# **Imaging Batteries Across Space and Time**
## Recent Progress in 2D, 3D, and 4D


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Battery Power | August 3, 2016

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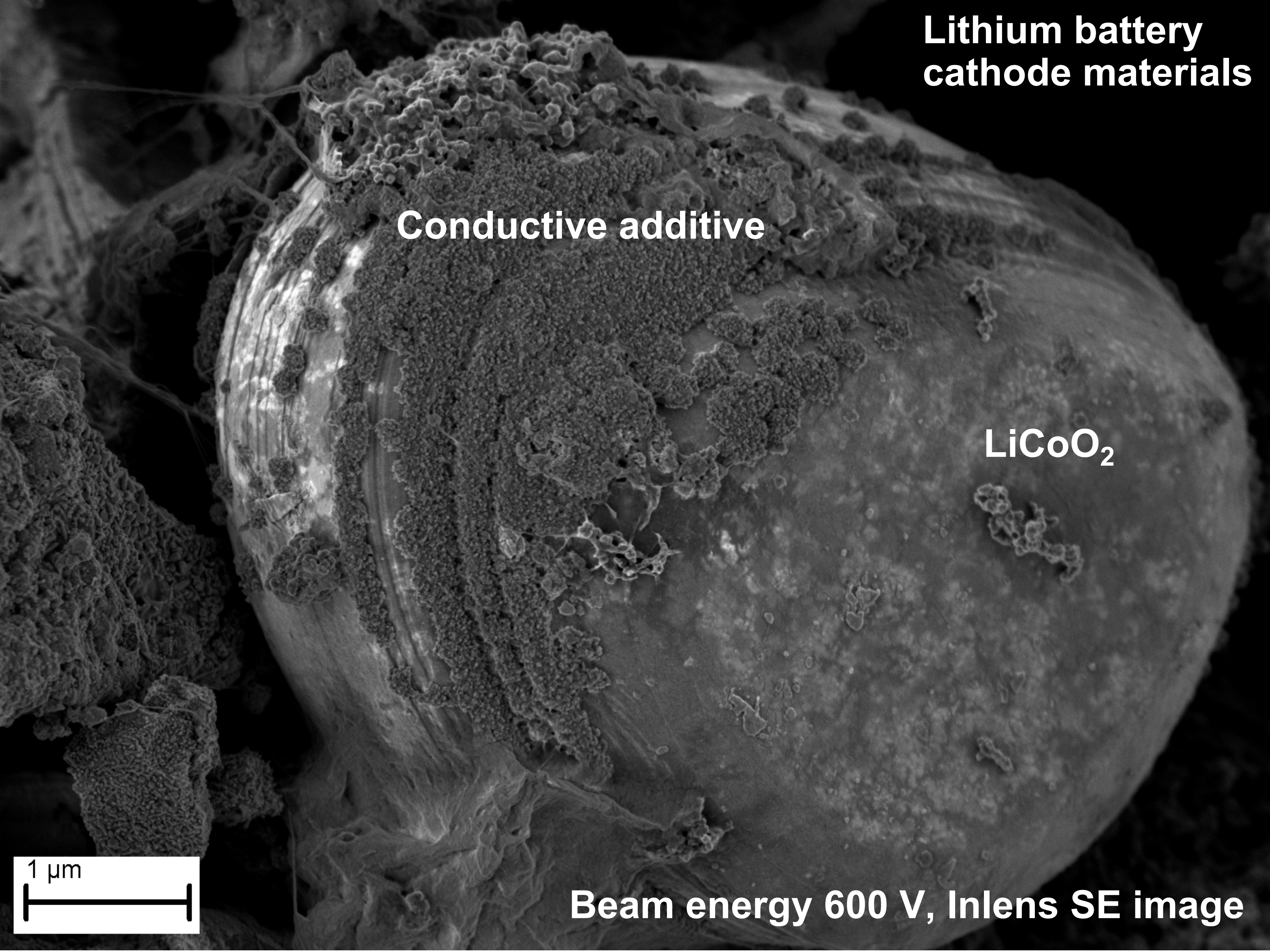
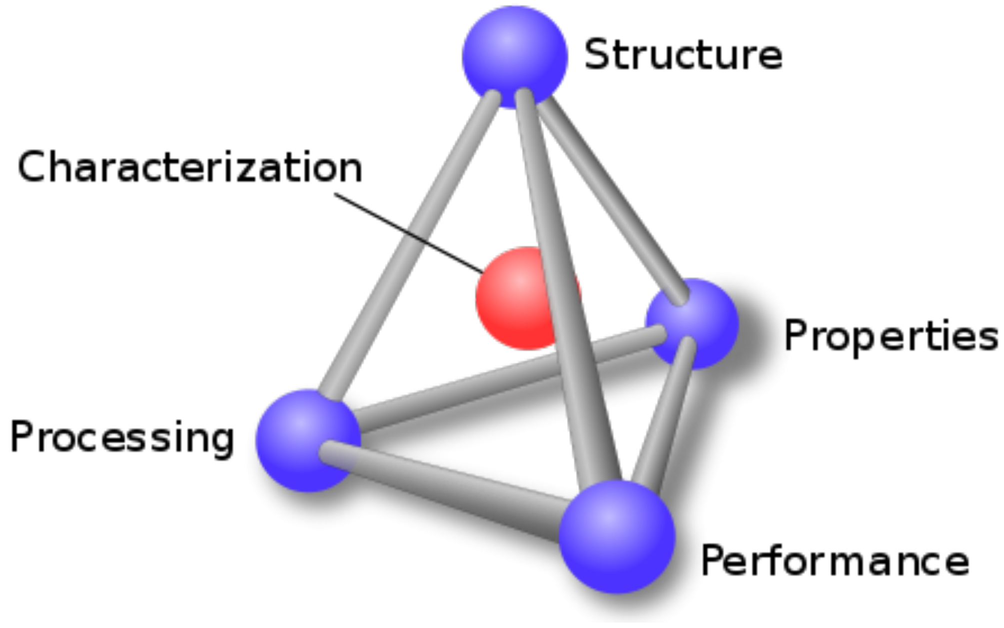

Lithium battery
cathode materials
Conductive additive
$LiCoO_2$
1 µm
Beam energy 600 V, Inlens SE image

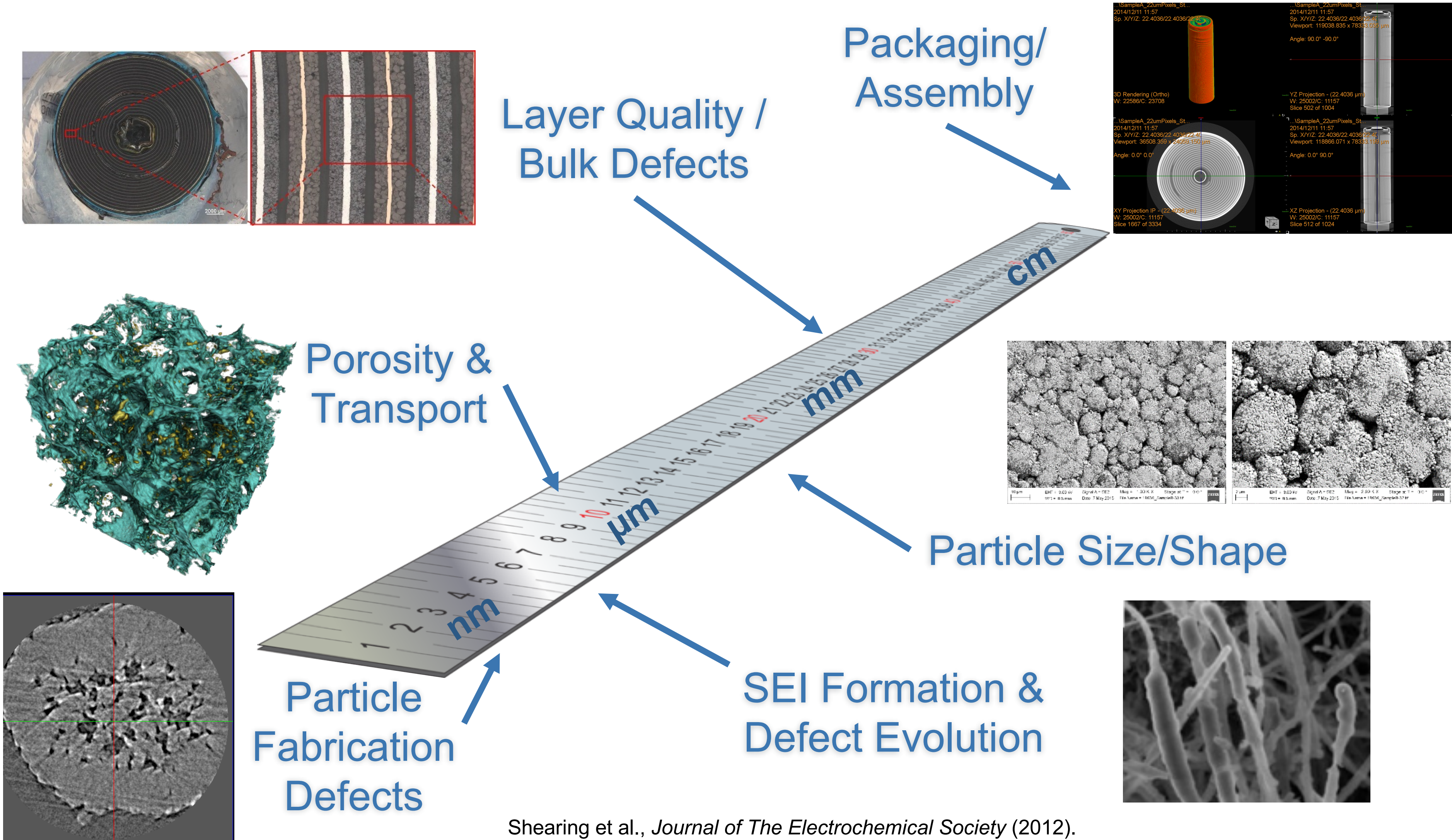
# Motivation

***Linking microstructure…***


***…with performance.***

# Li-Ion Batteries: A Complex, Multi-Scale Problem

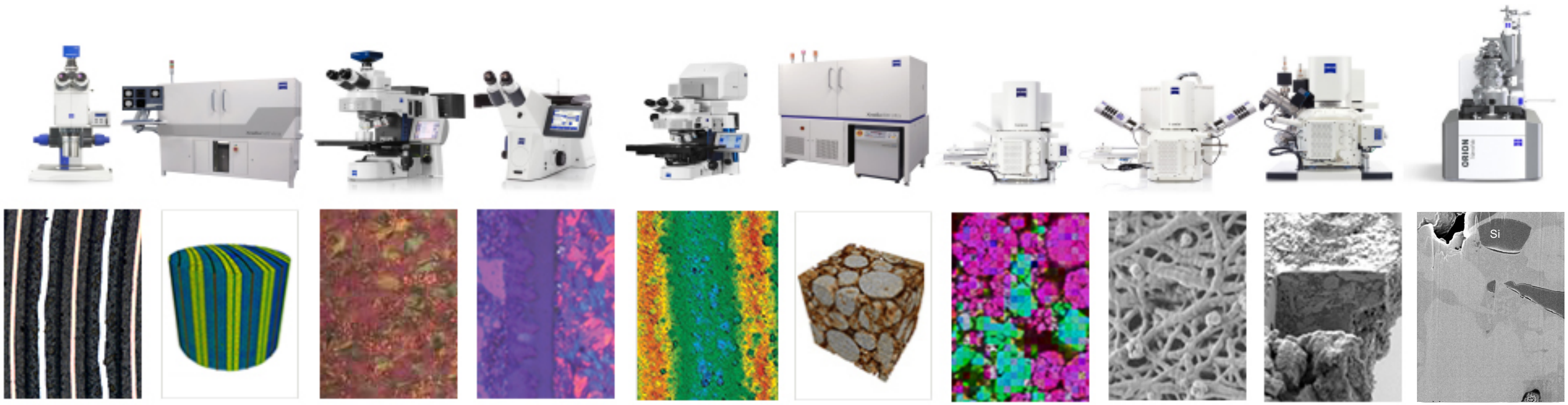



Shearing et al., *Journal of The Electrochemical Society* (2012).

# Industry Leading Integrated Microscopy Platform

## Multi-Scale Characterization for Multi-Scale Research

***A multi-scale platform…***




| Stereo | Sub-micron | Widefield | Polarized | Confocal | Nanoscale | SEM | FESEM | FIB-SEM | Helium Ion |
|---|---|---|---|---|---|---|---|---|---|
| LM | XRM | LM | LM | LM | XRM | EM | EM | EM | IM |
| 1 µm | 700 nm | 250 nm | 200 nm | 200 nm | < 50 nm | < 2 nm | < 1 nm | < 1 nm | < 0.5 nm |

***…to address multi-scale research challenges.***

Assembly → Particles → Pores → Defects

# ZEISS Light Microscopy

*Resolving Battery Structures from the Package to the Pore*

## Axio Zoom.V16

- High resolution and flexibility for larger samples
- Tunable, motorized zoom for precise magnification settings

## Axio Imager 2

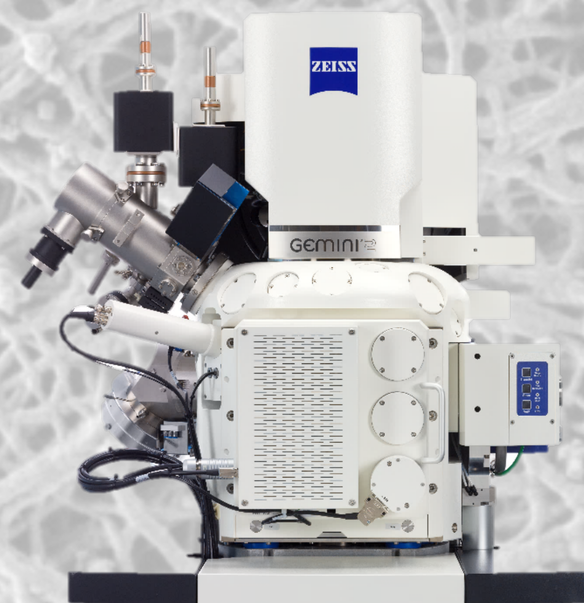
- Complete control over lighting, contrast, and magnification.
- Designed for accurate and repeatable results with complete motorization.

# ZEISS Electron Microscopy

*Highest Productivity FE-SEMs and FIB-SEMs for Li-Ion Batteries*


**FE-SEM: Merlin SEM, GeminiSEM**

- Best in class performance FE-SEM, resolution to sub-nm
- Simultaneously detect SE, EsB, AsB signals
- Additional ports for expandability
- High stability at low kV to reduce charging effects
- Optional transfer shuttle for air-sensitive specimens




**FIB-SEM: Crossbeam**

- Gemini column for sub-nm resolution in SEM mode
- Integrated FIB with currents up to 100 nA
- Optional load-lock laser ablation system for bulk removal
- Optional transfer shuttle for air-sensitive specimens

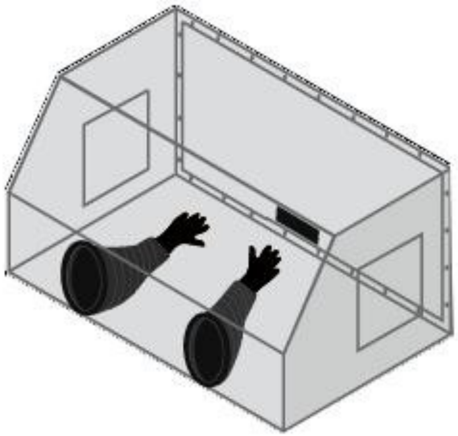
500 nm

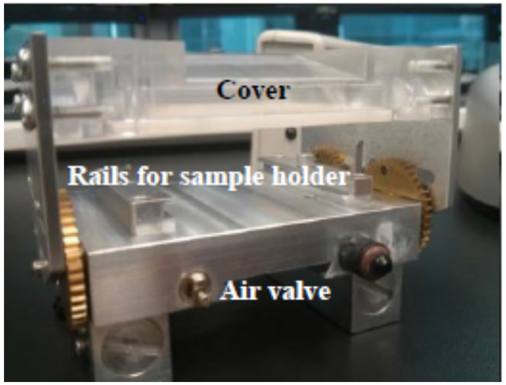
**Porous separator extracted from a mobile phone battery, imaged with Merlin FE-SEM.**

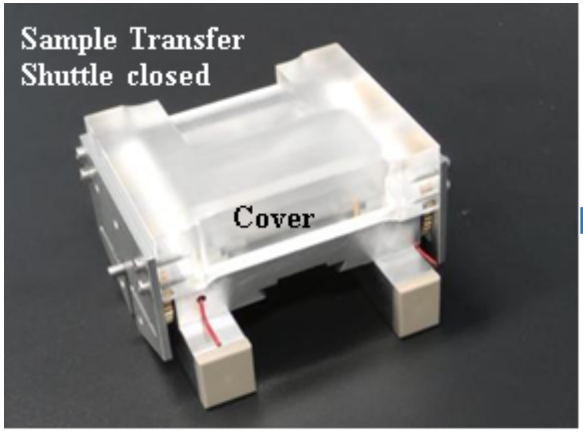
# Transfer Shuttle

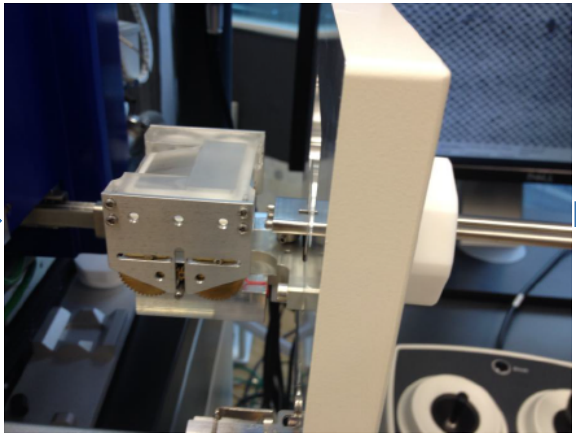
## Facilitating Multi-Scale Microscopy for LIBs

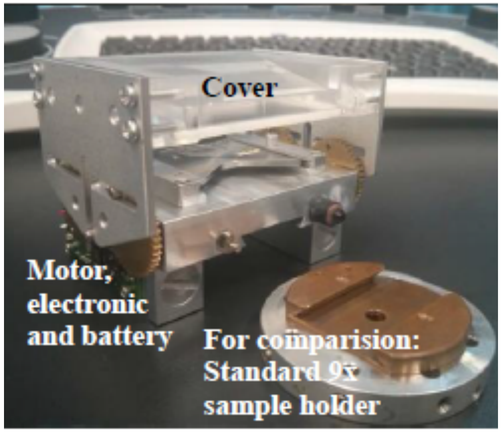
- **Protects** samples, mitigates air exposure during transfer
- **Sample only is transferred**, shuttle remains in the airlock
- Flexible chamber can handle **inert gas** atmosphere or **vacuum**
- **Autonomous** operation by infrared **remote control**
- Available for nearly **all ZEISS FE-SEMs** equipped with a ZEISS airlock





