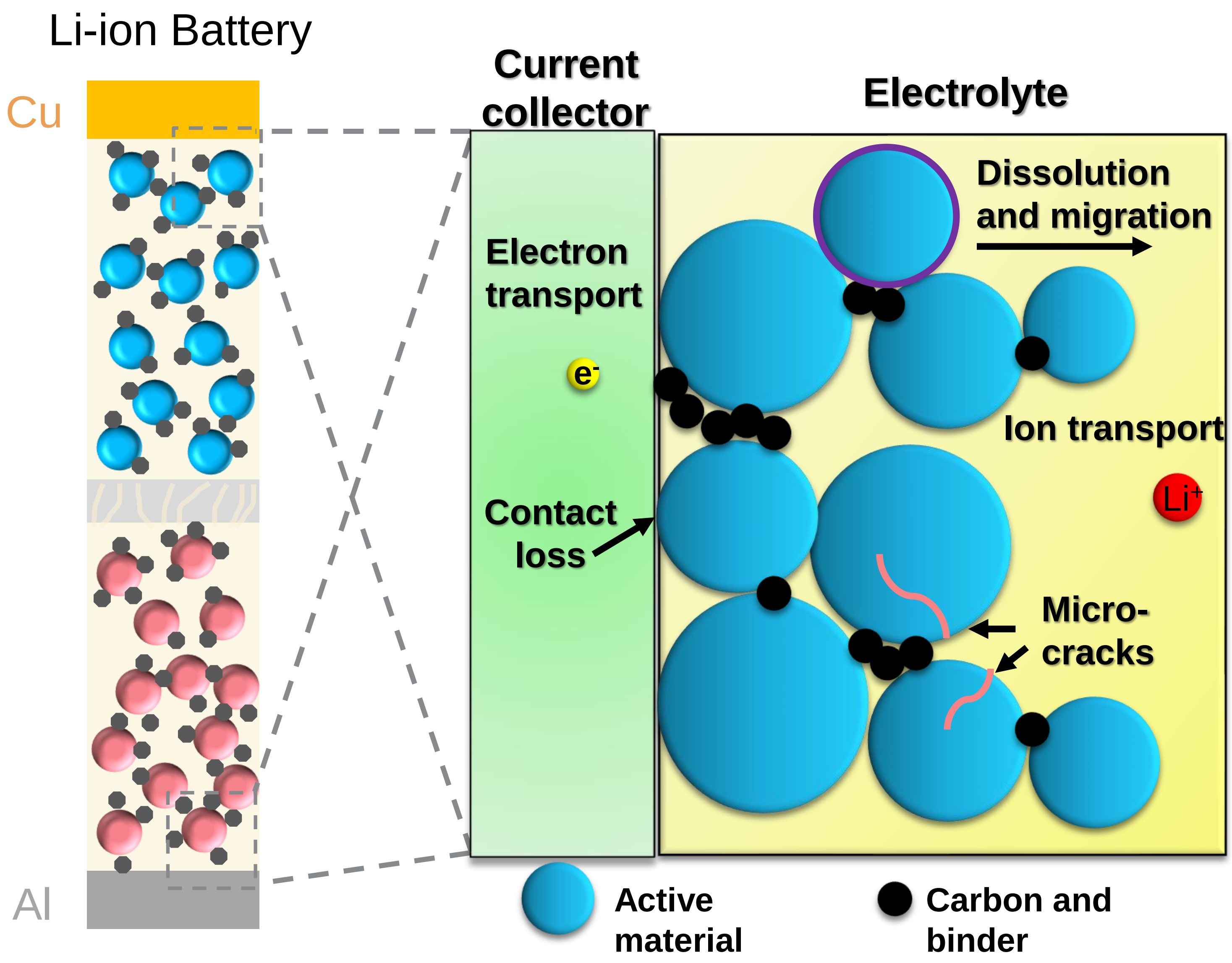
 Courtesy of Herman Lemmens, Devin Wu, Bart Winiarski, Dirk Laeveren, Chengge Jiao, Remco Geurts, Avizo Team

Thermo Fisher Scientific: The World Leader in Serving Science

Electron Microscopy	XPS	Raman	FTIR	XRF	XRD	IC	MS	Gauging
Multiscale imaging & analysis of various materials	Quantitative surface analysis	Chemical compound identification	Chemical compound identification	Bulk state elemental composition	Structure identification	Separating ionic components	Species identification	Inline coating thickness measurement

Multiple Analytical Solutions for Battery Research and Production

Motivation: Understanding Microstructure-Performance Correlation of Li-ion Battery



- **Understanding battery microstructure is critical for:**
  - Analyzing microstructure-performance correlation
  - Identifying degradation mechanisms
  - Improving battery performance
    - ✓ Energy density
    - ✓ Power density
    - ✓ Cycle life
    - ✓ Safety
- **Imaging technique is one of the key approaches for microstructural characterization**

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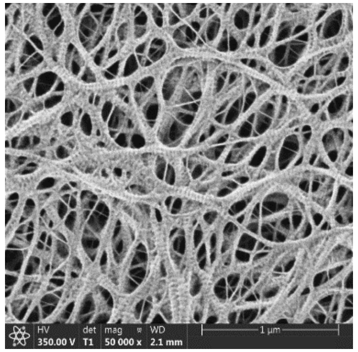
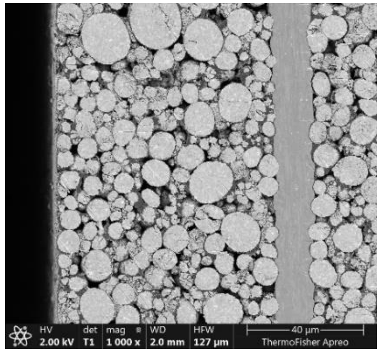
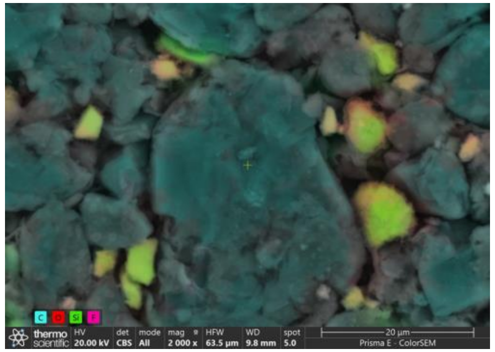
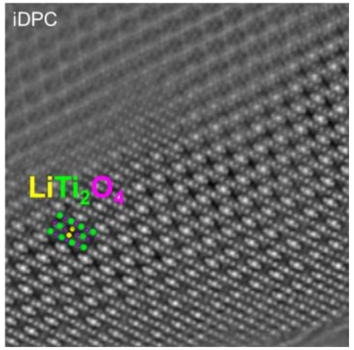
2D Imaging vs. 3D Imaging on Batteries

2D Imaging



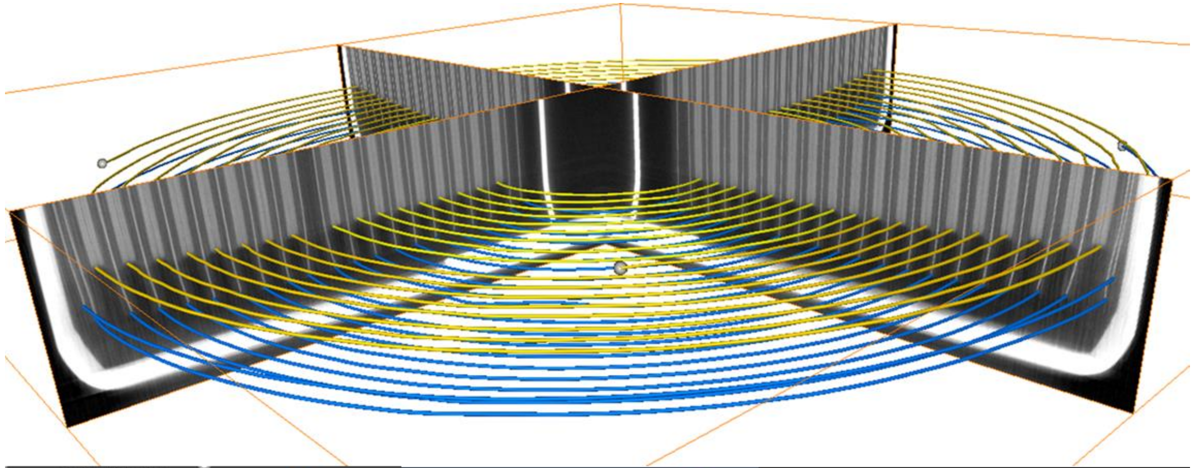


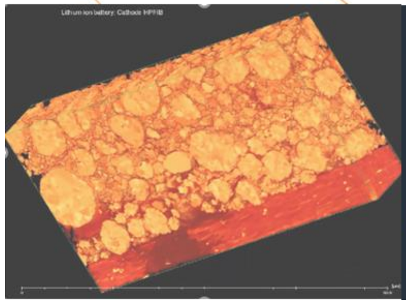


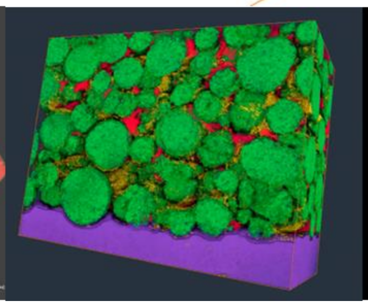


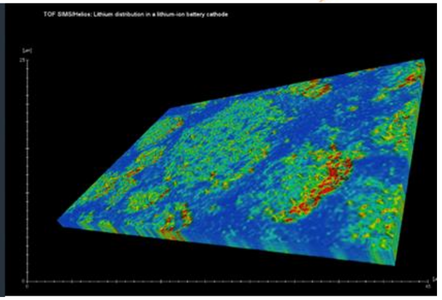
2D imaging mainly provides qualitative understanding on battery microstructure

3D Imaging





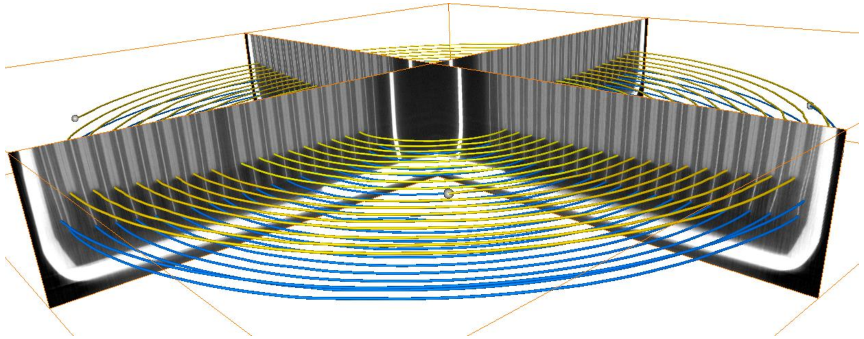




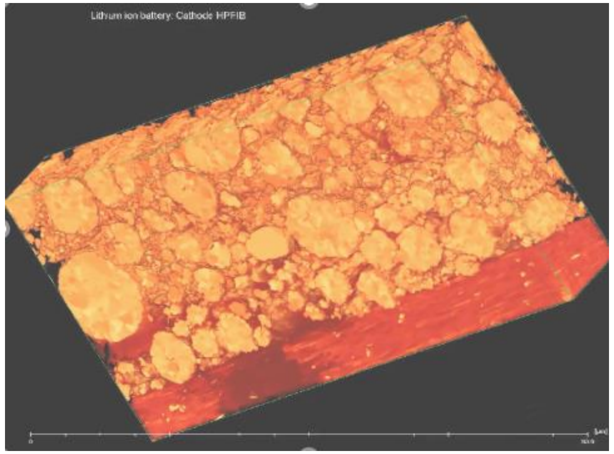
3D imaging provides in-depth quantitative understanding on battery microstructure

