TESCAN GnMEBA 2019

MEB-FIB TESCAN un outil polyvalent permettant l'intégration de multiples techniques innovantes - TOFSIMS

David BARRESI
Responsable TESCAN FRANCE

Décembre 2019

TESCAN
PERFORMANCE IN NANOSPACE

01

Product Portfolio
SEM

- **1991** — TESCAN, s.r.o. established
- **1999** — VEGA SEM introduced

- **2005** — MIRA Schottky FE-SEM introduced
- **2007** — LYRA FIB-SEM introduced

- **2009** — Chinese branch established
- **2010** — Acquisition of TESCAN USA
- Third generation of TESCAN SEMs introduced

- **2011** — FERA3 and TIMA introduced
- 1000 SEM installed & ISO certification
- **2012** — MIRA3 AMU introduced

- **2013** — Merger of TESCAN and ORSAY PHYSICS resulted in TESCAN ORSAY HOLDING, a.s.
- TESCAN-UK Ltd. established
- **2014** — Acquisition of App Five
- GAIA3 and RISE introduced

- **2015** — XEIA3 and Q-PHASE introduced
- TESCAN Benelux + TESCAN Do Brasil established
- **2016** — NEW UHR Series Triglav™

- **2017** — TESCAN S8000 series introduced

- **2018** — TESCAN Germany established
- TESCAN XRE established
- TESCAN Medical established
- TESCAN S9000 series introduced

TESCAN ORSAY HOLDING Product Range

SEM

Thermal Emission SEM

TESCAN VEGA3

FEG-SEM

TESCAN MIRA3

TESCAN CLARA

TESCAN MAGNA

Special Solutions

TESCAN TIMA-X

TESCAN MIRA AMU

TESCAN RISE

FIB-SEM

Ga FIB-SEM

TESCAN LYRA3

TESCAN AMBER

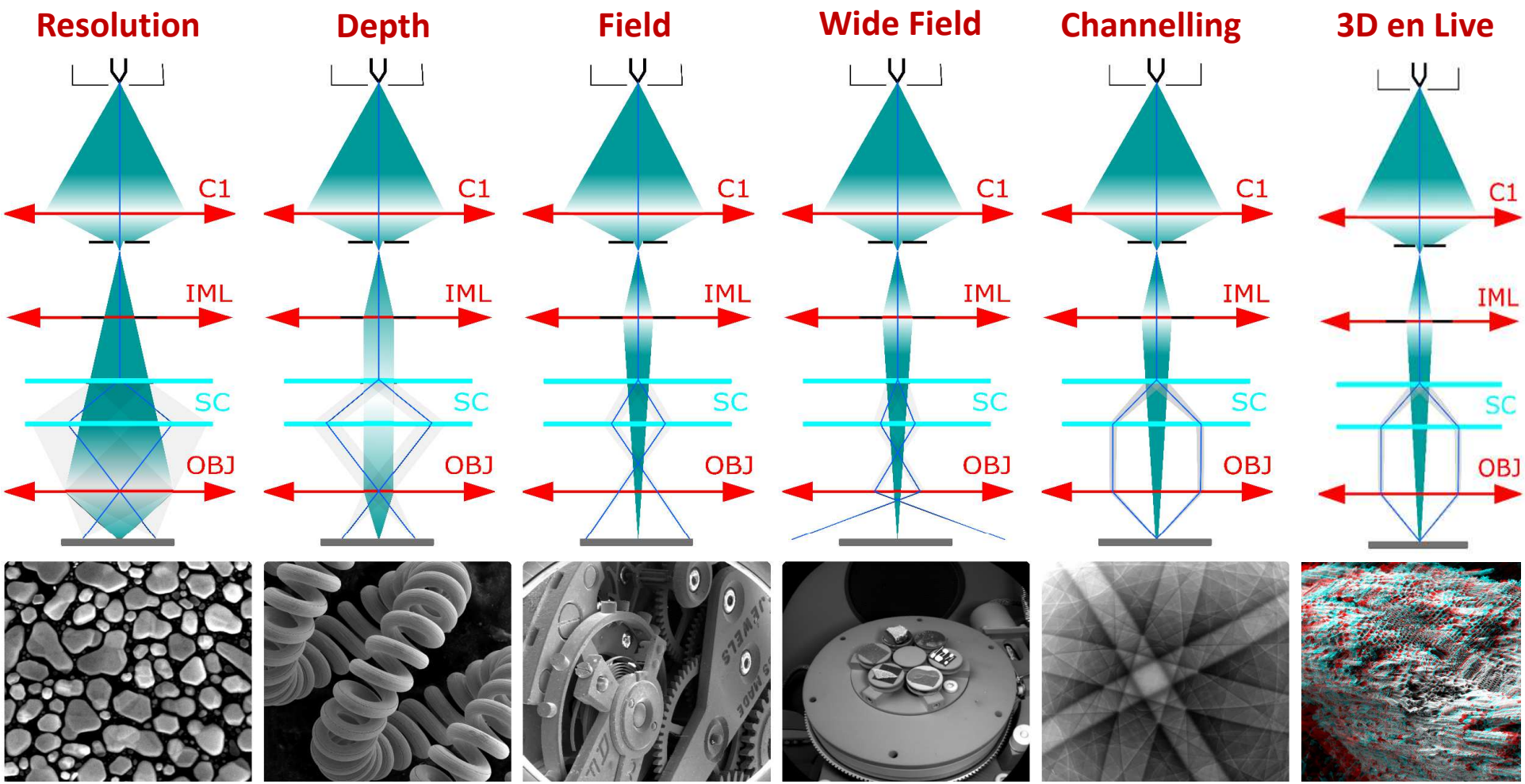
TESCAN SOLARIS

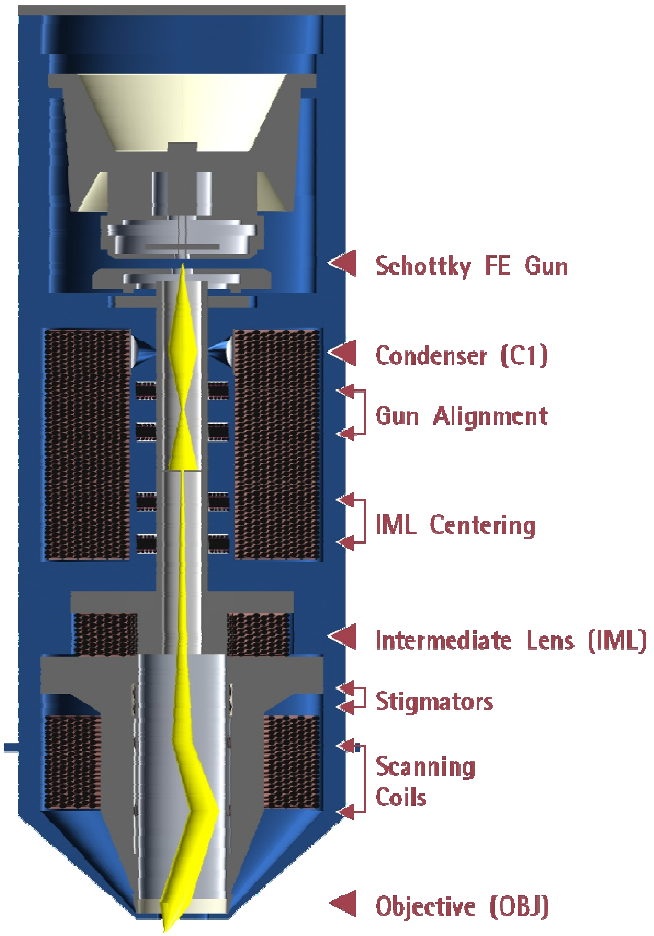
Xe plasma FIB-SEM

TESCAN AMBER X

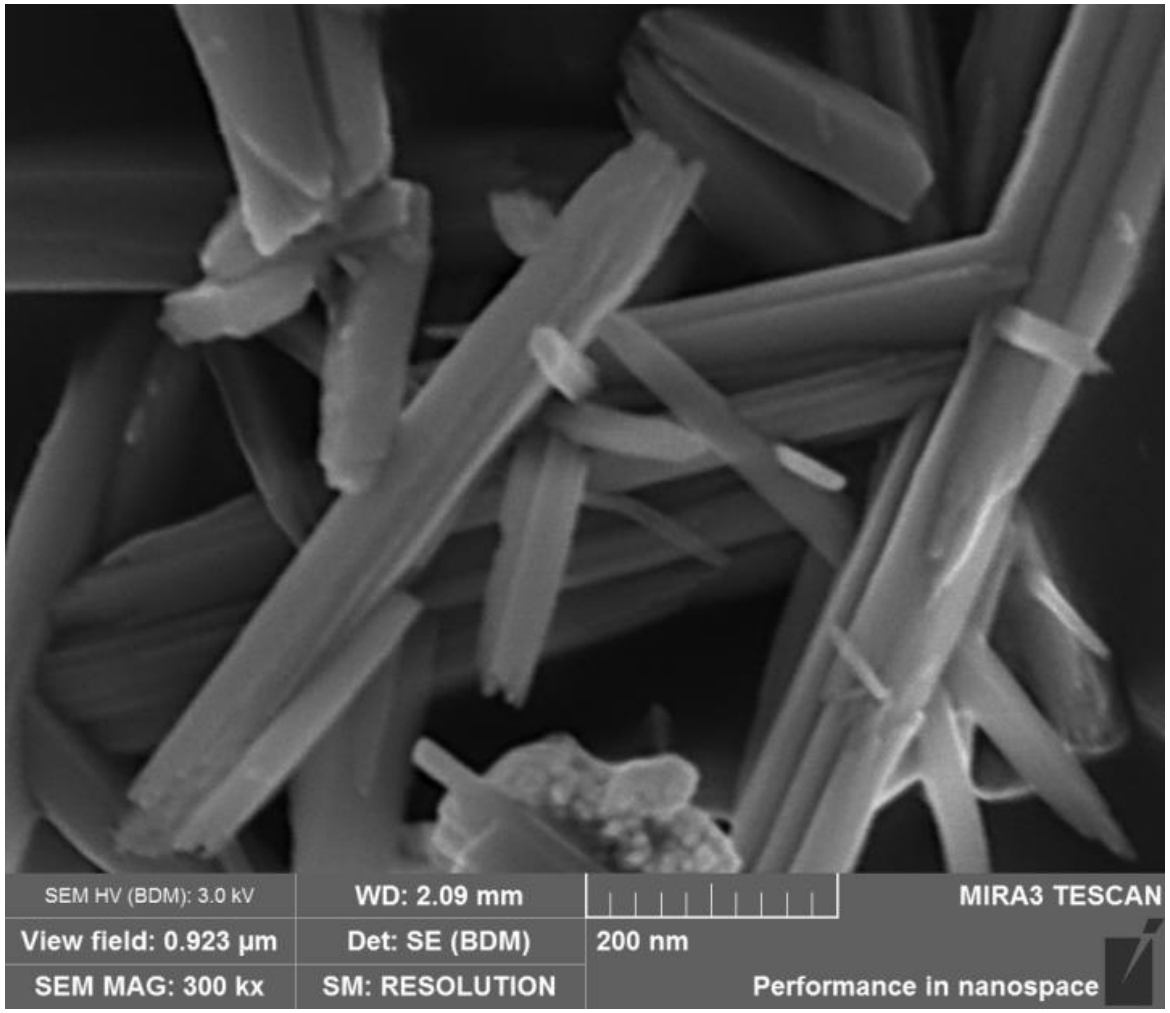
TESCAN SOLARIS X

TESCAN X-ray MicroCT

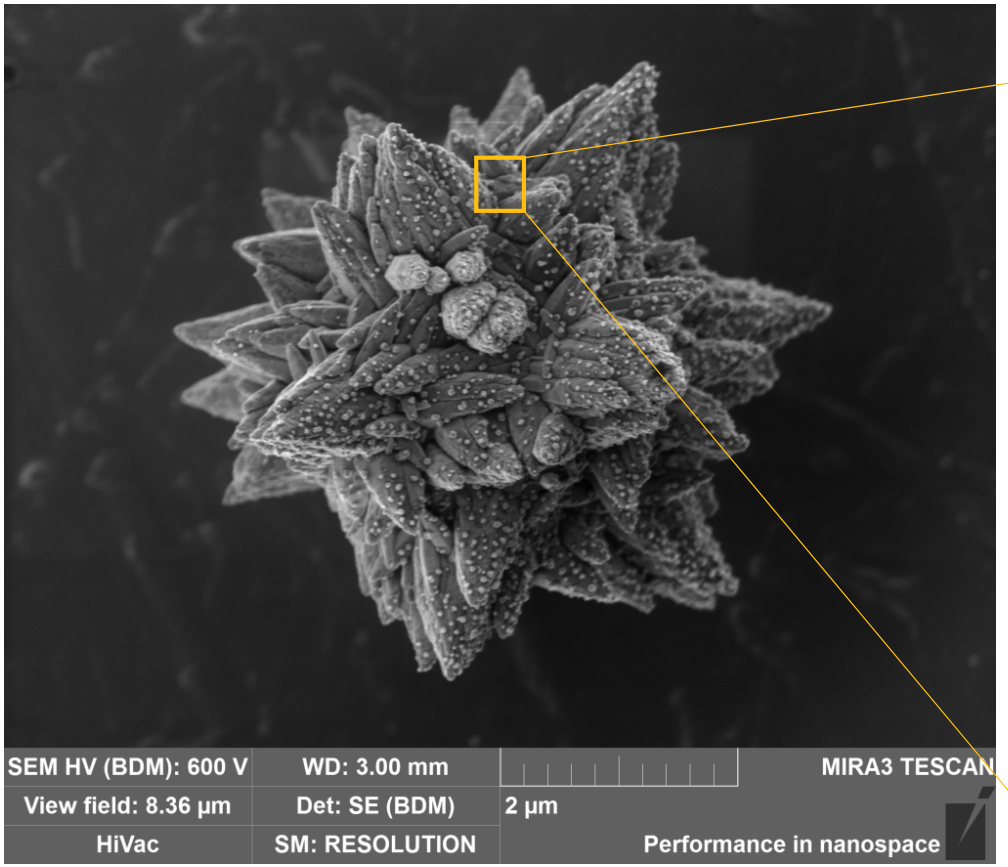

Resolution
Depth
Field
Wide Field
Channelling
3D en Live
C1
IML
SC
OBJ



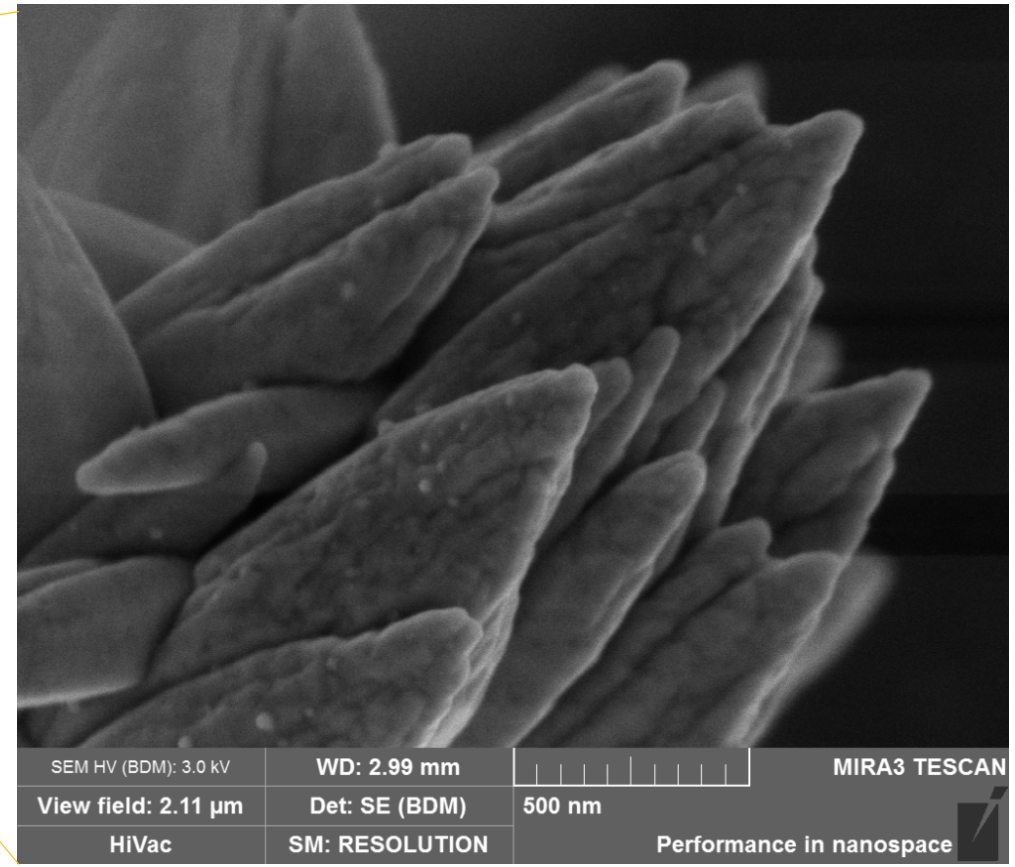
Sample: Goethite powder FeO(OH)
Magnification: **300 000×** Image at **3 keV**



Sample: ZnO with metallic nano-particles

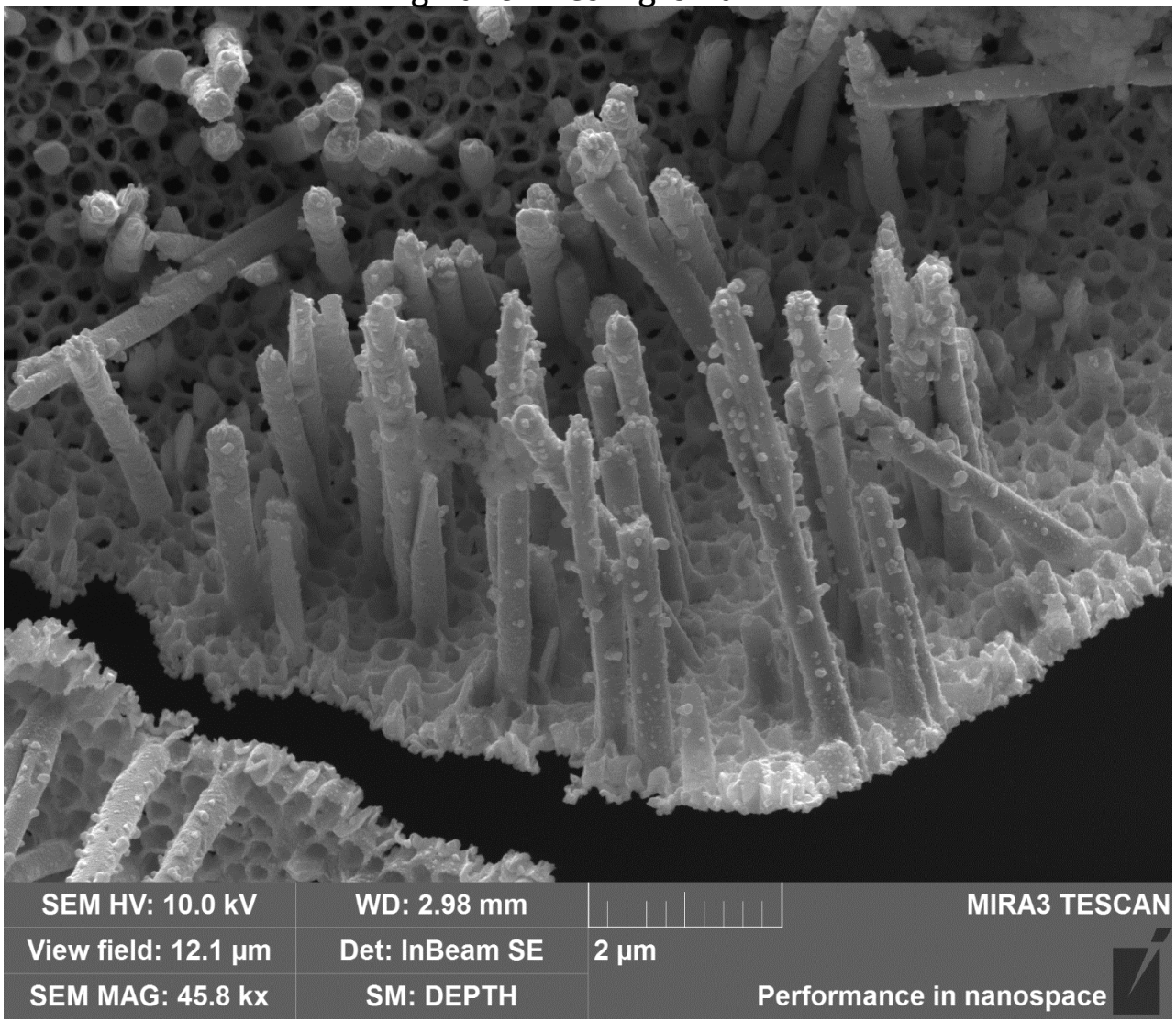


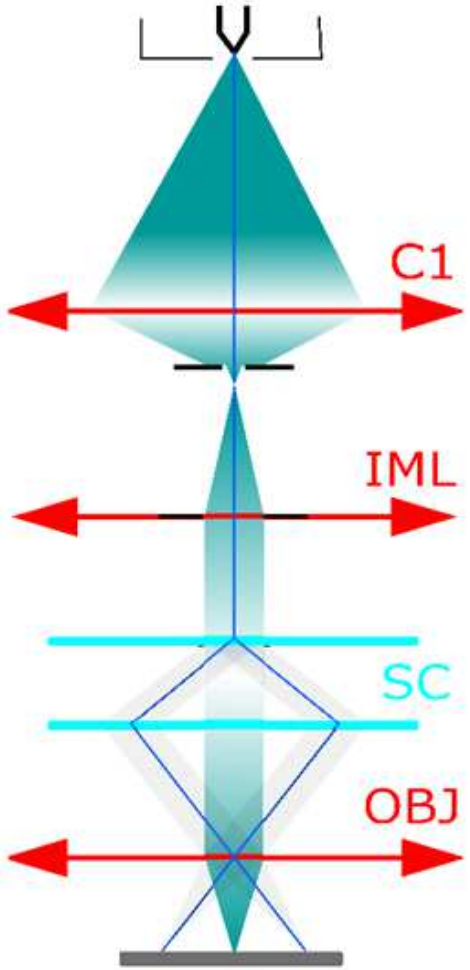
Magnification: **66 256 ×**
Imaged at **600 eV** with the SE (BDM) detector