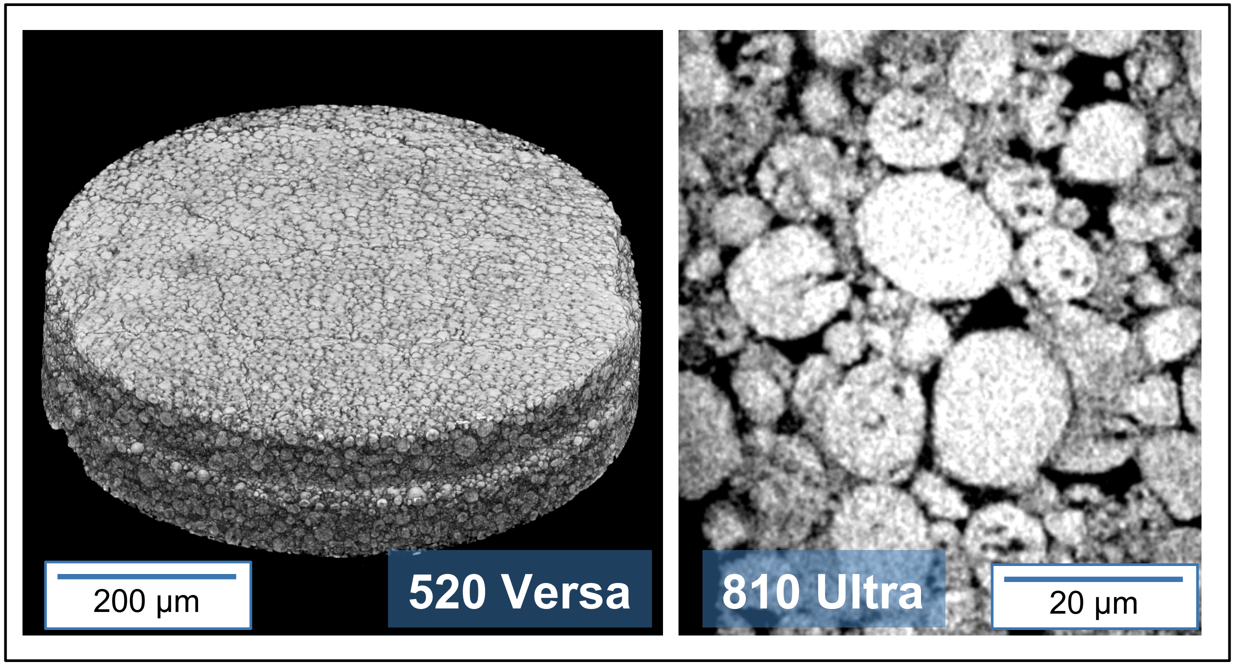


# ZEISS X-ray Microscopy

*Non-Destructive 3D/4D Imaging of Battery Evolution*

ZEISS

- **Highest 3D resolution for non-destructive imaging**
- Enables time-resolved (4D) studies of microstructure evolution
- **Highest contrast for segmenting materials**
- Particles vs. pores, separator vs. air




NCA Cathode→ Sub Micron to nanoscale resolution

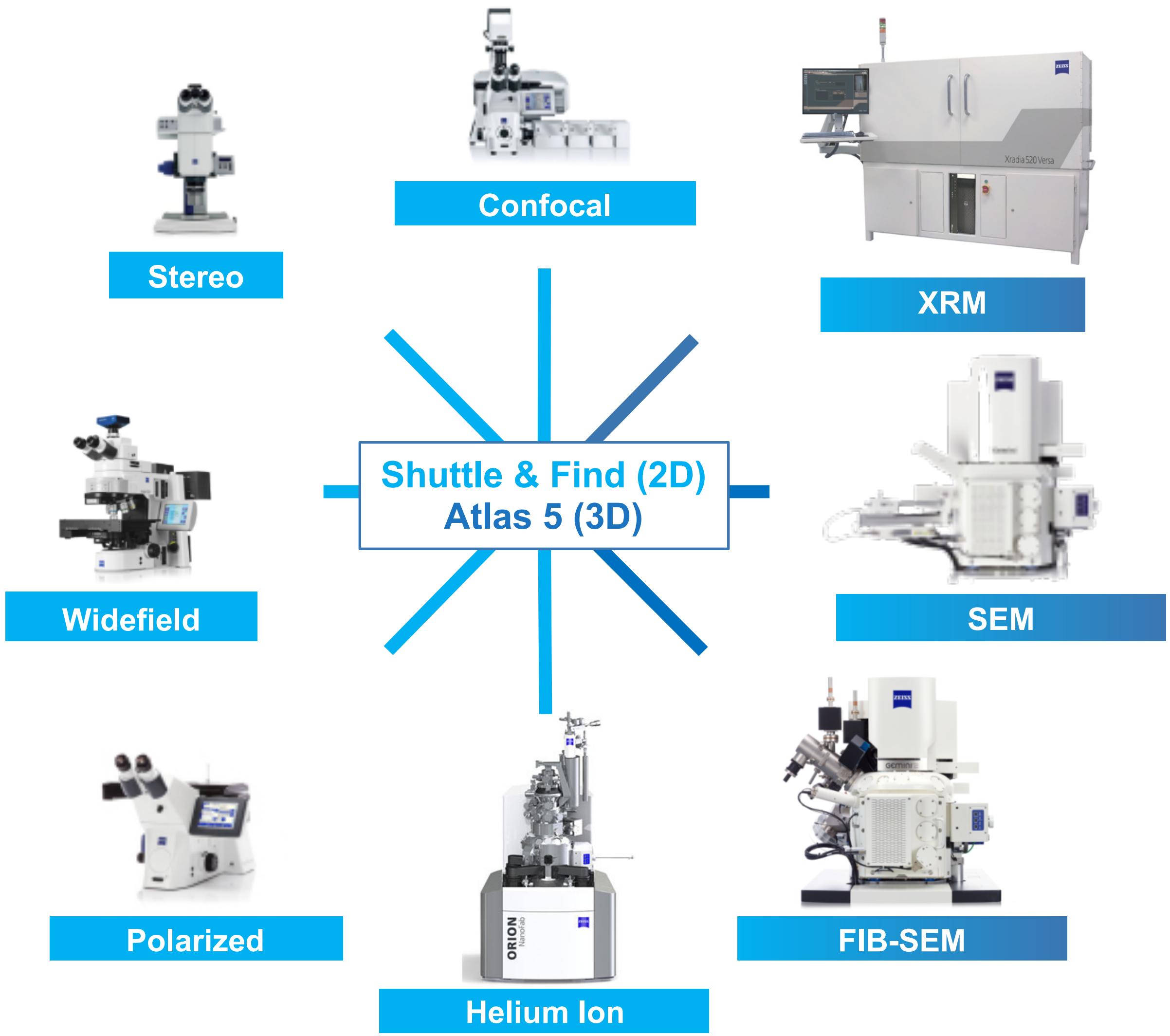
**Xradia Versa Family**

0.7 µm Resolution
70 nm Minimum Voxel

**Xradia 810 Ultra**

50 nm Resolution
16 nm Minimum Voxel

# **ZEISS Correlative Microscopy**
## Mastering the Multi-scale Challenge




- Datasets from various sources (instruments, modalities, resolutions) may be imported and co-registered in 2D and 3D.
- **Shuttle & Find** links the light microscopy workflows with electron microscopy, providing easy ROI co-registration for correlative microscopy.
- **Atlas 5** ***uniquely*** performs advanced on-line control of acquisition for ZEISS SEM and Crossbeam systems, boosting productivity and enabling new science.

# ORS Visual SI Advanced
## Complete Visualization and Processing Solution

### Full featured 3D Visualization and Data Analysis platform

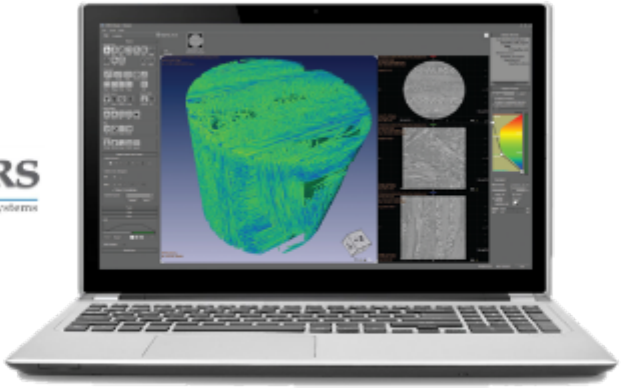
- Highly interactive and user-friendly
- Implement your workflow start to finish
- Find quantitative answers
- Tell compelling visual stories through rich graphics and movies

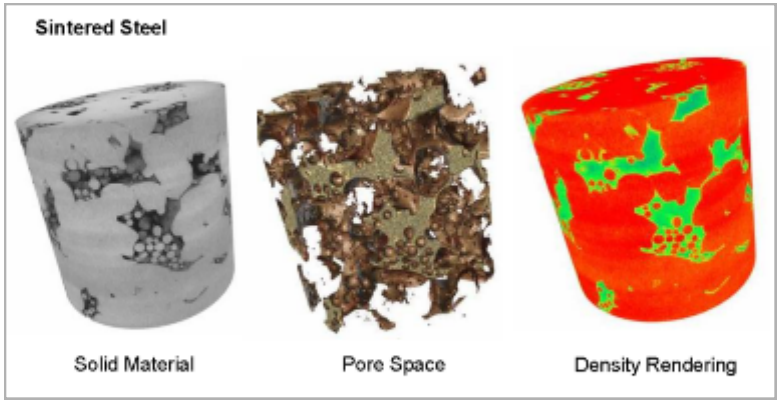



### Engineered to support the needs of XRM, FIB-SEM, and SEM microscopists

- Real-time, high impact 3D volume renderings
- Transparency, texture, and lighting features
- 32-bit color depth
- User friendly image inspection and analysis tools
- Easy-to-use image segmentation and analysis including:
  - Pore connectivity
  - Porosity
- Flexible volume and surface area analysis
- Volume and mesh picking in 2D and 3D
- Measure and annotate graphics
- Create, edit, and export movies
- Flexible data import/export utilities

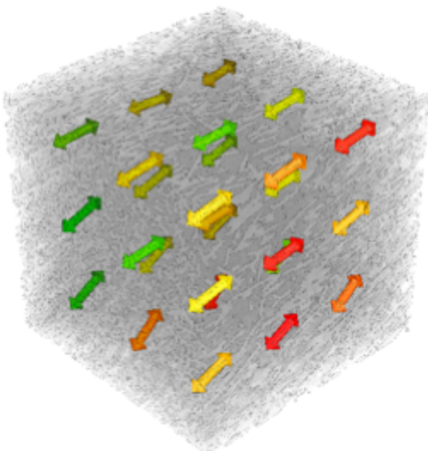
ORS object research systems

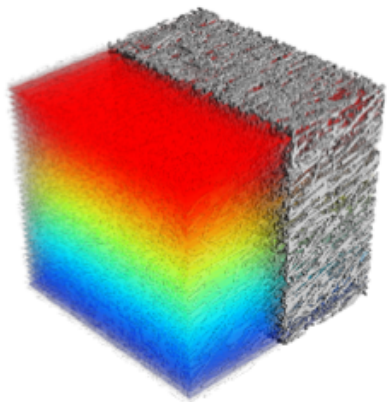


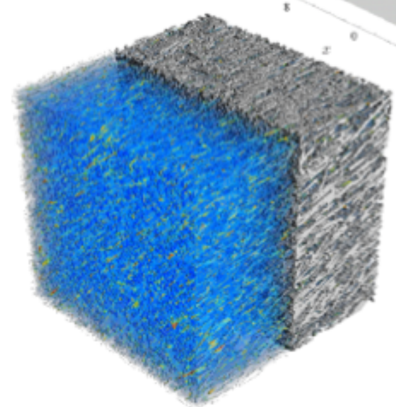


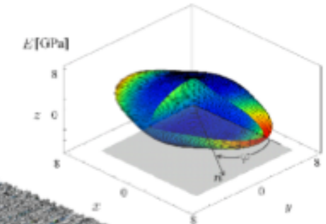
# Math2Market GmbH, GeoDict
# Digital Experiments on CT-Scans

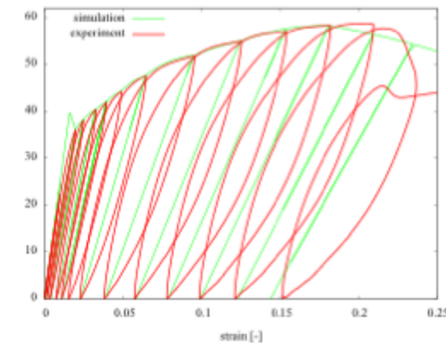
Visit us at: www.geodict.com












| Geometrical Parameters | Flow & Conduction Parameters | Mechanical Parameters | Large Deformation, Damage & Failure |
|---|---|---|---|
| ■ Fiber volume fraction | ■ Absolute permeability | ■ Elastic moduli | ■ Hyperelastic materials |
| ■ Fiber diameters | ■ Thermal conductivity | ■ Stiffness tensor | ■ Plastic deformations |
| ■ Fiber orientation | ■ Electrical conductivity | ■ Full anisotropy | ■ Viscous effects |
| ■ 3d structure modelling | ■ Tortuosity | ■ Thermal expansion | ■ Failure and damage |
| | ■ Diffusivity | ■ Stress-Strain curves | ■ Structure change |