Overview

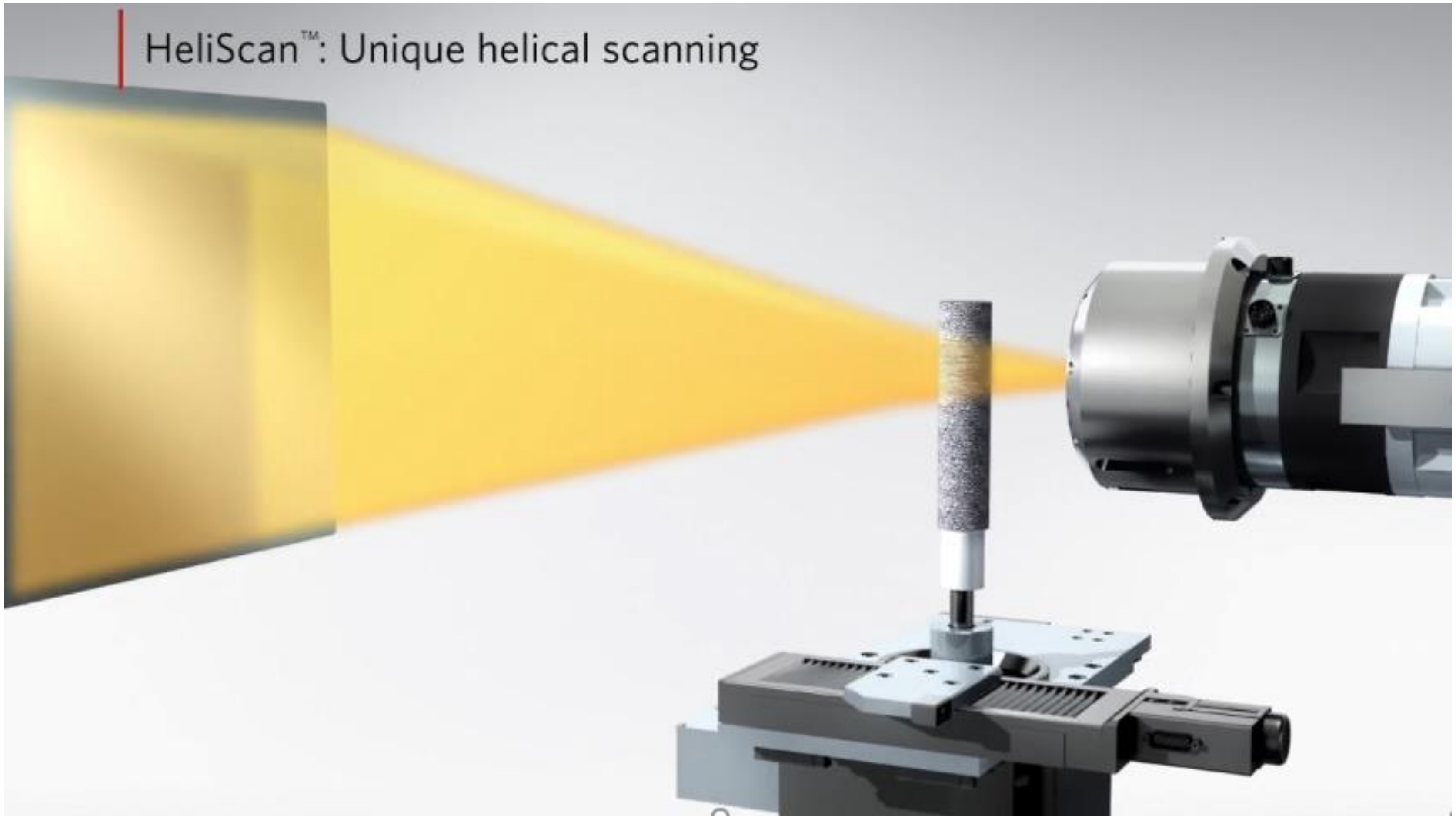
- **3D Imaging Solution via microCT**
  - 3D imaging on 18650 full cell via HeliScan microCT



- **3D Imaging Solution via DualBeam (FIB-SEM)**
  - 3D imaging analysis of battery electrode



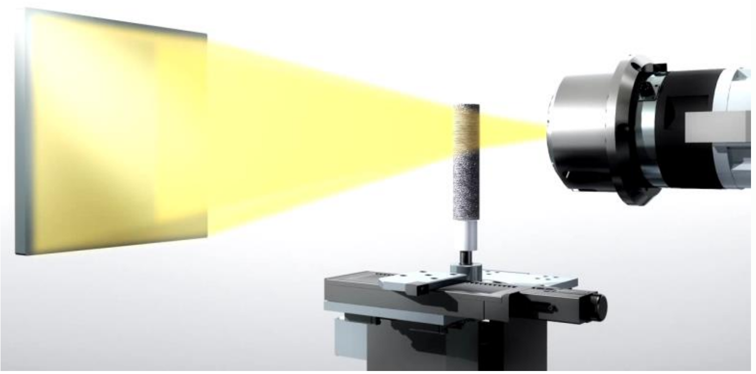
Introduction: HeliScan microCT



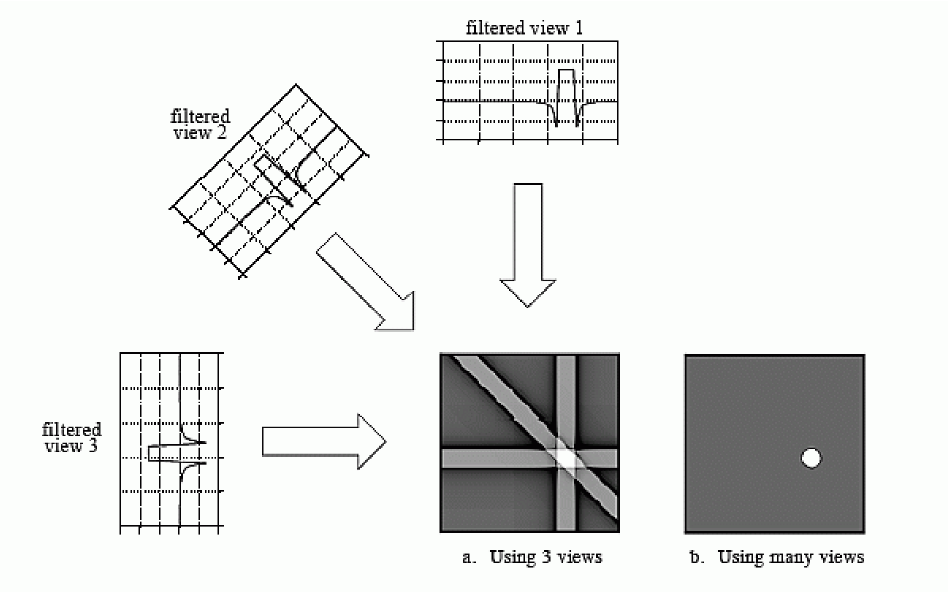
- **Stitch-free** scanning of larger volumes and regions of interest with **Helical** scanning **trajectory**
- **Fast acquisition** and **high resolution (below 400nm)** with new **high cone-angle x-ray source**
- **Highest image fidelity** with **iterative reconstruction** algorithm and **patented** correction software
- Built for **versatility**