Magnification: **131 470 ×**
Imaged at **3 keV** with the SE (BDM) detector

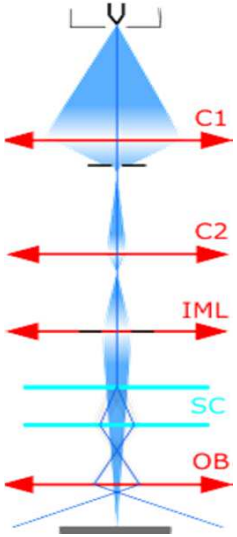
Ag nanowires – growth

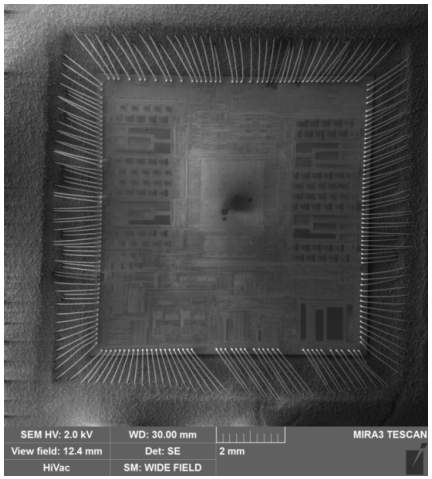




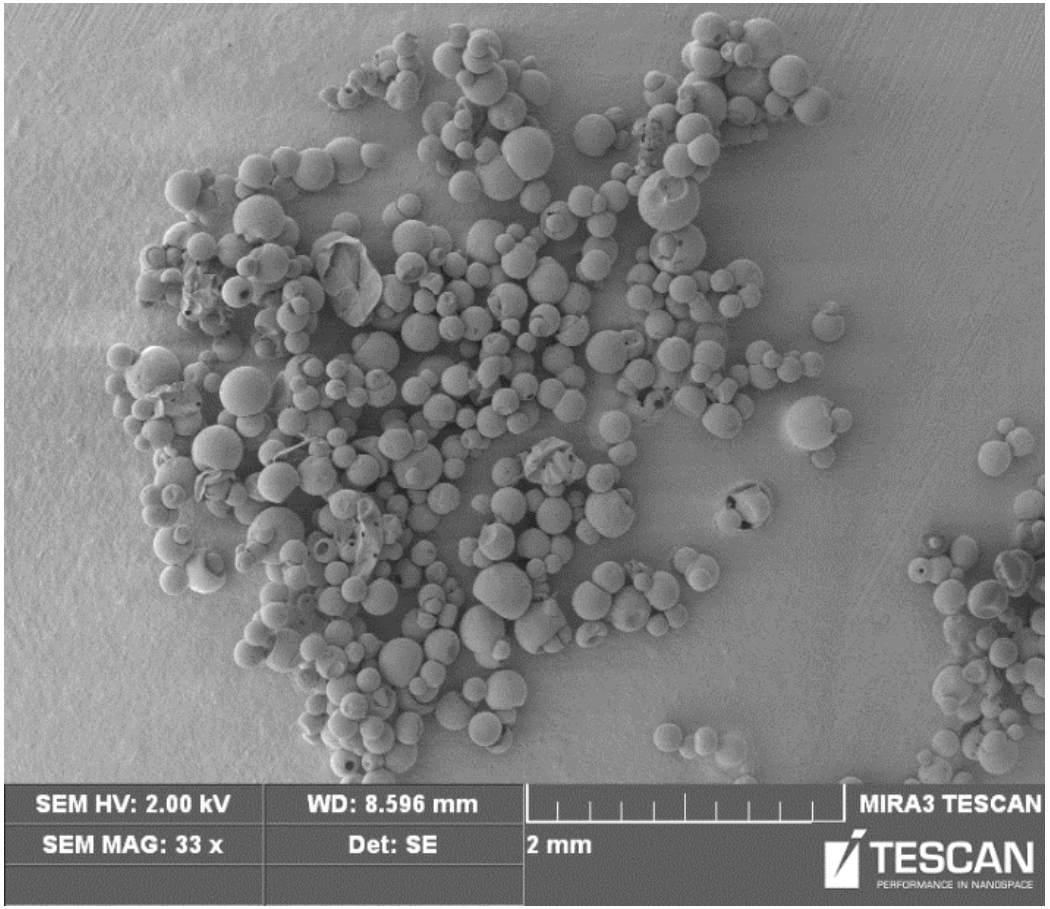
The Wide Field Mode

- Caractéristique Unique du MEB
- Grandissement extra-faible (jusqu'à x1)
- Angle de balayage jusqu'à 45 degrés
- Pas de distorsions d'image
- Possibilité de faire des mesures



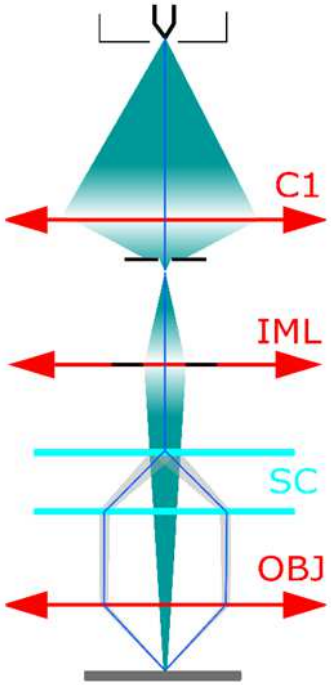


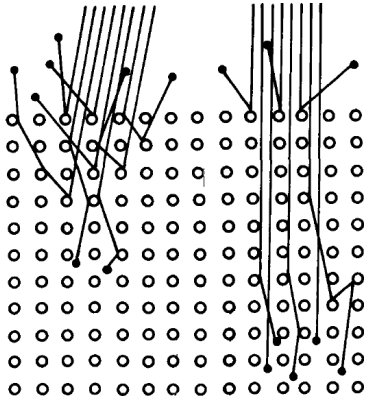
Integrated circuit

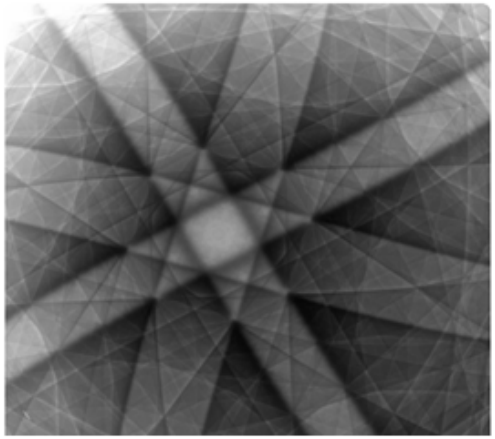


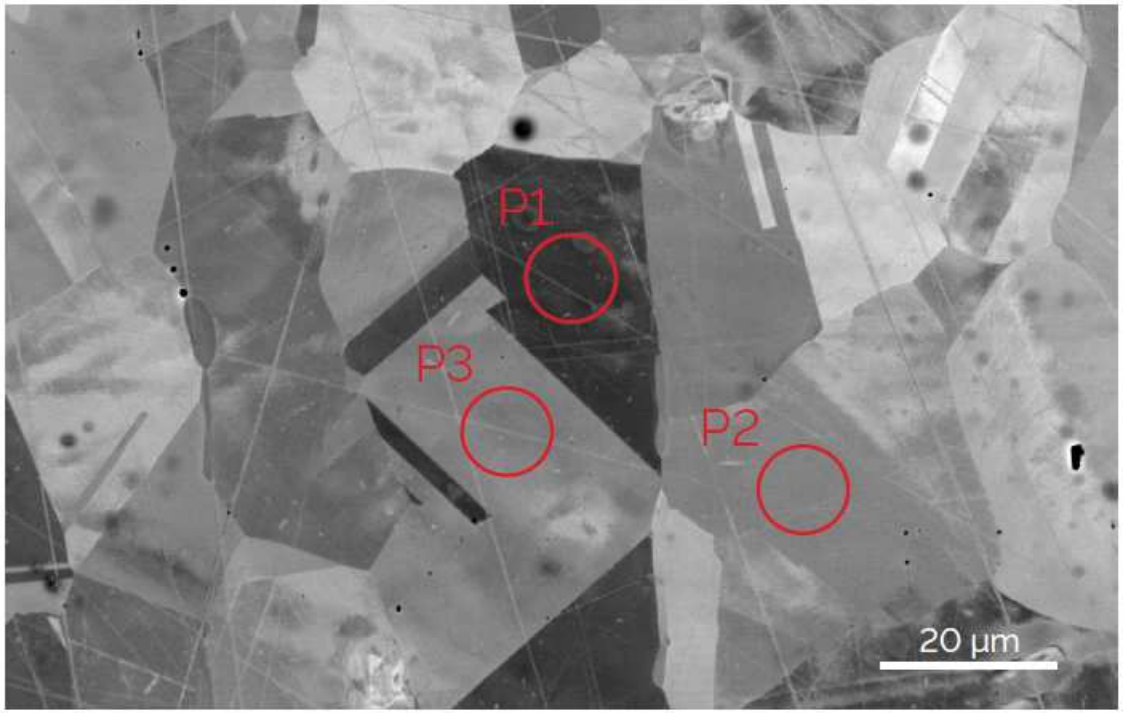
Tramadol

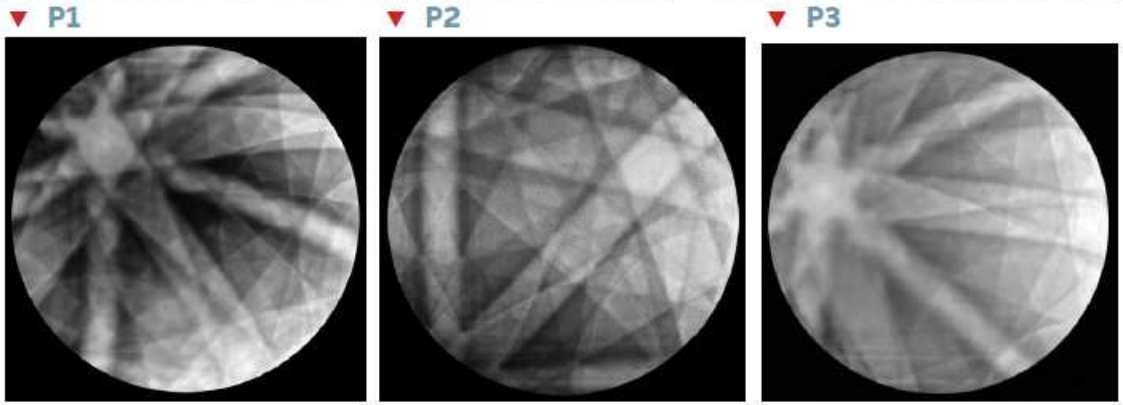
- **Information cristallographique en standard sur toute la gamme de MEB Tescan,**
- **Complete la gamme des signaux BSE : représente une structure particulière du cristal de la zone balayée**

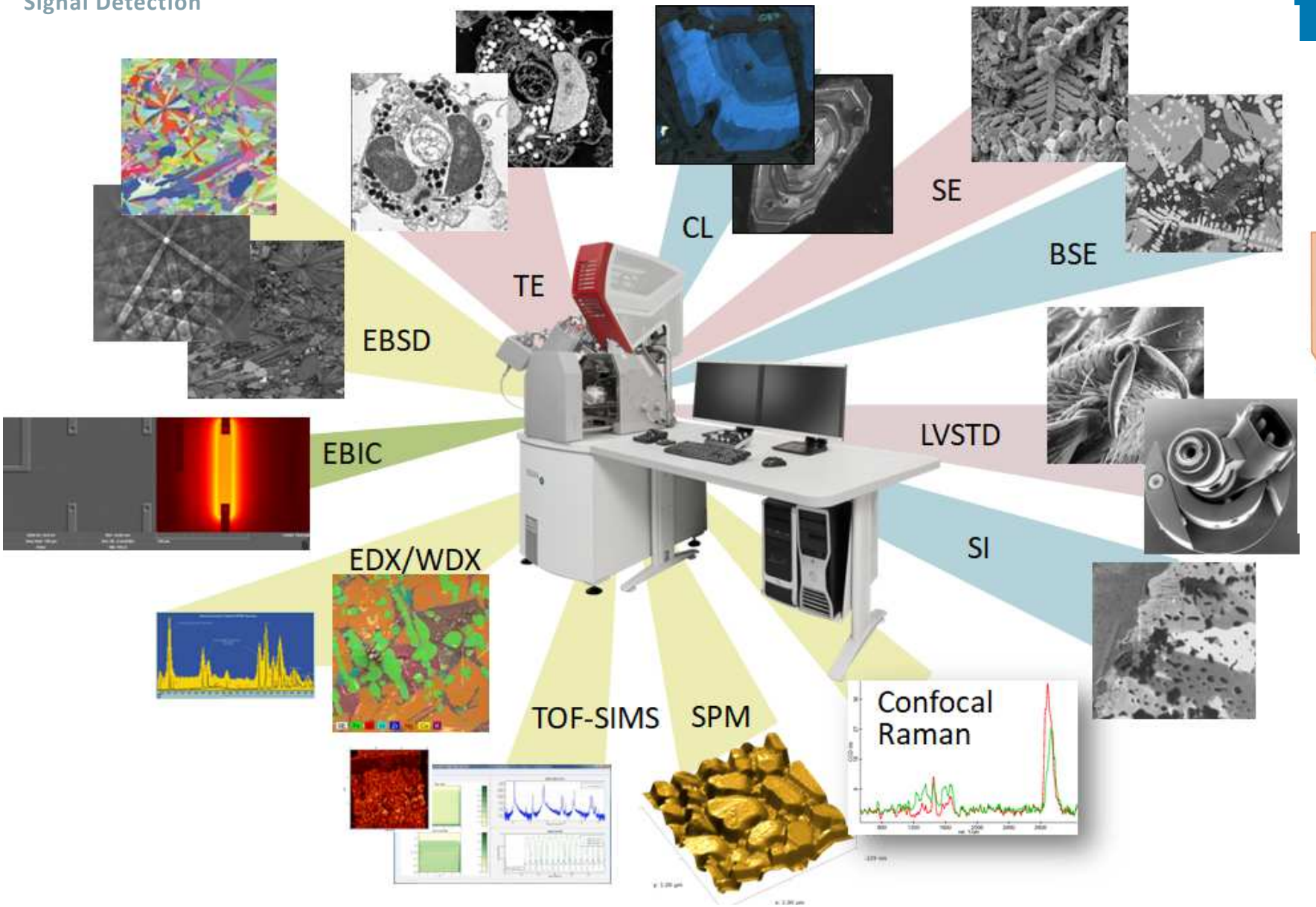


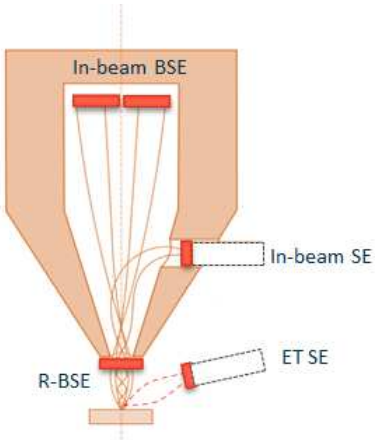




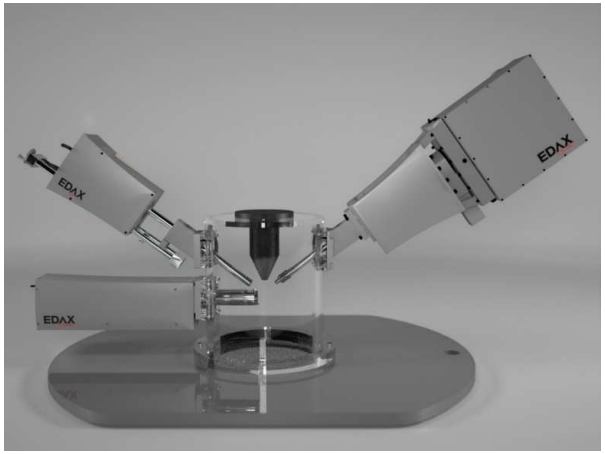




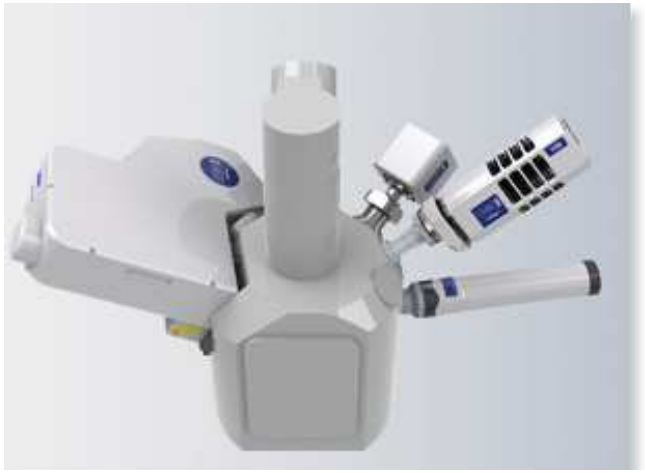

TE
CL
SE
BSE
EBSD
EBIC
LVSTD
EDX/WDX
SI
TOF-SIMS
SPM
Confocal
Raman


In-beam BSE
In-beam SE
ET SE
R-BSE

EDAX

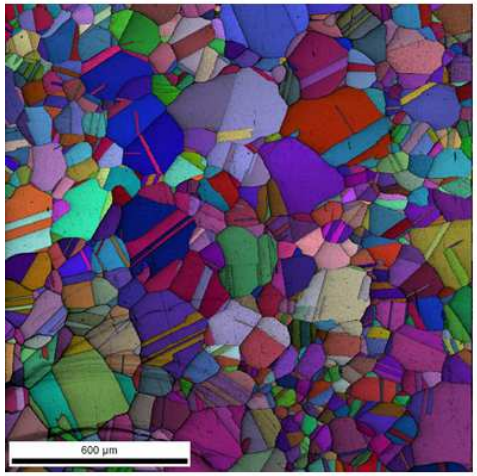


OXFORD



BRUKER

acier inox 316L



acier Duplex 2204

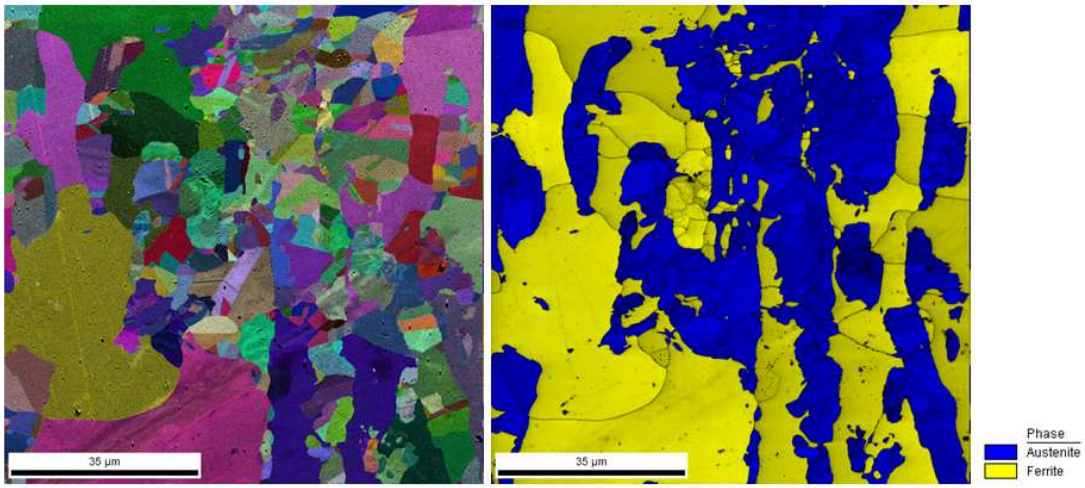
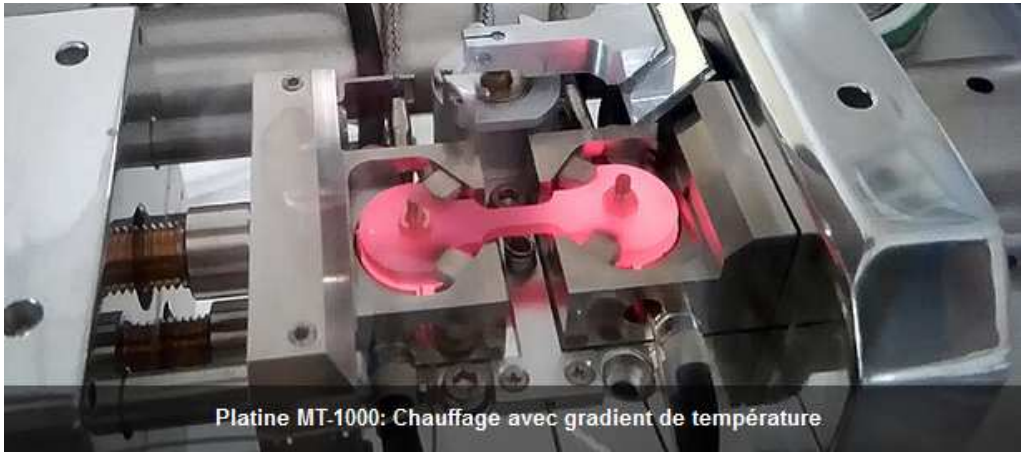
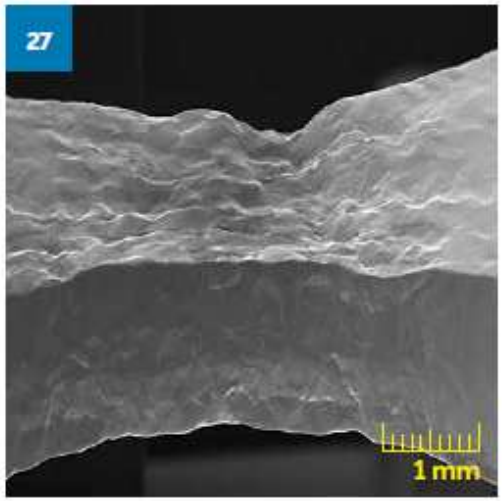
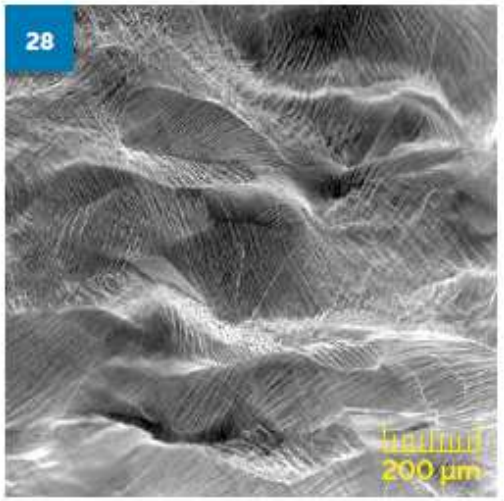


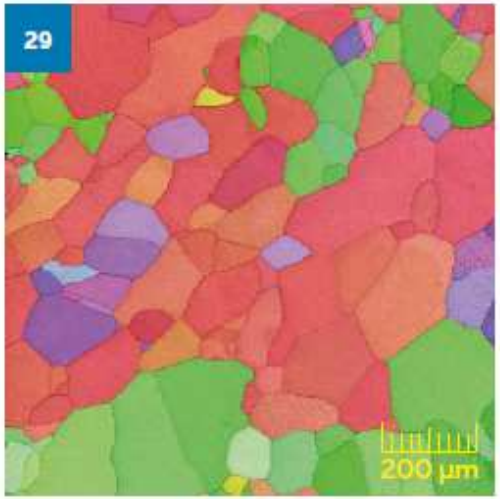
Image Quality & Phase Map

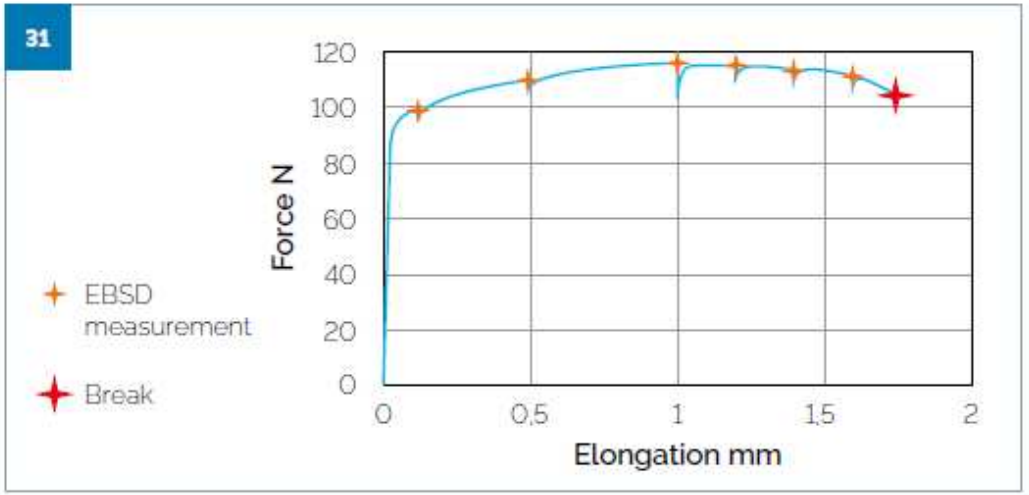
Echantillon d'aluminium analysé par EBSD après traitement thermique