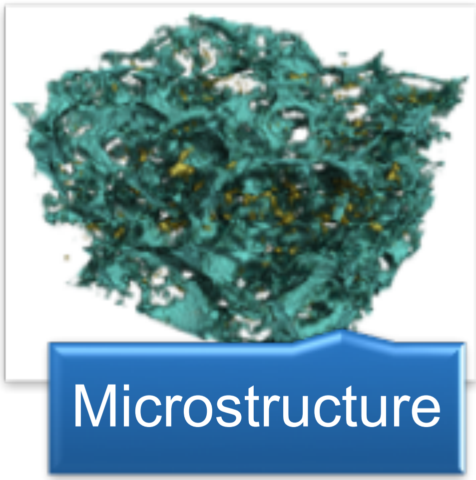
GeoDict

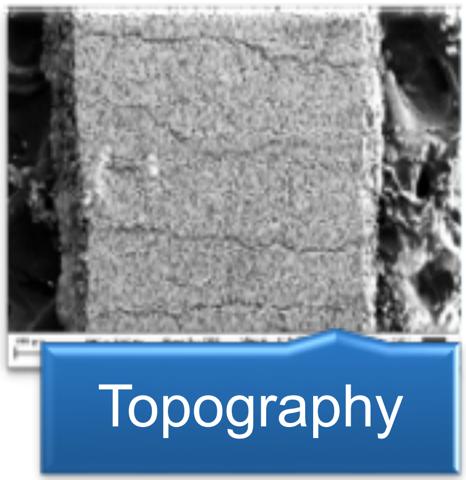


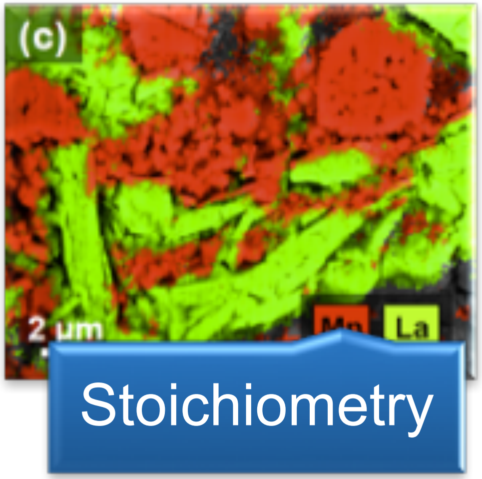


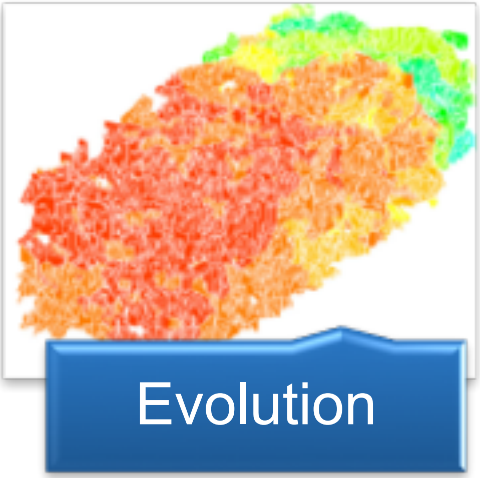
MATH 2 MARKET

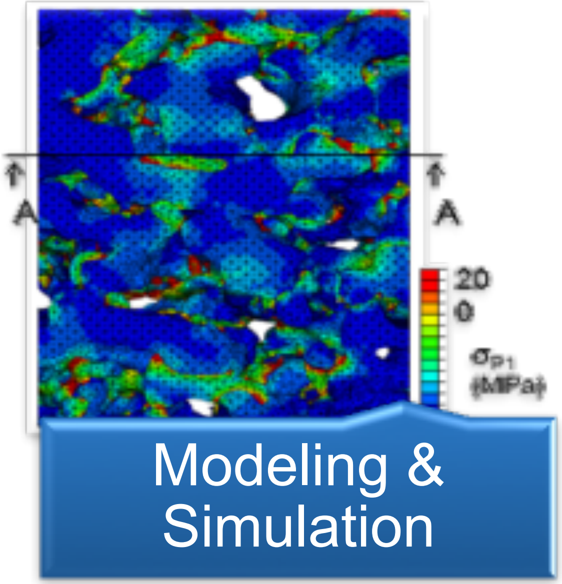
# Battery Characterization Overview

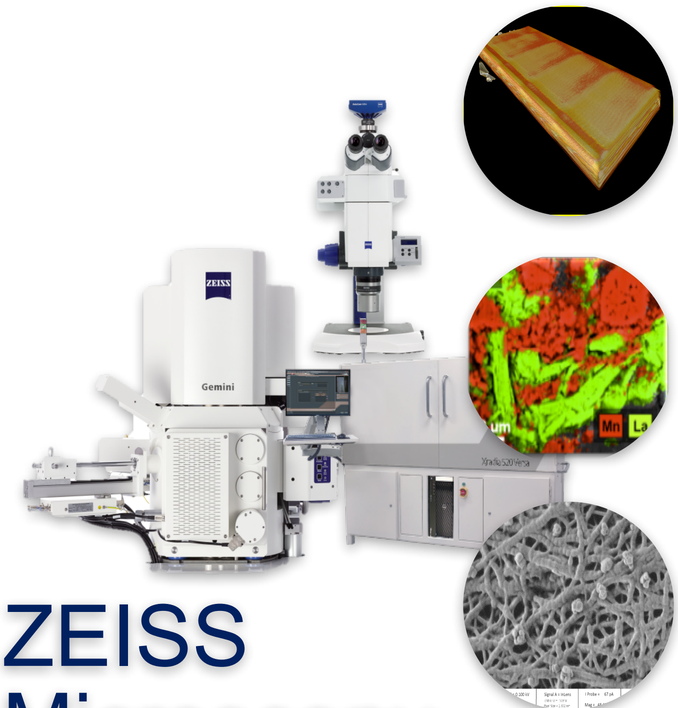


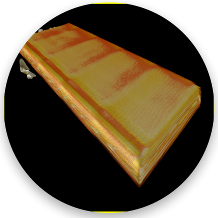



Package

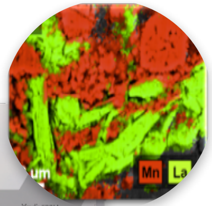
Electrode

Separator

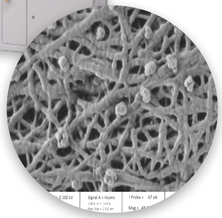
ZEISS Microscopy

Package




Electrode



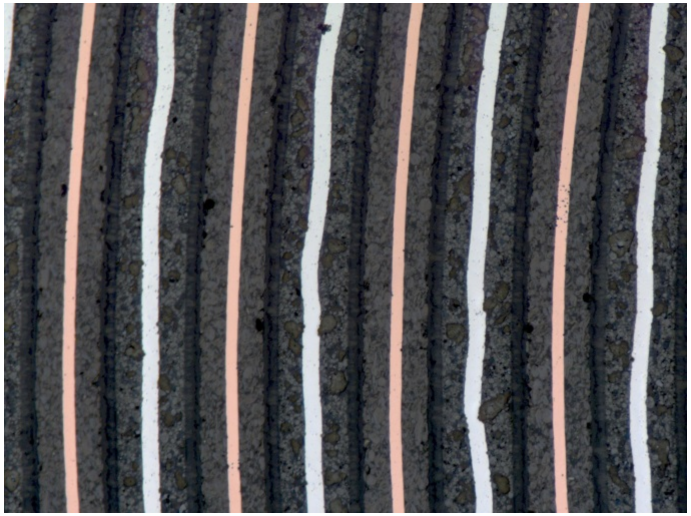
Separator

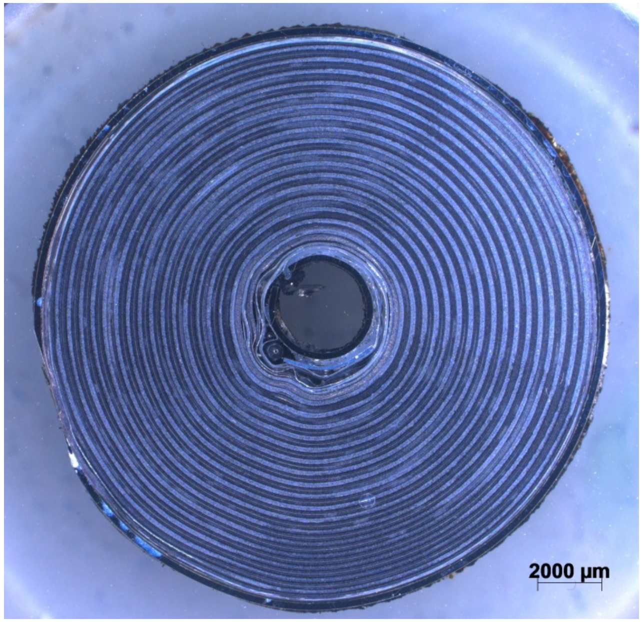
ZEISS
Microscopy

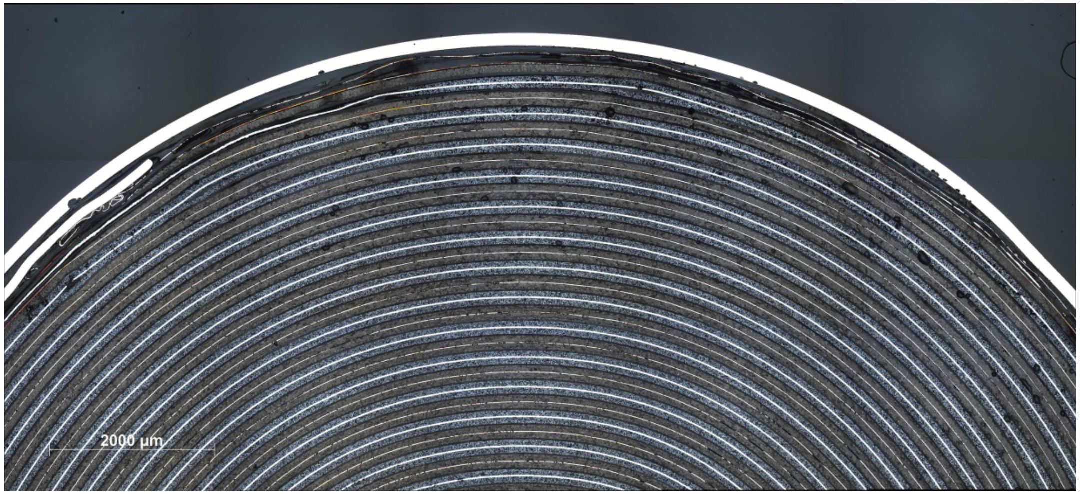
# **High-Resolution Inspection of Sectioned Cell**
## With Brightfield Stereo Microscopy

- Lithium-ion battery inspected after polishing
- Brightfield microscopy with **Axio Zoom.V16**

- Geometric architecture of electrodes
- Details such as the thickness and integrity of active material layers, current collectors, and separators are visible





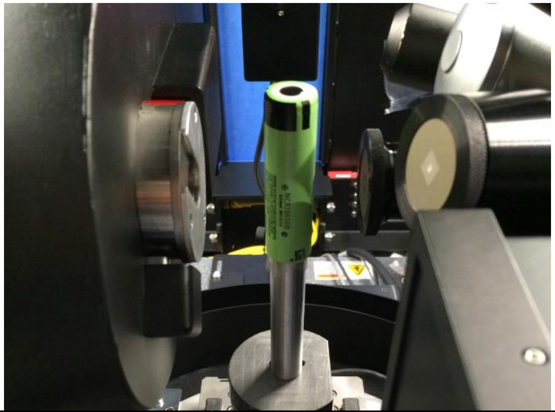

**Sample courtesy of T. Bernthaler, Materials Research Institute Aalen, Germany.**

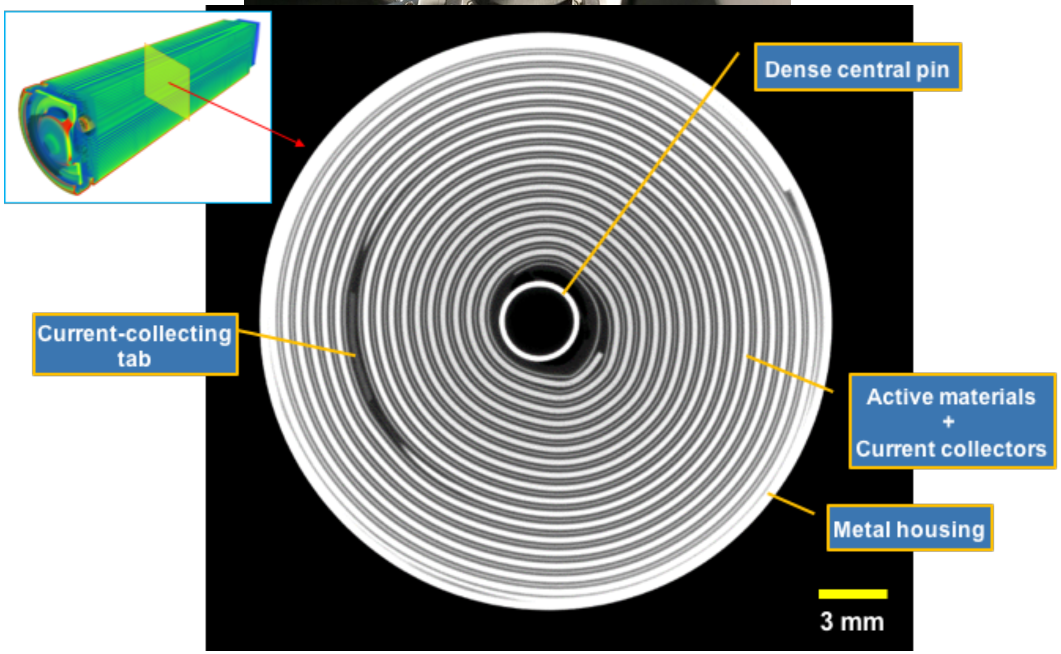
# Commercial 18650 Battery
## Full Battery Inspection

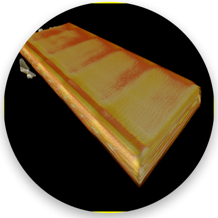
- Specimen imaged **non-destructively** with **520 Versa XRM**.

- The XRM technique allows specimens to be imaged intact, providing **high-resolution** data **without sectioning**.

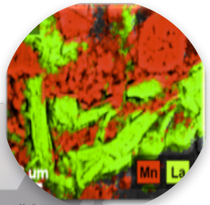
- Workflow:
  1. **Inspect** the specimens
  2. **Identify** regions for higher resolution analysis
  3. **Drive** the microscope to enlarge those regions



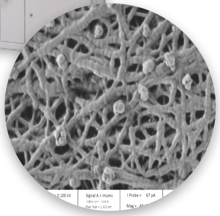




Package




Electrode



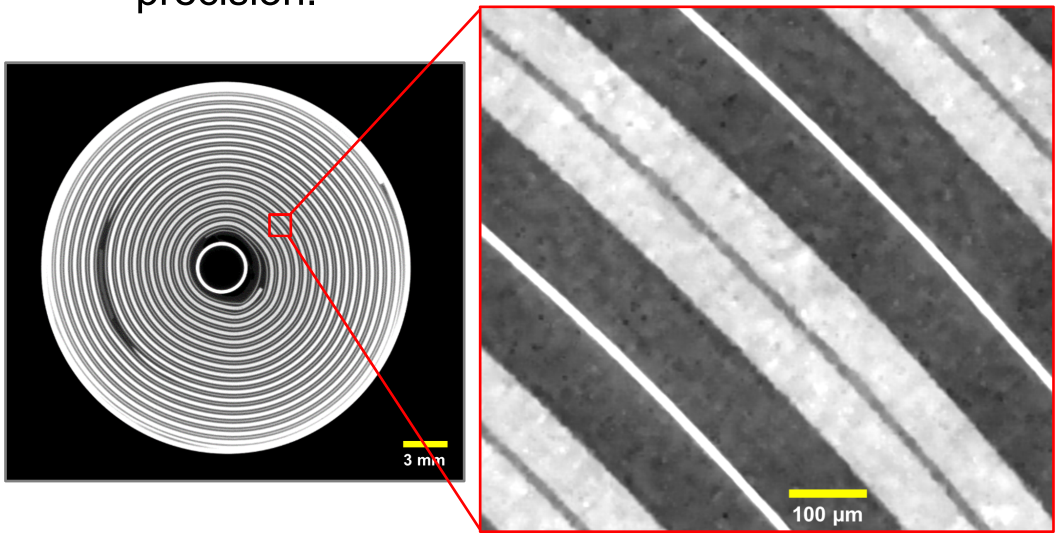
Separator


ZEISS
Microscopy

# Non-destructive Imaging: Central Section
1.8 µm Voxel Size

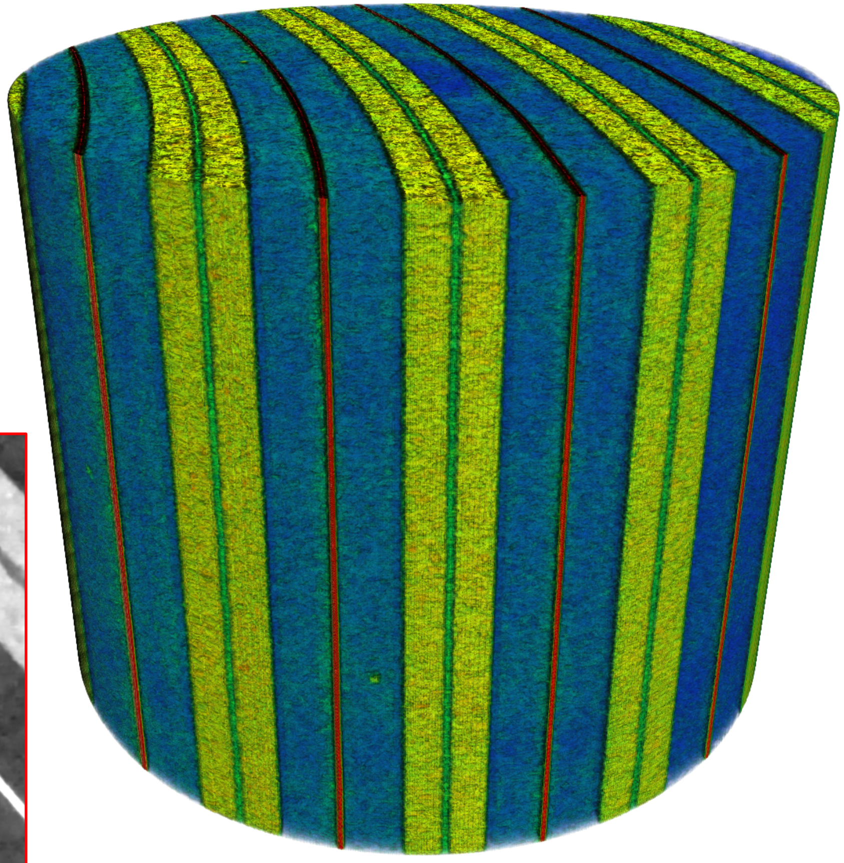
## Zeiss Xradia 520 Versa

- A small region of jelly-roll near the central pin was arbitrarily selected for higher-resolution X-ray imaging.
  - Voxel size: 1.8 µm
- This allowed the different layers to be **non destructively** inspected with higher precision.

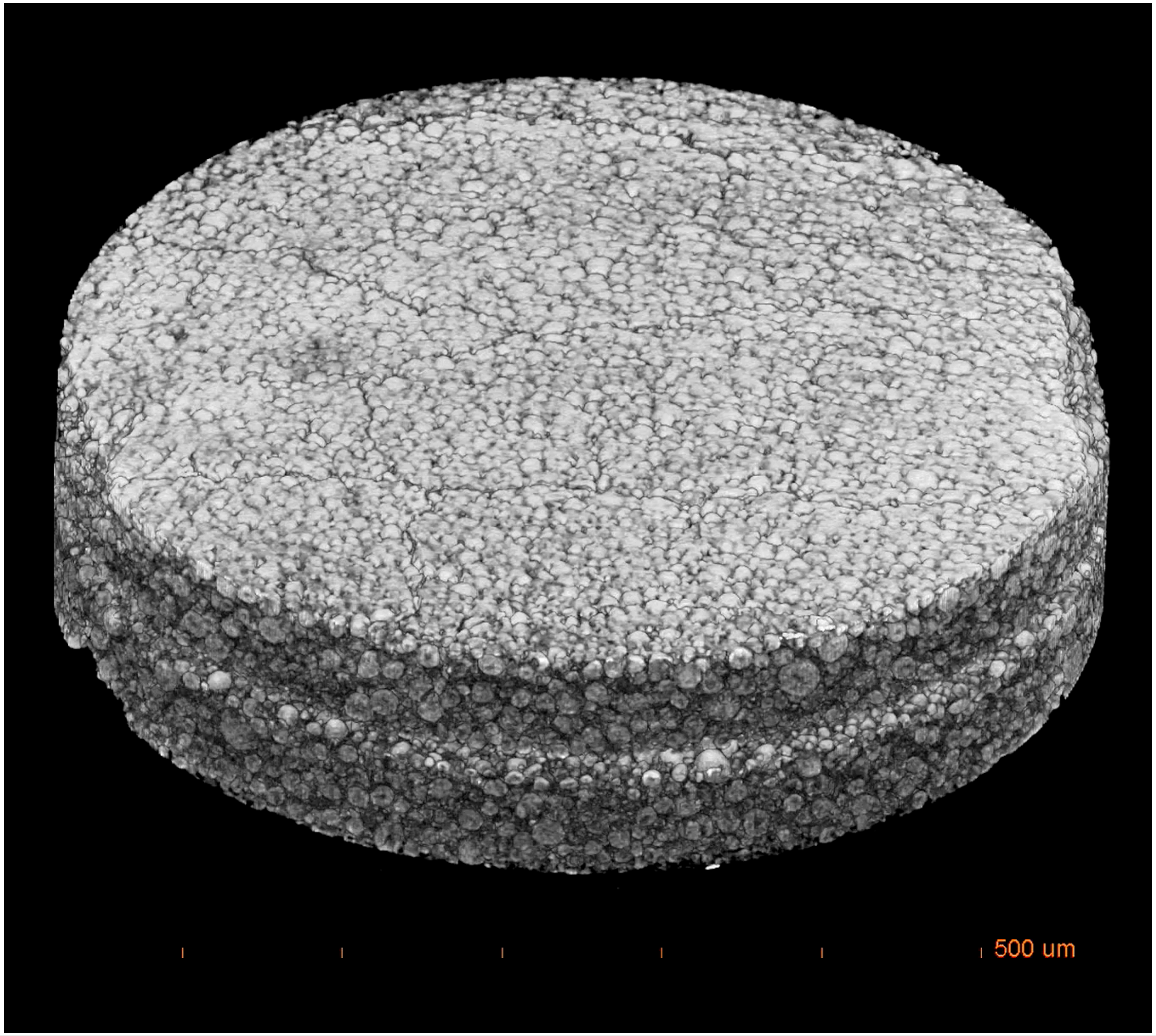



Virtual Slices from the 3D Volume

3D Volume Rendering



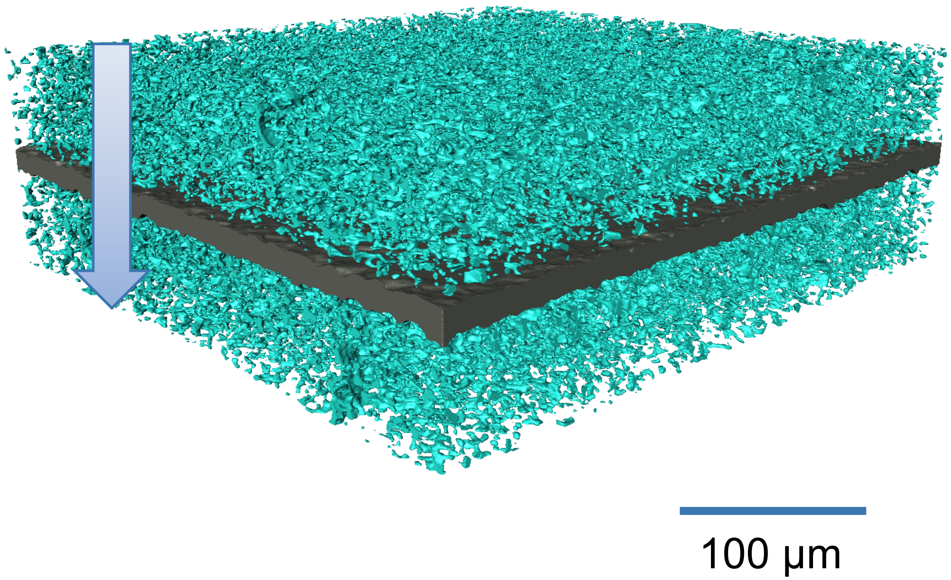
# **520 Versa Imaging: NCR-18650B**
Depackaged Cathode (350 nm Voxel Size)