HeliScan microCT 3D Imaging Workflow

1. Acquisition

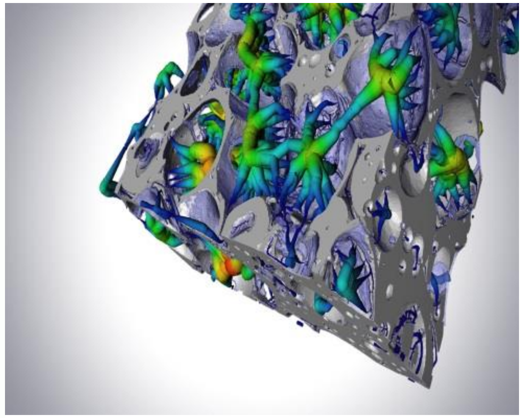


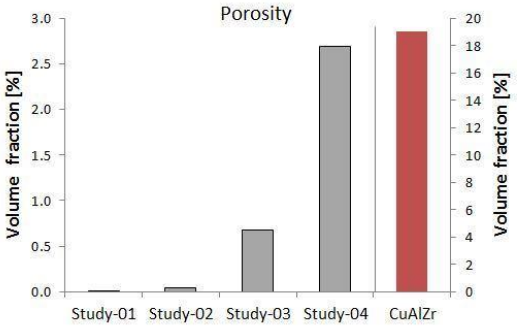
2. Reconstruction



Iterative reconstruction on GPU-Cluster

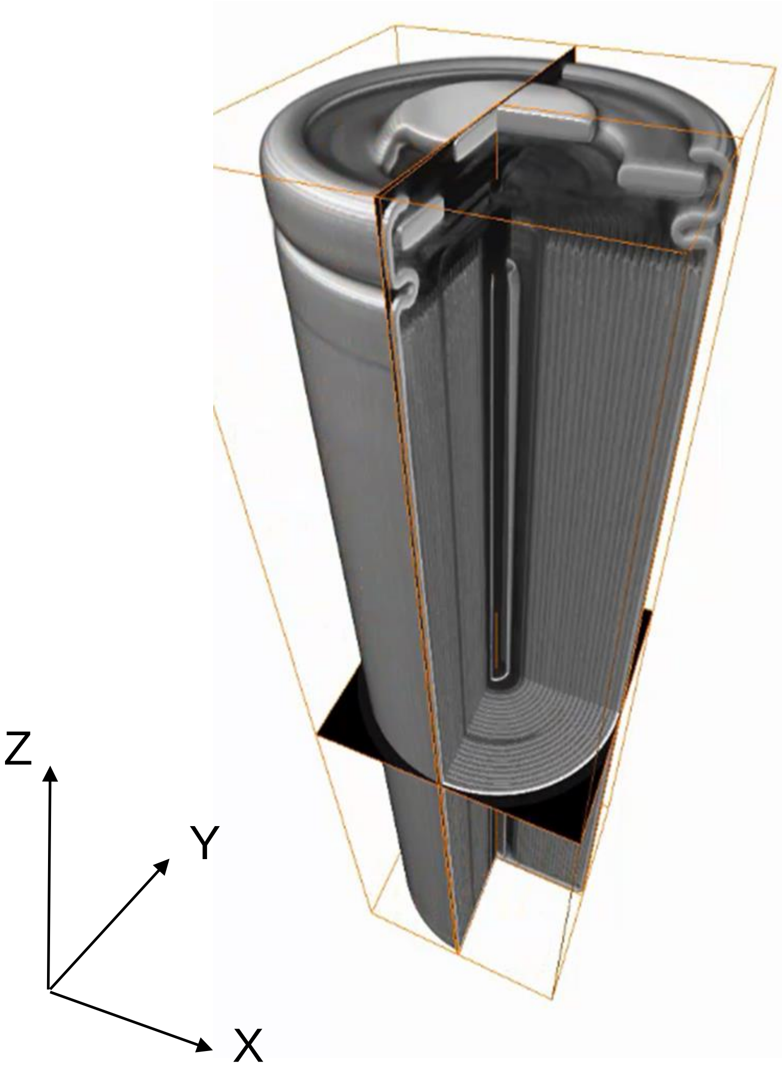
3. Visualization & analysis



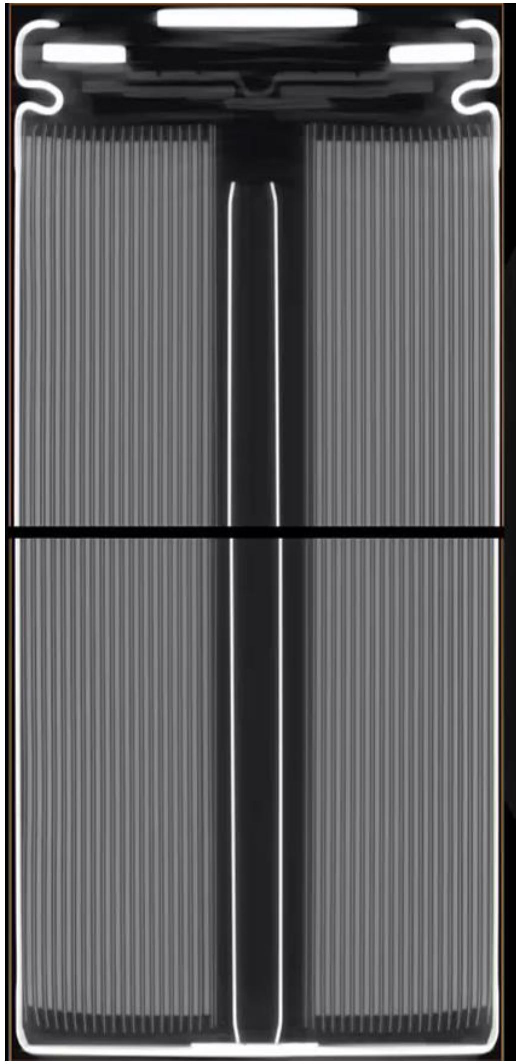


Avizo for Materials Science software

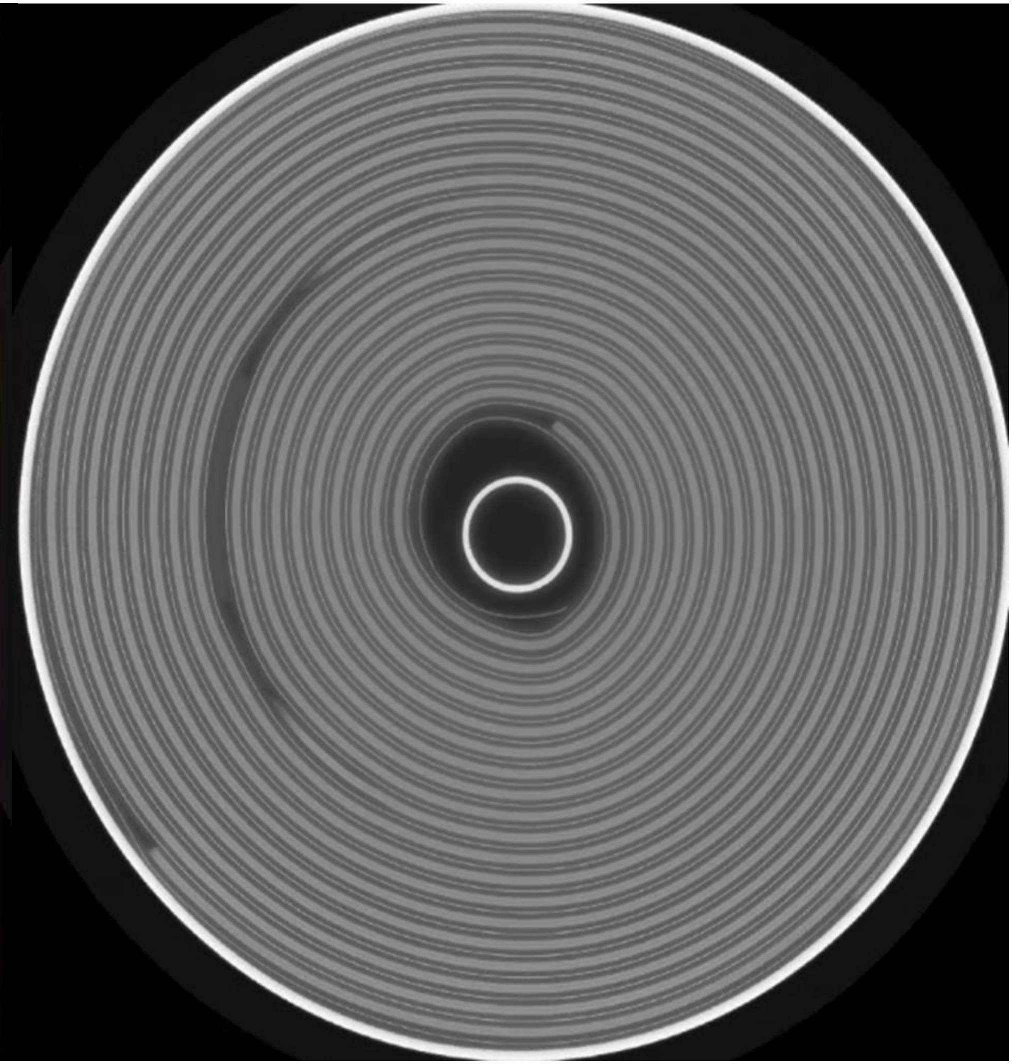
3D Imaging at The Cell Level: microCT



X (Y) – Z Plane

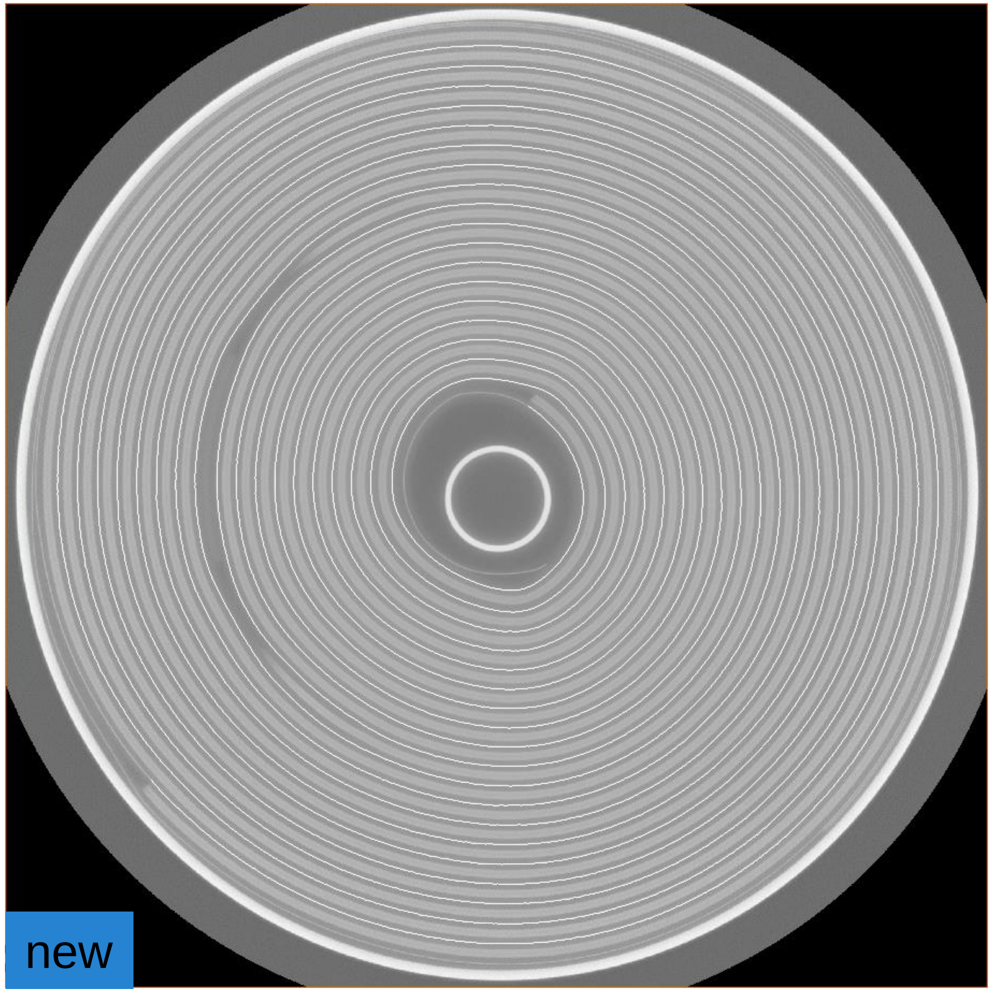


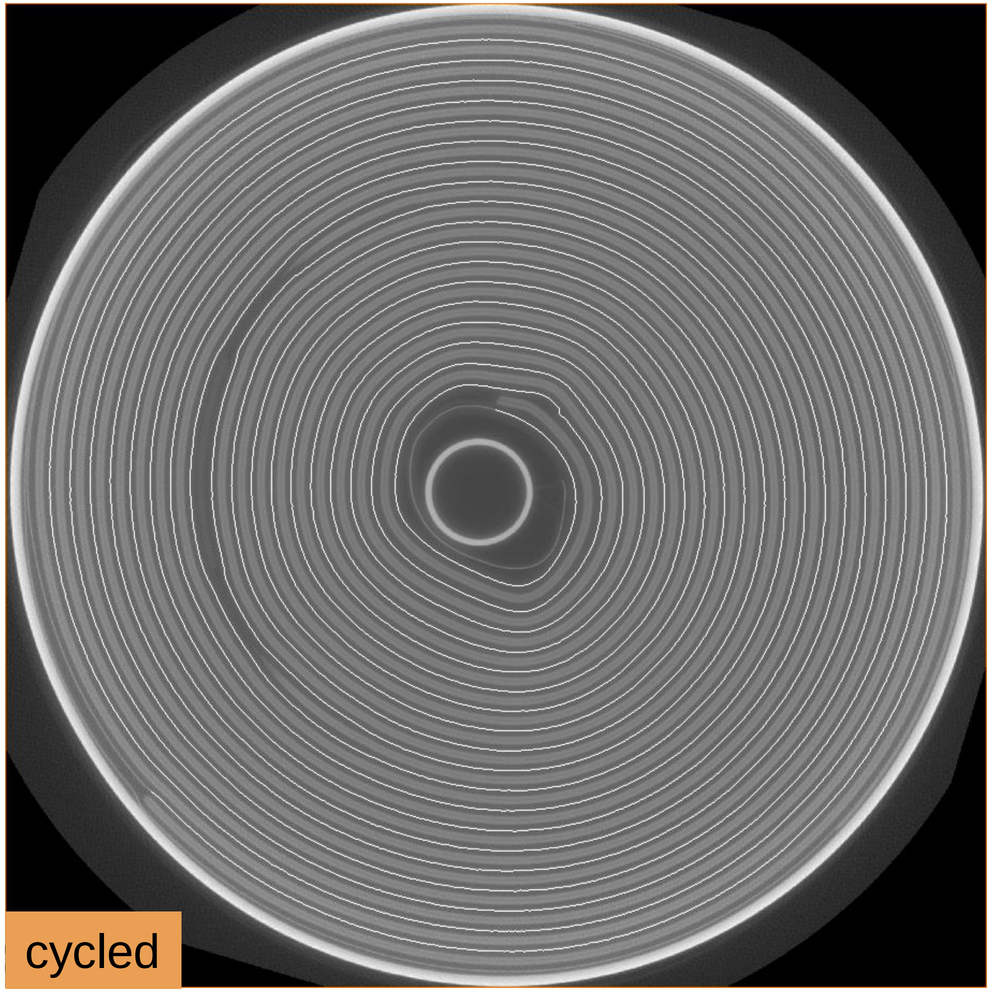
X –Y Plane



Comparing Cu Collector Shape on Each Horizontal Slice

- Extracting spirals following the Cu collector, starting and ending where the cathode starts & ends
- Segmentation is automated and performed on every x,y slice

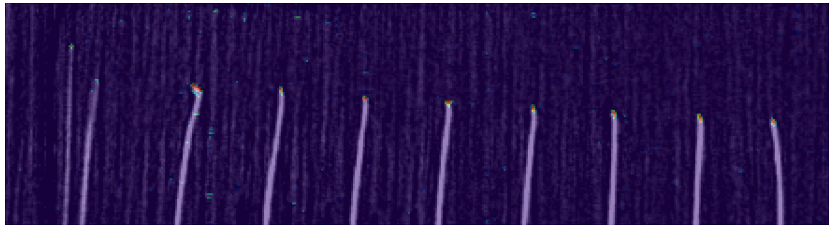




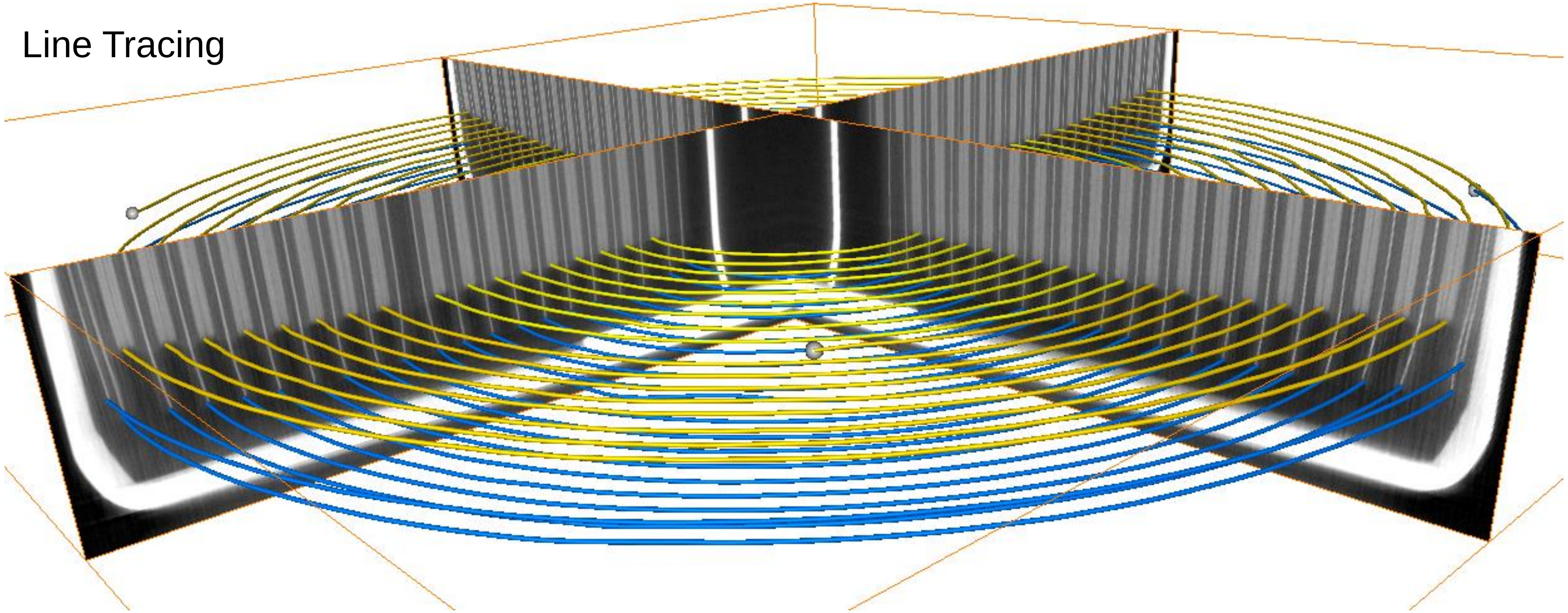
Sample courtesy: University of College London

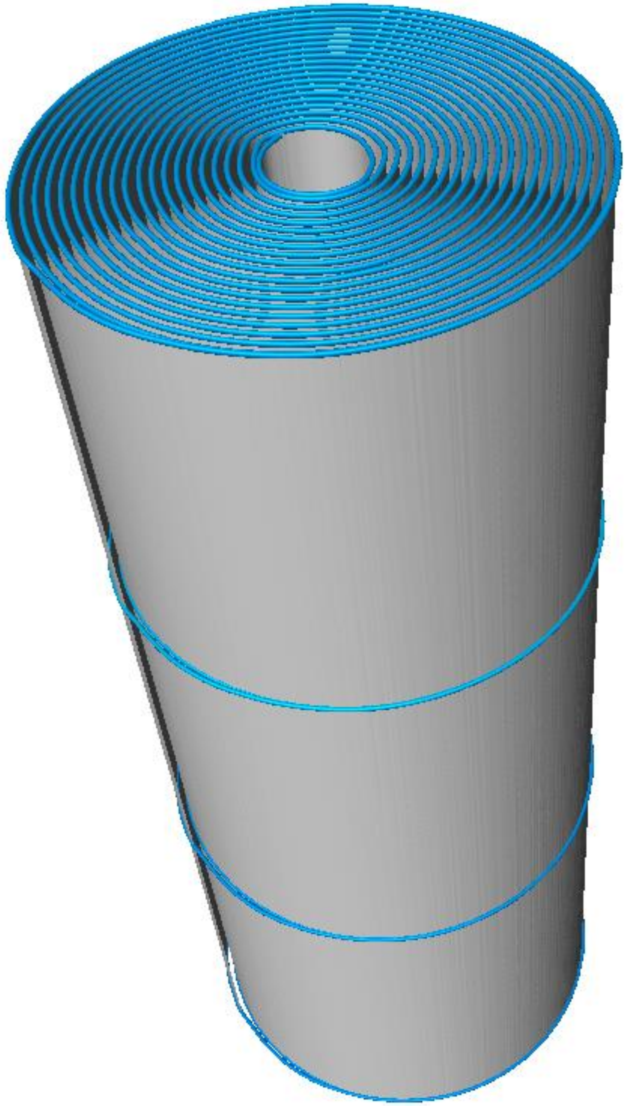
Geometry Extraction from the microCT Dataset

In each horizontal slice; the foil locations are tracked and co-registered to allow comparison between the new state and the cycled state.