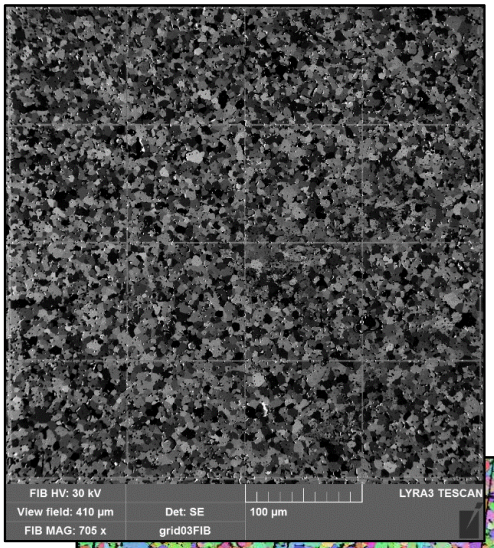


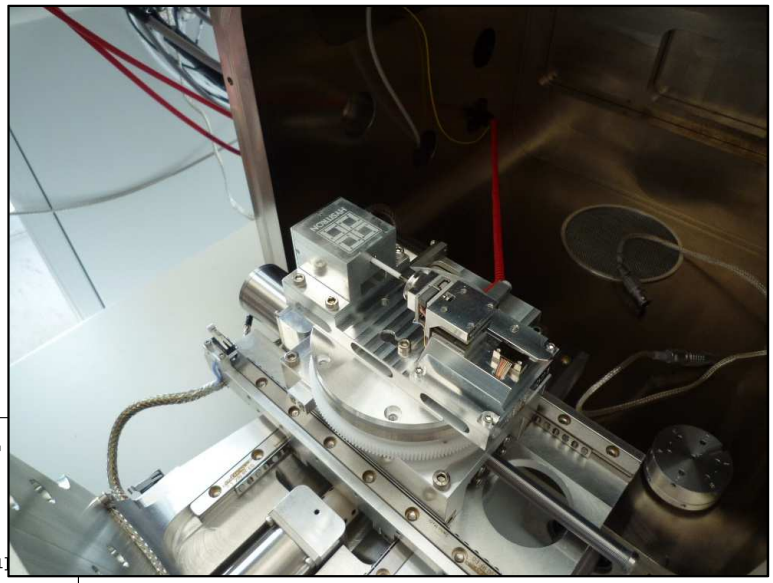


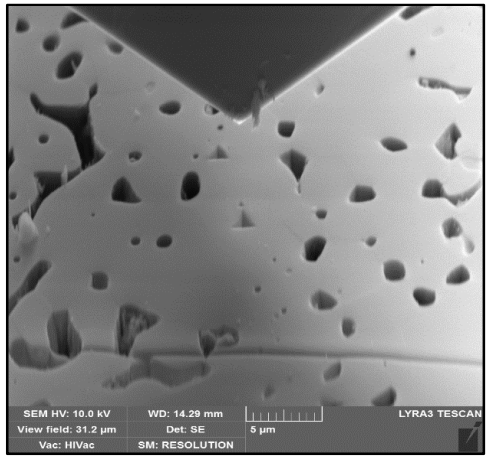


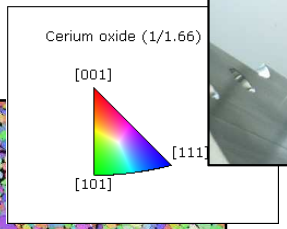


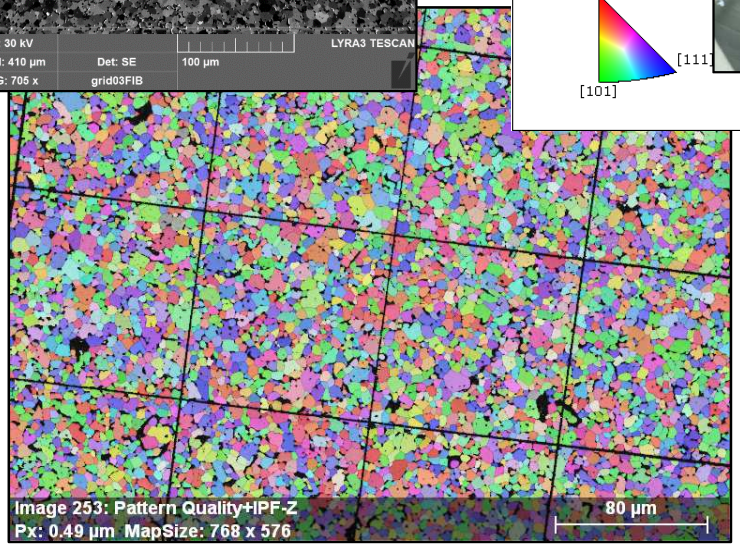
Echantillon d'Oxide de Cerium

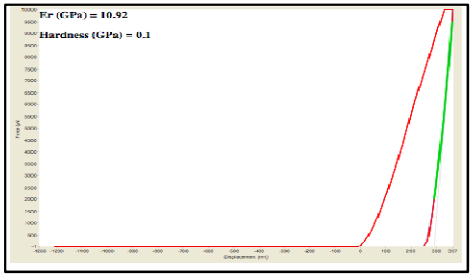


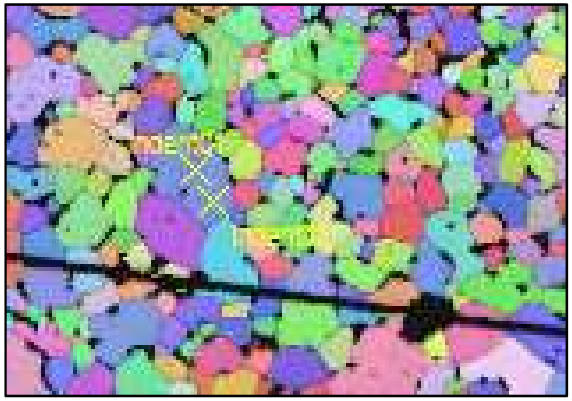




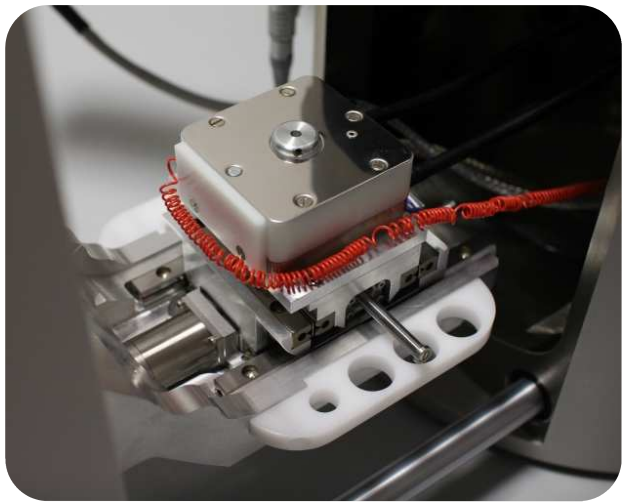






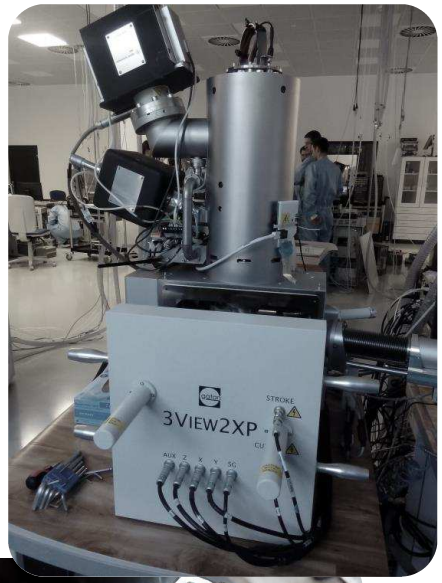


CryoSEM

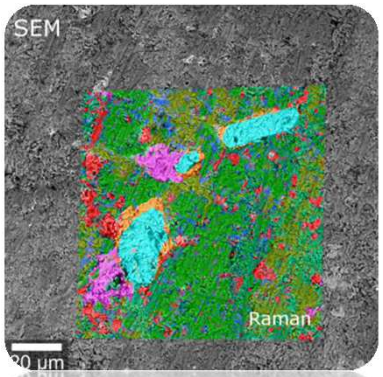


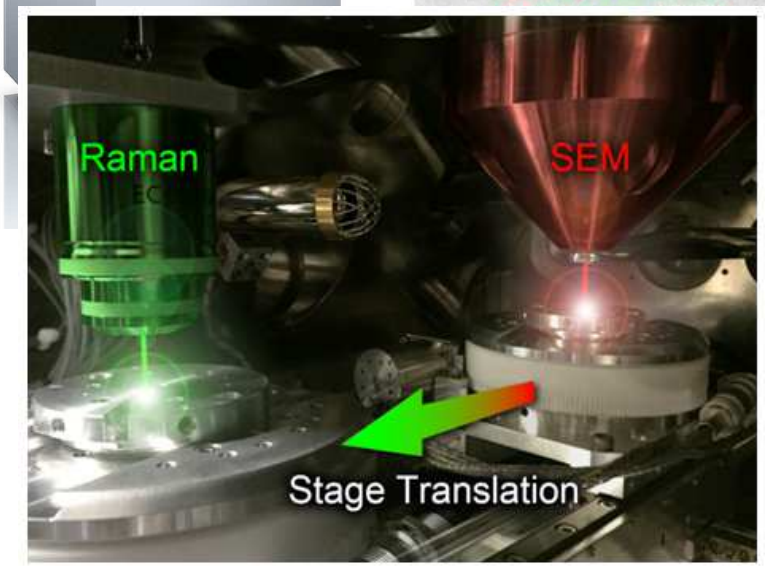
Cooling stage

GATAN 3View

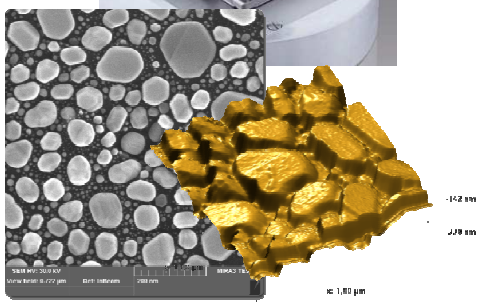


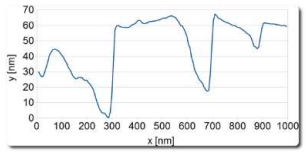
RAMAN



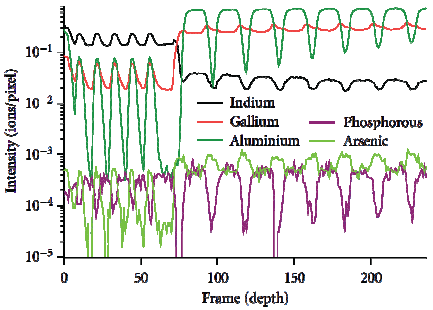


AFM





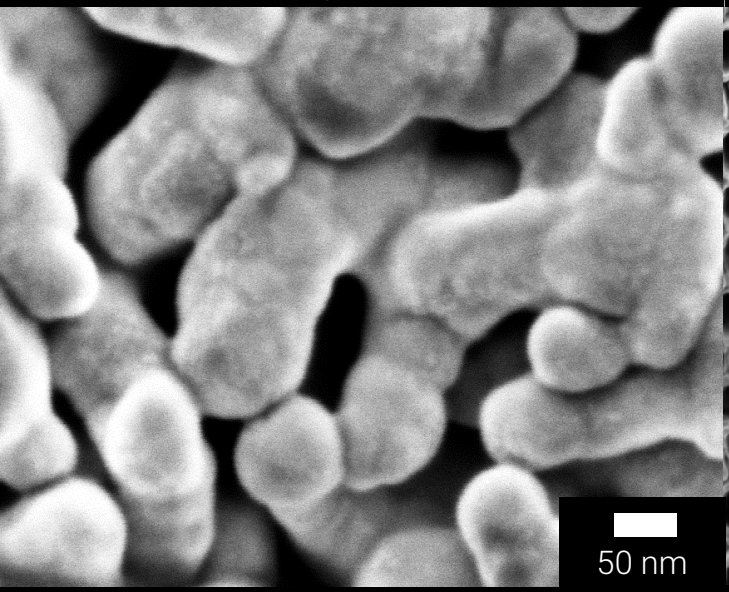
TOF-SIMS



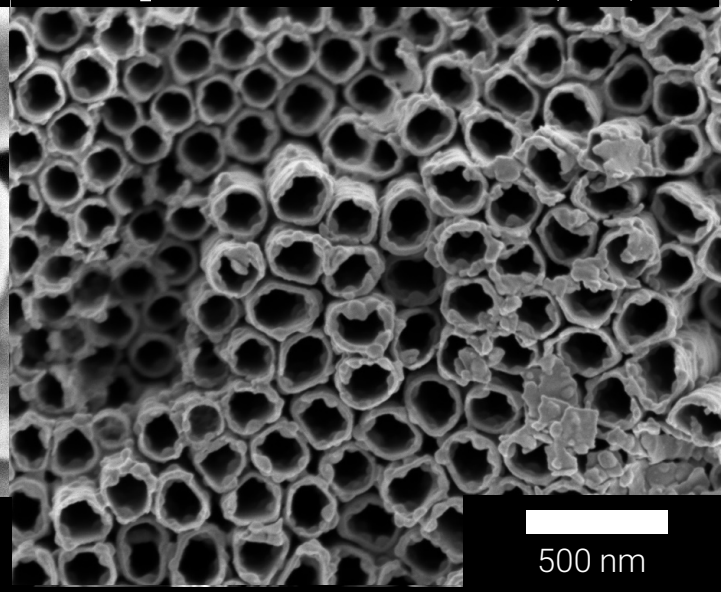
TESCAN CLARA

Field-free analytical UHR SEM for materials characterization at the nanoscale

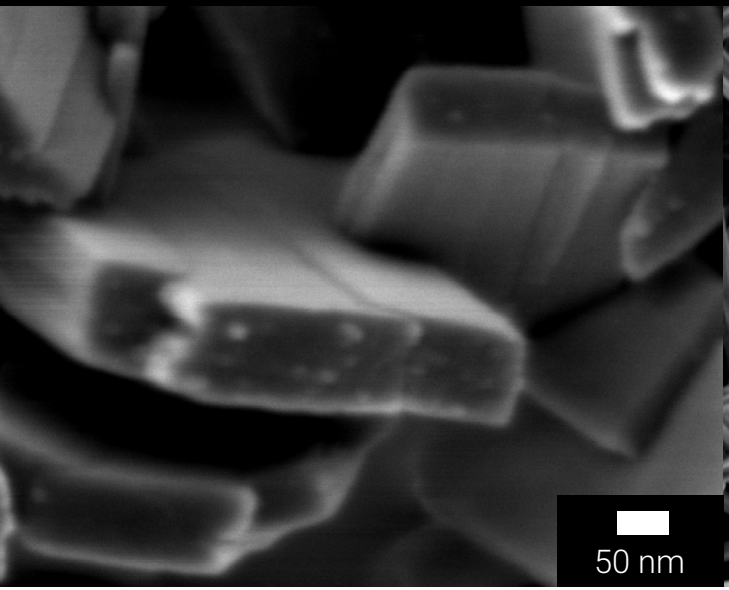
Nanoporous gold 1 keV Axial SE



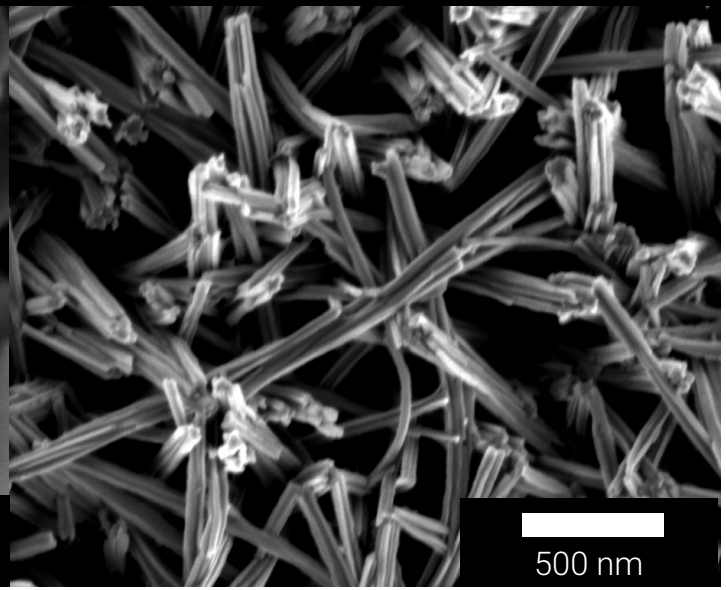
TiO_2 nanotubes 500 eV Axial SE (BDM)



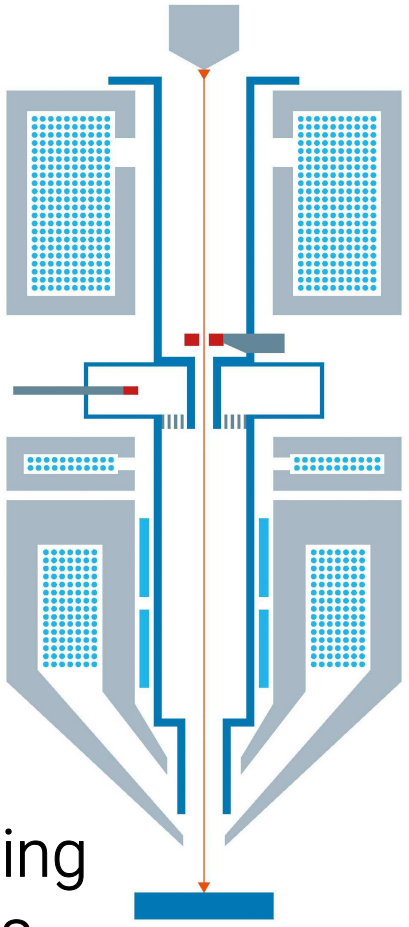
Ceramic nanoparticles 1 keV Axial SE



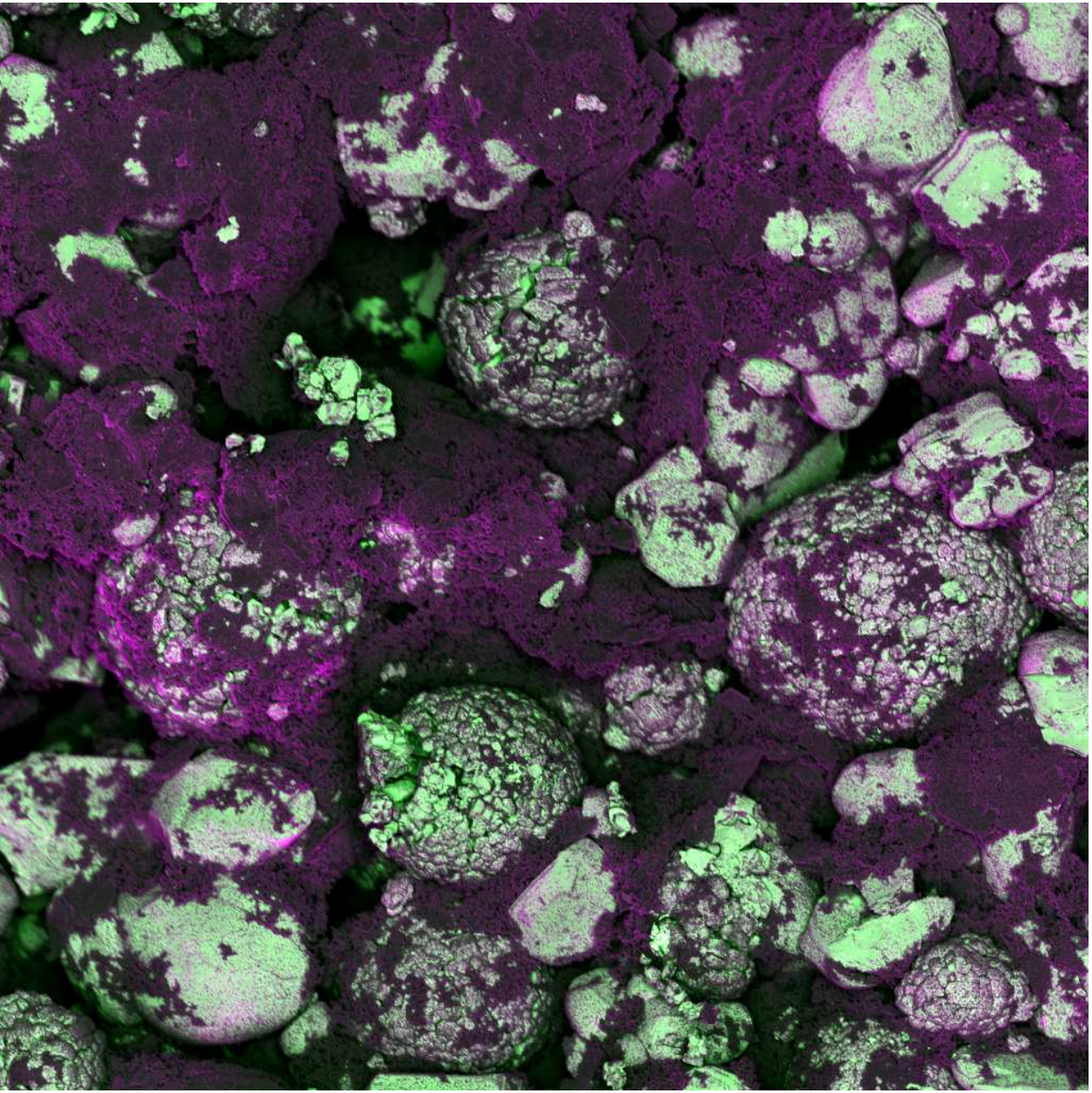
Ceramic nanoparticles 1 keV Axial SE

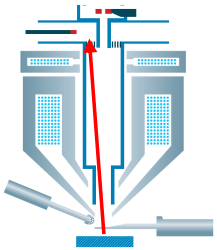


TESCAN CLARA



UHR imaging capabilities





In-column Multidetector

BSE contrast
With topography

Unique for
In-column
Axial BSE

Unique for
In-column
(f) Multidetector

Sample: Li battery catohde imaged at 2 keV

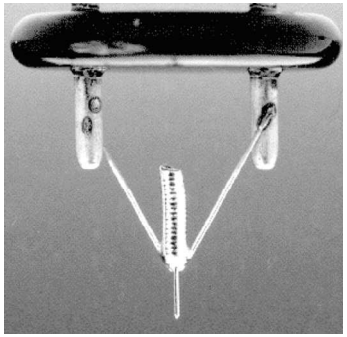
TESCAN
PERFORMANCE IN NANOSPACE

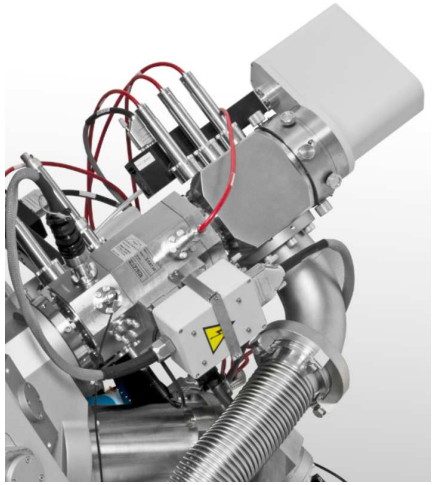
02

Product Portfolio
FIB

Orage Column - Gallium

- **Resolution: < 2.5 nm**
- **Excellent high current performance (100nA)**
- **Ecellent performance at low kV**