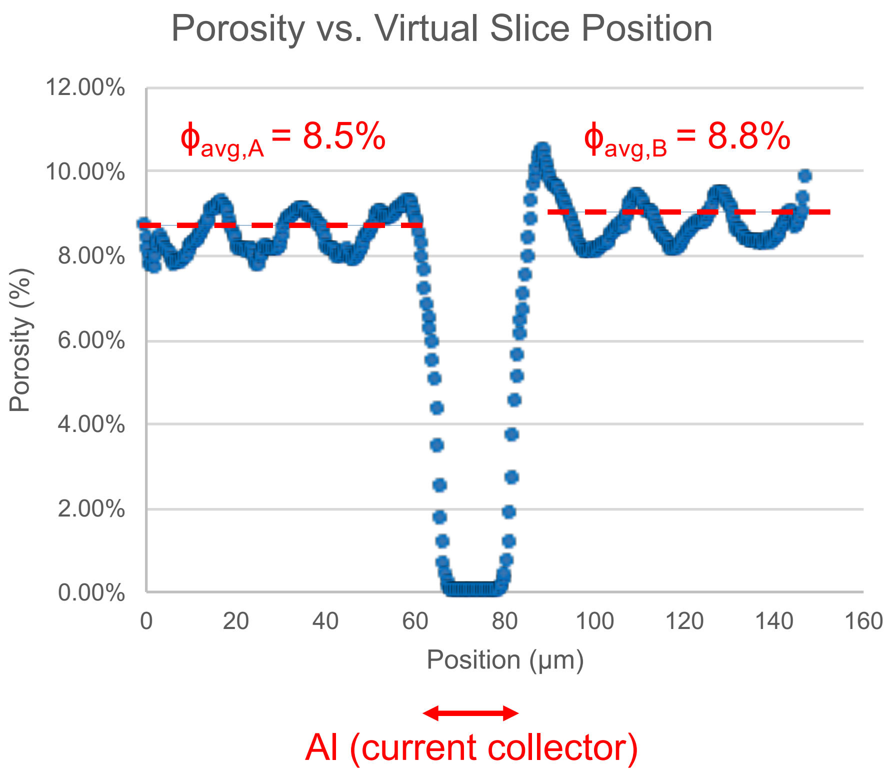



Voxel size:
350 nm

# 520 Versa Imaging: NCR-18650B
Depackaged Cathode (350 nm Voxel Size)

*Porosity quantified on a slice-by-slice basis:*

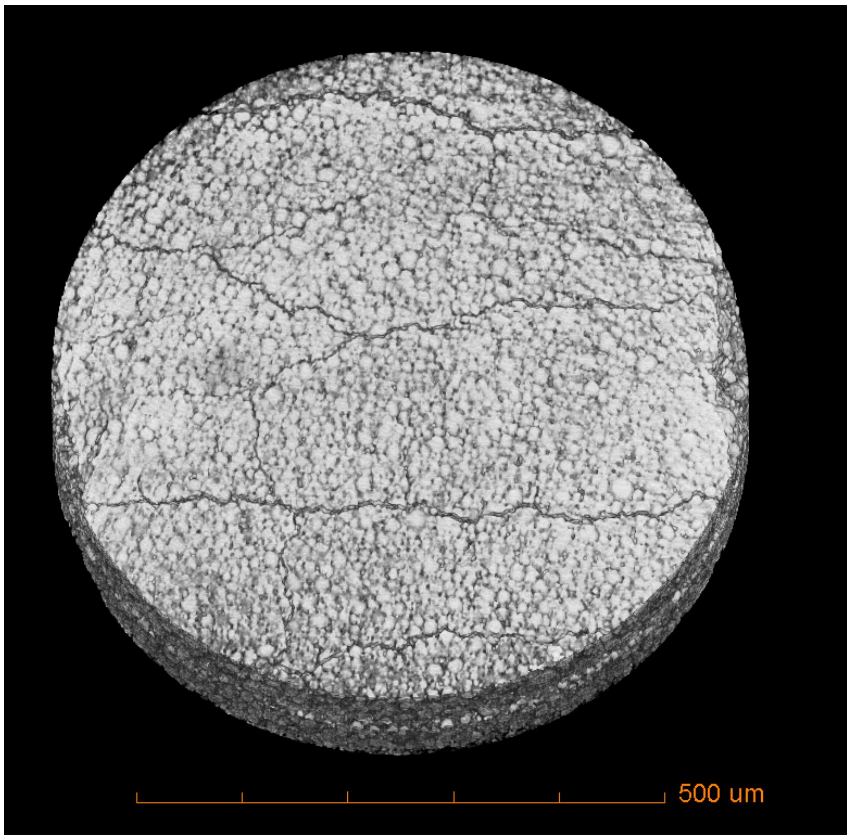


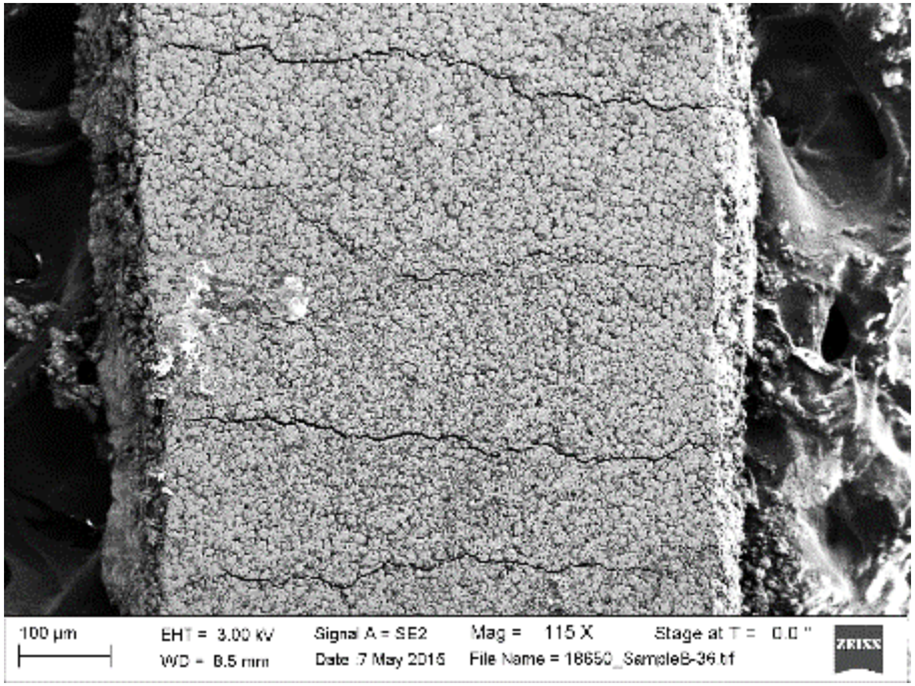
# **18650 Cathode**
# Correlating XRM with FE-SEM


+


## 520 Versa (XRM)

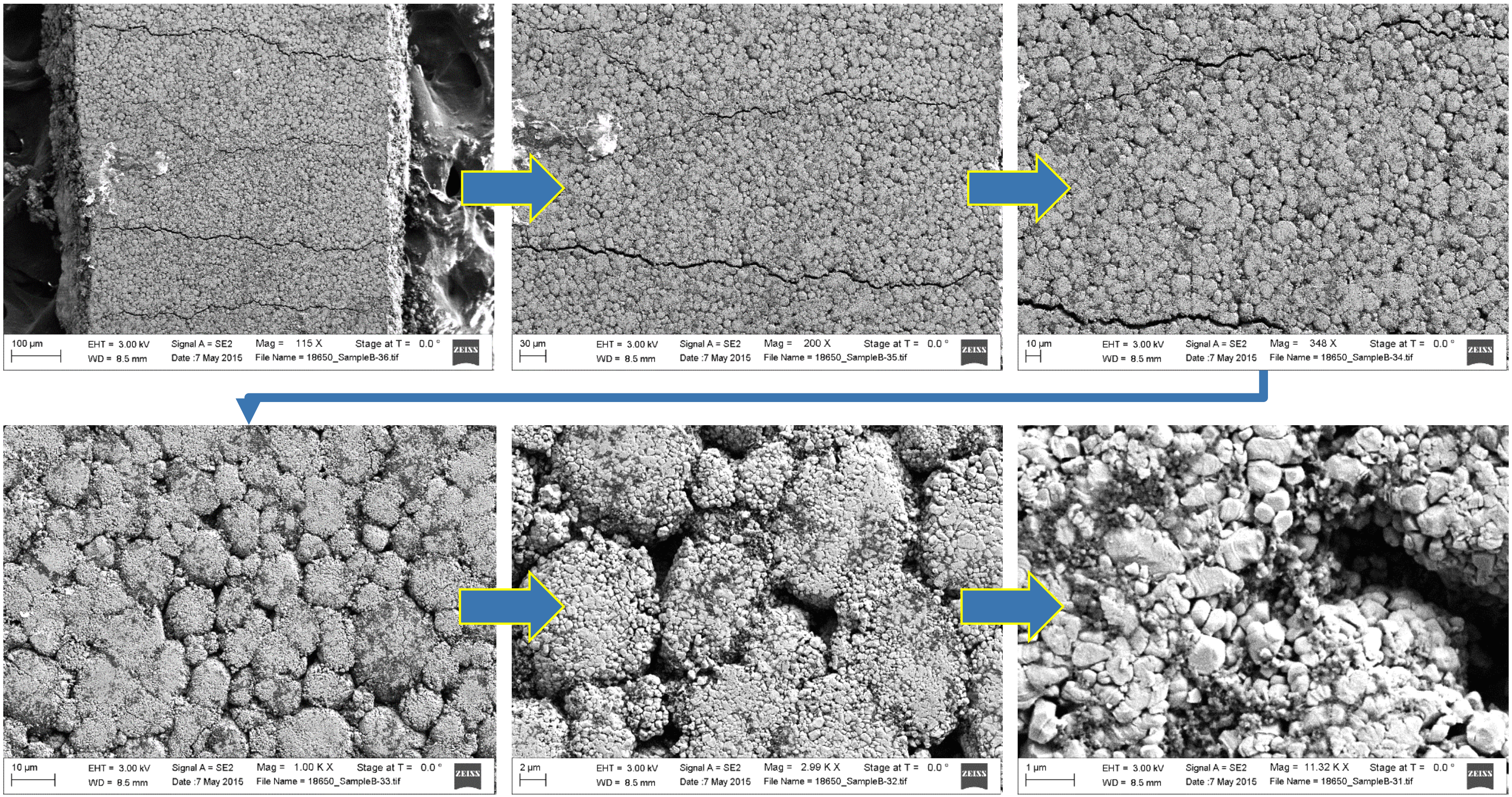



## Sigma (FE-SEM)



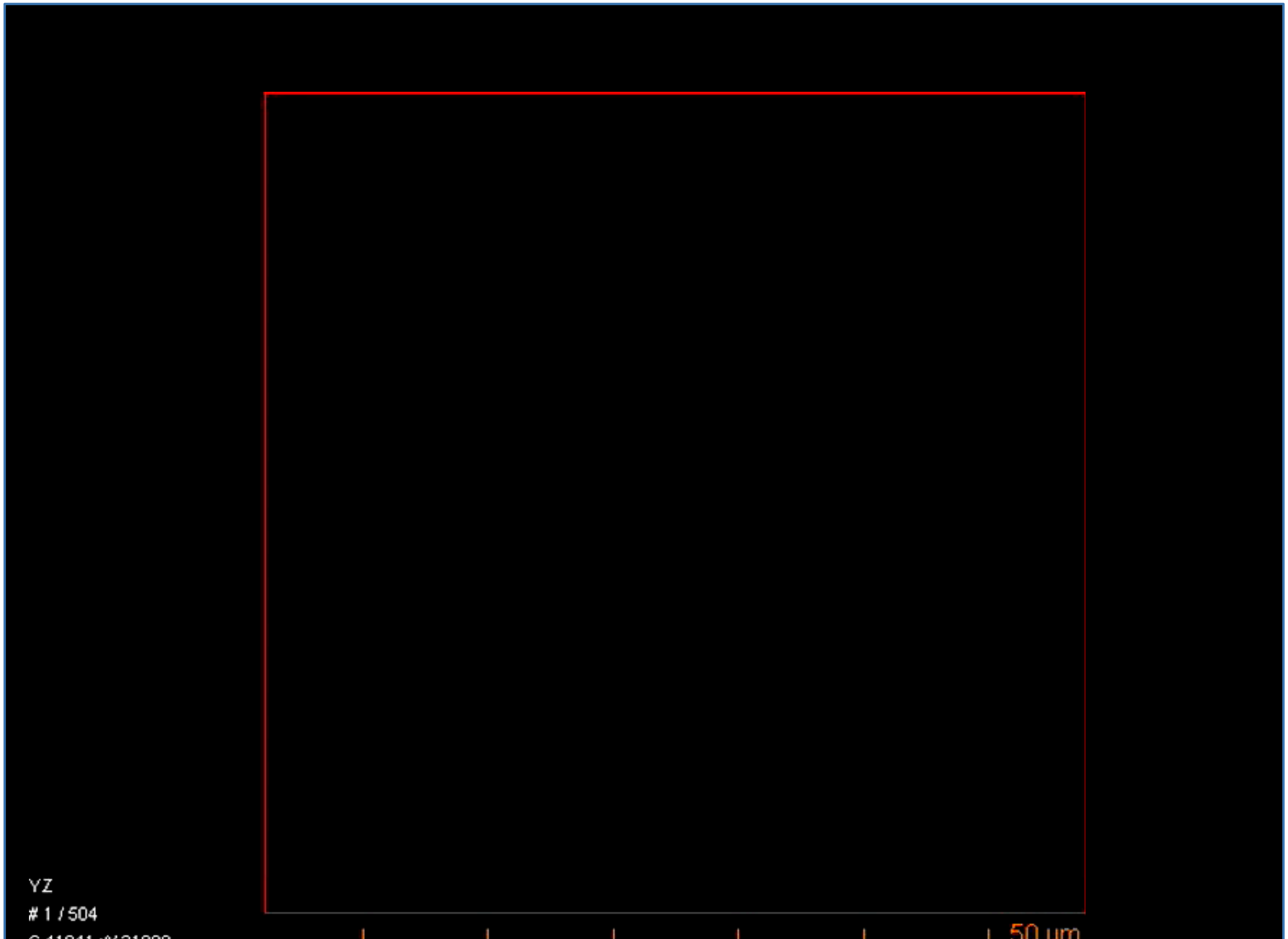
# **18650 Cathode**
## Multi-Scale Imaging with FE-SEM

Data collected with Sigma FE-SEM:



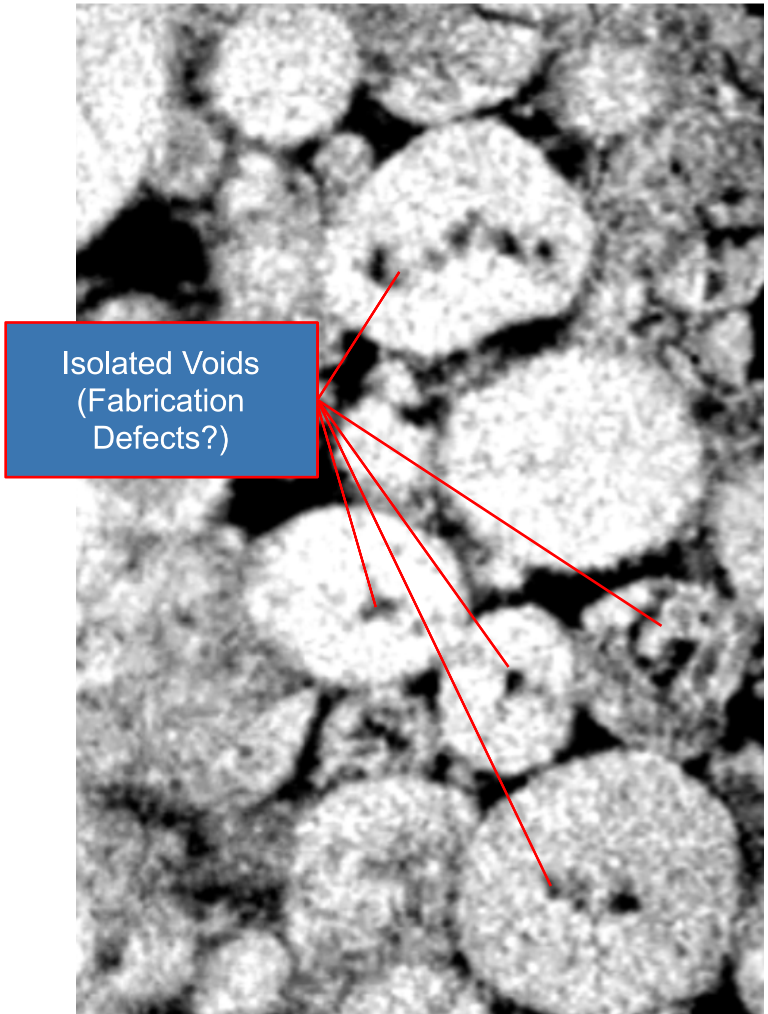
# **Ultra Imaging: NCR-18650B**
## Depackaged Cathode (130 nm Voxel Size)