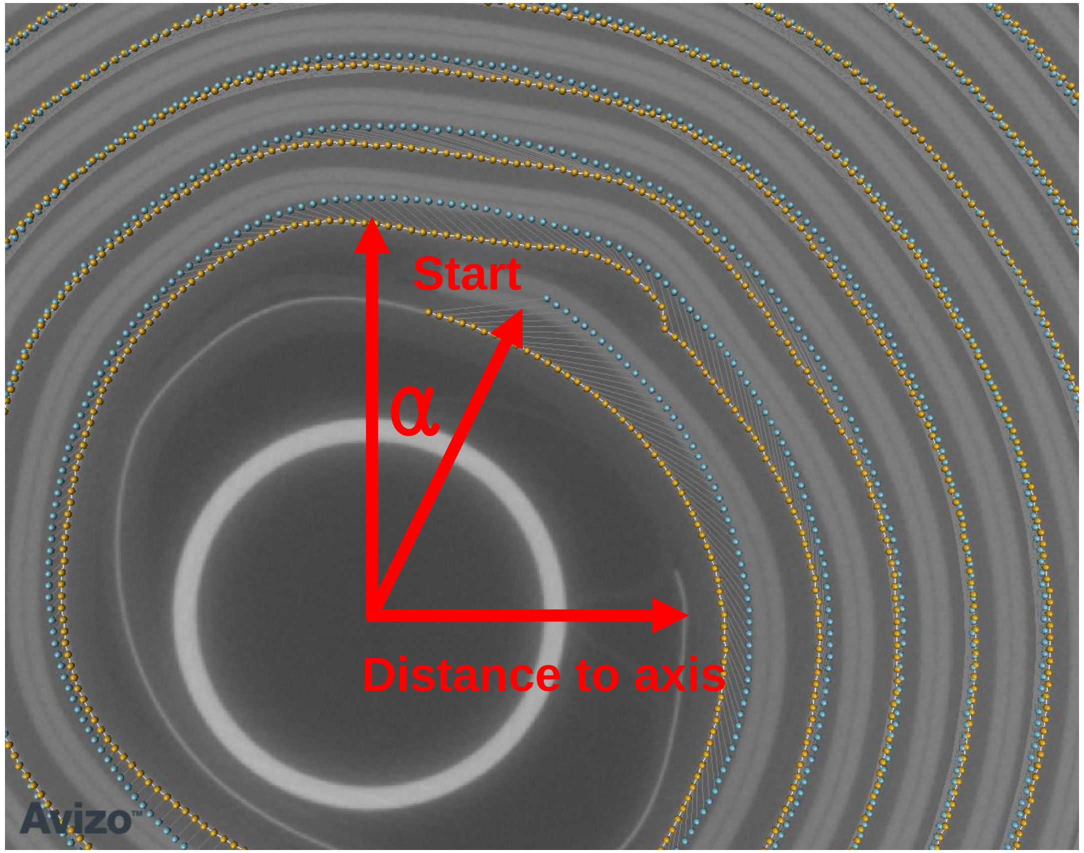
Line Tracing



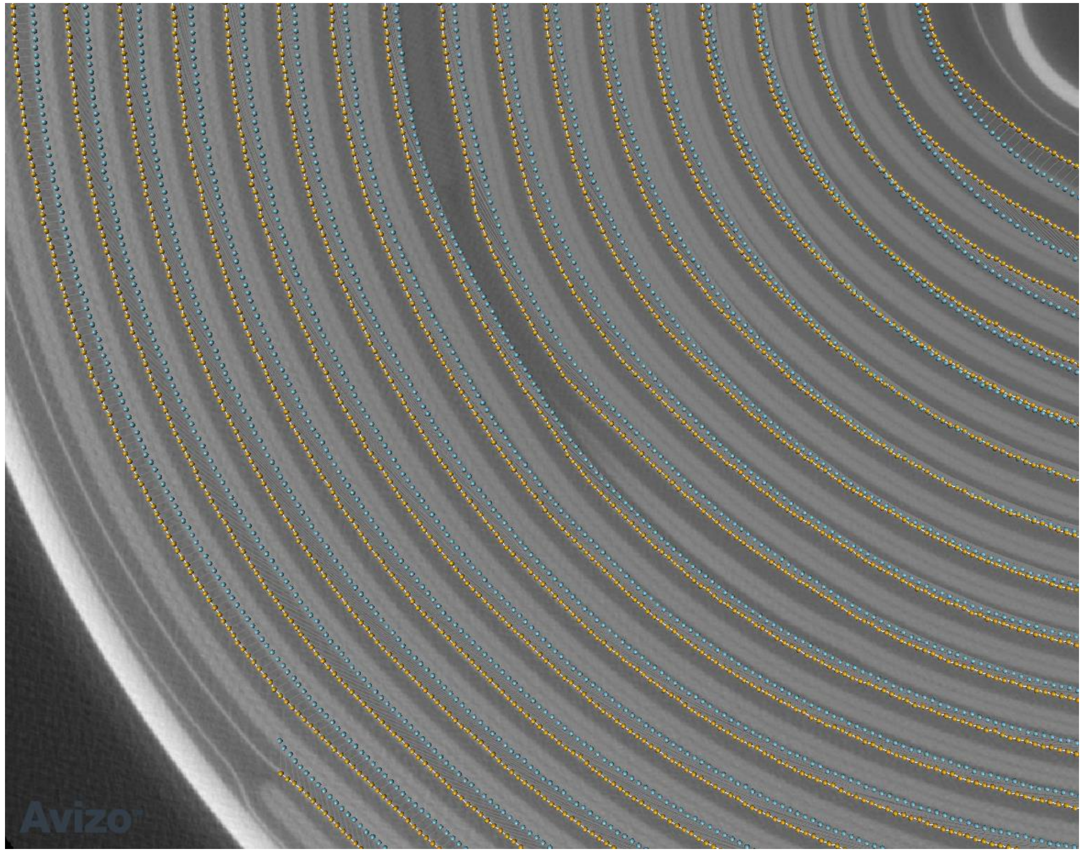


Collector shape change is quantified by digitally correlating the position of the spiral in the fresh and aged battery and plotting the distance from the center versus the rotation angle α

Center of the cell

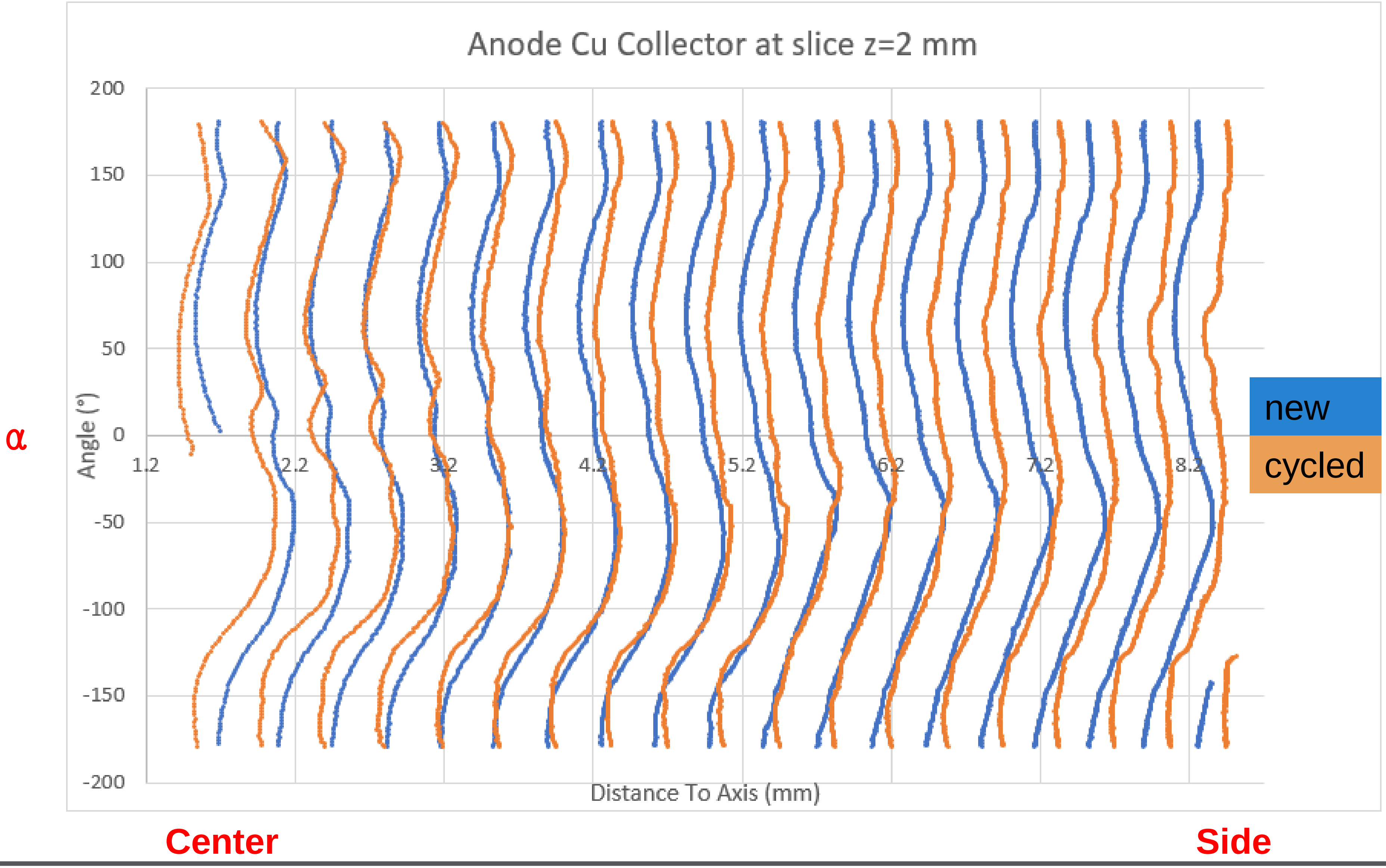


Edge of the cell



new
cycled

Comparing Cu Collector Shape on Slice Z=2mm



At the center, the cycled battery collector is closer to the middle; this situation reverses towards the edge of the battery. It suggests an electrode volumetric expansion.

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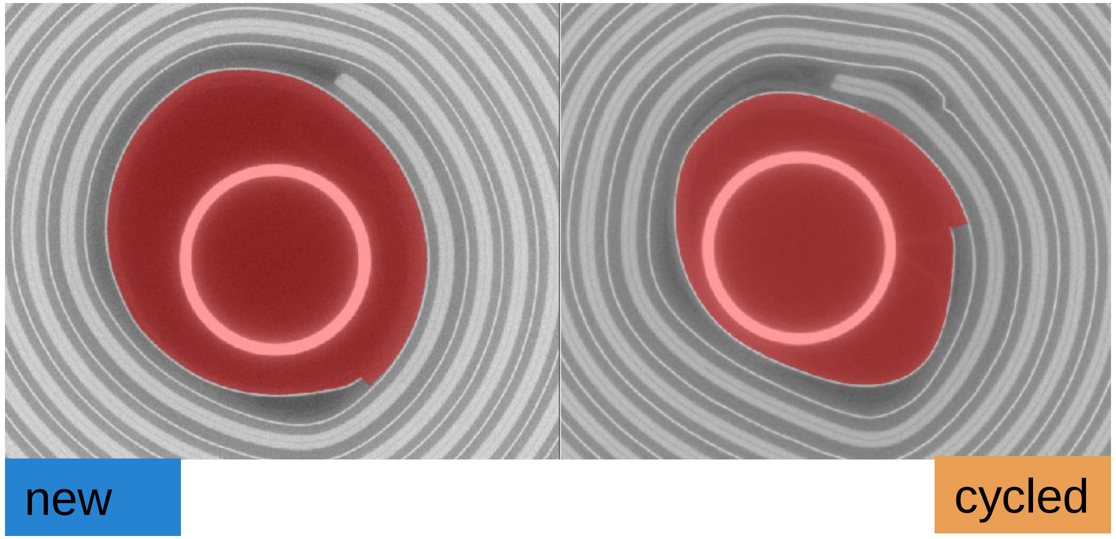
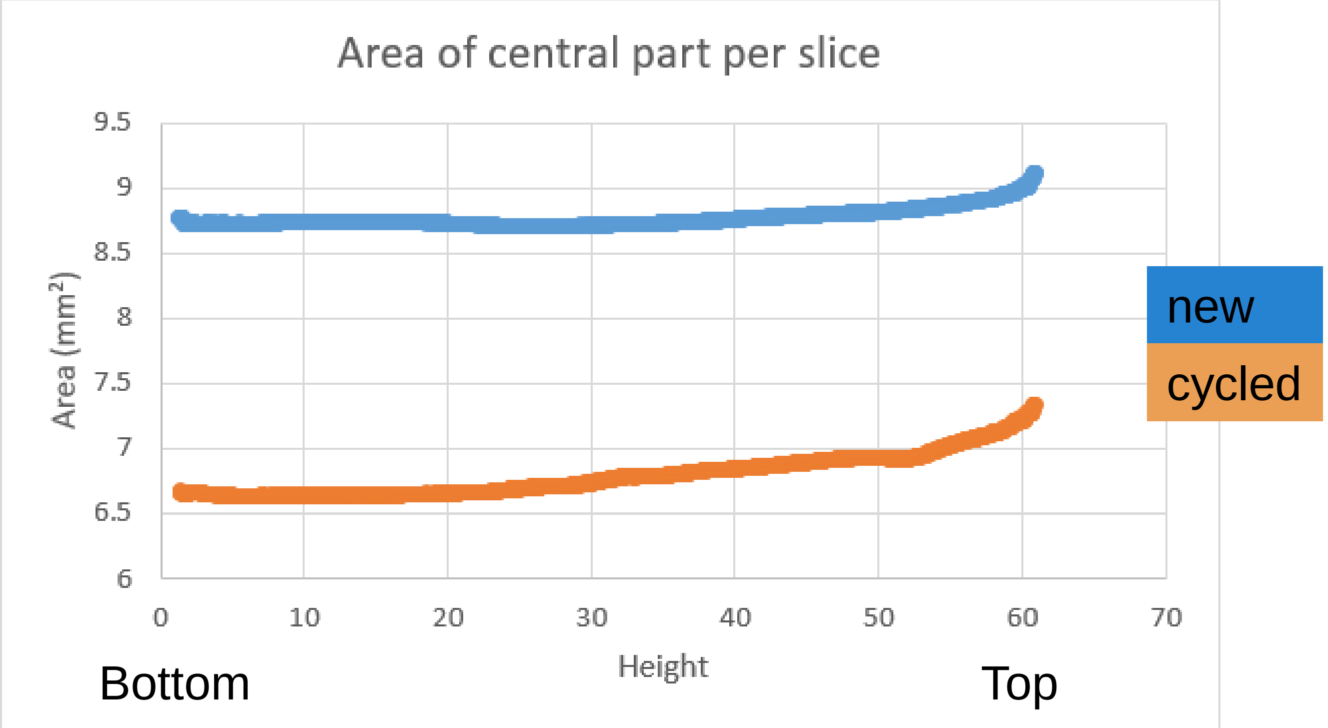
Comparing Central Rod Area