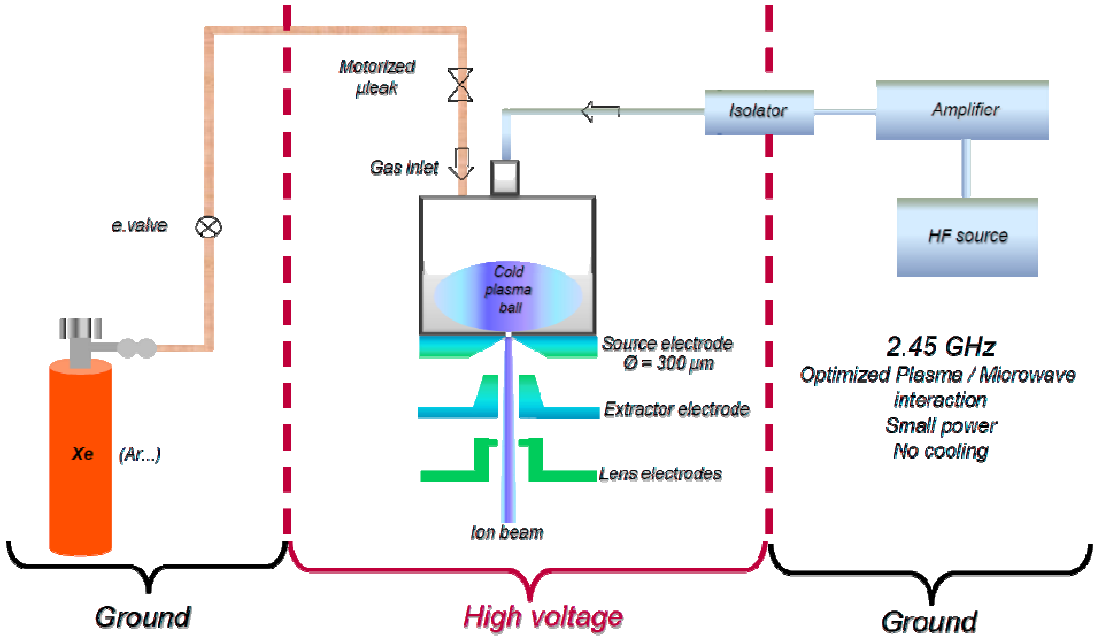


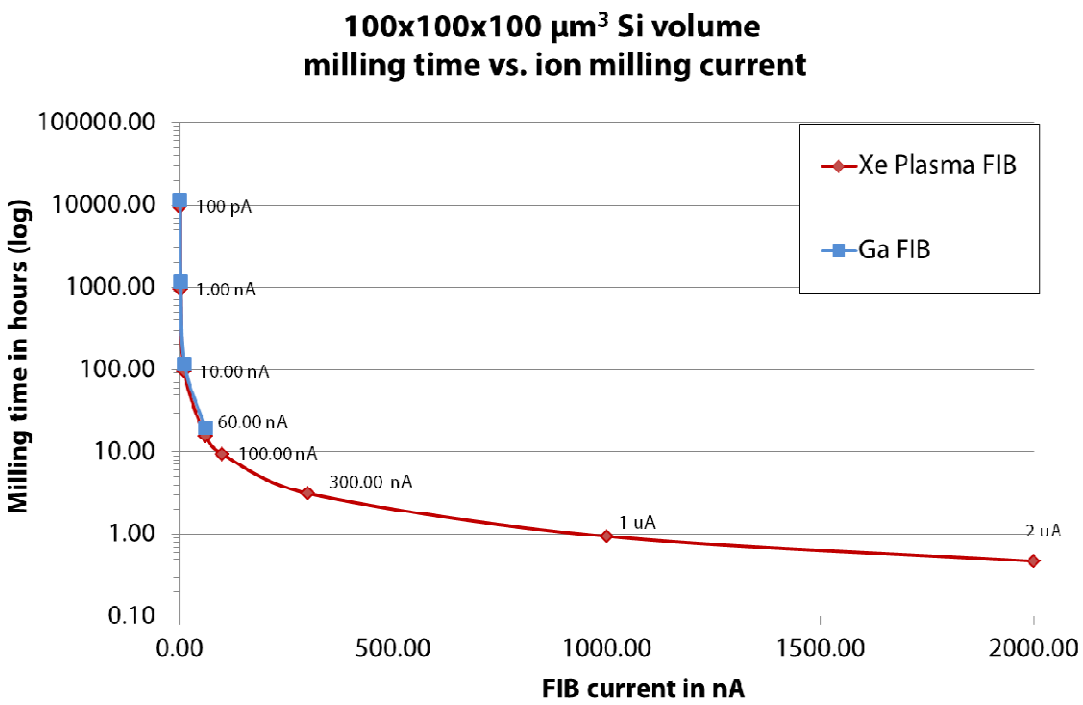


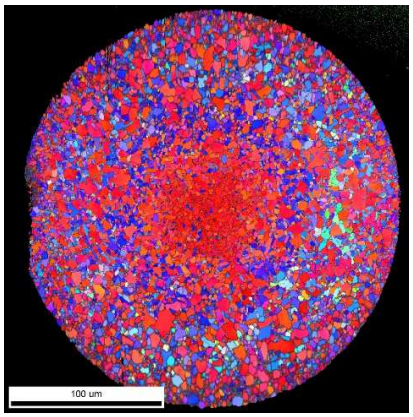
iFIB+ HR

- **High resolution Xe Plasma FIB (< 15nm at 30keV)**
- **High throughput using ≥ 1µA beam currents**

Patented OP source

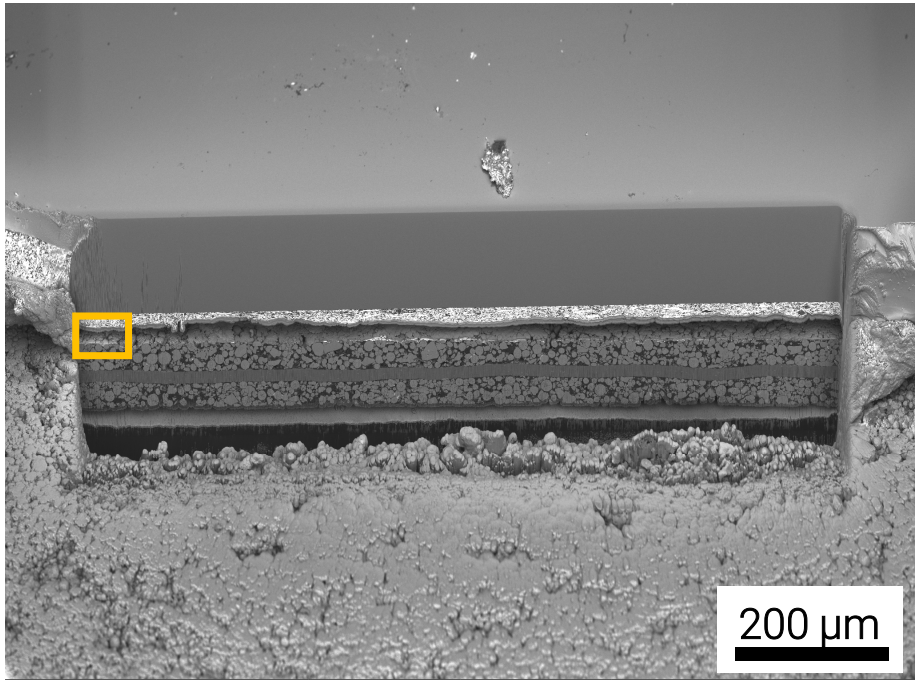




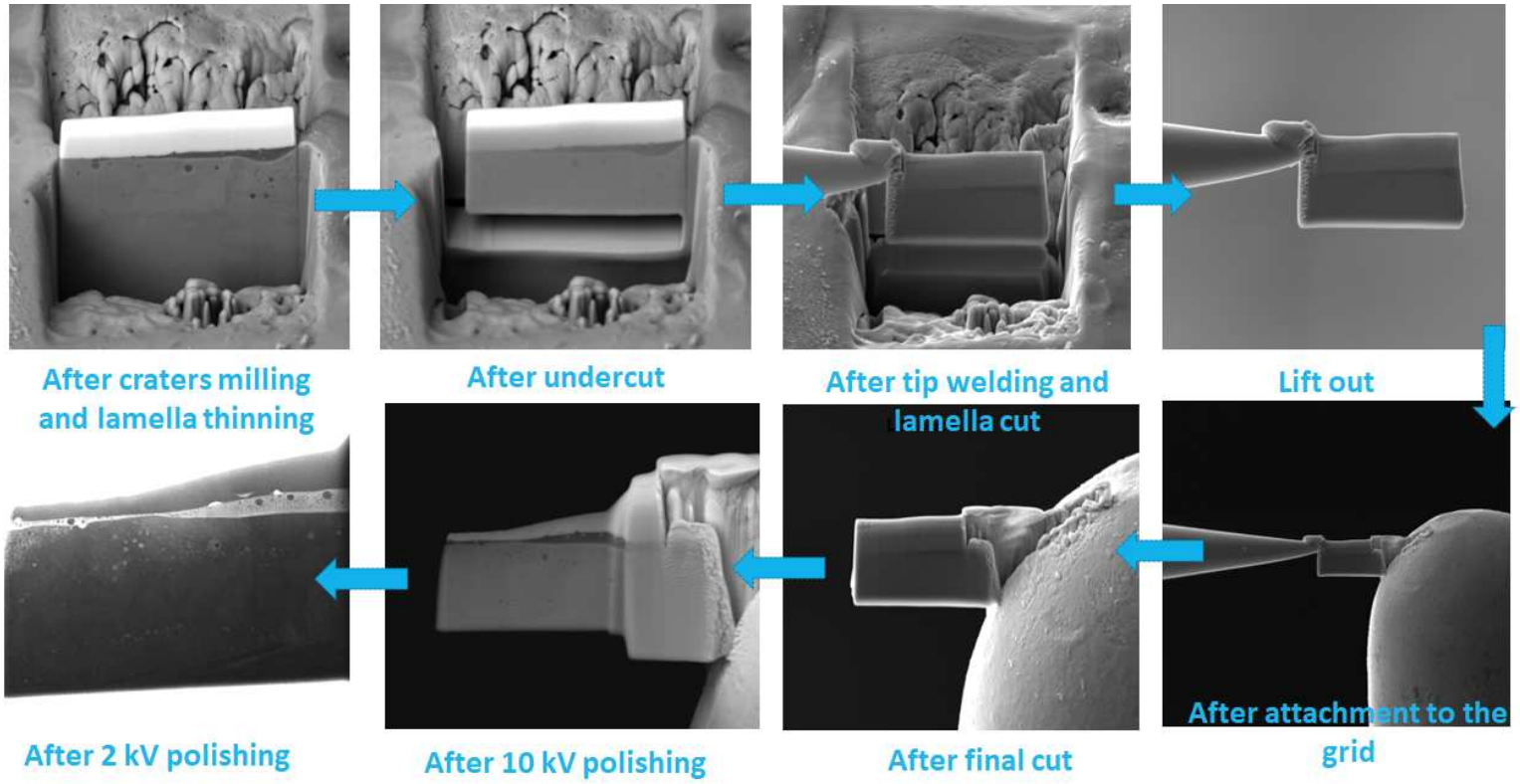


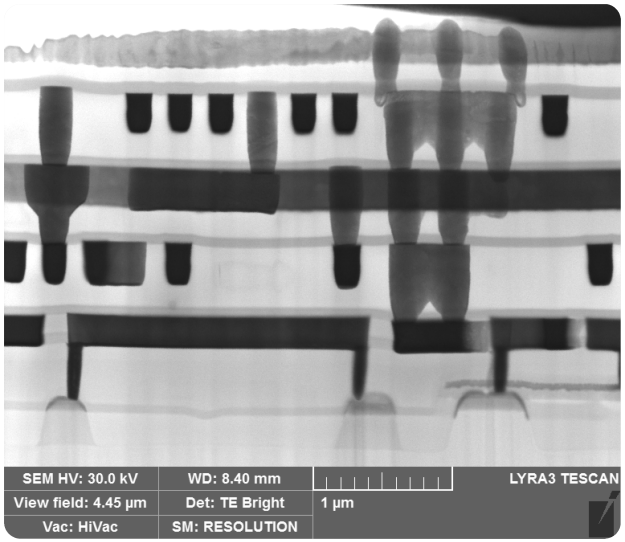
EBSD map from a cross-section of a 300 µm diameter Copper wire (prepared in 1 h).

Ga⁺ FIB: 50 µm wide cross-section of a Li-ion battery electrode



Xe⁺ Plasma FIB: 1 mm wide cross-section of a Li-ion battery electrode

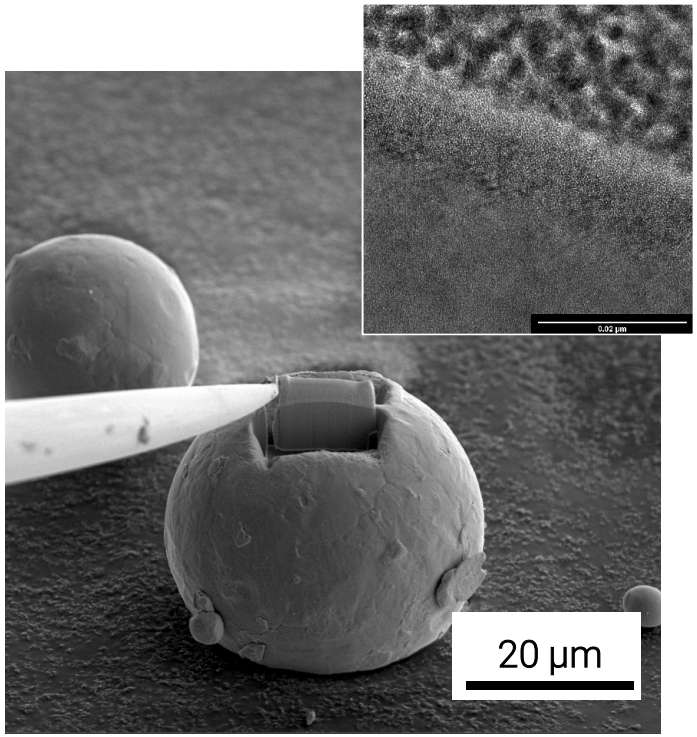

After craters milling and lamella thinning
After undercut
After tip welding and lamella cut
Lift out
After attachment to the grid
After final cut
After 10 kV polishing
After 2 kV polishing


SEM HV: 30.0 kV
WD: 8.40 mm
LYRA3 TESCAN
View field: 4.45 µm
Det: TE Bright
1 µm
Vac: HiVac
SM: RESOLUTION

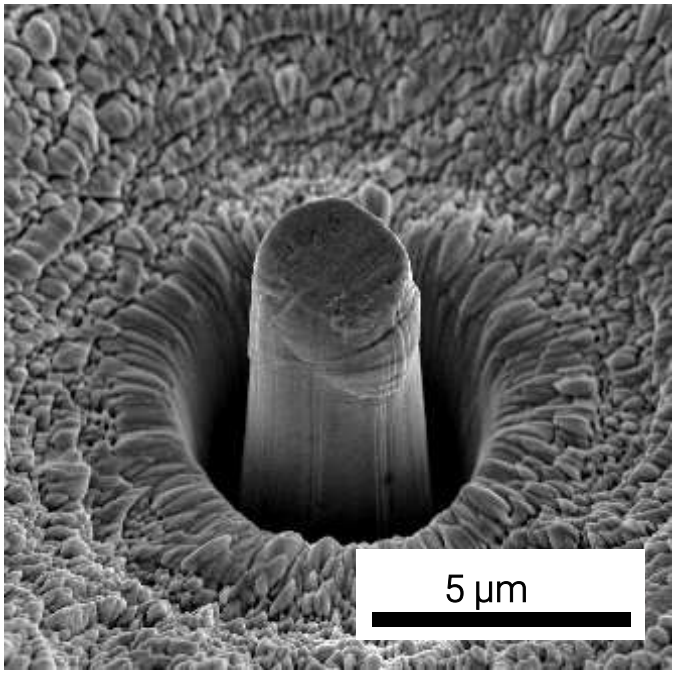

SEM HV: 30 kV
WD: 2.98 mm
MIRA3 TESCAN
View field: 1.47 µm
Det: TE-BF
200 nm
SEM MAG: 294 kx
SM: RESOLUTION
TESCAN

TESCAN AMBER X

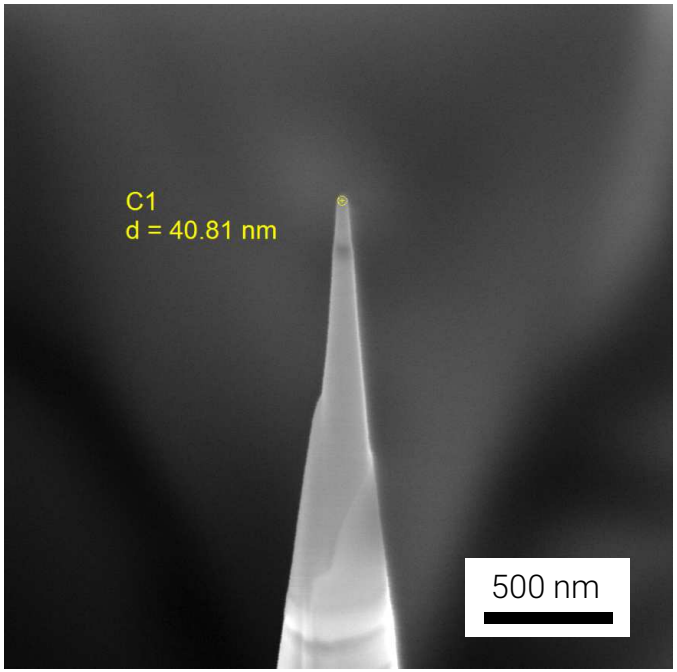
High precision Ga-Free Sample Preparation



TEM sample prepared from a Ti6Al4V powder particle, showing the oxidation layer in the TEM image.



A micro-pillar from ultra-fine-grained aluminum subjected to compression testing.

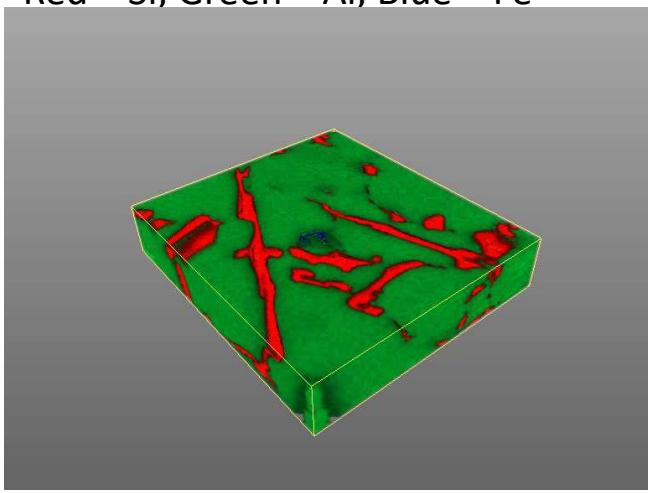


Ga-free Atom Probe Tip sample prepared using Xe PlasmaFIB

3D EDS – (alloy A380; Mg Alloy)