**Zeiss Xradia 810 Ultra**

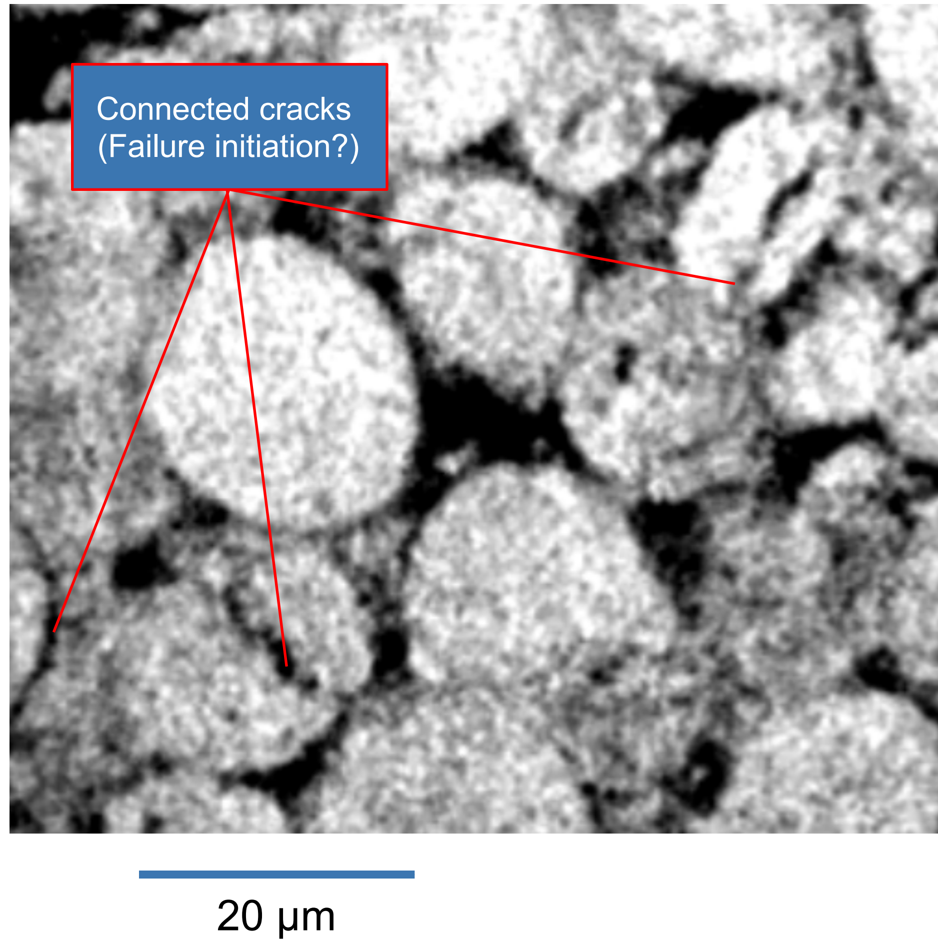



10 µm

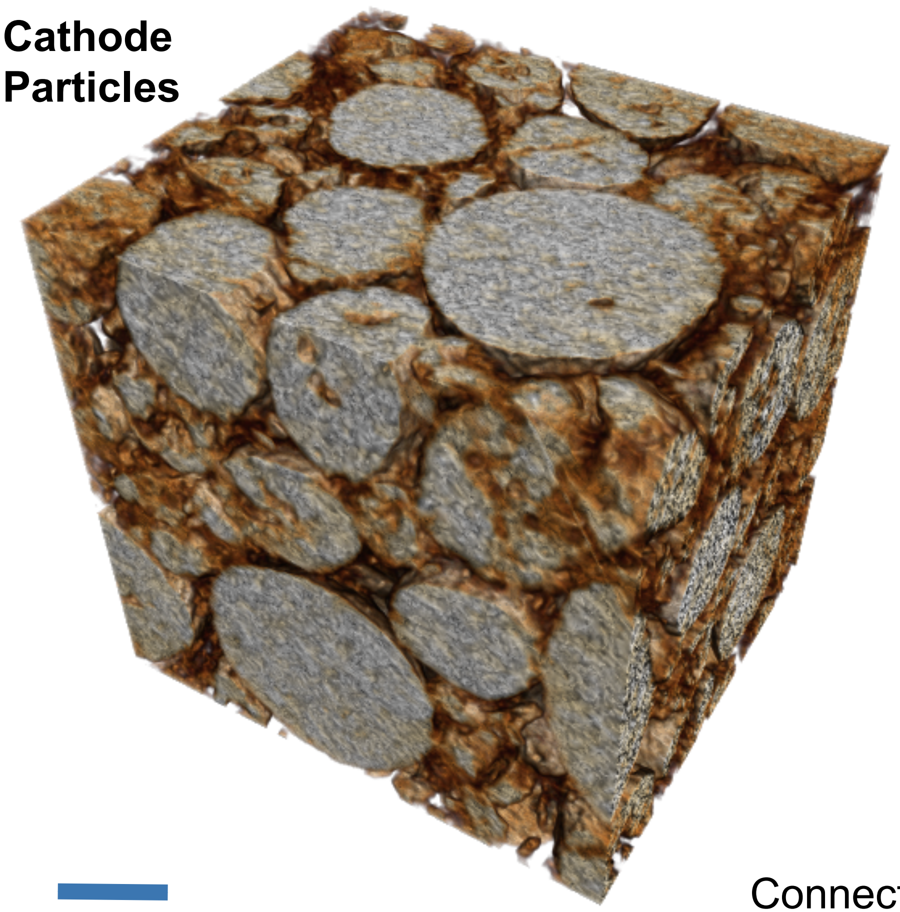
# **Ultra Imaging: NCR-18650B**
# Depackaged Cathode (130 nm Voxel Size)

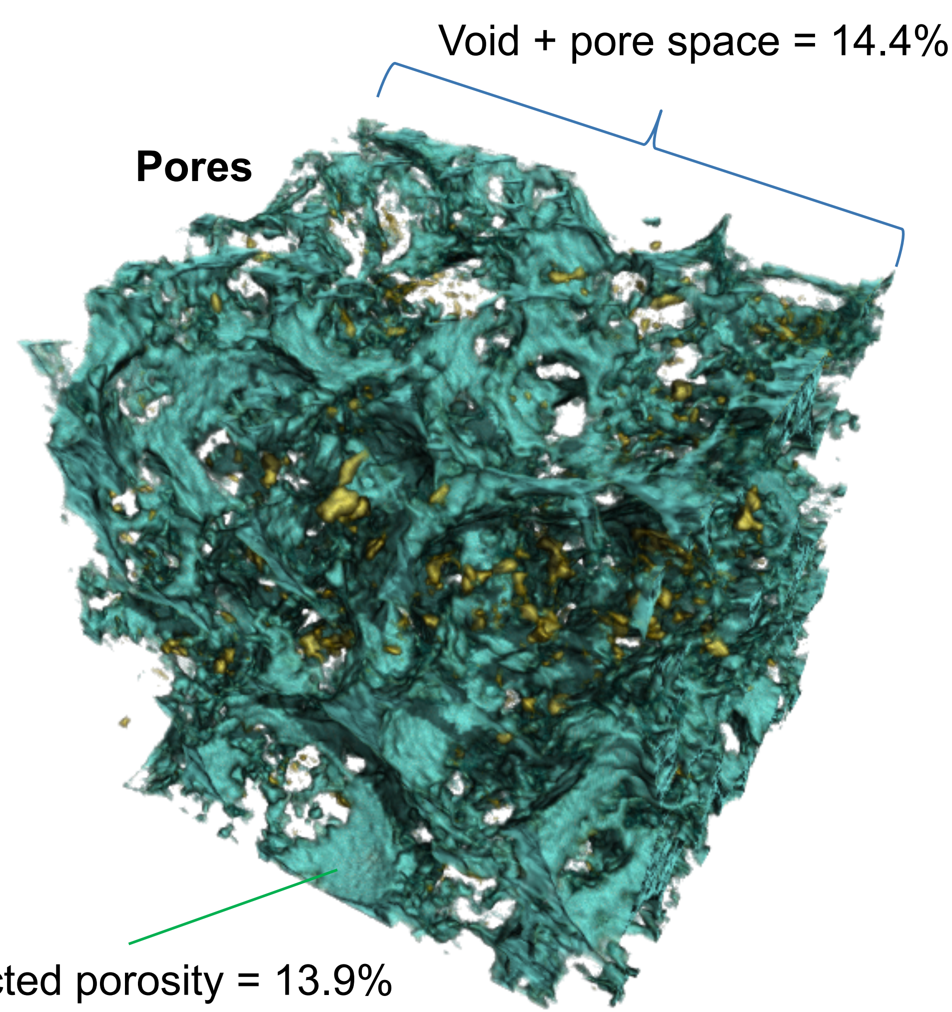



**Zeiss Xradia 810 Ultra**



# Ultra Imaging: NCR-18650B
Depackaged Cathode Segmentation



# Tortuosity: How "tortuous" (curved) is the path?

Tortuosity (τ) is defined as the **ratio** of **length of the path** (L) to the **distance between the ends** (C):

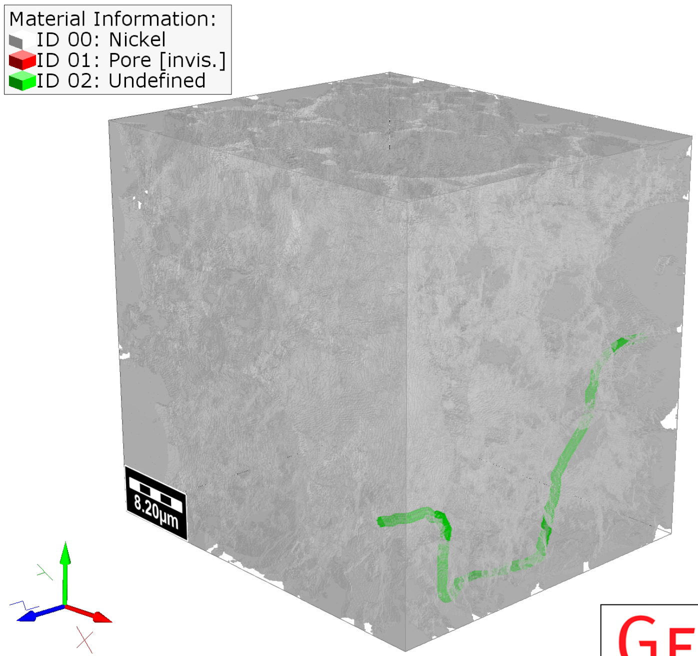
$$\tau = \frac{L}{C}$$

← Low tortuosity, τ~1

High tortuosity, τ >> 1 →

# **Percolating Pore Pathway**
130 nm Voxel Size

ZEISS

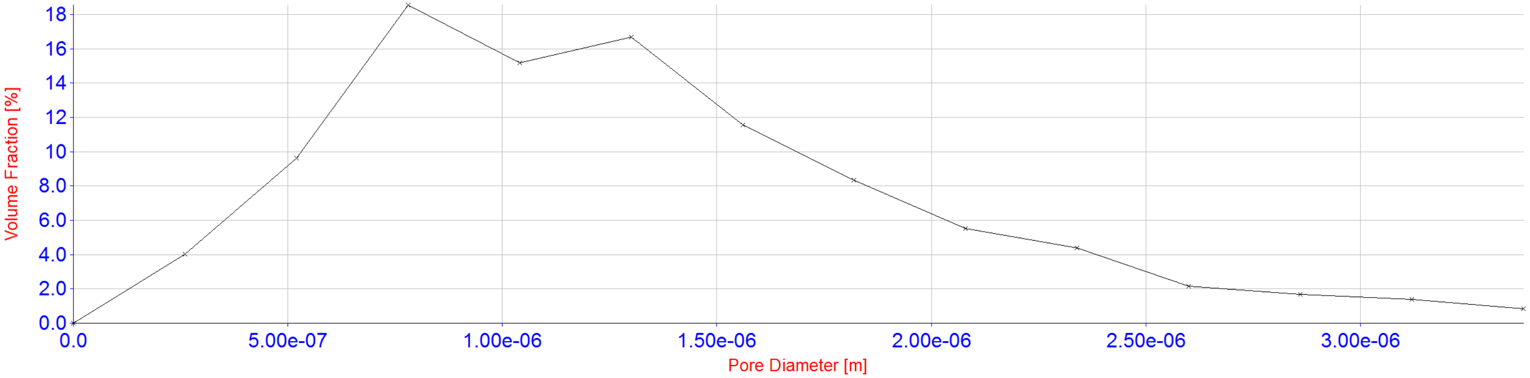



**Percolating pore pathway shaded with green**

**Pathway = ~2x straight line**

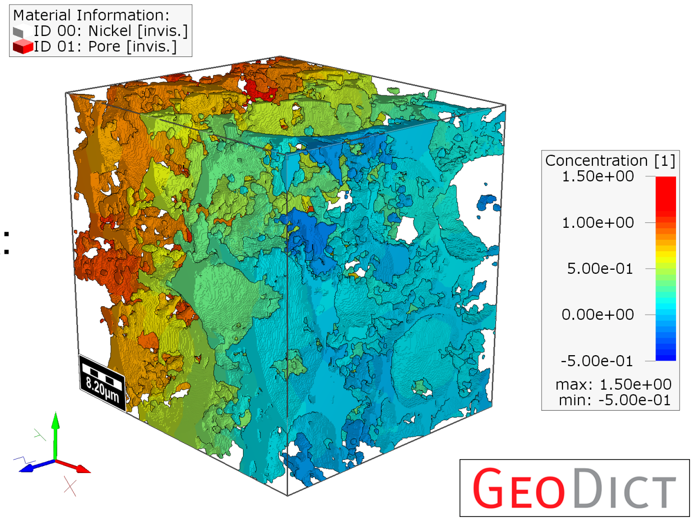
GeoDict

**Pore size distribution**

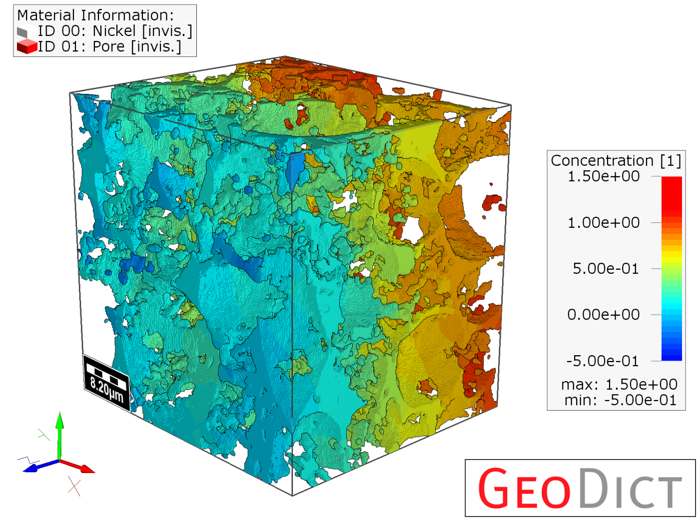


# **Diffusivity Simulations: X, Y, Z**
## 130 nm Voxel Size

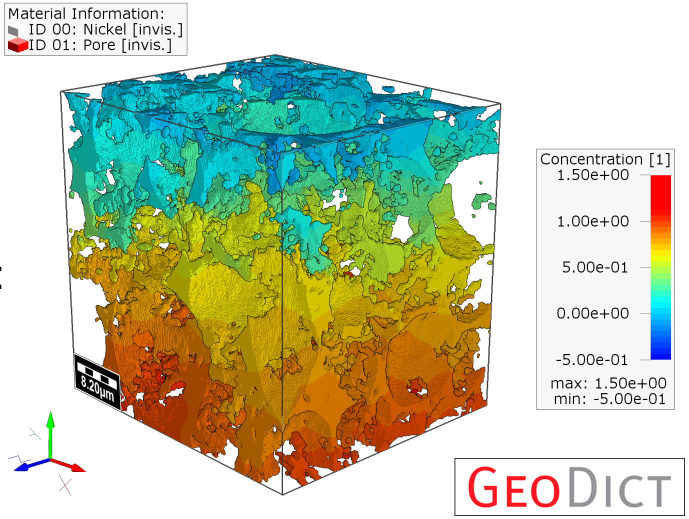
X:




Z:




Y:



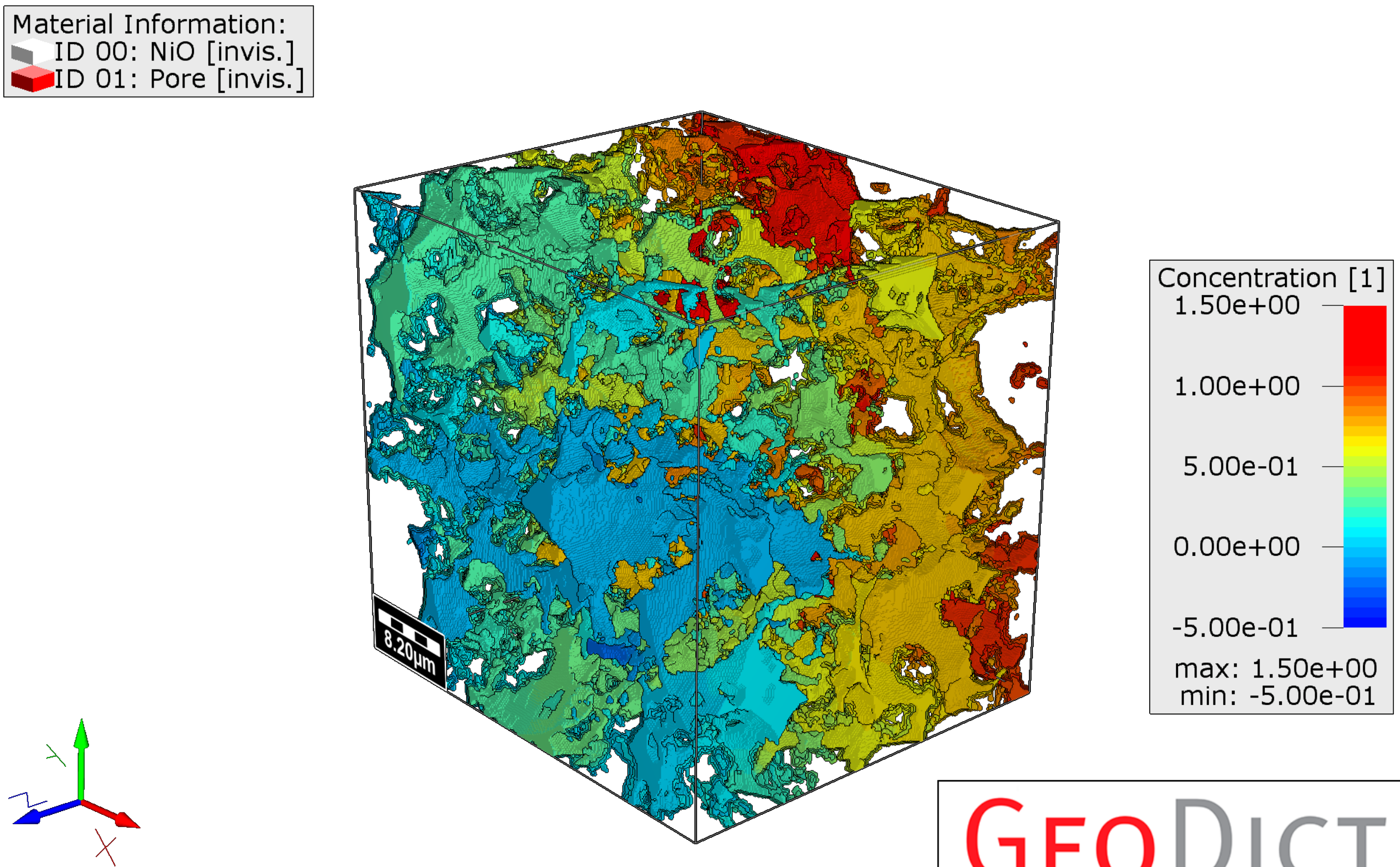

Diffusivity Tensor

| | | |
|---|---|---|
| 2.47 | 0.09 | -0.06 |
| 0.09 | 2.55 | 0.03 |
| -0.06 | 0.03 | 2.30 |