- Area around the central rod, 'inside' the anode



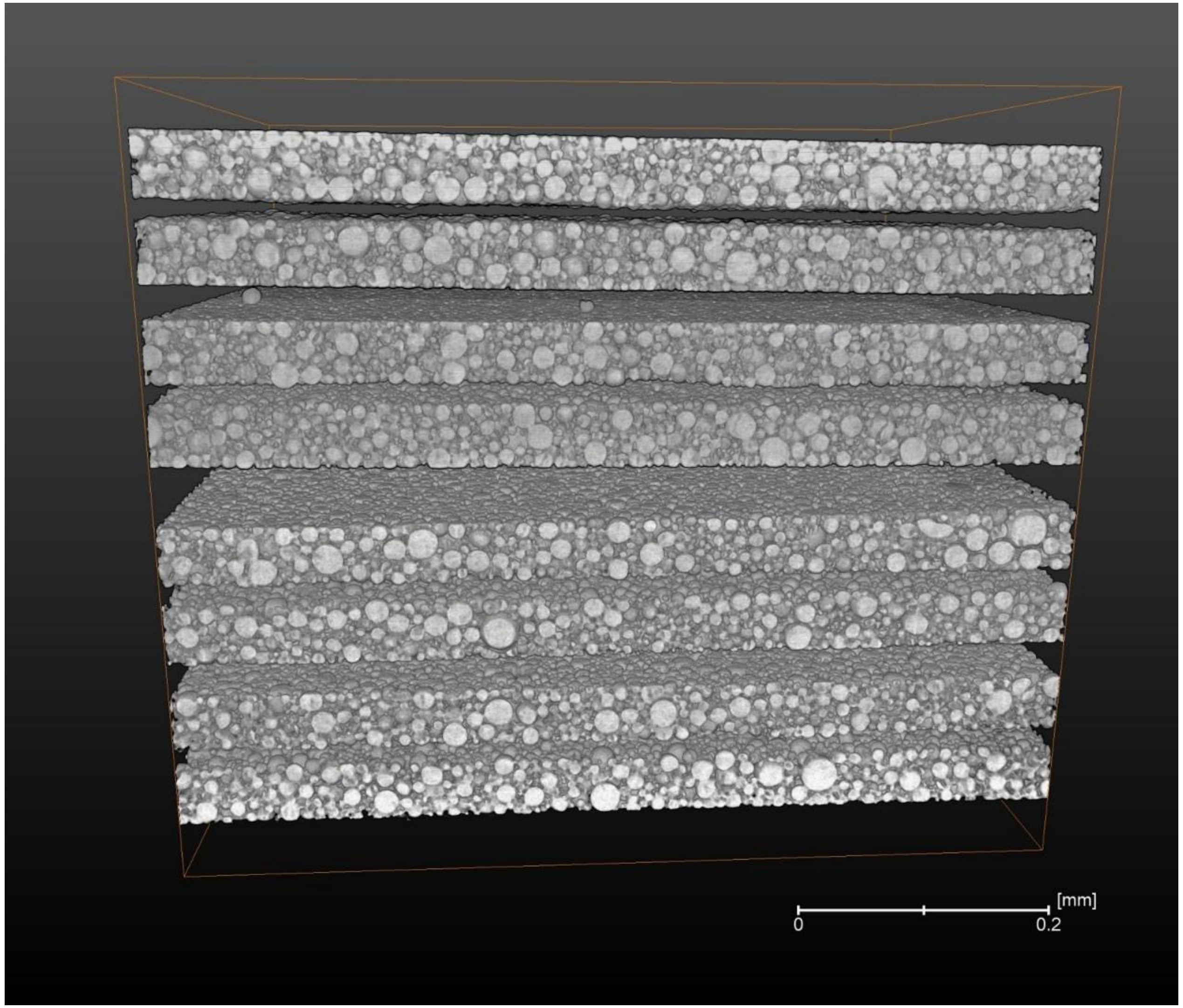
Average area:

New = 8.76 mm², Cycled = 6.78 mm² (77%)

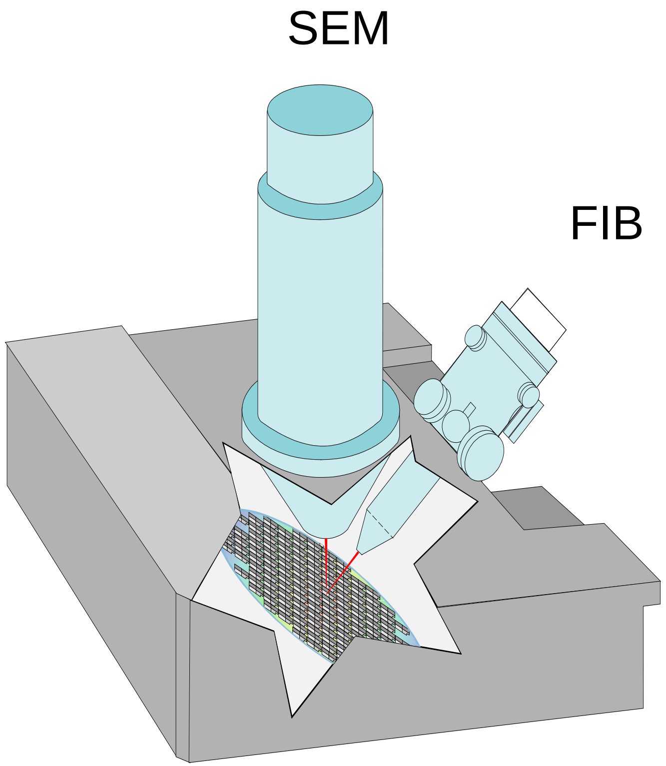


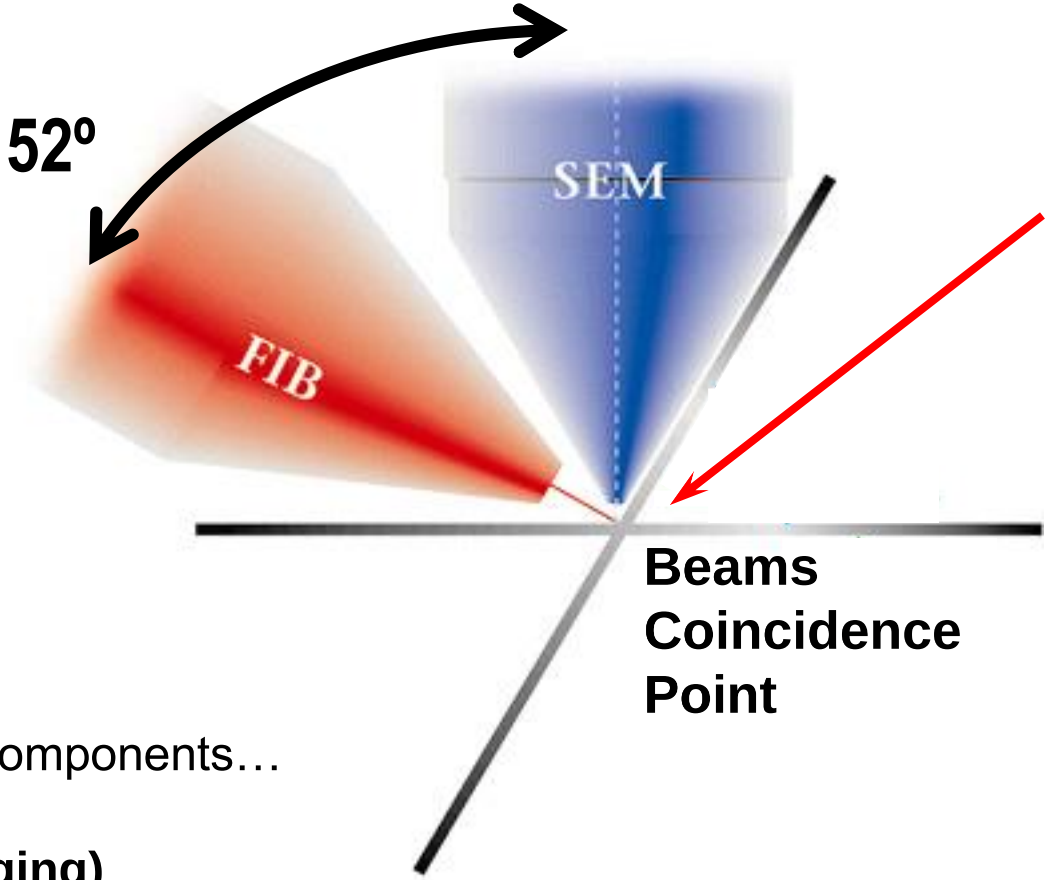
HeliScan microCT + Avizo allows to quantify structural changes in a cycled battery

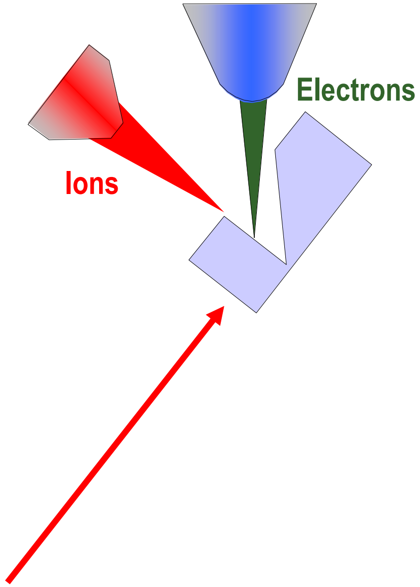
Challenges of the microCT for Battery Imaging



- Not enough resolution to see fine-structure within the electrode particles (e.g. cracks)
- Lack of chemical compositional/elemental information
- DualBeam (FIB-SEM) technique provides 3D imaging solution at electrode and particle level





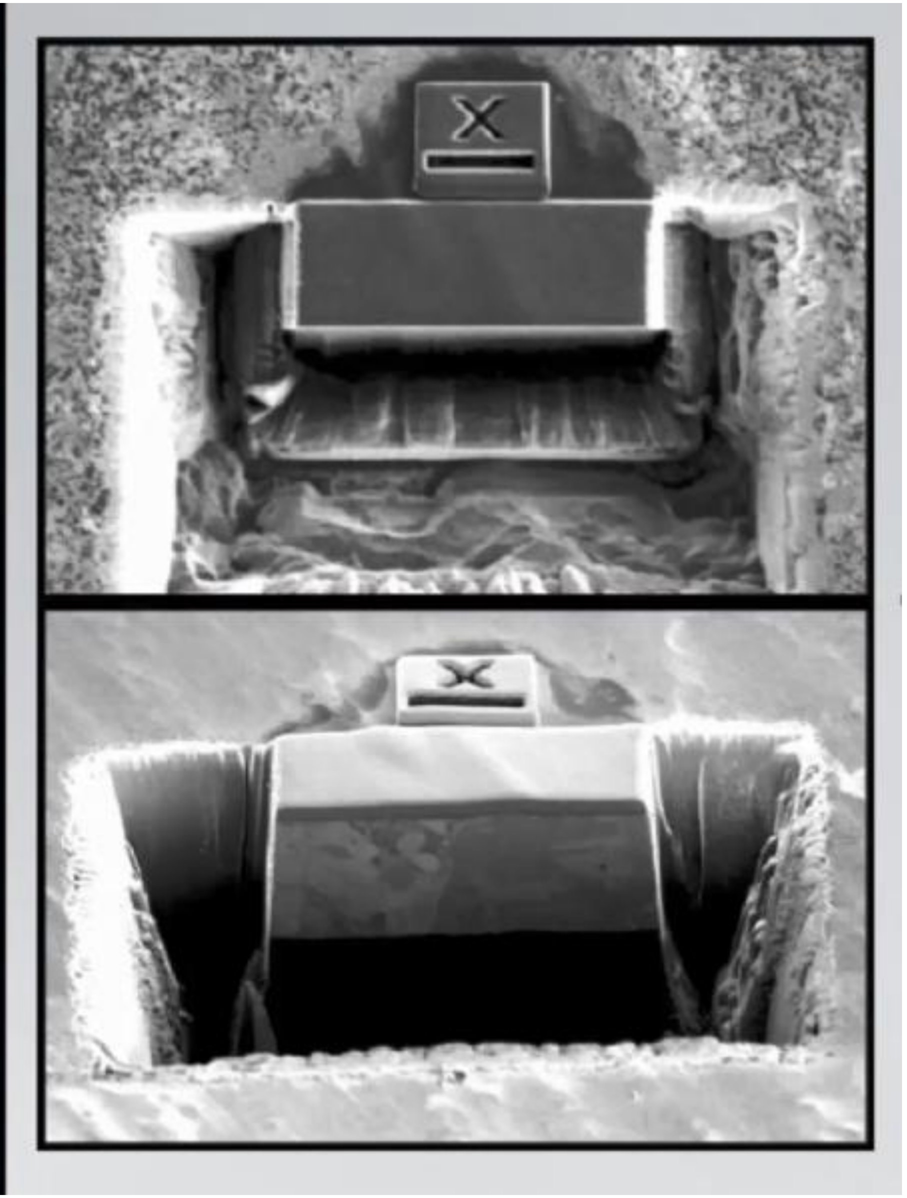


A DualBeam is defined by of two primary components…

Scanning Electron Microscope (for imaging)
+
Focused Ion Beam (milling)