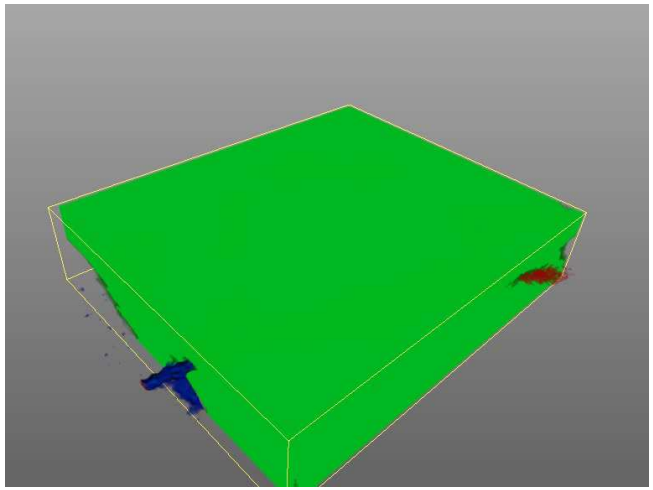
Total acquisition time: 19h 5 min

Red = Si, Green = Al, Blue = Fe

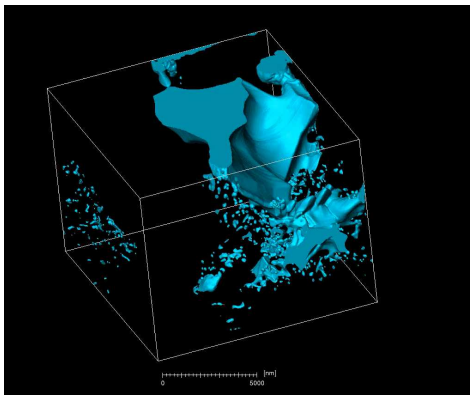


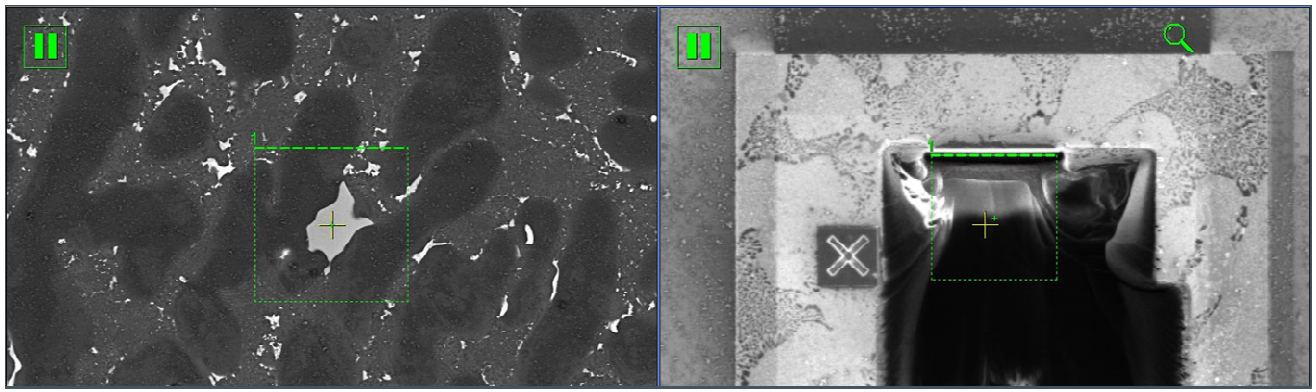
Green = Mg, Red = Al, Blue = Fe

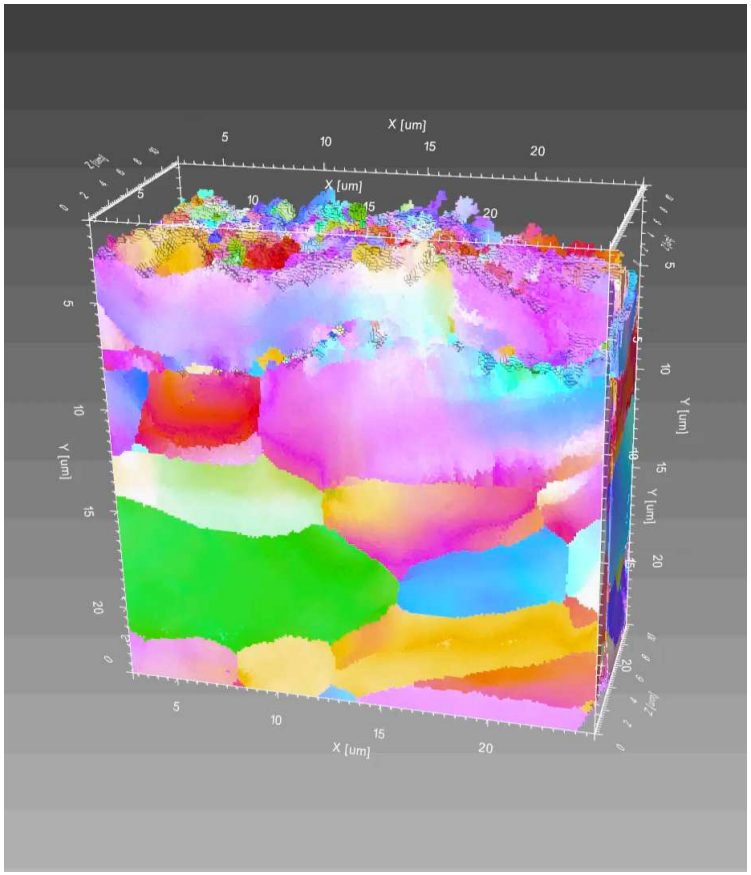
Total acquisition time: 17h 38 min



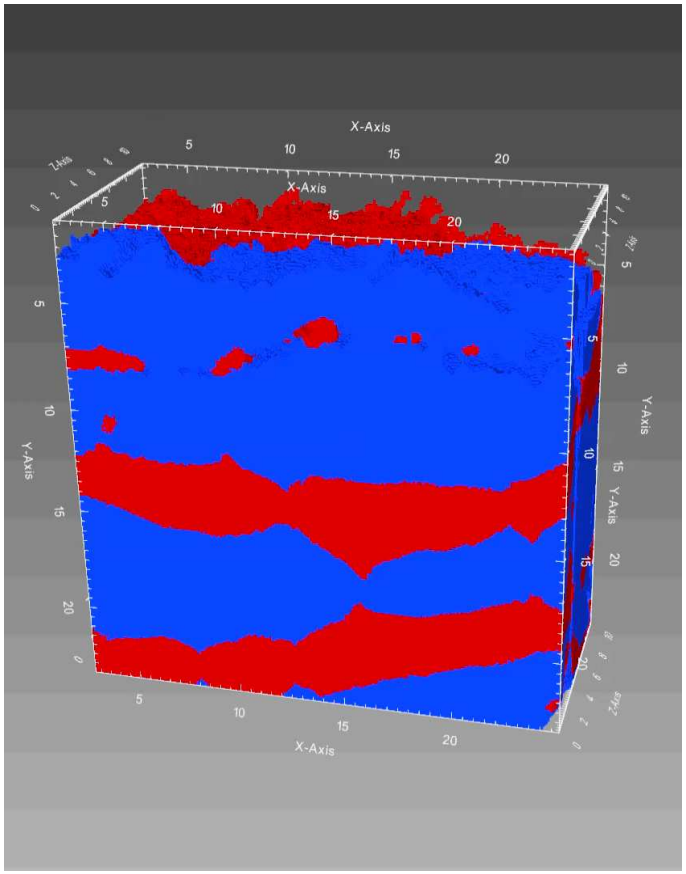
Al-Si: Fe-rich intermetallics



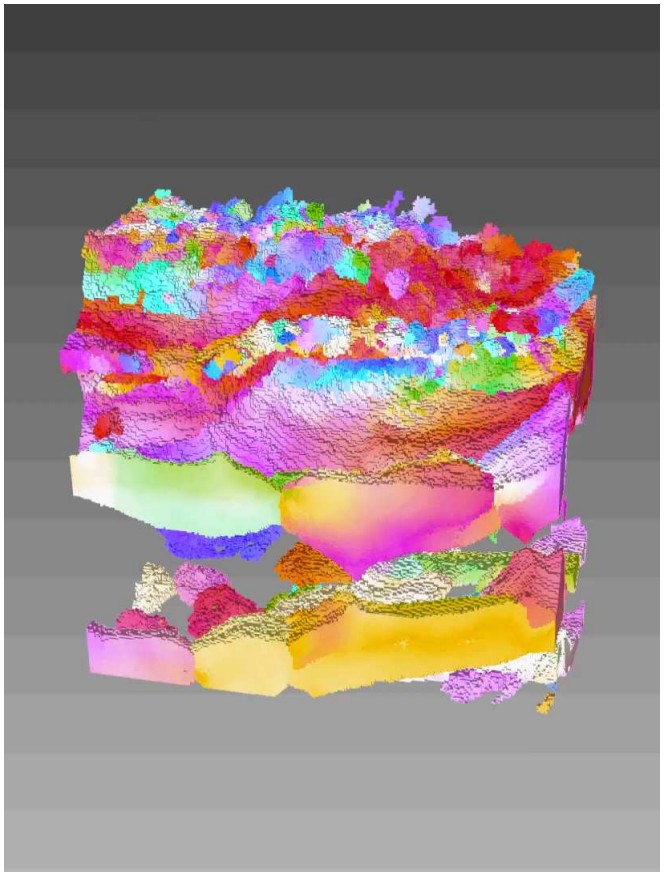




IPF map



Phase map



IPF map (ferrite only)

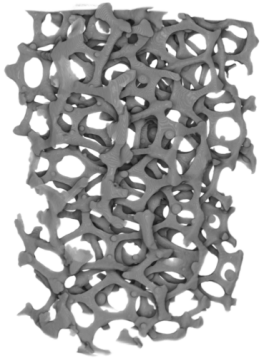
TESCAN
PERFORMANCE IN NANOSPACE

Product Portfolio
MicroCT

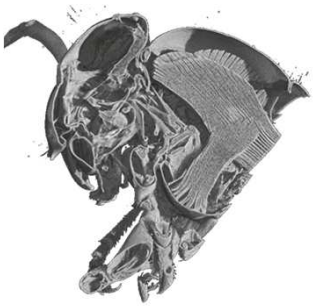
03

A new alternative in 3D X-ray imaging
Dynamic solutions for your lab

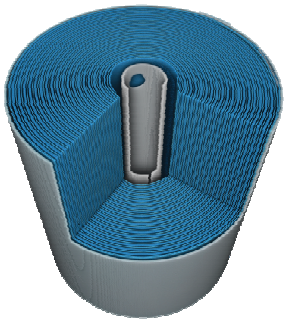
Compression of metal foams



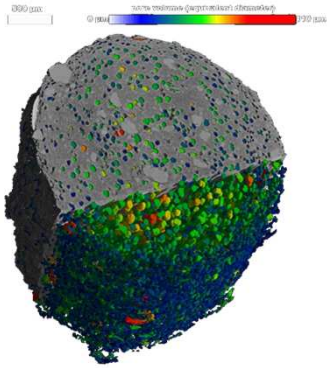
Insect



Lithium ion Battery



Pharmaceutical Tablet

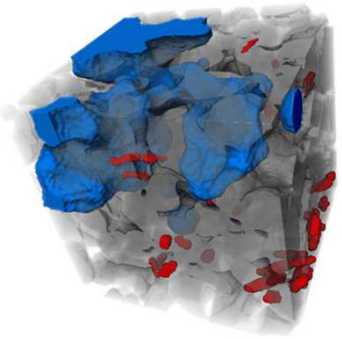


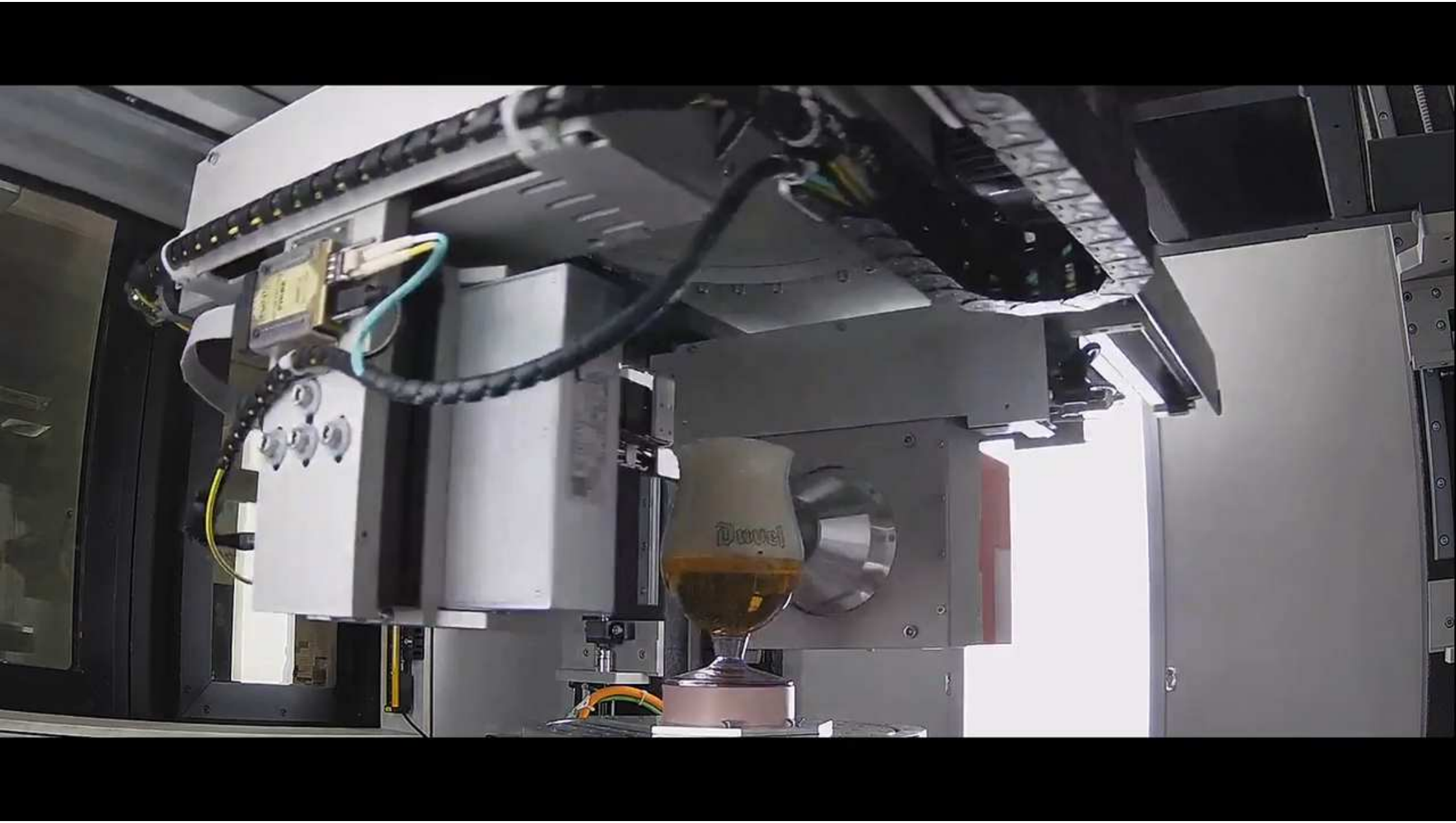
Carbonates

In situ Flow in Sandpack

Fractures in concrete

In situ mineralization

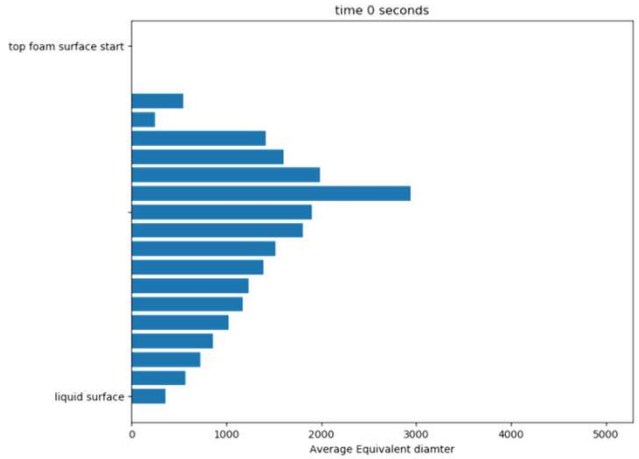


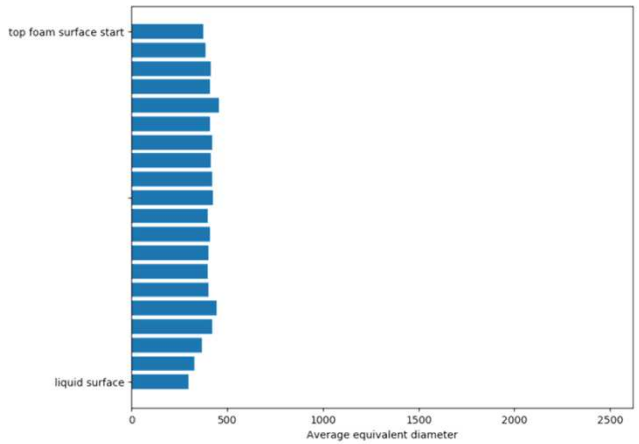


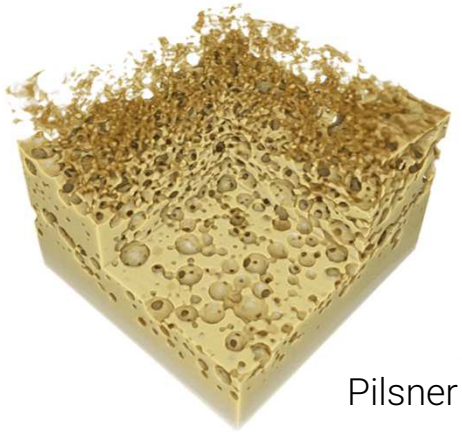
TESCAN CoreTOM – Foam Collapse Studies

BPA foam shows
greater stability and homogeneous bubble distribution compared to pilsner.

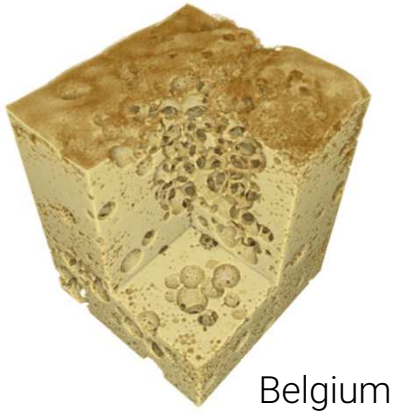
Foam collapse study
FOV ~ 10 cm







Pilsner

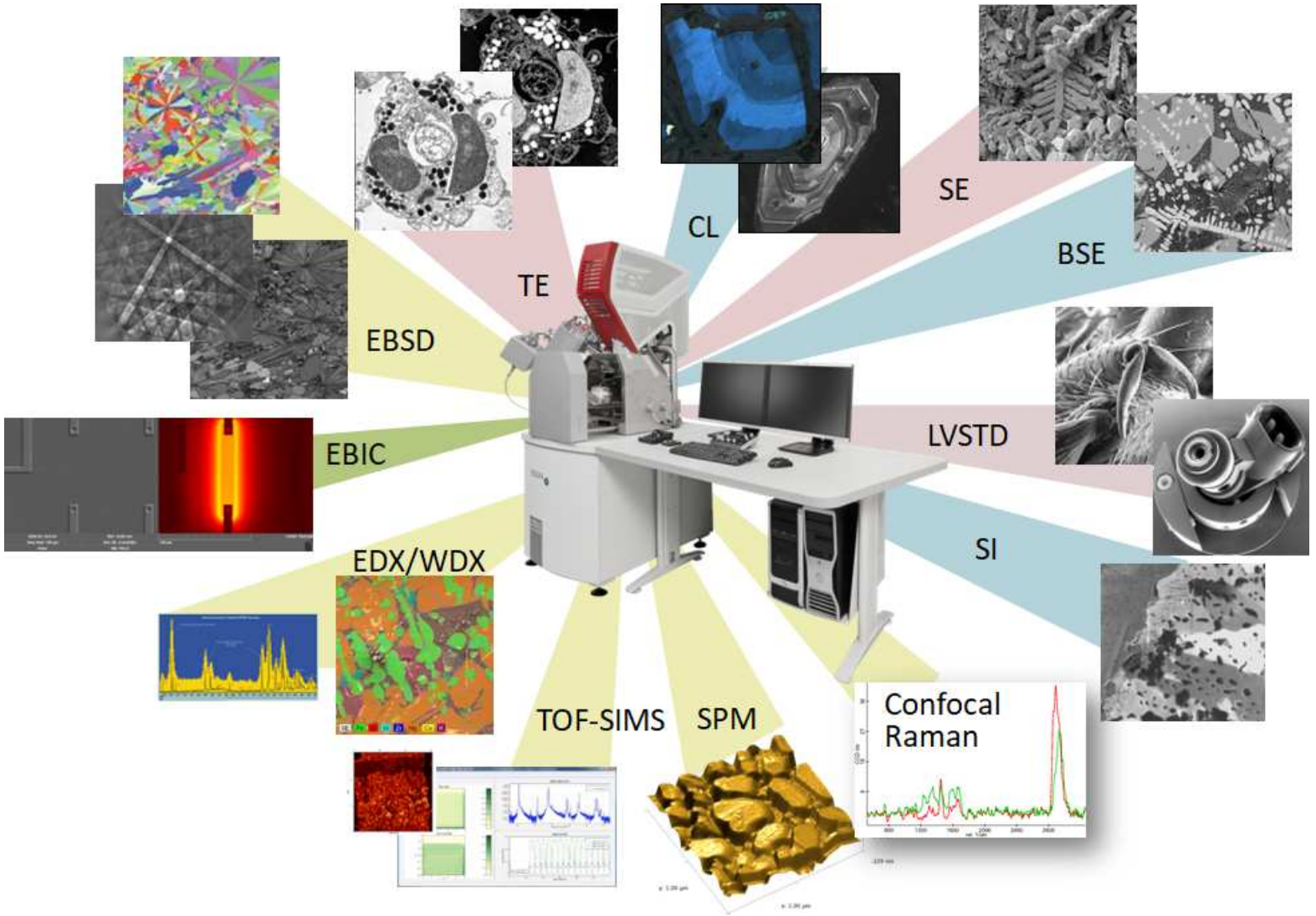


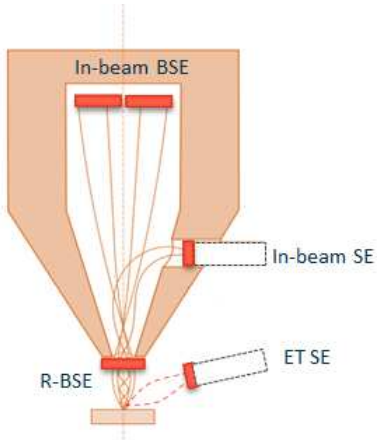
Belgium Pale Ale

TESCAN
PERFORMANCE IN NANOSPACE

TOF-SIMS

03

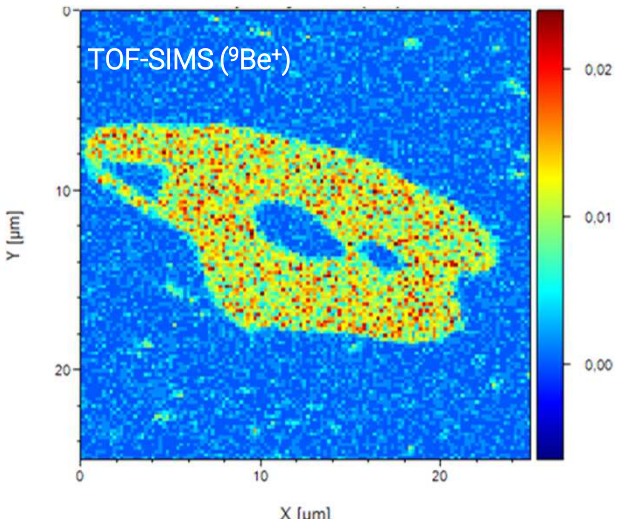

TE
CL
SE
BSE
EBSD
EBIC
LVSTD
SI
EDX/WDX
TOF-SIMS
SPM
Confocal Raman


In-beam BSE
In-beam SE
ET SE
R-BSE

TOFWERK
Time-of-Flight Mass Spectrometry

CTOF - Compact retractable TOF-SIMS

Berylium Mapping

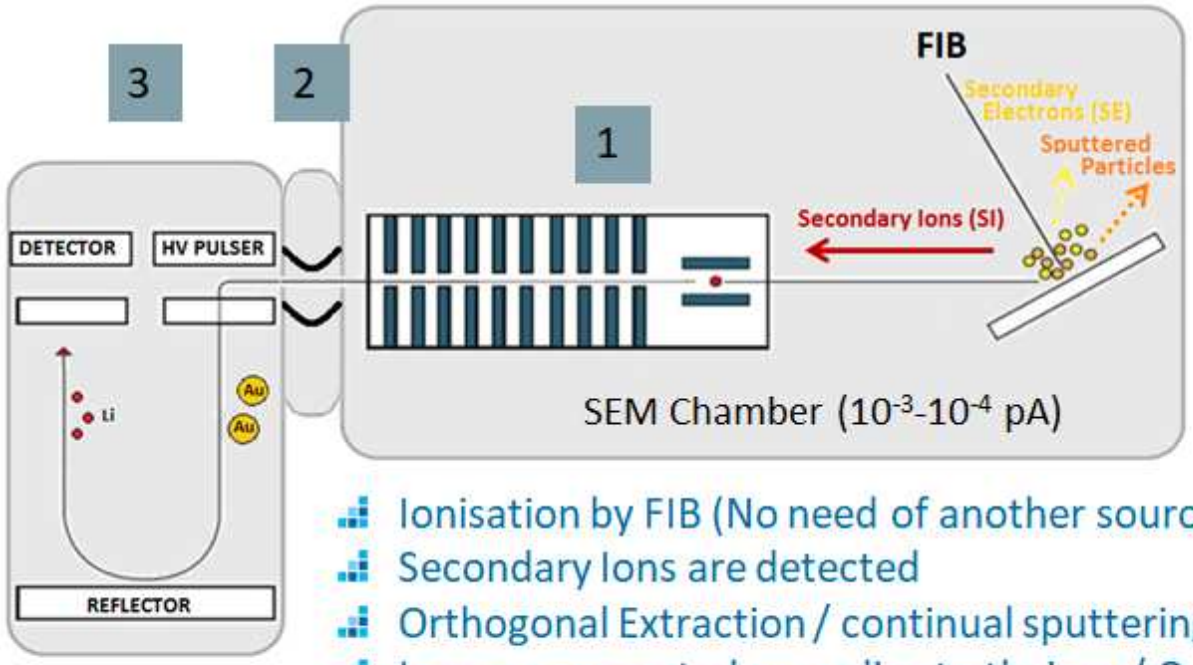


HTOF - High resolution TOF-SIMS

Longer time of flight: Higher mass resolution

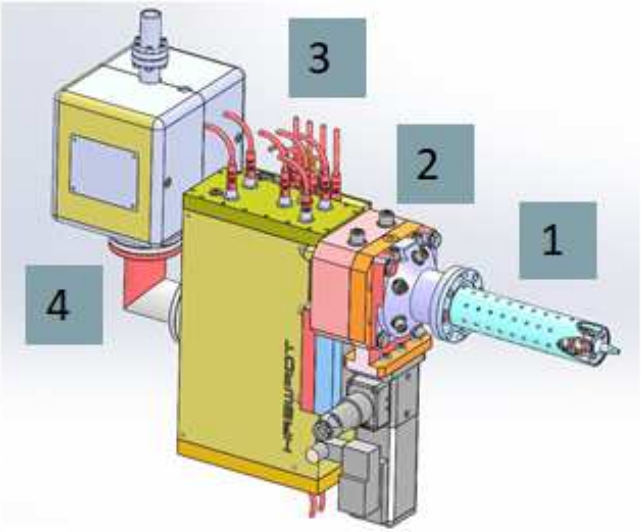
DESCRIPTION OF THE TECHNIQUE

Schematic drawing



- Ionisation by FIB (No need of another source)
- Secondary Ions are detected
- Orthogonal Extraction / continual sputtering
- Ions are separated according to their m / Q
- Time of Flight is measured

1 Ion Transfer Optics
2 Separating valve
3 TOF chamber
4 TOF ion pump



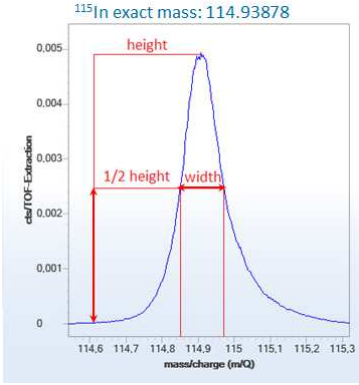
3D visualization

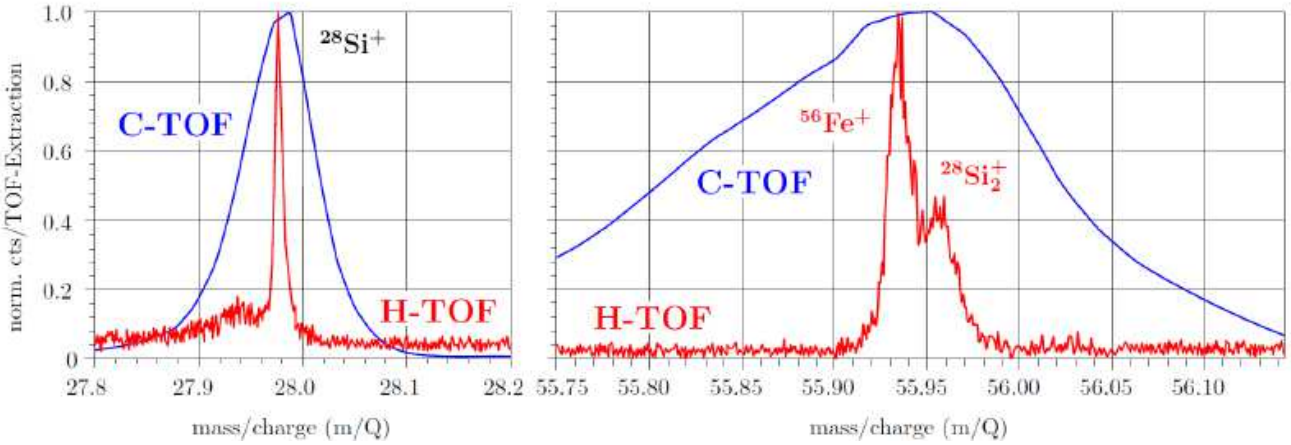
	C-TOF		H-TOF	
	Ga⁺ FIB	Xe⁺ FIB	Ga⁺ FIB	Xe⁺ FIB
Lateral resolution (nm) *	40	60	40	60
Detection limit (ppm)	3	1,5	10	5
Depth resolution (nm)	3		6	
Mass resolution	>800		>3500	

*Measured on the certified reference material BAM L200.