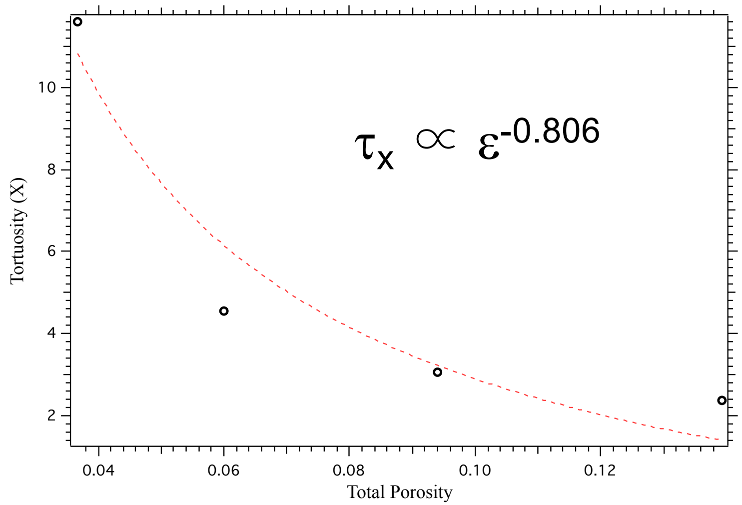
Tortuosity

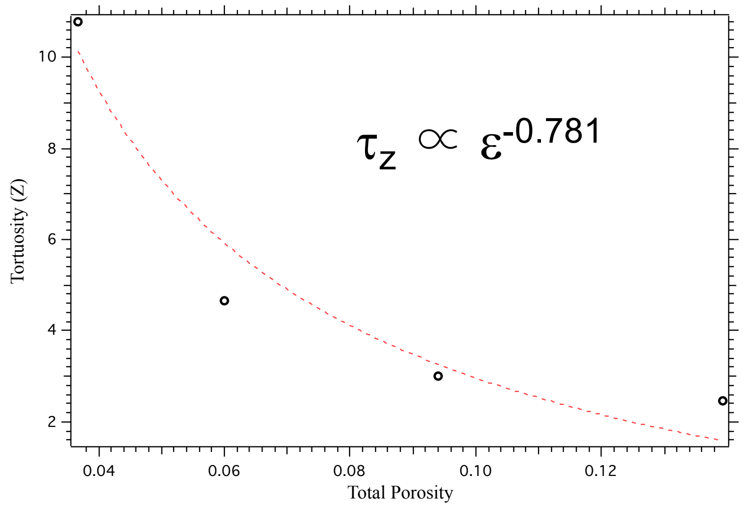
| | |
|---|---|
| Tortuosity (X) | 2.38 |
| Tortuosity (Y) | 2.34 |
| Tortuosity (Z) | 2.46 |

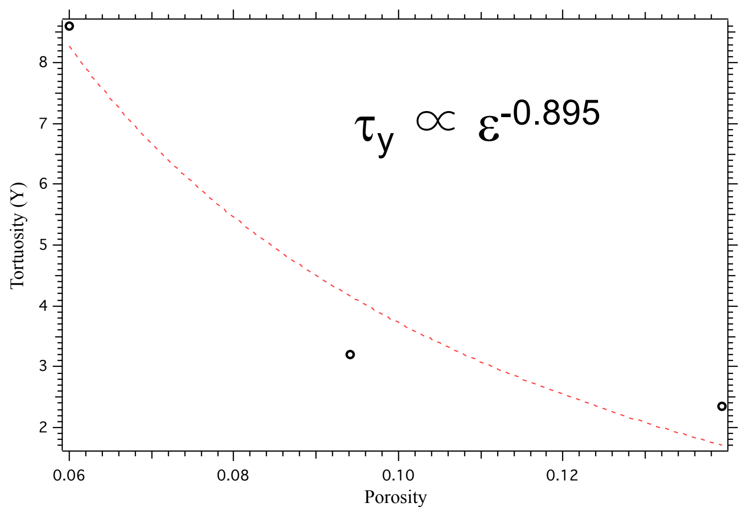
# Evolution of Tortuosity / $D_{eff}$ (Simulation)



# Tortuosity vs. Porosity – Simulation Results



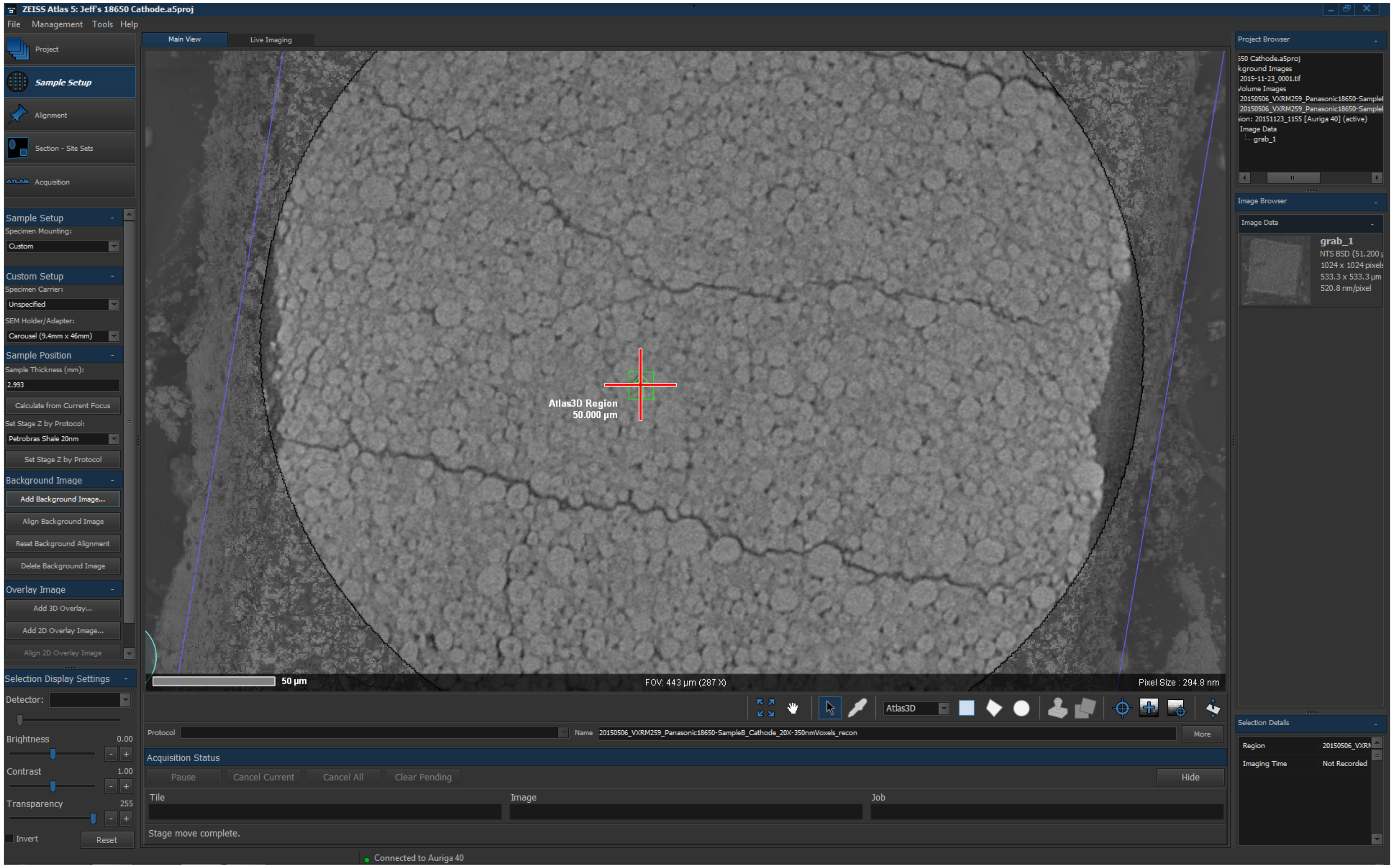




| Direction | Bruggeman Exponent |
|---|---|
| X | 0.806 |
| Y | 0.895 |
| Z | 0.781 |

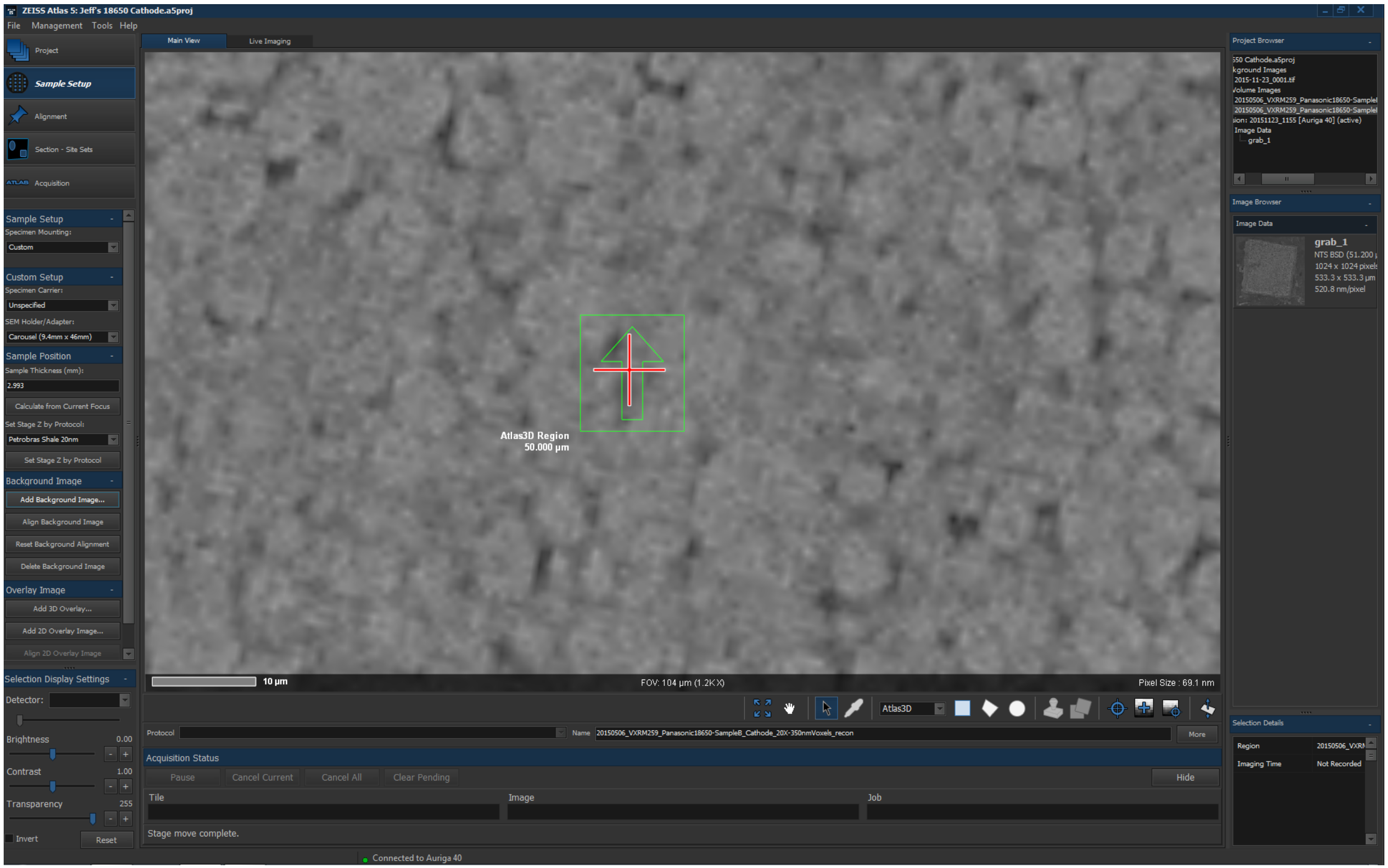
# Correlative FIB-SEM Analysis
Using Atlas 5

**XRM data was used to identify a representative region within the cathode specimen:**

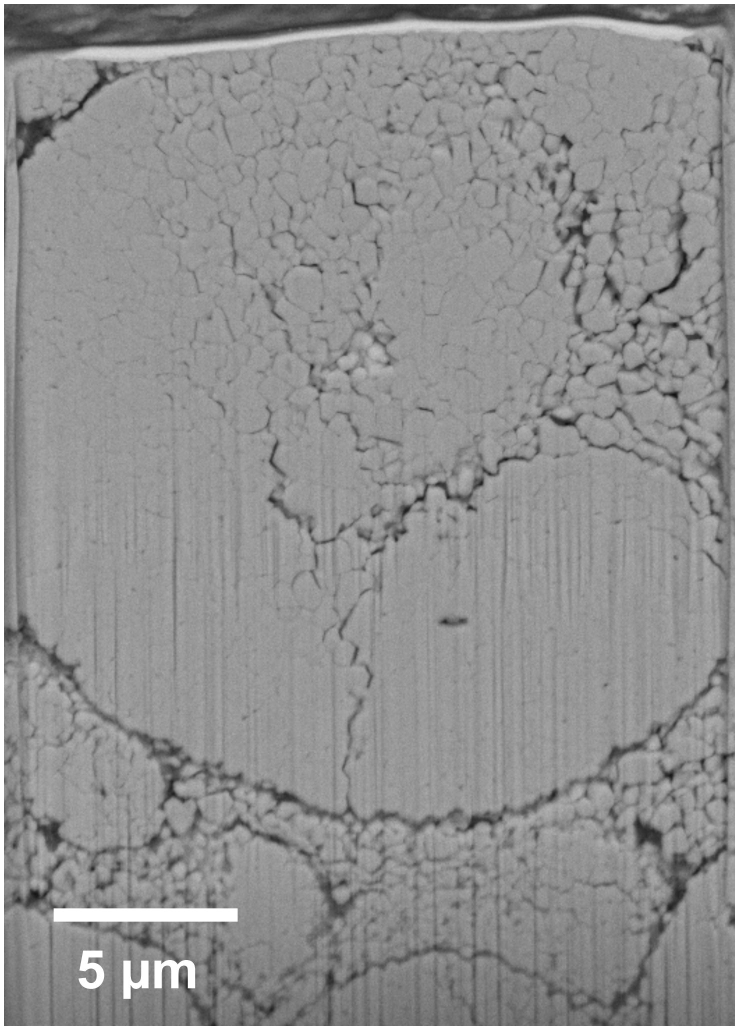


# Correlative FIB-SEM Analysis
Using Atlas 5

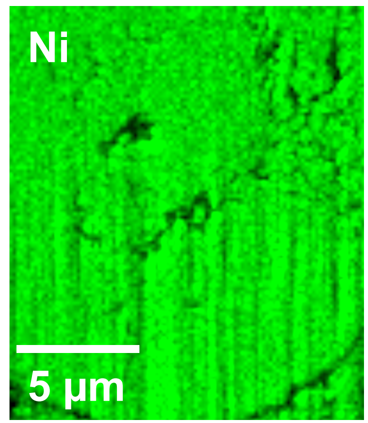
## Identified cathode particle that indicated signs of an internal crack below the surface:

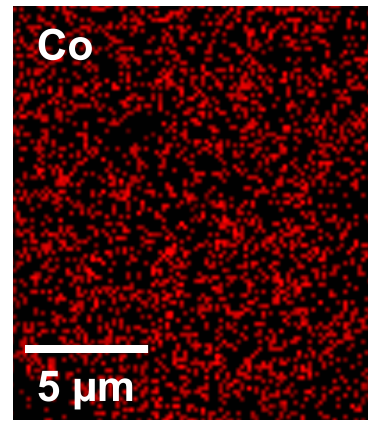


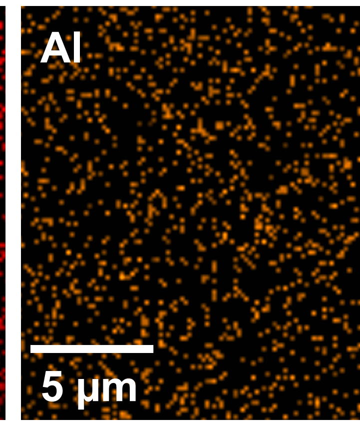
# Correlative Chemical Analysis
## Targeted ROI from XRM Data

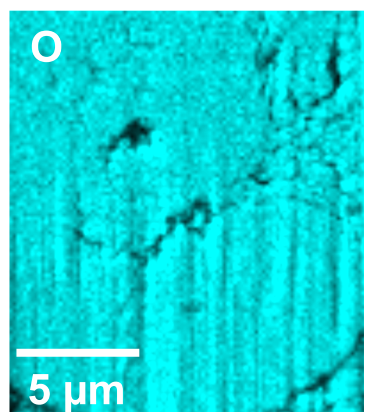



- Hayashi et. al. *JECS* (2014): $LiNi_{0.82}Co_{0.15}Al_{0.03}O_2$
- Mapped composition with EDS at 20 kV, fit to Hayashi data



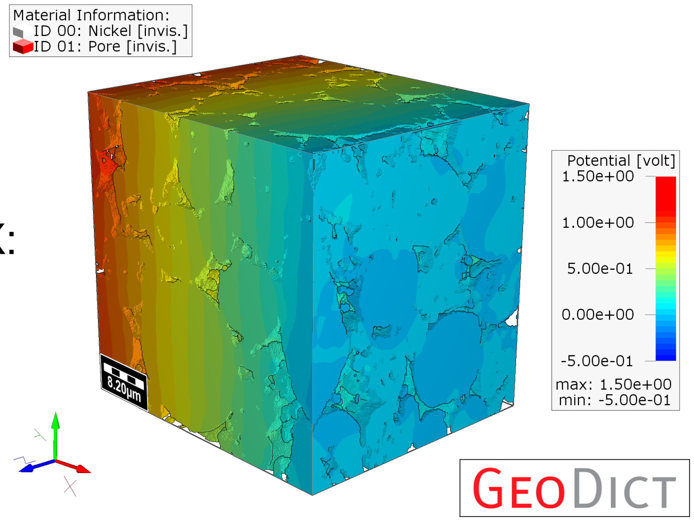




| Element | Wt% |
|---|---|
| Ni | 30% |
| Co | 7% |
| Al | 1% |
| O | 61% |

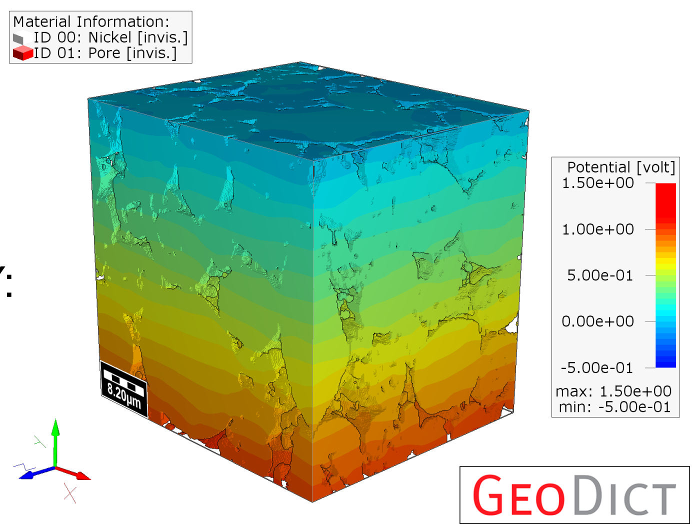
# Electrical Conductivity Simulations: X, Y, Z