The sample and stage are maneuvered beneath the beams to optimize imaging and milling

The DualBeam in Action…



FIB

SEM

DualBeam Technologies

40x40x40 μm³/hr (Si) @65nA

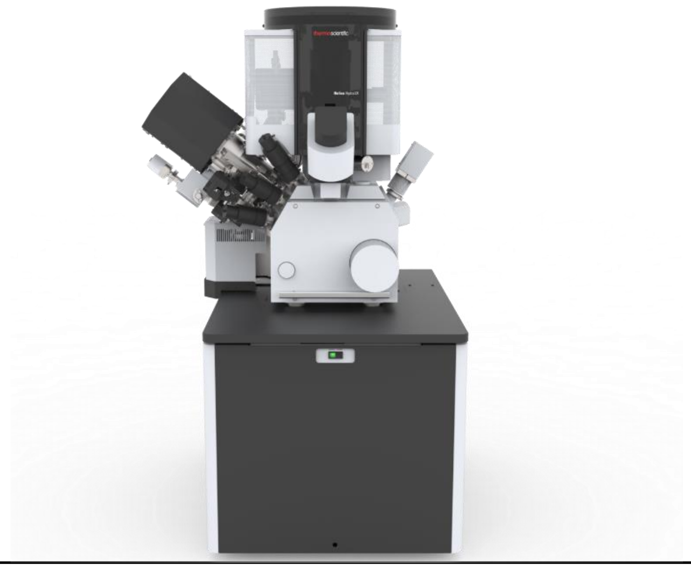
Ga⁺ LMIS

Helios (FIB)

150x150x150 μm³/hr (Si) @2.5μA

(~**40x** faster than FIB)

Multi chem plasma source
(Xe, Ar, N, O)



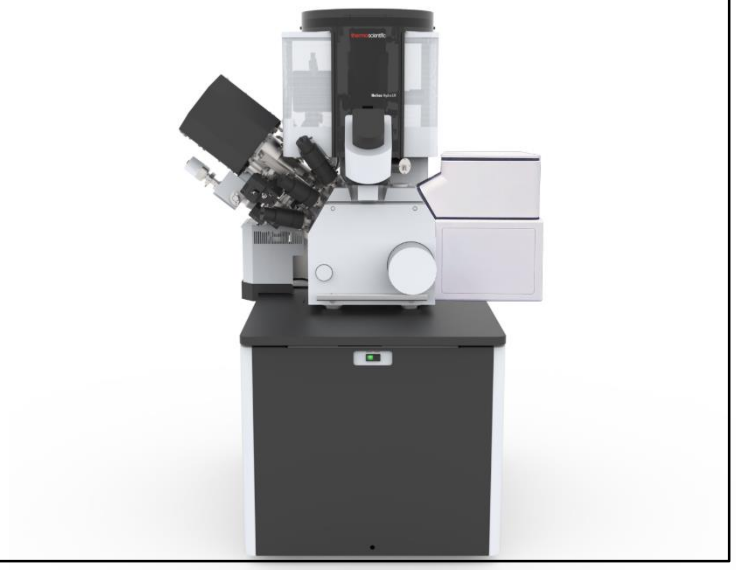
Helios Hydra DualBeam

1200x1200x1200 μm³/hr

(**>15.000x** faster than FIB, or >1000μA)

Ultra short pulse laser

(515nm,/1030 nm)



Helios PFIB UXe Laser

Increasing 3D Volume for Analysis

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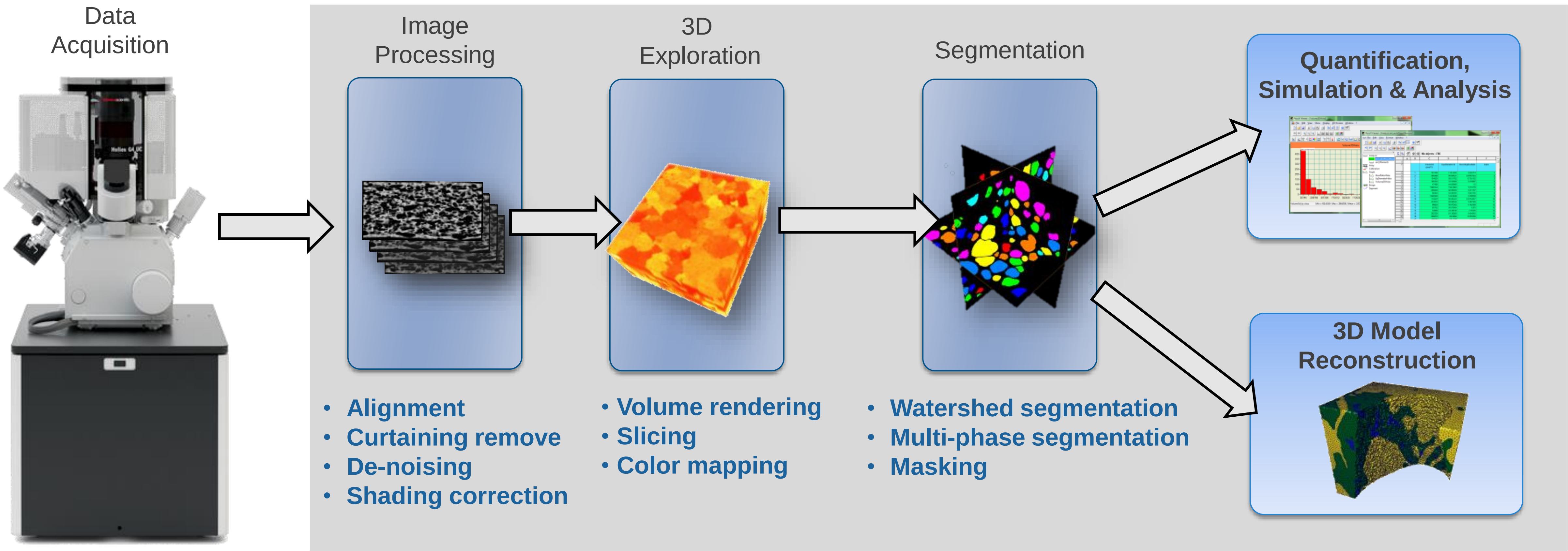
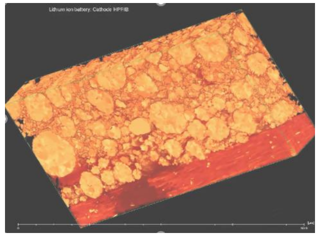
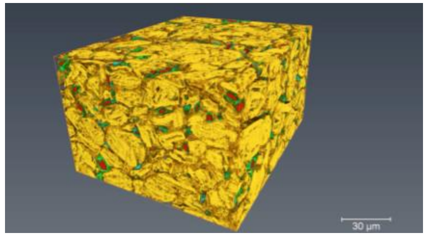
DualBeam 3D Imaging Workflow



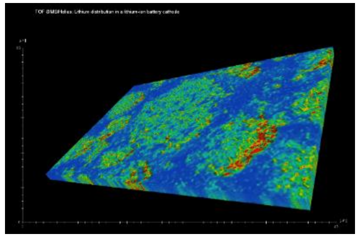
3D SE/BSE Images



3D EDS

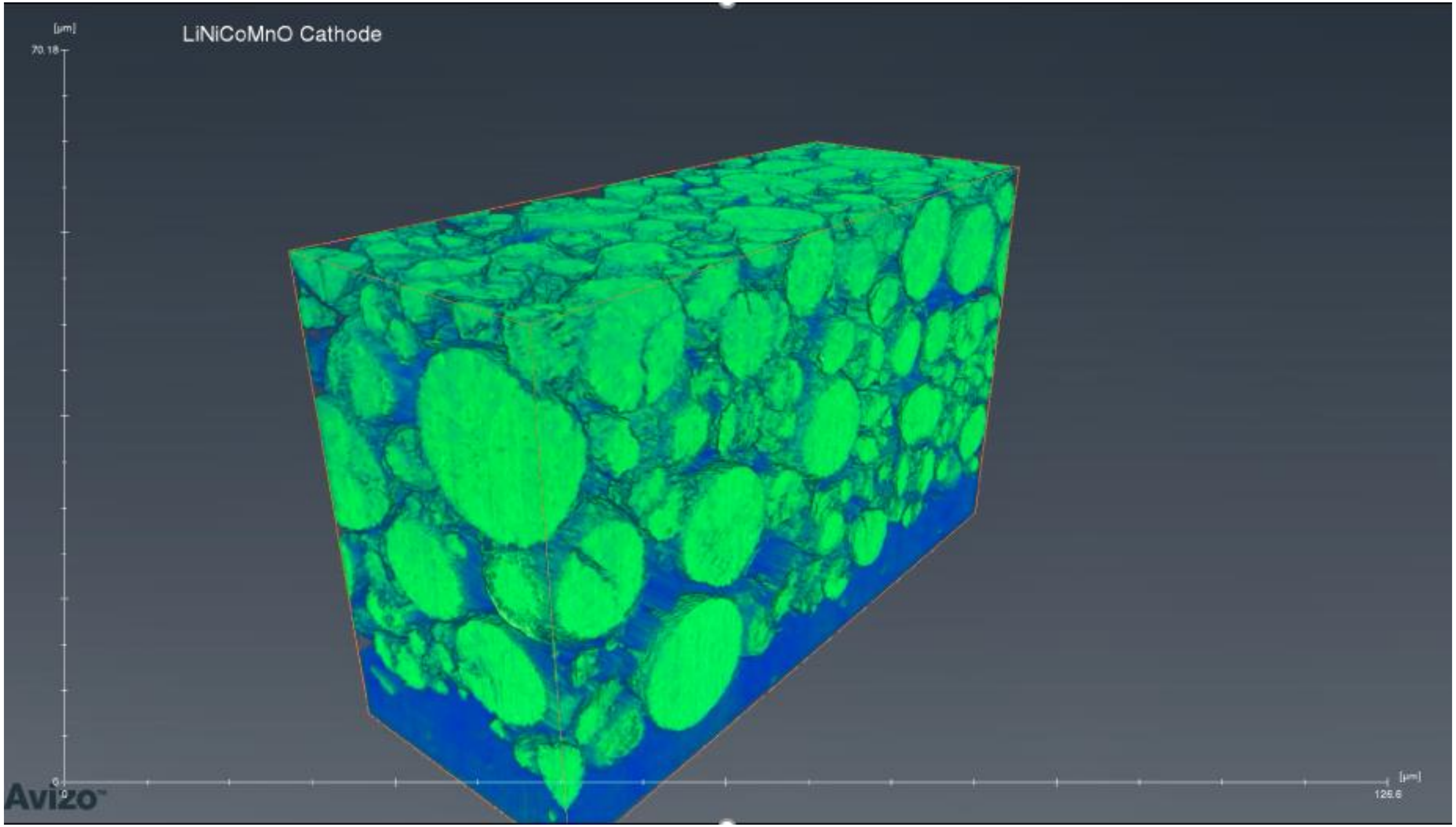


3D TOF-SIMS

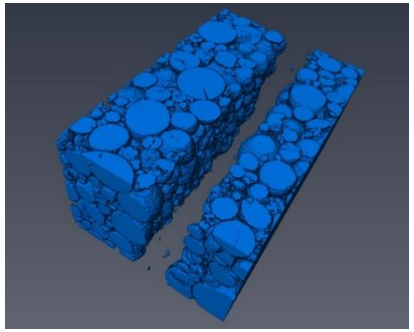


DualBeam can perform accurate multi-scale, multi-modal 3D characterization

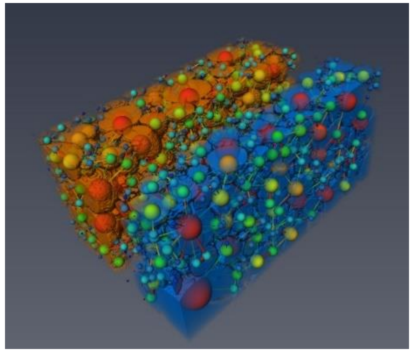
3D Characterization through BSE/SE Image