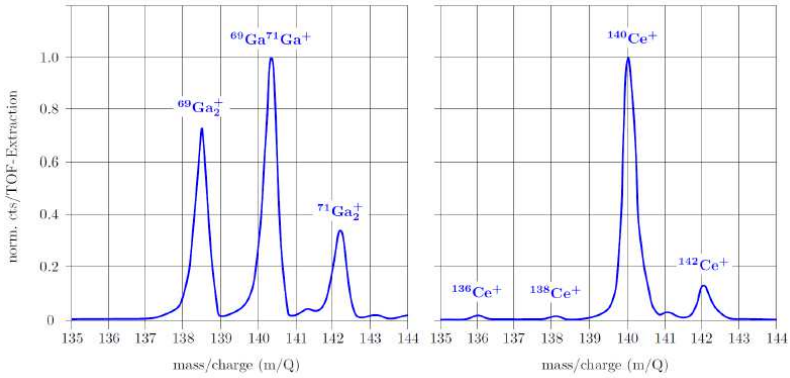
MASS RESOLUTION

isotope mass (114.93878) / peak width at half of its maximum (FWHM)



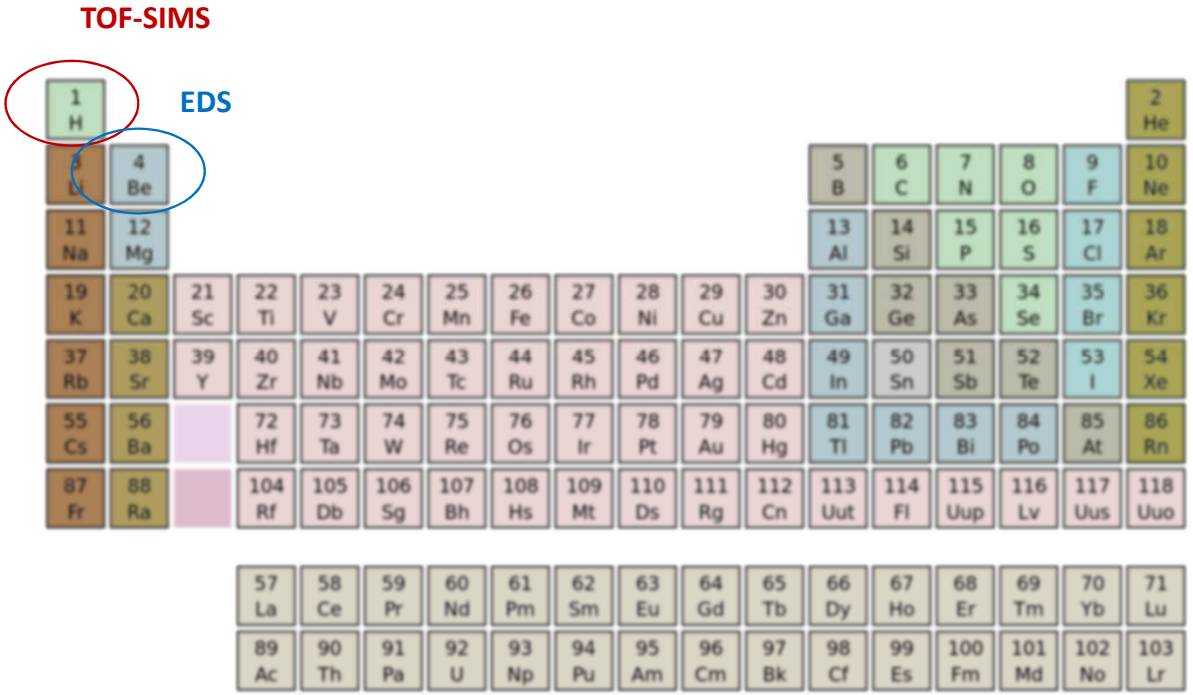


- **Ga⁺ primary ions**
  - high lateral resolution
  - low currents
- **Xe⁺ primary ions**
  - high detection limit
  - limited ion implantation



Unique features – compared to EDS / WDS systems

- **Detection of light elements**
- Better limits of detection
- Depth profiling
- Better lateral resolution
- Isotopes can be distinguished



Unique features – compared to EDS / WDS systems

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- **Better limits of detection**
- Depth profiling
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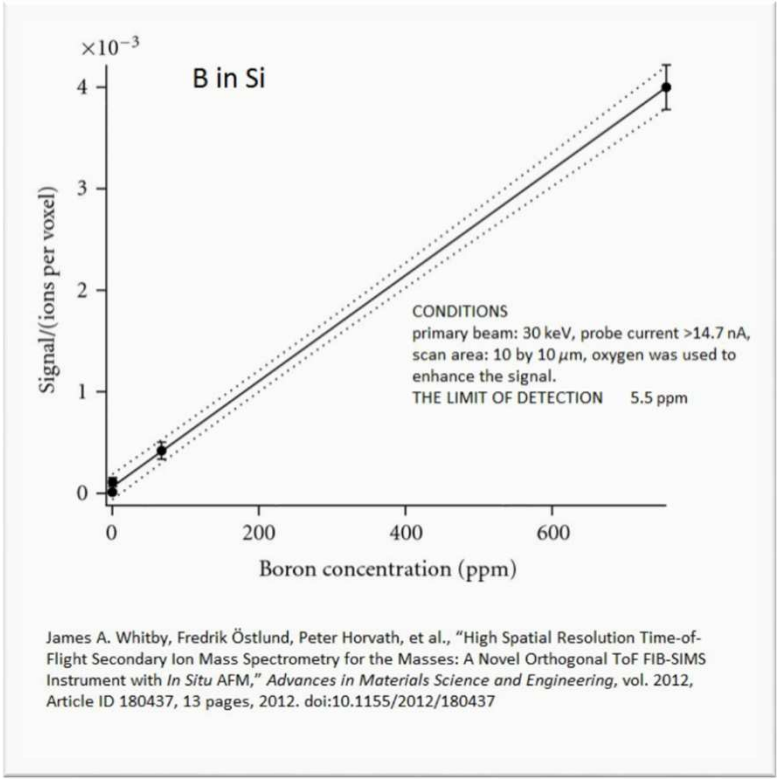
- Isotopes can be distinguished

EDS: 0.1 (mass %)
WDS: 0.01 (mass %)
TOF-SIMS: a few ppm



James A. Whitby, Fredrik Östlund, Peter Horvath, et al., "High Spatial Resolution Time-of-Flight Secondary Ion Mass Spectrometry for the Masses: A Novel Orthogonal ToF FIB-SIMS Instrument with *In Situ* AFM," *Advances in Materials Science and Engineering*, vol. 2012, Article ID 180437, 13 pages, 2012. doi:10.1155/2012/180437

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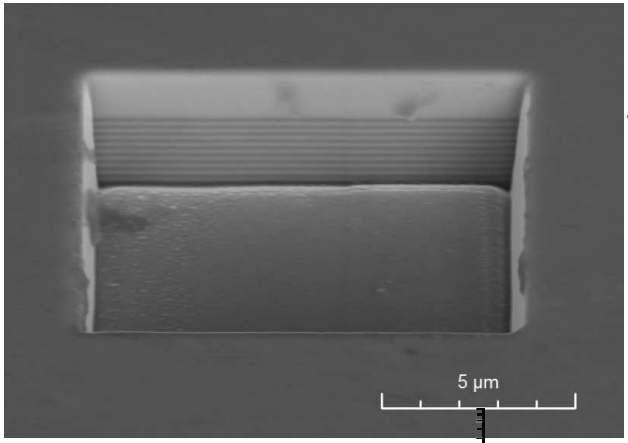
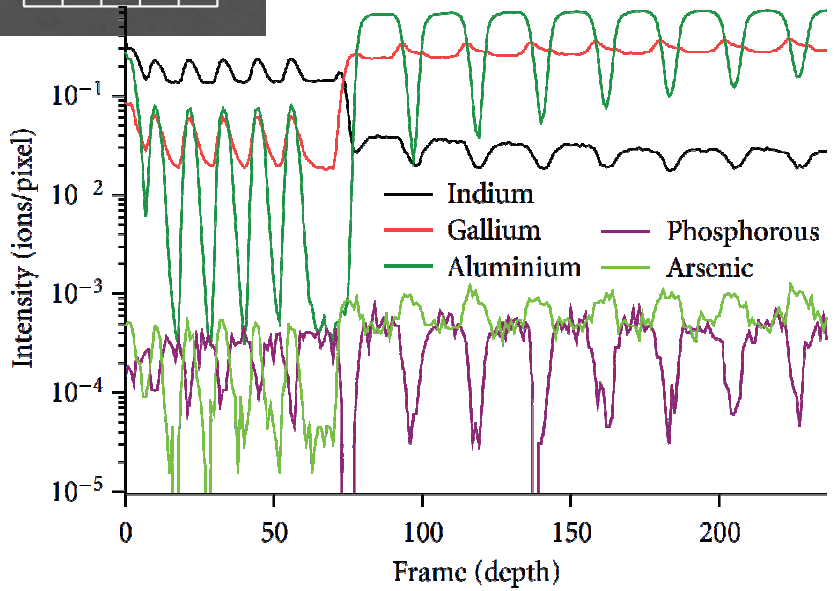


Vertical Cavity Surface Emitting Laser (VCSEL)

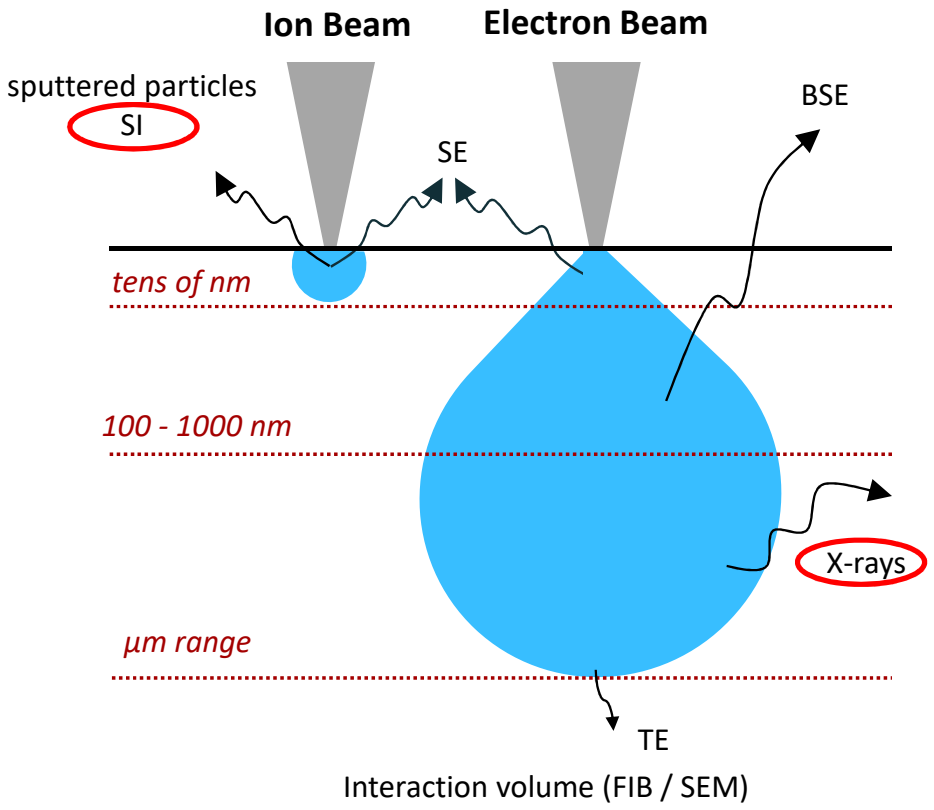
multi-layered sample



James A. Whitby et al., "High Spatial Resolution Time-of-Flight Secondary Ion Mass Spectrometry for the Masses: A Novel Orthogonal ToF FIB-SIMS Instrument with *In Situ* AFM," *Advances in Materials Science and Engineering*, vol. 2012, Article ID 180437, 13 pages, 2012.

Unique features – compared to EDS / WDS systems

- Detection of light elements
- Better limits of detection
- Depth profiling
- **Better lateral resolution**
- Isotopes can be distinguished



Unique features – compared to EDS / WDS systems

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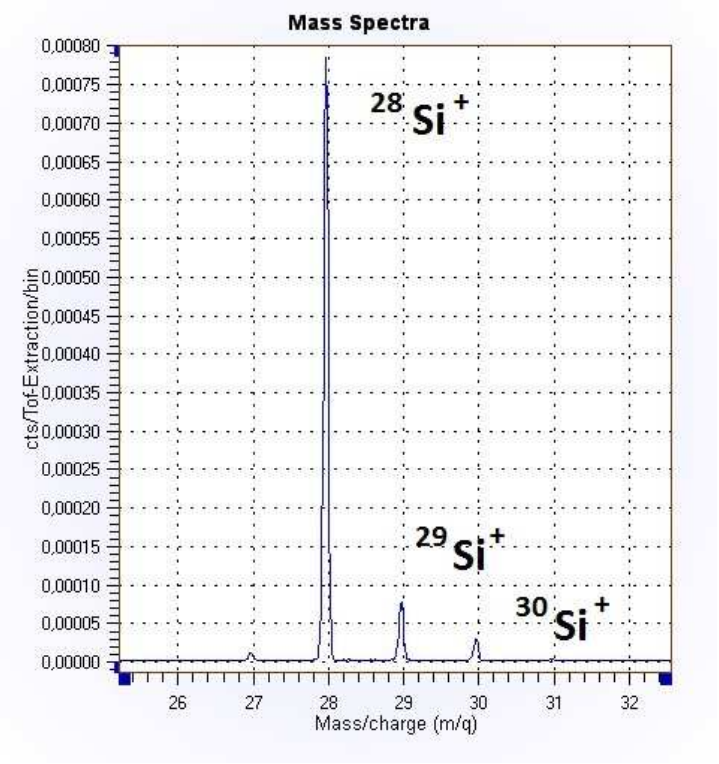
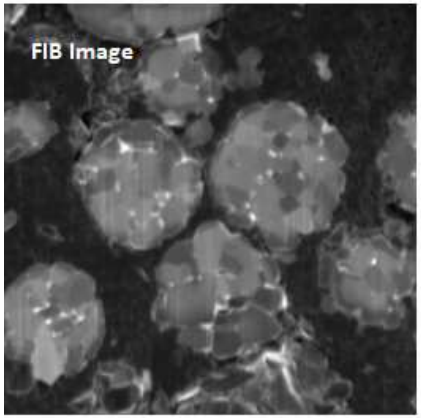
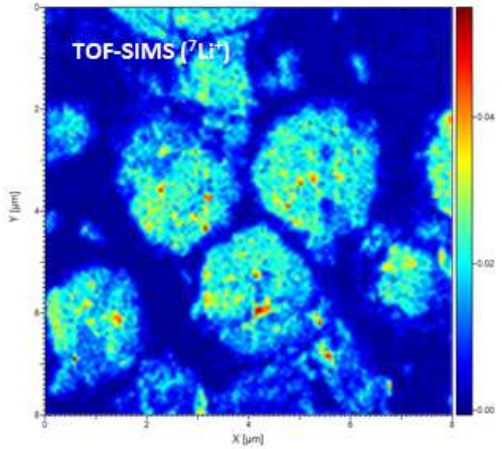


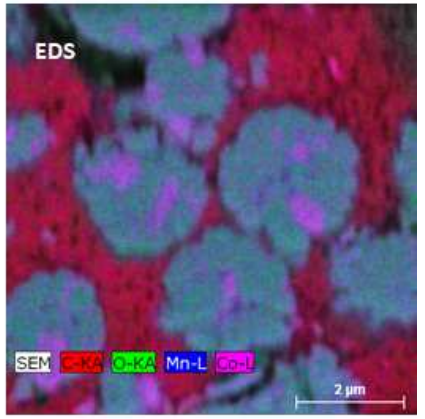
- Hydro Quebec – Electricity supplier (Canada)
- University of Maryland (USA)

Lithium Mapping

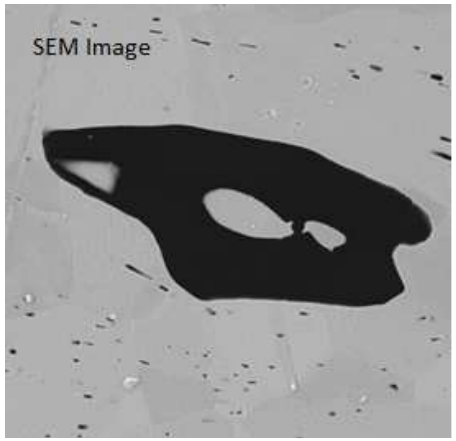


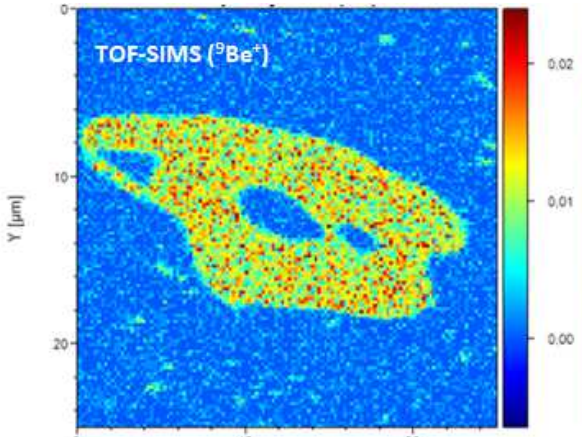
Li Battery

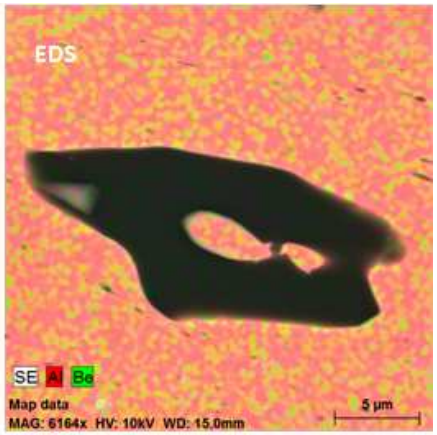




Berylium Mapping



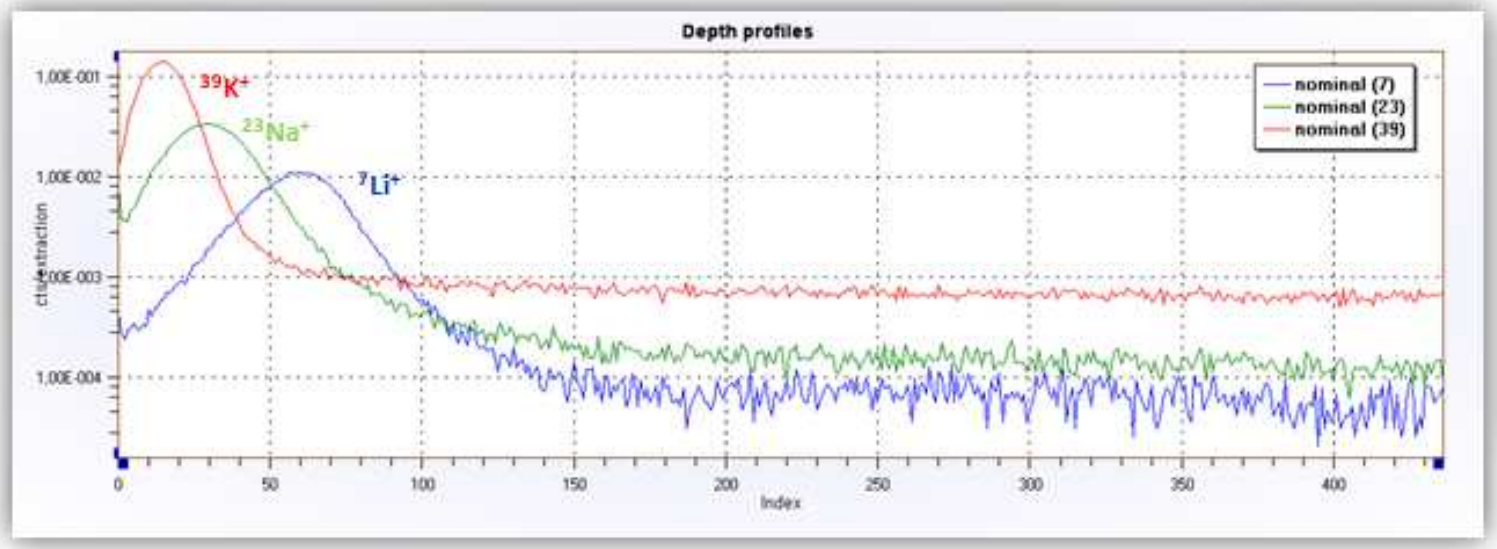


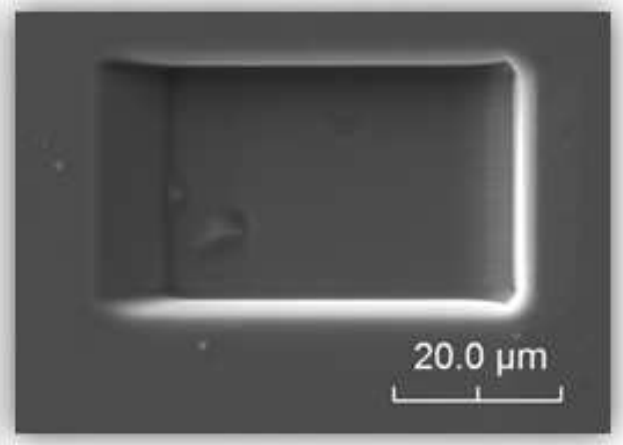


- Semiconductor company (South Korea)
- Texas A&M (USA)

Trace element analysis

- *Elements like K, Cs, Na, B, Li can be detected in ppm.*
- *Elements like C, H, N can be detected in (tens of) percents.*
- *Different sensitivity for different elements.*