130 nm Voxel Size

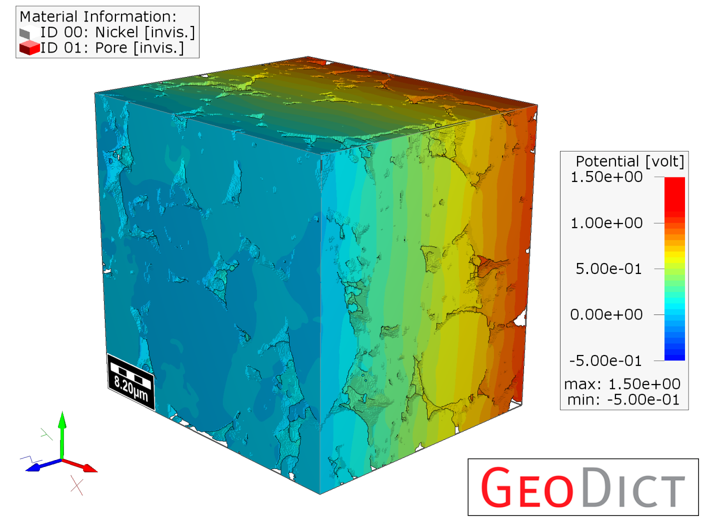
X:




Y:

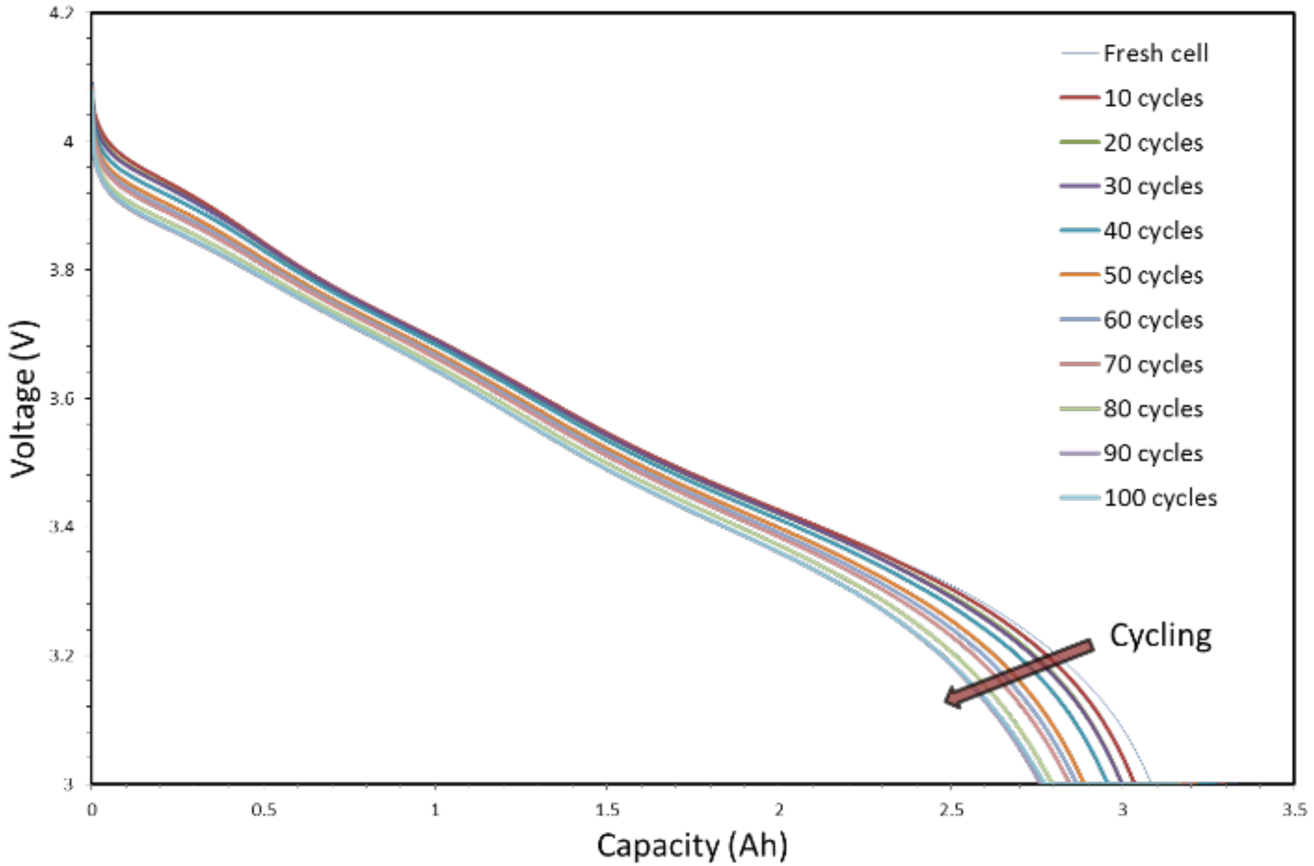



Z:

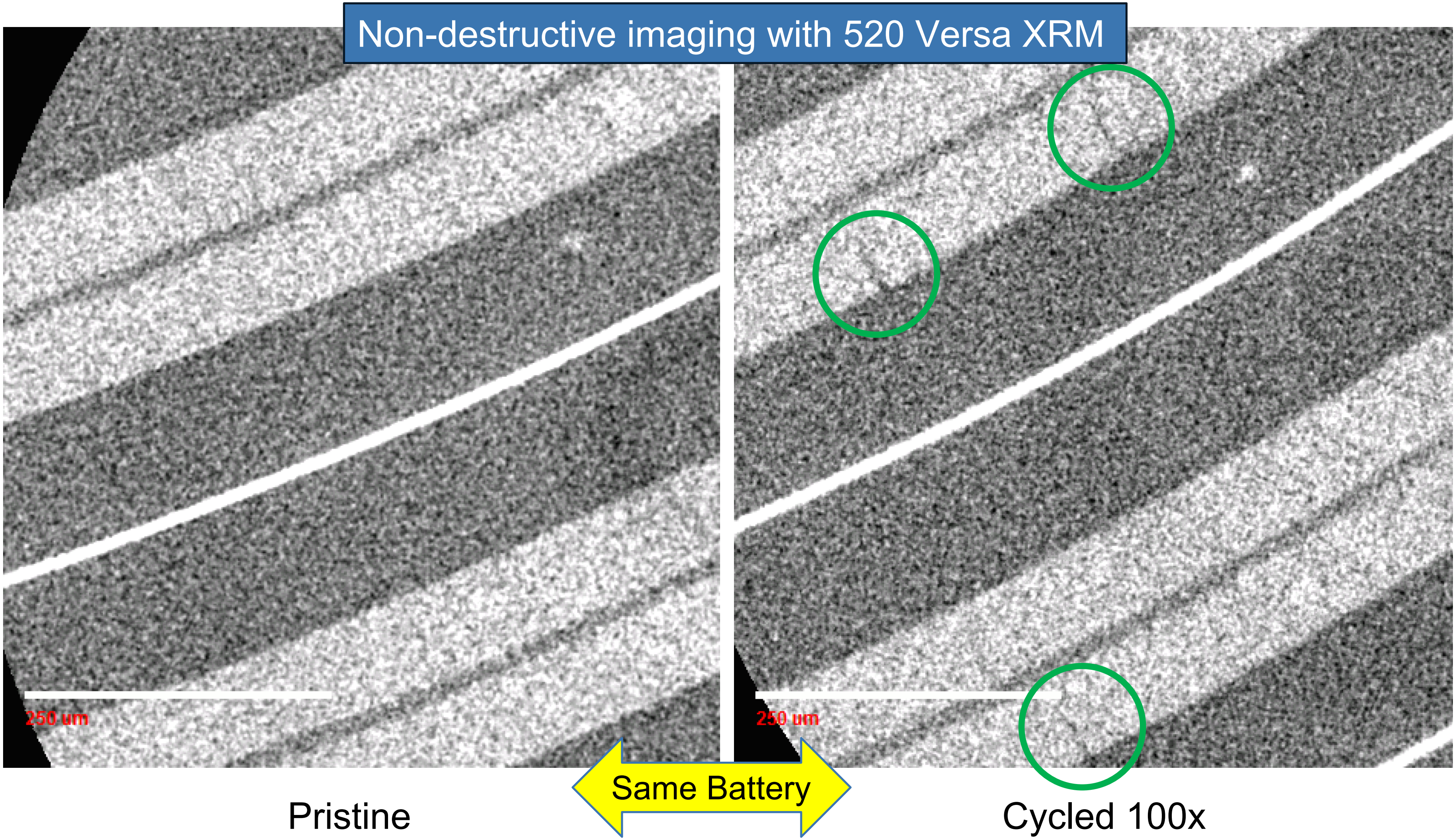


# 18650 Cathode
## Entering the 4th Dimension: Charge Cycling Behavior

- One cell was charge cycled 100x at 0.5C, imaged non-destructively before and after using a **520 Versa XRM**.
- Observed ~6% capacity fade after 100 charge cycles.

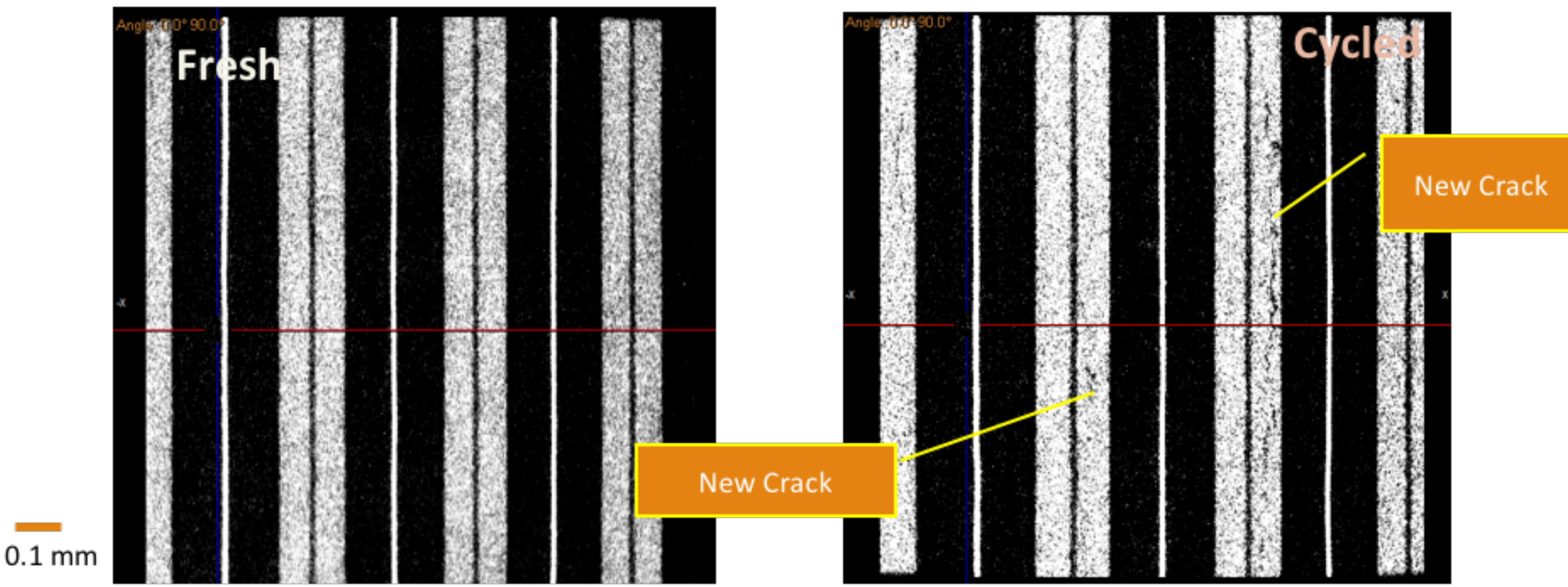


# **Defects Observed After 100 Charge Cycles**
## Commercial 18650 Li-Ion Battery Cell Cathode
## 1.8 µm Voxel Size



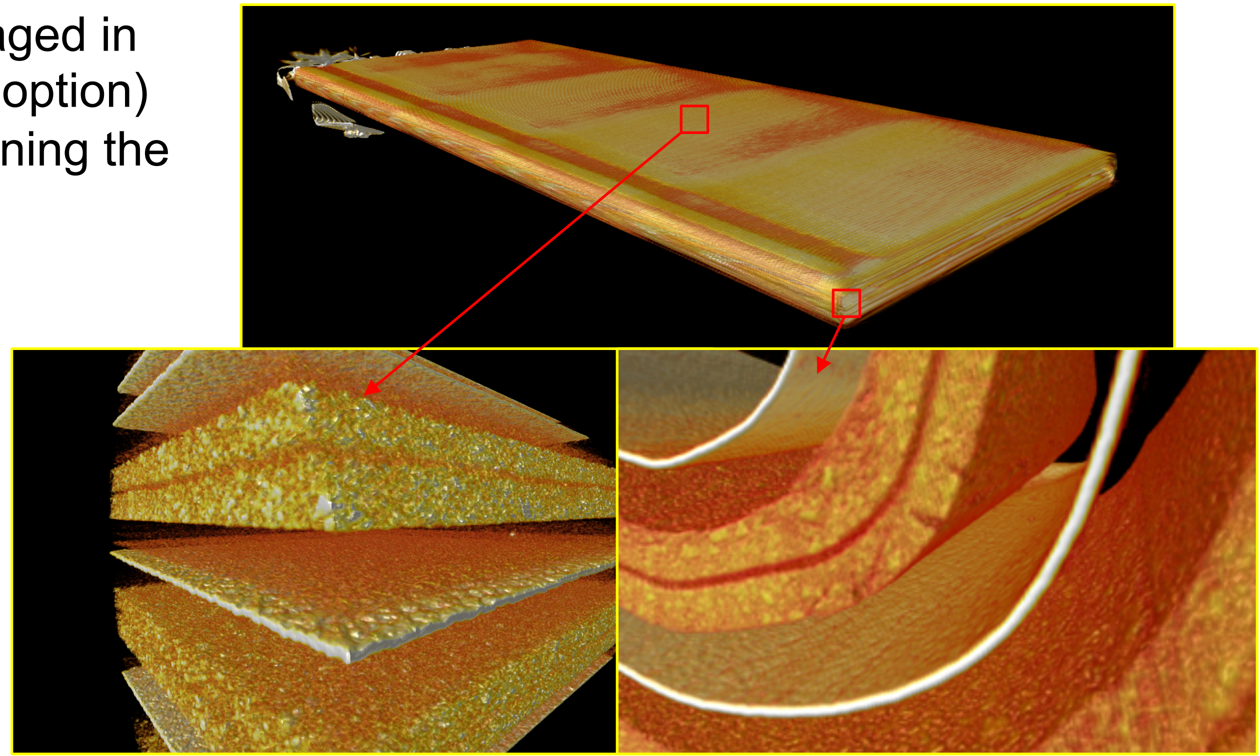
## **Defects Observed After 100 Charge Cycles**
Commercial 18650 Li-Ion Battery Cell Cathode
1.8 µm Voxel Size

Examining from another direction:



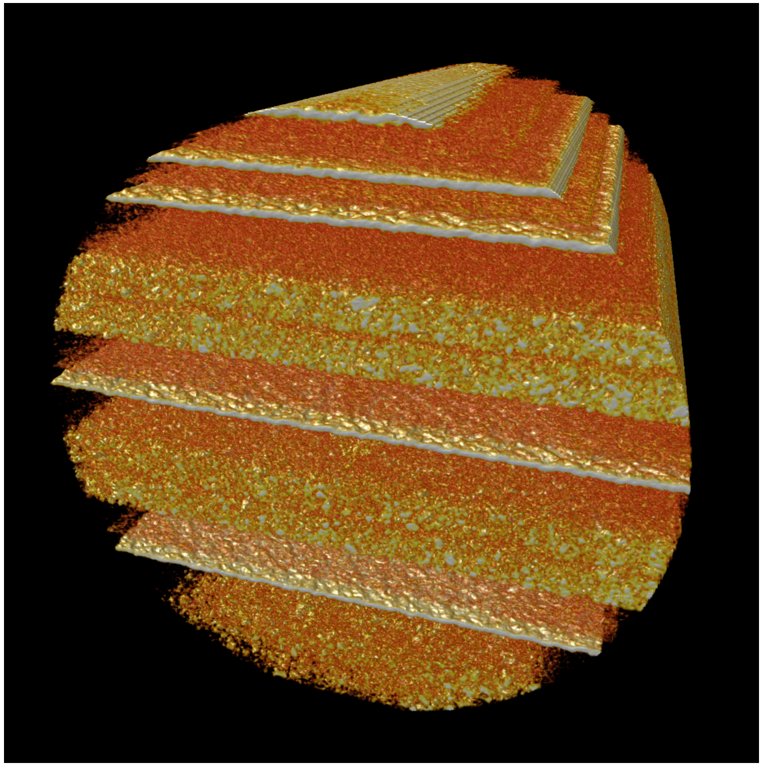
# Packaging/Assembly – Large Scale Assembly to Small Scale Defects

Mobile phone battery imaged in 3D with **520 Versa** (**FPX** option) without sectioning or opening the package.

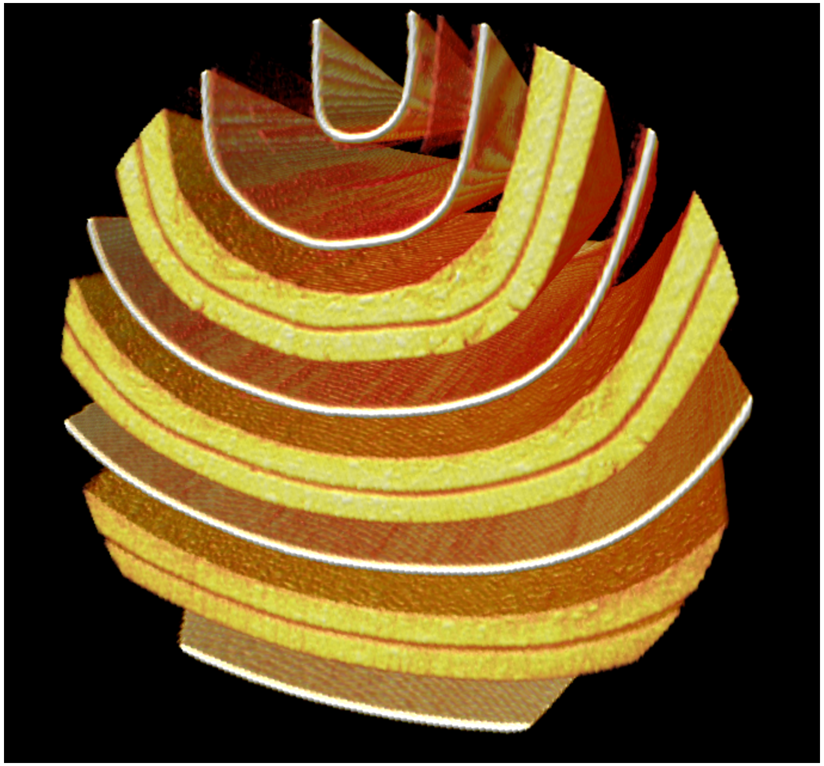



Results showed more cracks in the bent regions (fold of jelly roll) than in the straight regions (middle of battery), suspected to be due to high tensile stresses in those positions.