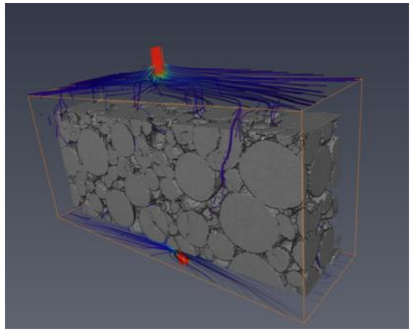
Volume



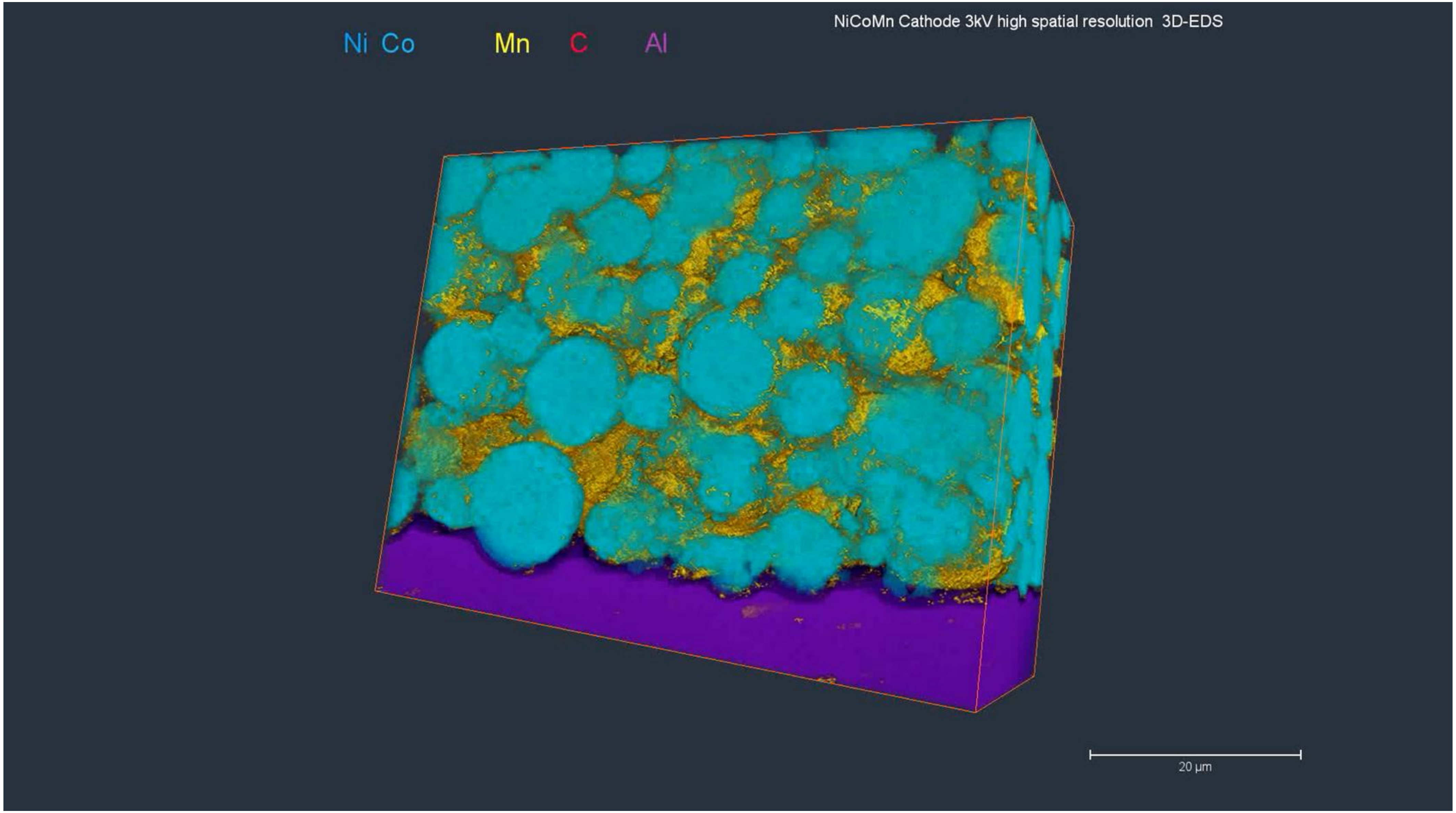
Connectivity



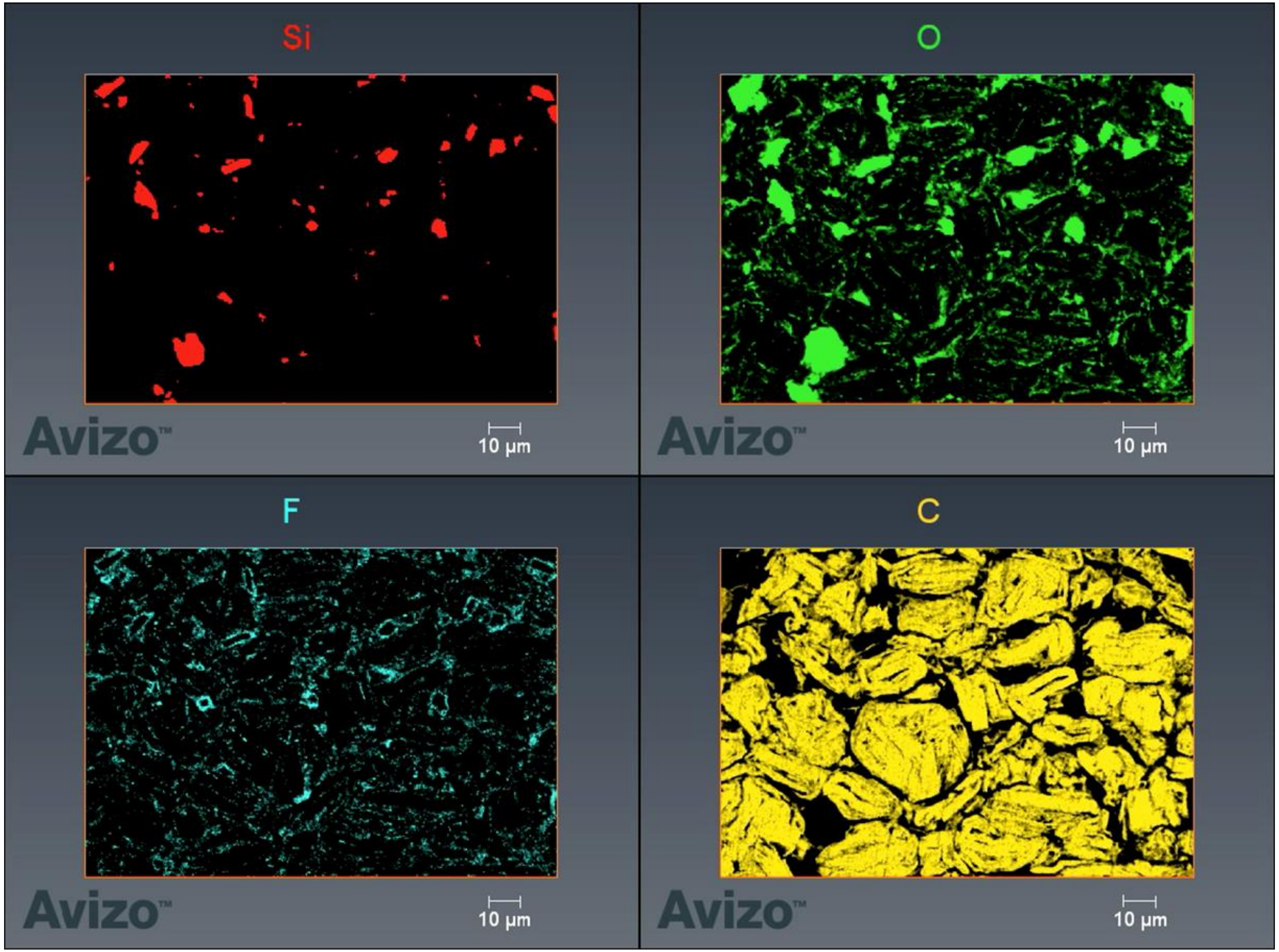
Tortuosity



3D EDS on $Li(Ni_xMn_yCo_{1-x-y})O_2$ Cathode

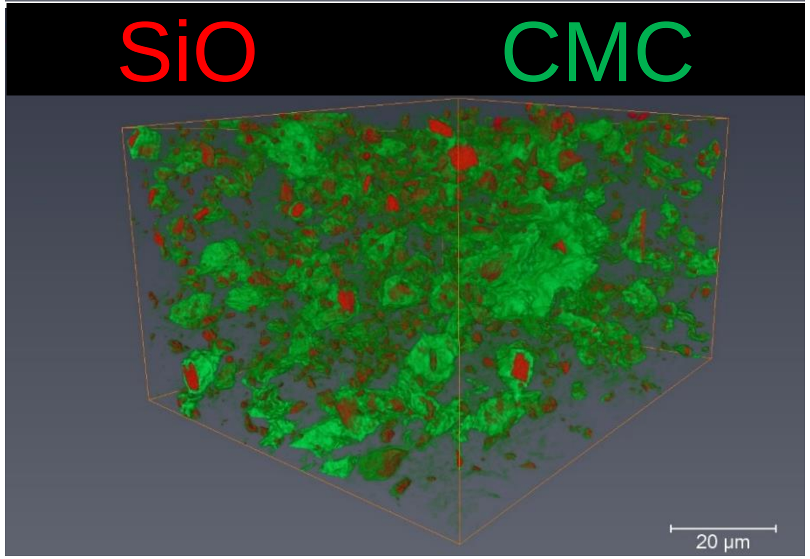


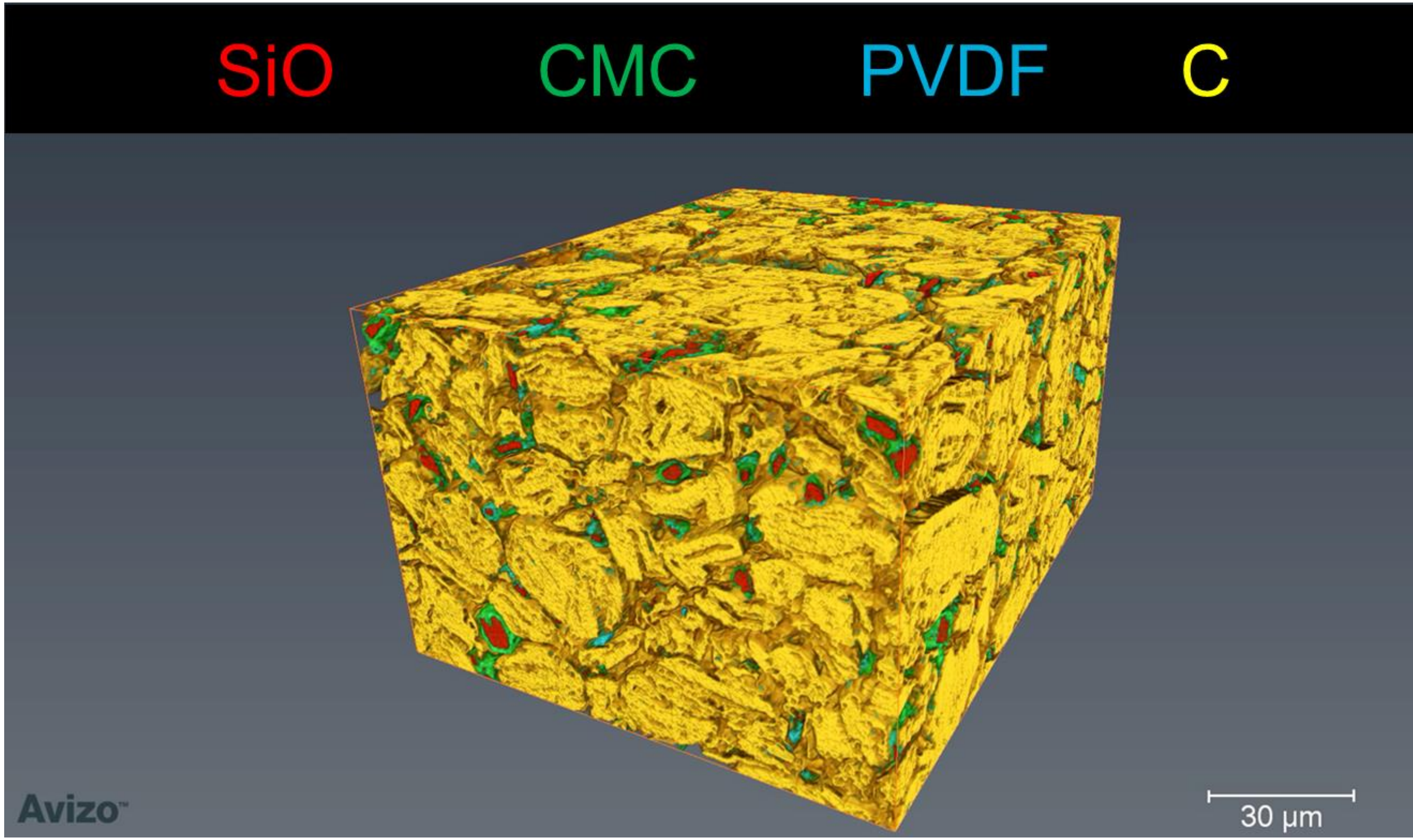
3D EDS on SiO/C Anode: Enables 4-phase Identification