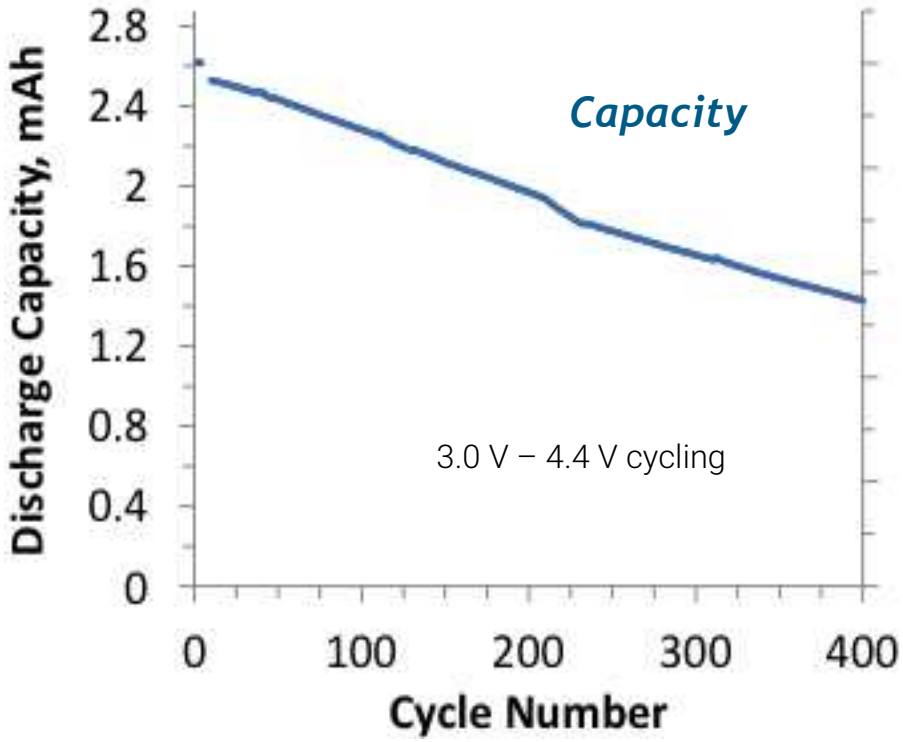


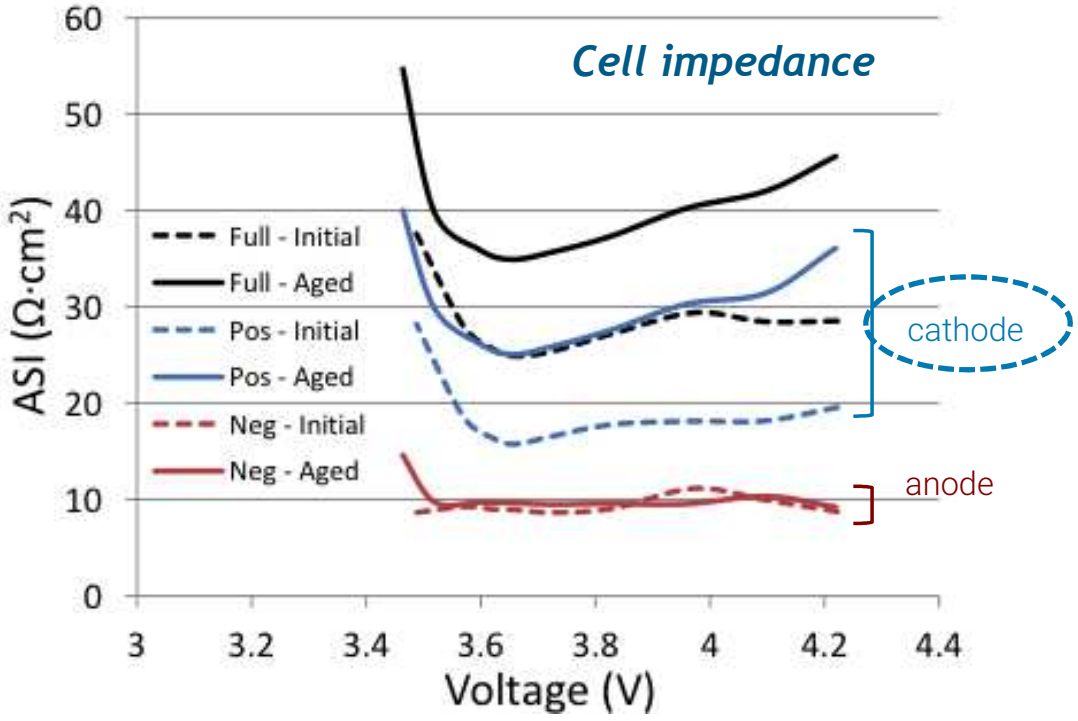
Crater after analysis

Addressing capacity fade in Li-ion batteries

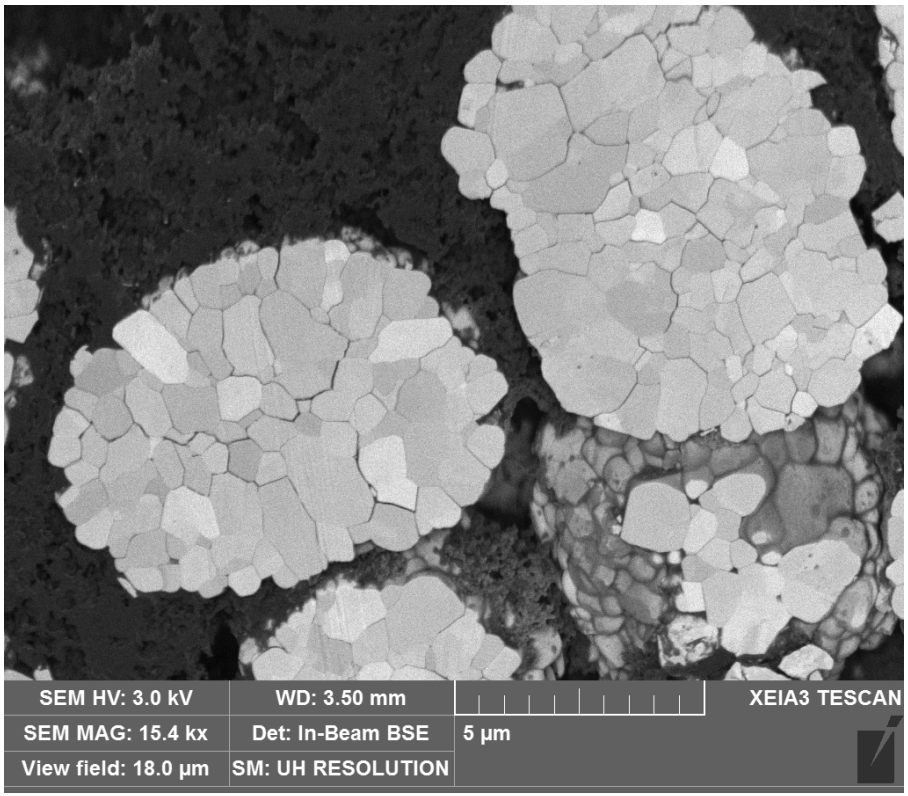
Layered oxides offer high capacity, but can lose of capacity as function of cycling, especially when cycled at higher voltages and fast charge rates

"NCM 523" - $Li_{1.03}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{0.97}O_2$

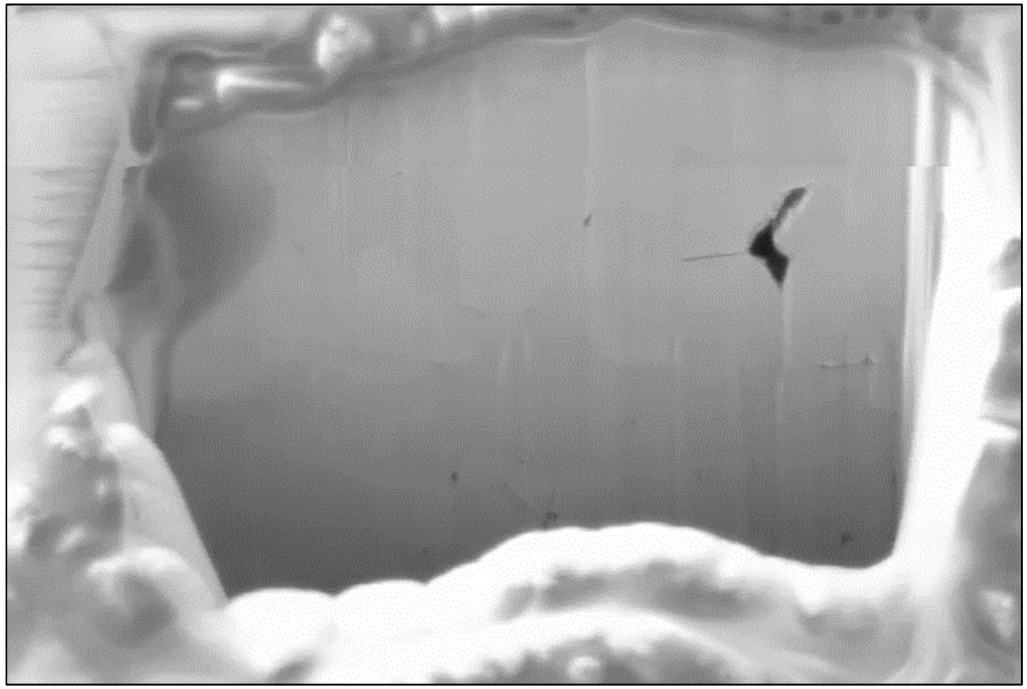




FIB-SEM can provide new insight into degradation mechanisms in Li-batteries

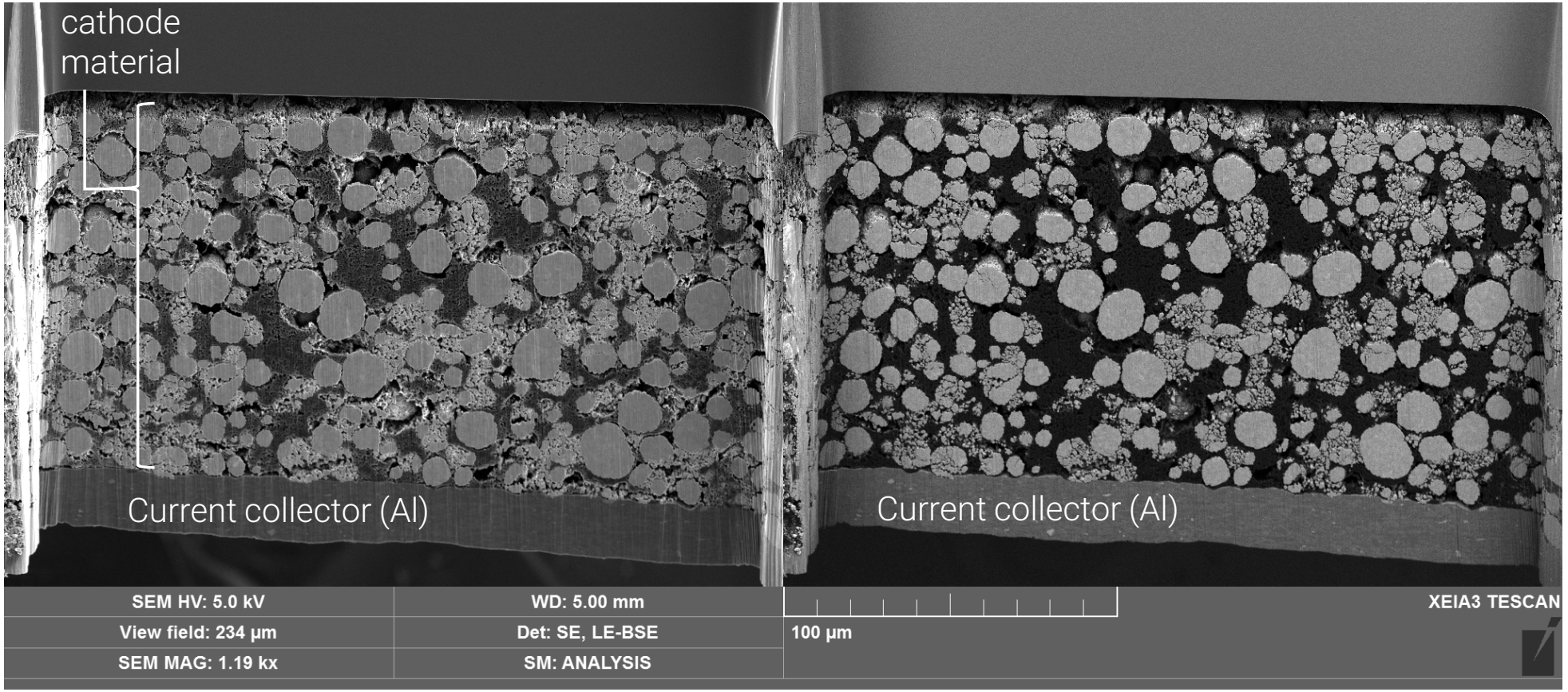


Structure and morphology



In situ and operando characterization

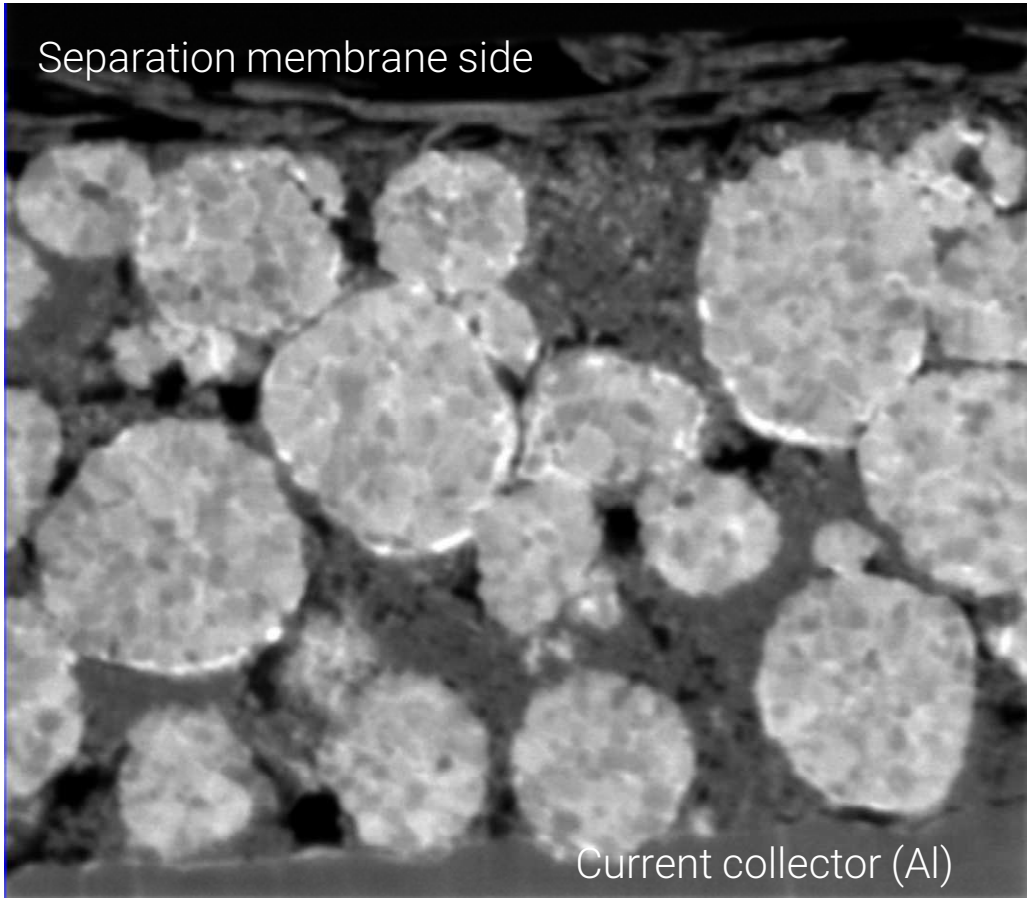
TOF-SIMS in FIB-SEM

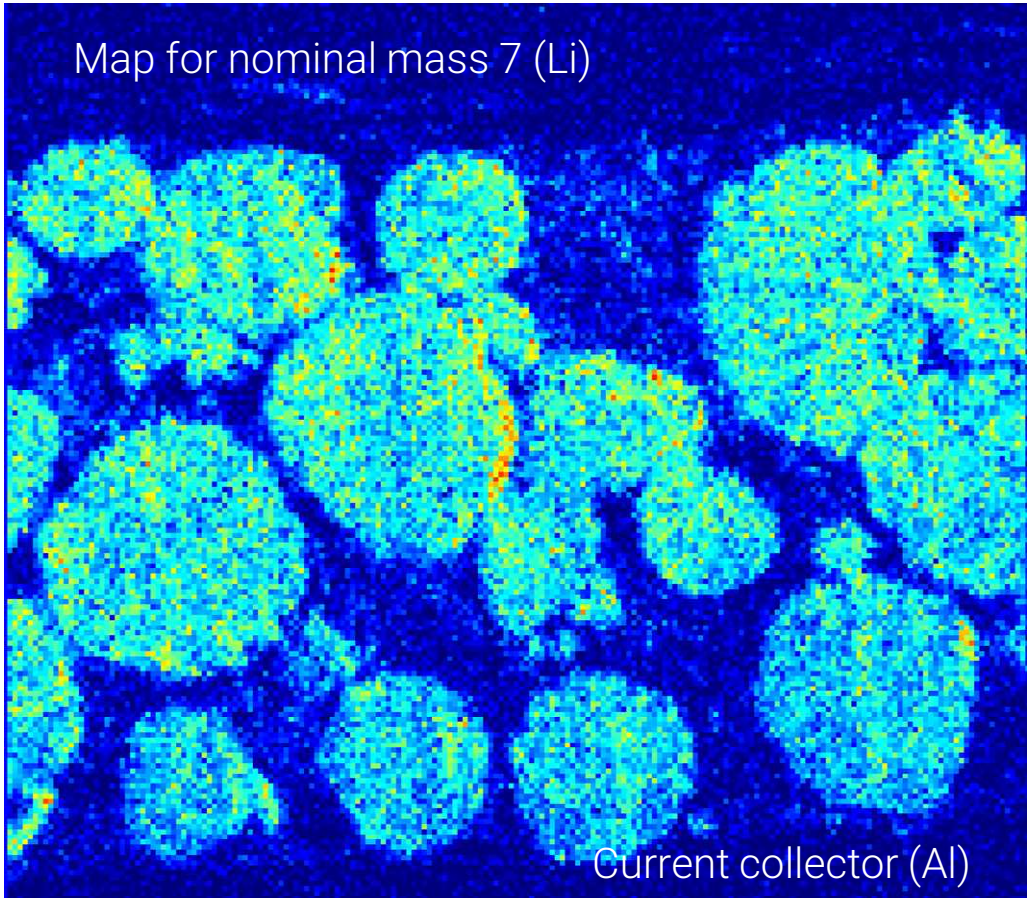


- $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) electrode
- 400, 3.0–4.4 V cycles at 30 °C (against graphite)
- examined in “fully lithiated” state

Cross-section of thick electrode prepared *in situ* using plasma FIB

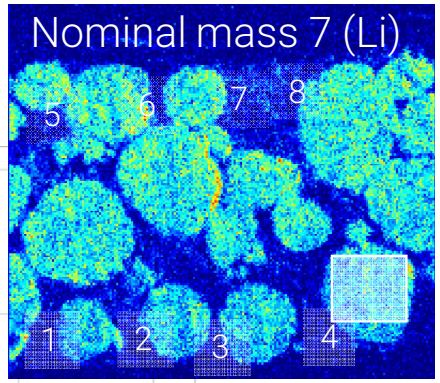
Evidence for global inhomogeneity in Li distribution across cathode - mapping

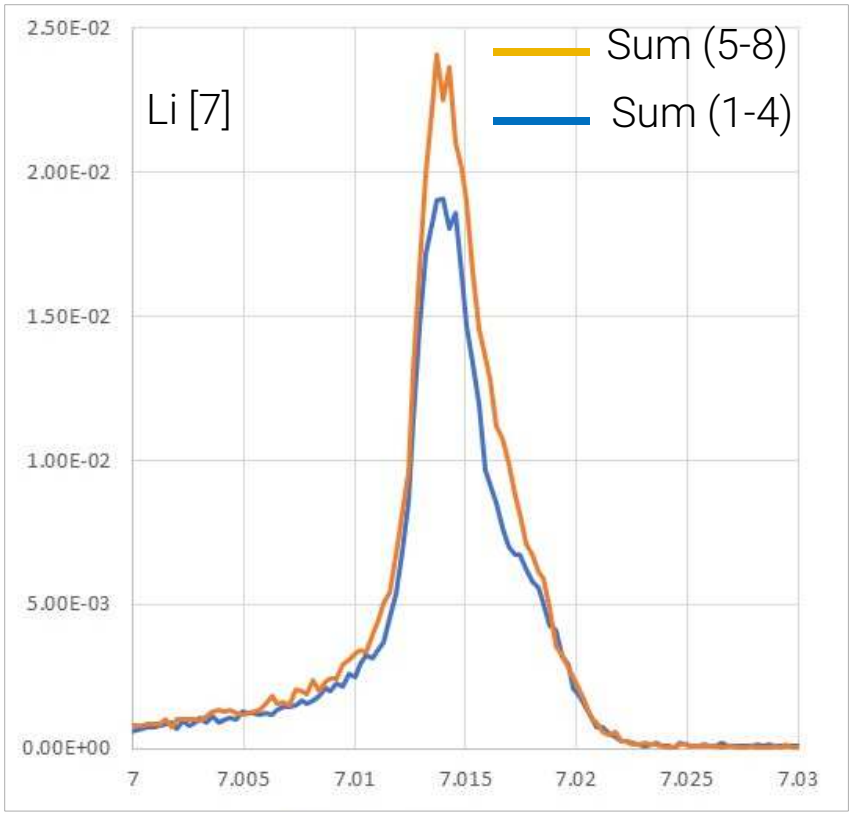


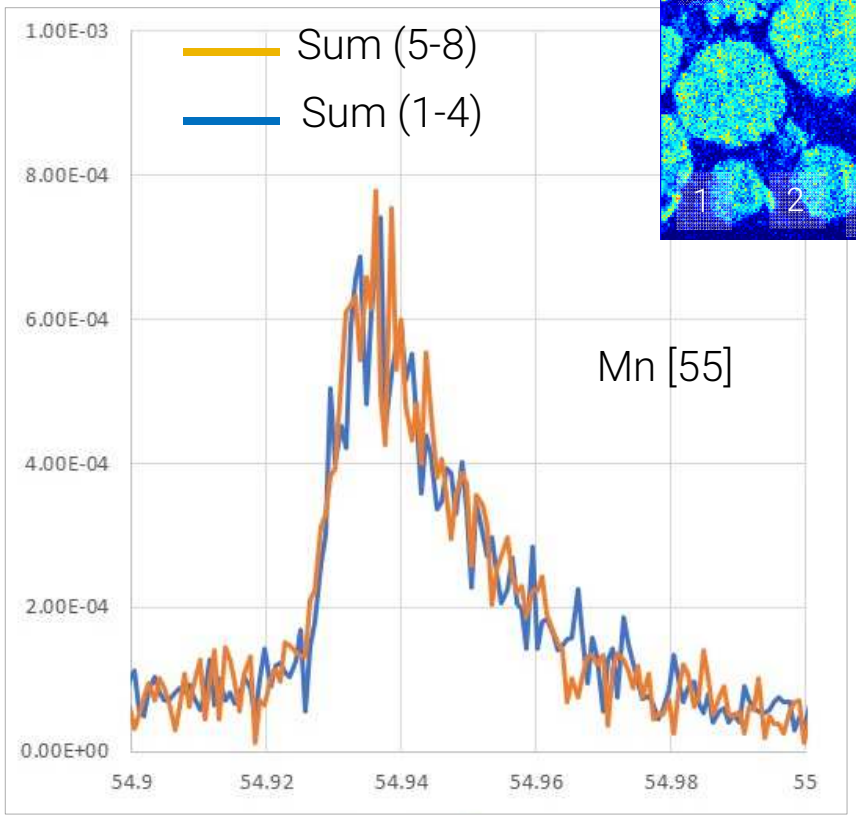


- Li content often seems to be higher in particles closest to separation membrane, lower in particles closest to current collector

Evidence for global inhomogeneity in Li distribution across cathode – spectrum analysis