# Packaging/Assembly – Large Scale Assembly to Small Scale Defects

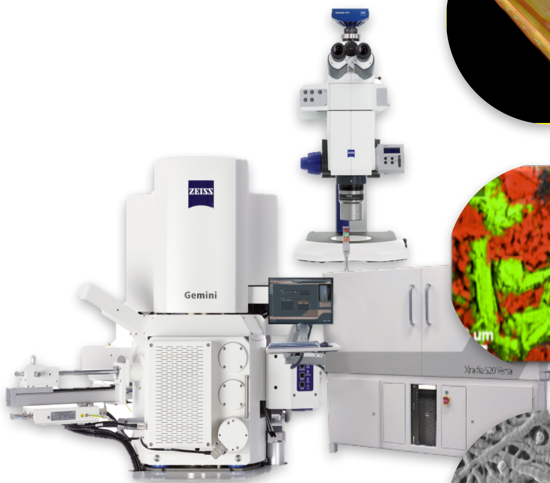


Flat interior section

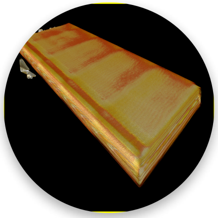


Corner (bent) region

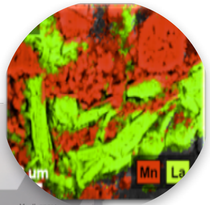
**Higher radii of curvature were observed to correspond to higher densities of cracks.**



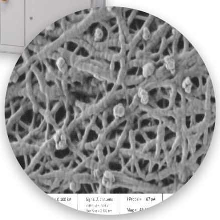

ZEISS Microscopy



Package

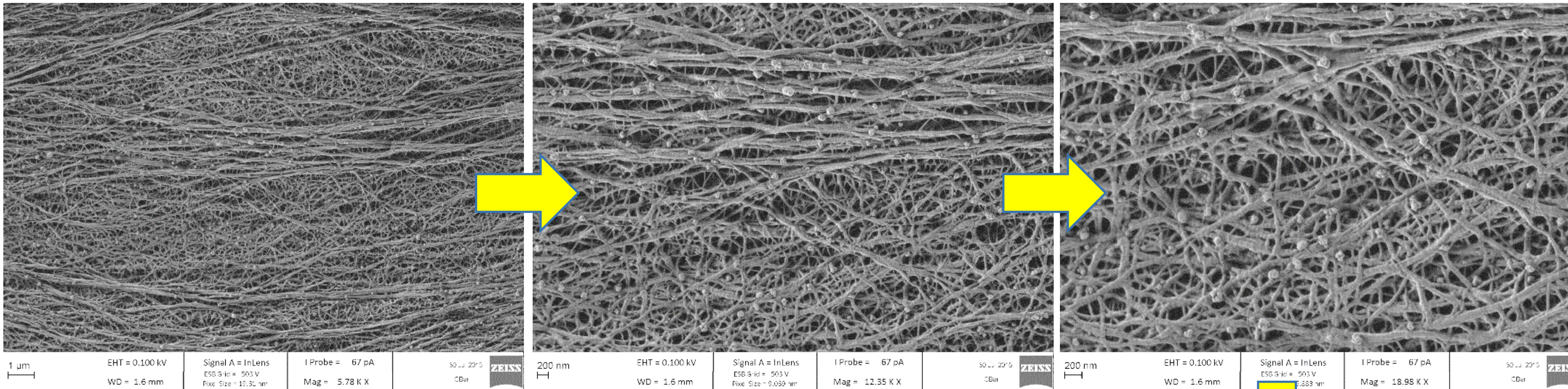



Electrode



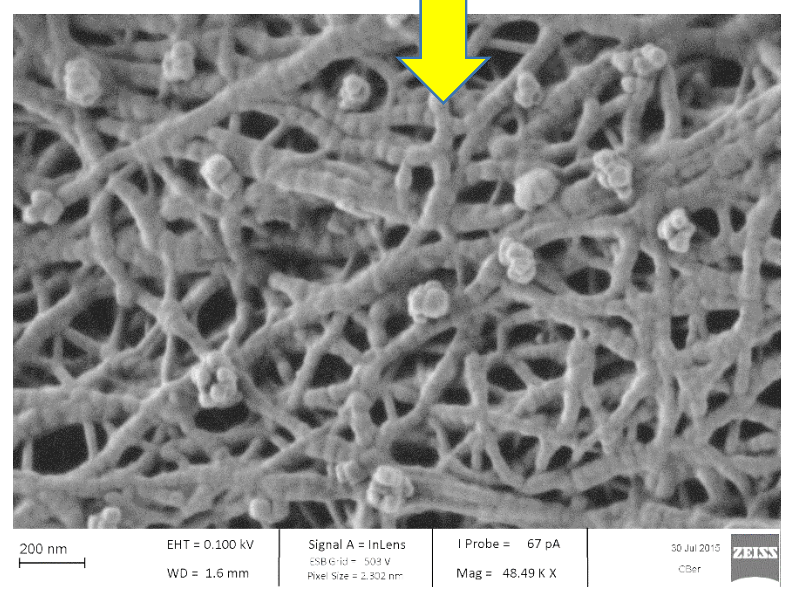
Separator

# Separator Case Study: Topography & Microstructure with Merlin FE-SEM



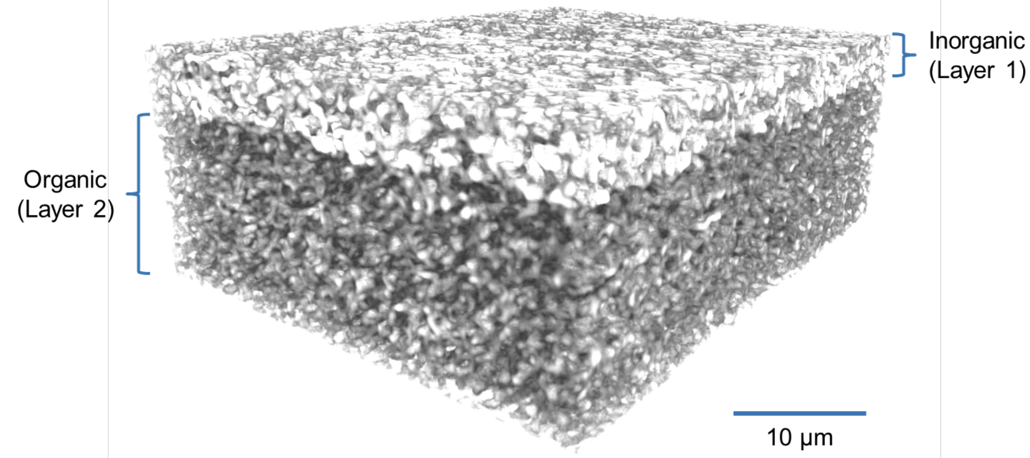

- **Merlin FE-SEM** with **at 0.1 kV** reveals multi-scale heterogeneity of separator topography

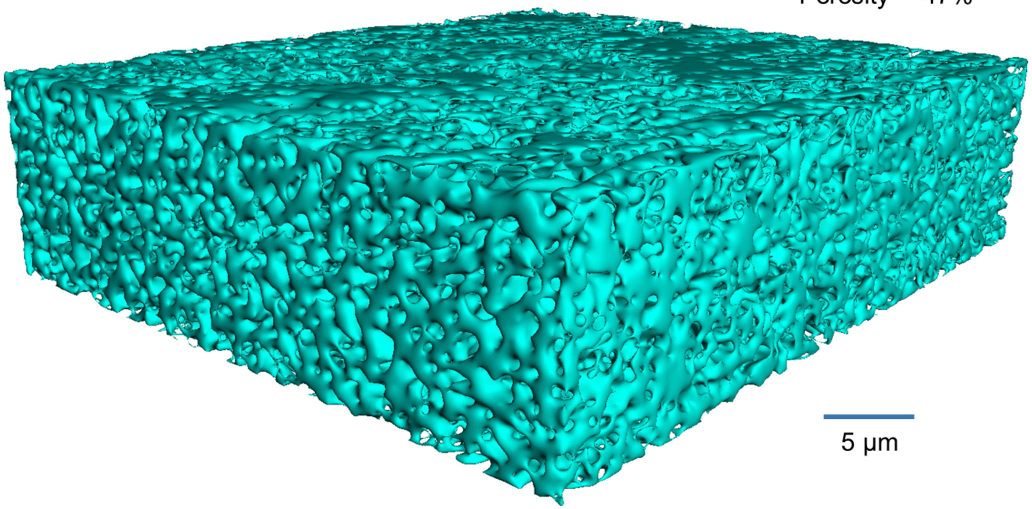
- Tunable magnification delivers large area overviews and localized images with sub-nm resolution



# Separator Case Study: Microstructure/Porosity

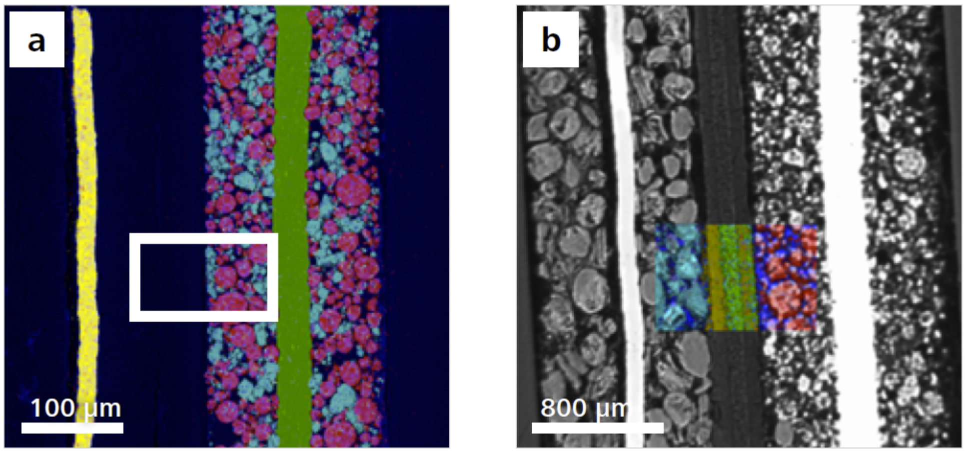
## From 2D to 3D with X-Ray Microscopy

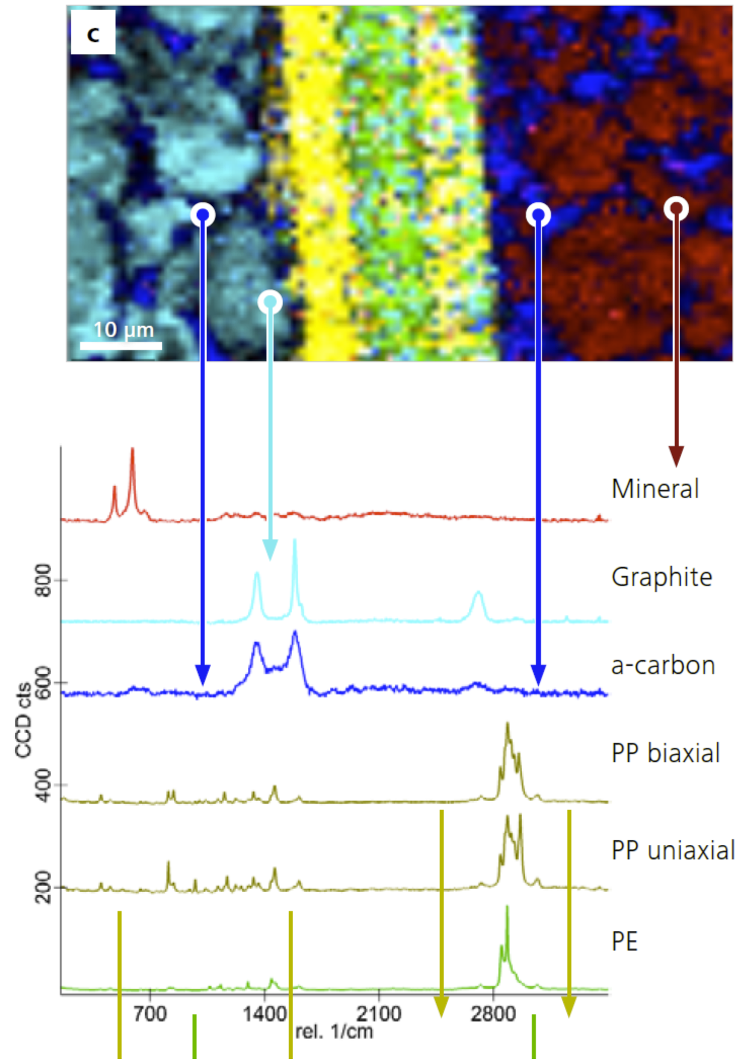



- Separator extracted from commercial 18650 battery.
- Imaged in 3D using the **810 Ultra XRM** with 150 nm resolution.
- Identified thick organic and thinner inorganic layers in the separator.
- Virtually isolated the organic layer and computed porosity.
- Results useful for modeling & simulation studies.

# Separator Case Study: Chemical Composition
## Fusing FE-SEM with Raman



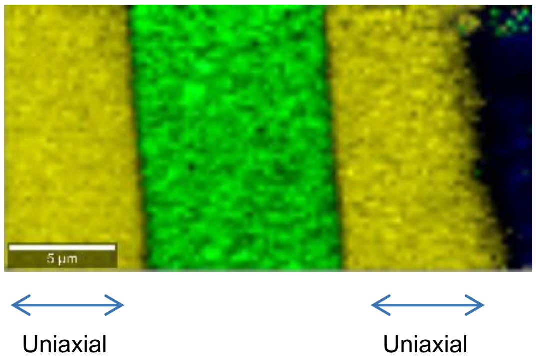




- Commercial 18650 battery was cross-sectioned and imaged using the **GeminiSEM** with *in situ* Raman spectrometer.

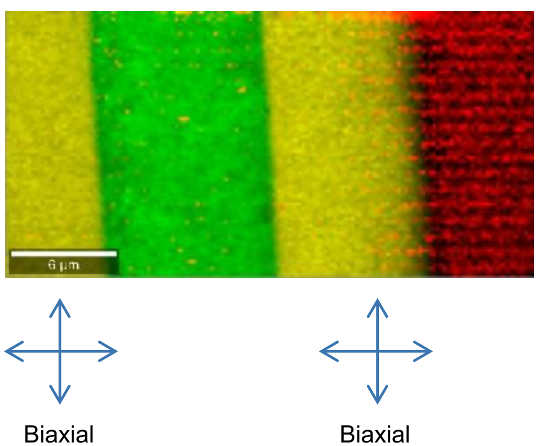
- Results reviewed the multi-phase nature of the separator, including:
  - Uniaxial PP
  - Biaxial PP
  - PE

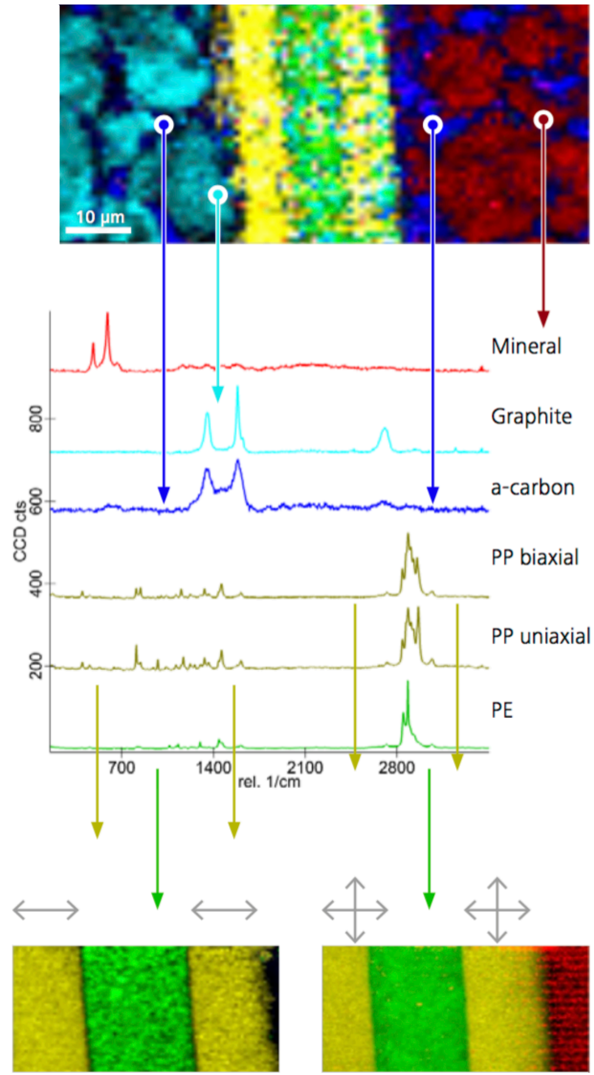
# Separator Degradation after Aging
## GeminiSEM with Raman Spectrometer

Before aging:




After aging:




- Raman mapping reveals change of poly-propylene from uniaxial to biaxial after altering
- Loss of Li ions from anode to cathode expected thus impedance increases
- Separator degrading results in shorter battery lifetime

# ZEISS Microscopy Portfolio for Li-Ion Battery Research

## Beyond electrochemical analysis…

Desired

| Cathode | Anode, SEI | Separator | Binder | Electrolyte |
|---|---|---|---|---|
| • Micro structure<br>• Topography<br>• Material contrast<br>• Crystal structure, phases<br>• Chemical analysis<br>• Stoichiometry | | • Micro structure<br>• Topography<br>• Chemical analysis | • Micro structure<br>• Chemical analysis | • Chemical analysis |
| LM<br>EM SE, BSD, EDX, WDX<br>EBSD<br>X-ray<br>Raman<br>AFM | LM<br>EM SE, BSD<br>SIMS<br>X-ray<br>Raman<br>AFM | LM<br>EM SE | LM | |
| | | Raman | Raman | Raman |

ZEISS offers

**Upright Light** Microscopes

**X-ray** Microscopes

**Focused Ion Beam** Microscopes

**FESEM** Microscopes



# Acknowledgements & Collaborators


- Dr. Paul Shearing, Dr. Donal Finegan, & Prof. Dan Brett (Electrochemical Innovation Laboratory, University College London)
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