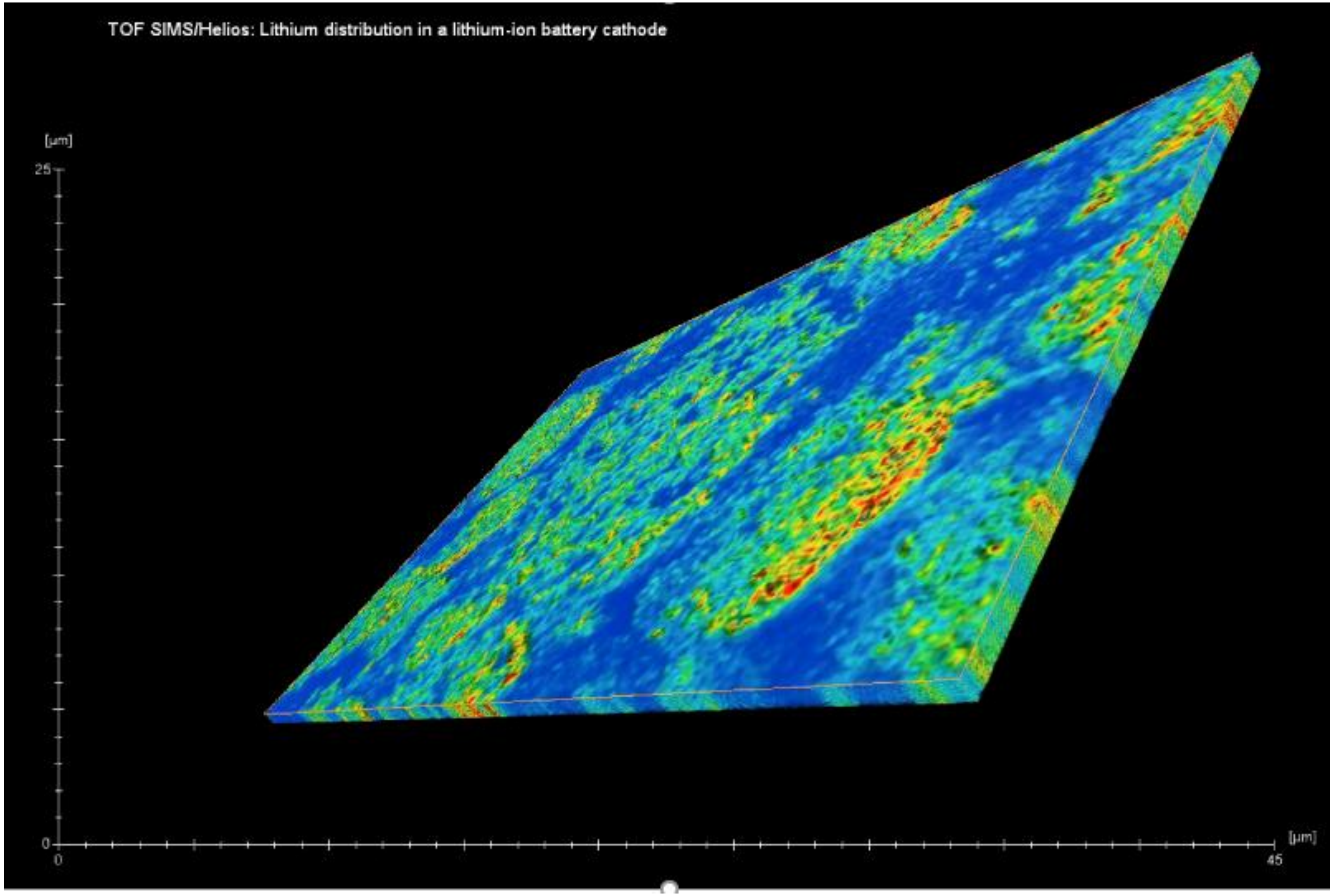
- **High-res 3D EDS on SiO/C anode at low kV to enable 4-phase identification in 3D volume**
  - Not achievable via SE/BSE imaging due to low contrast among phases
- **Identification of each phase provides critical information to understand structure-performance correlation in the battery**
  - Phase distribution
  - CMC coating on SiO
  - Carbon/SiO ratio optimization

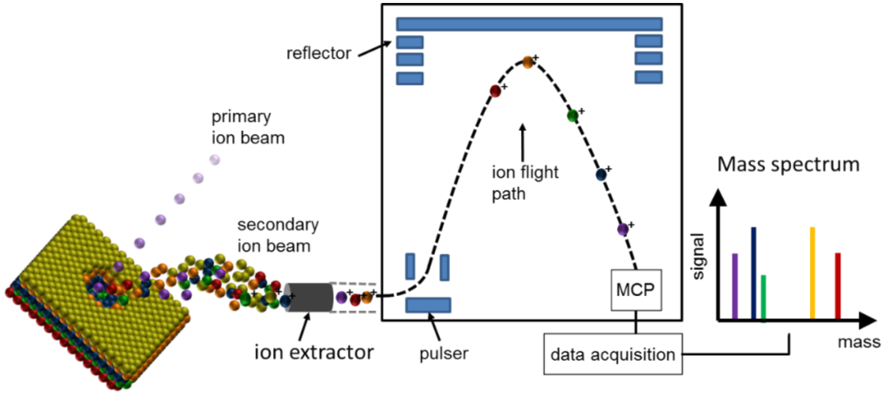
3D EDS on SiO/C Anode: Enables 4-phase Identification





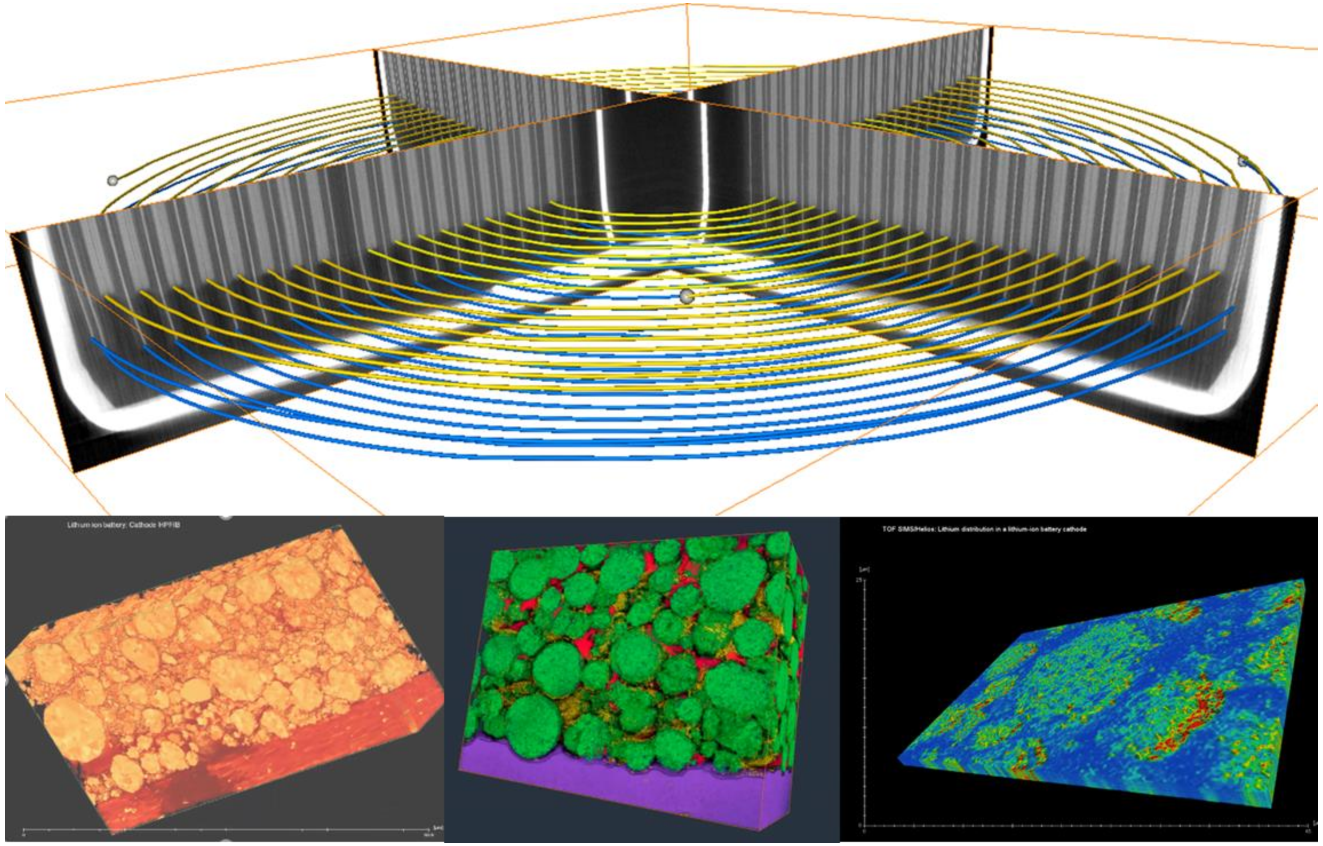
TOF-SIMS: $^{7}Li^{+}$ Distribution in 3D





- **TOF-SIMS on DualBeam enables the measurement of 3D distribution of the lithium ions within the electrode**
  - Effective in mechanism study, e.g. SEI layer, fresh vs. cycled cell structure

Summary



- **3D imaging technique provides a quantitative approach to understand battery structure-performance correlations**
  - Heliscan microCT allows for quantitative study of the battery structure evolution at the cell levels
  - DualBeam technique allows for 3D characterization at electrode level for both morphology and chemical information

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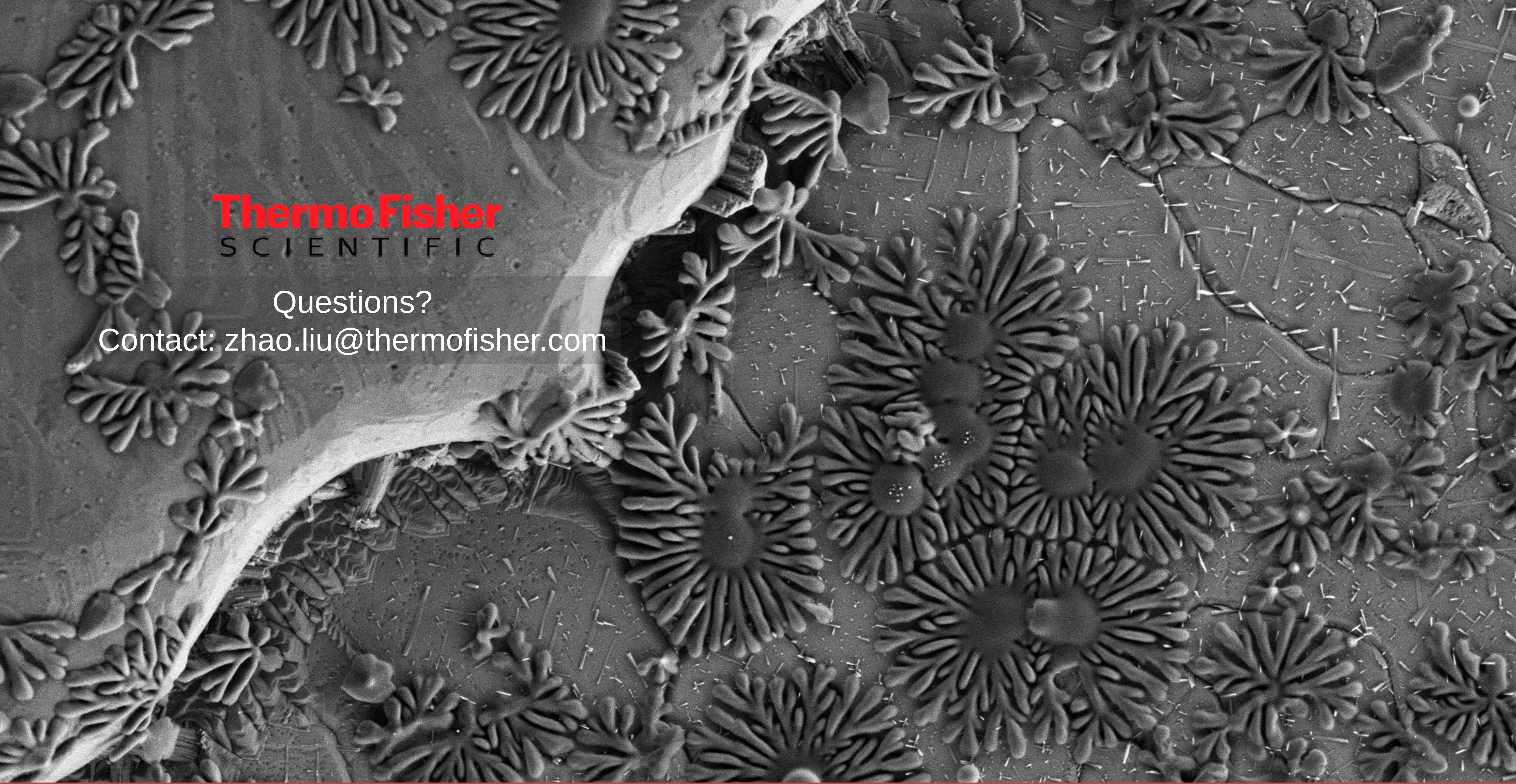

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Questions?

Contact: zhao.liu@thermofisher.com