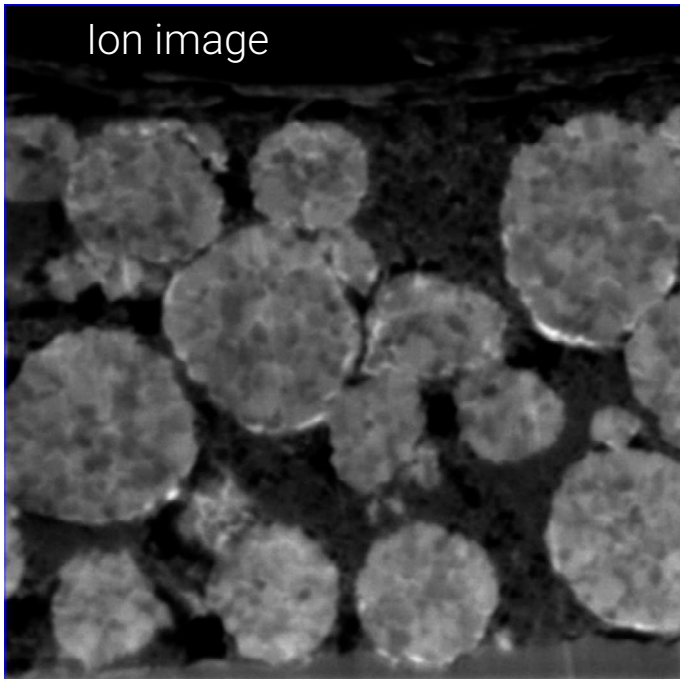


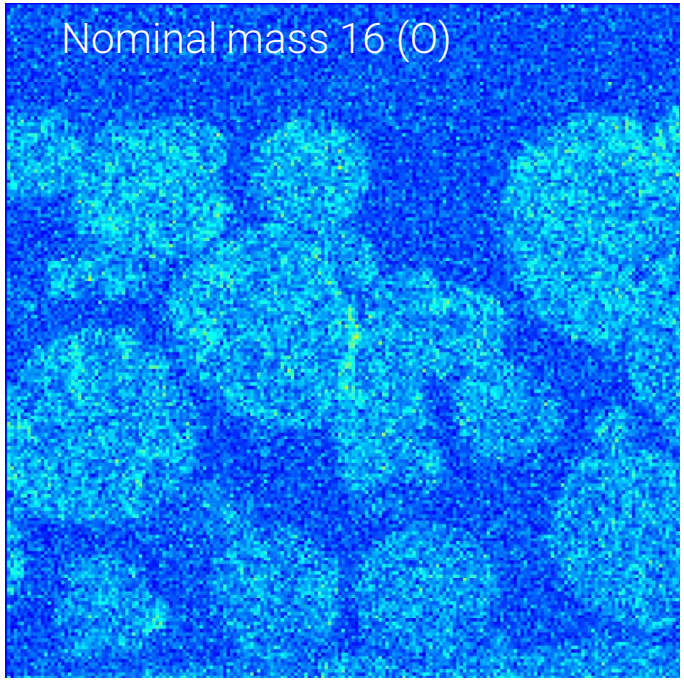


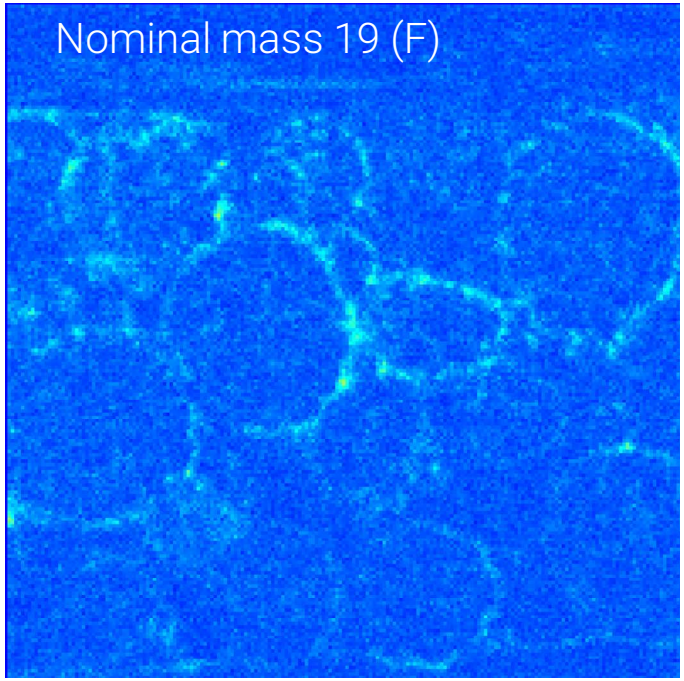


- Li content is higher in particles close to separation membrane and lower in those close to the current collector while transition metal content is equal (Mn shown)

Evidence for inhomogeneity in Li distribution and reaction product surface deposits across cathode

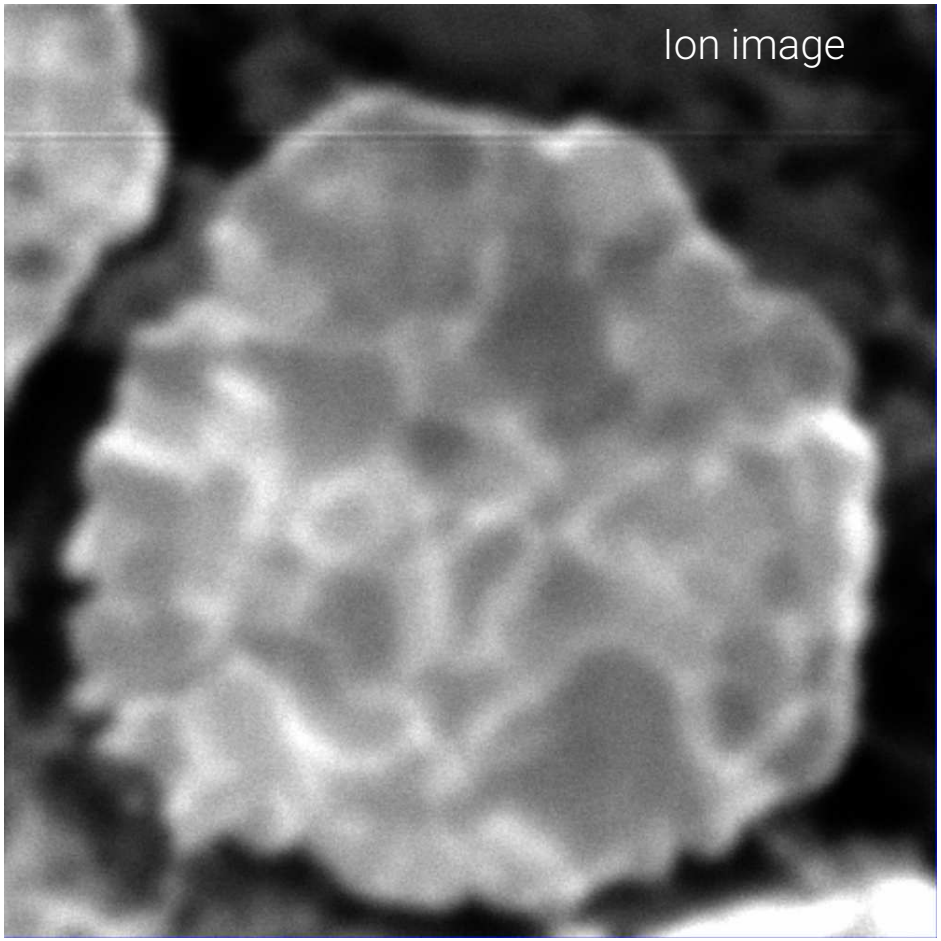


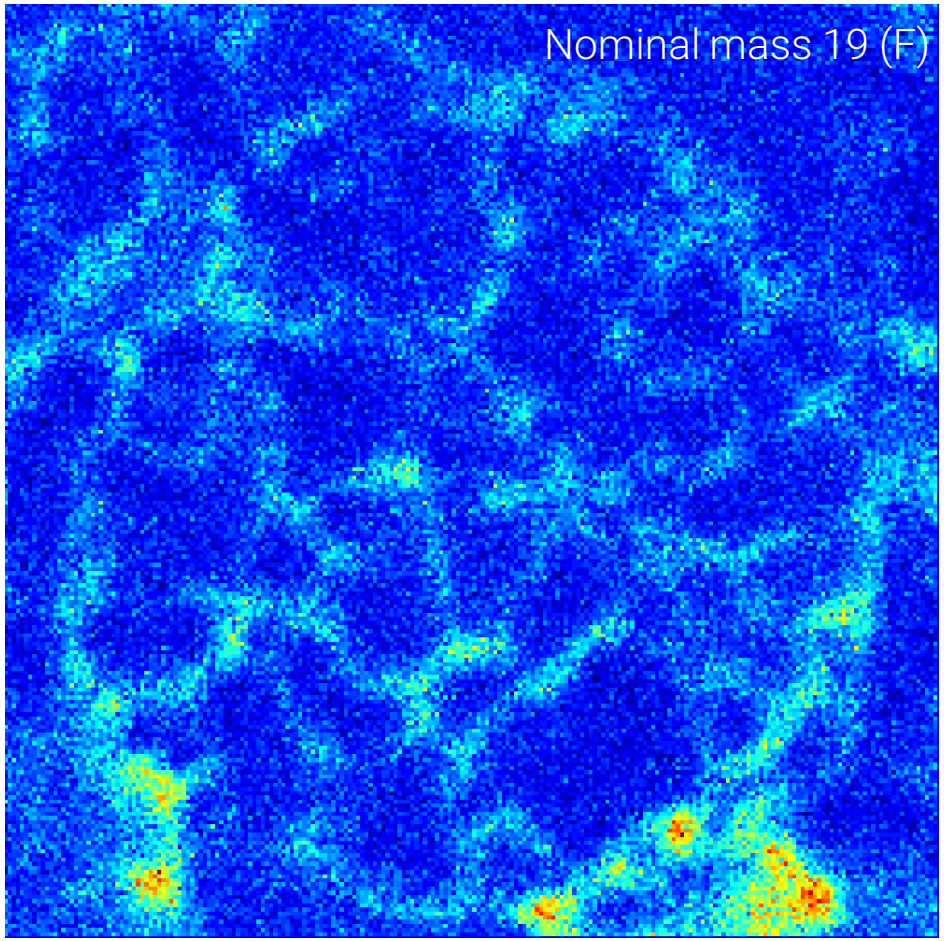




Negative ion scan

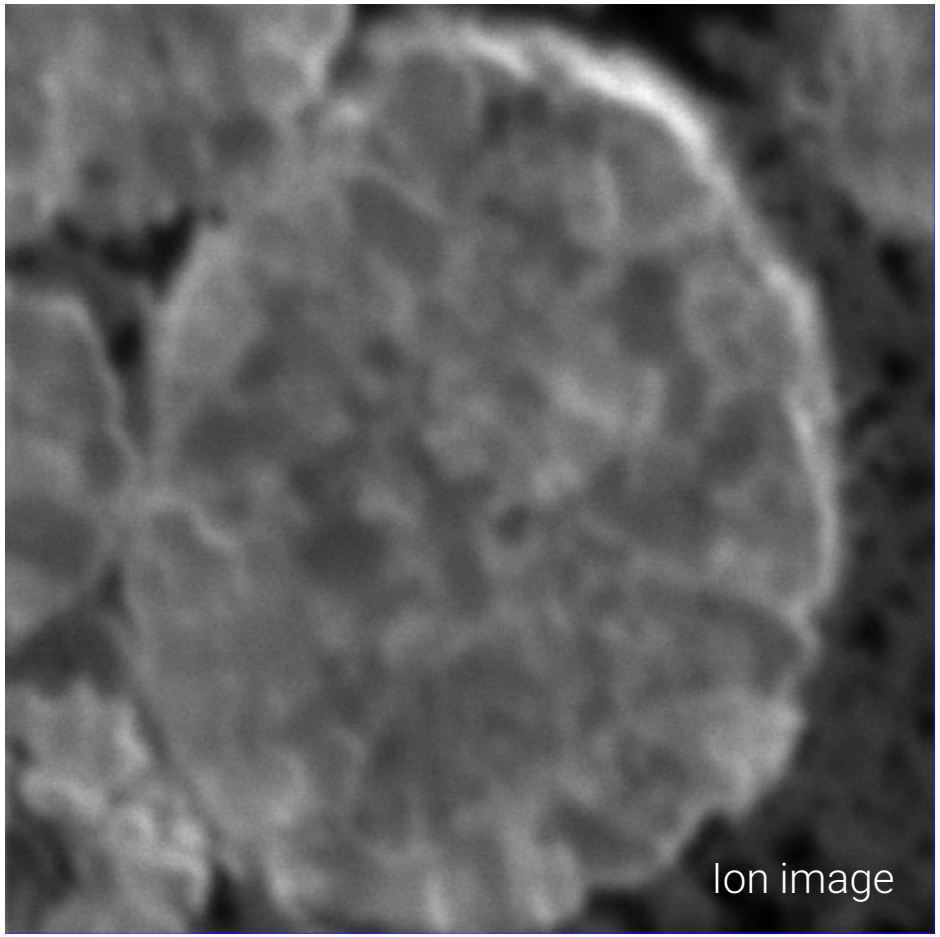
Evidence for electrolyte penetration into cathode particles

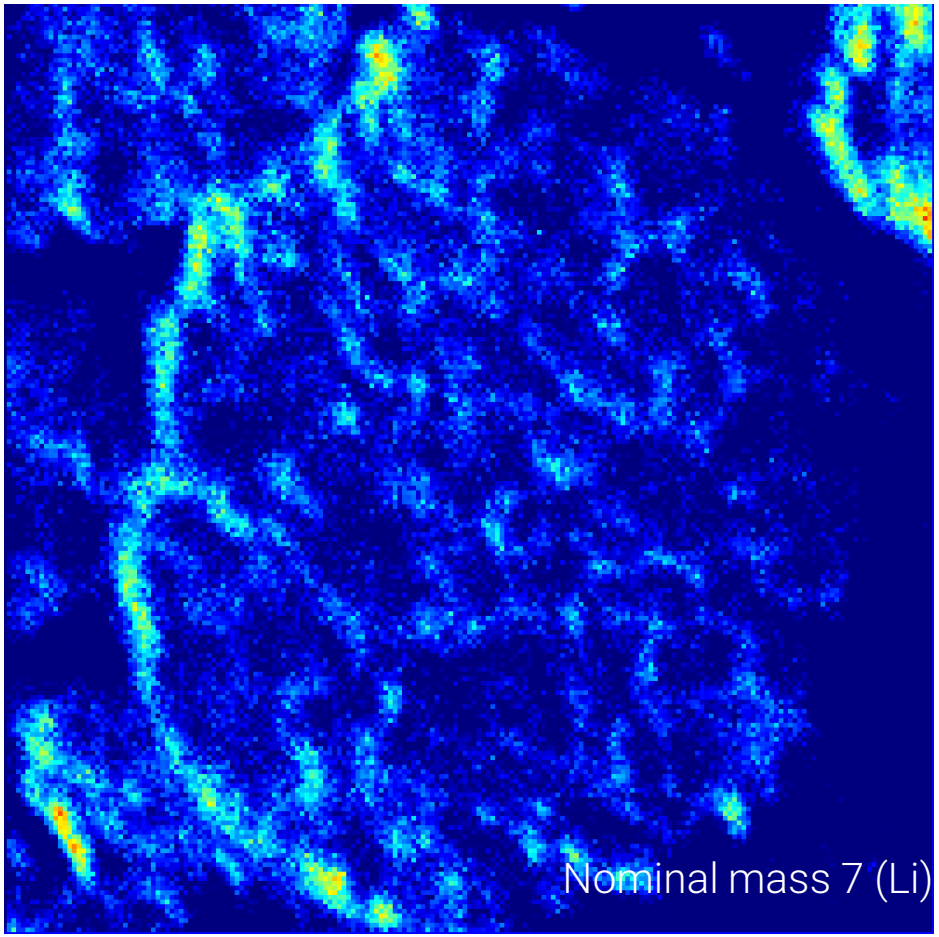




- Li mapping shows F is present at grain boundaries within individual particles, consistent with electrolyte penetration into particles along grain boundaries

Local inhomogeneity in Li distribution within individual cathode particles

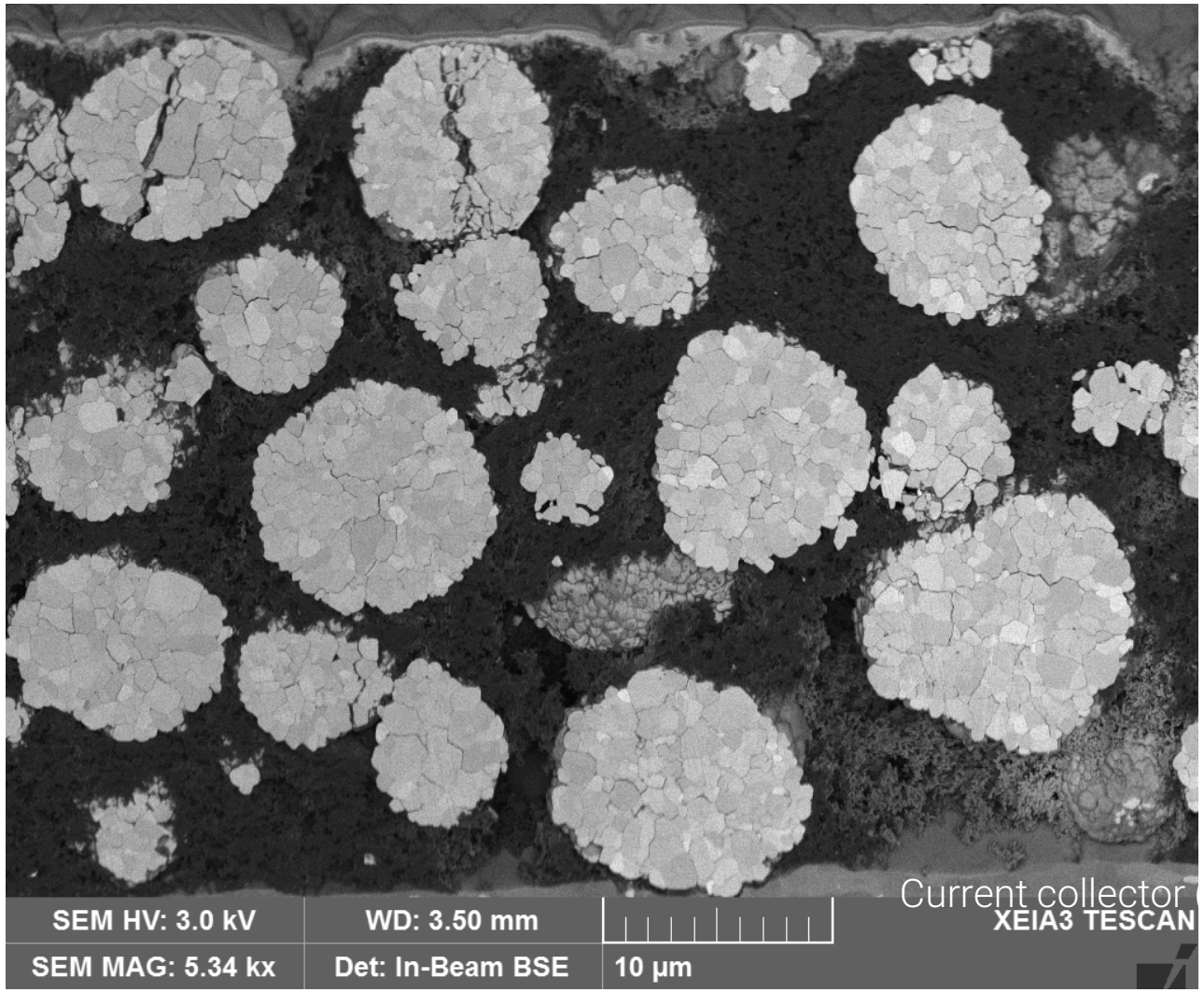




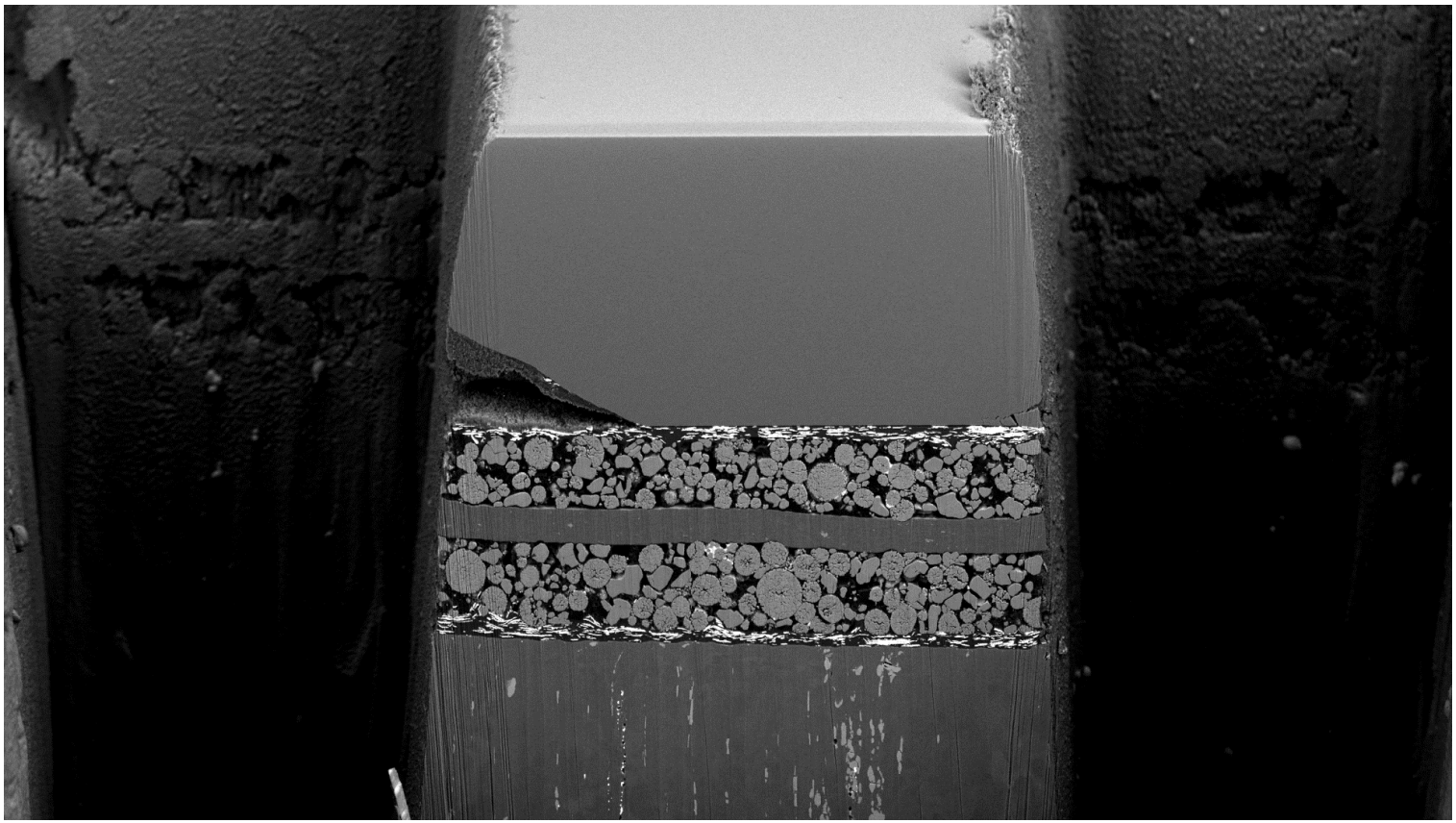
- Li mapping shows higher Li content at grain boundaries and suggests some variation of Li content from grain to grain within a single particle

Global inhomogeneity in microstructural degradation and cracking

- More significant cracking near the separation membrane side is consistent with inhomogeneous degradation under high voltage, fast cycling



Li-ion battery electrode



Volume:
200x100x80um^3
Voxel size: 100 nm

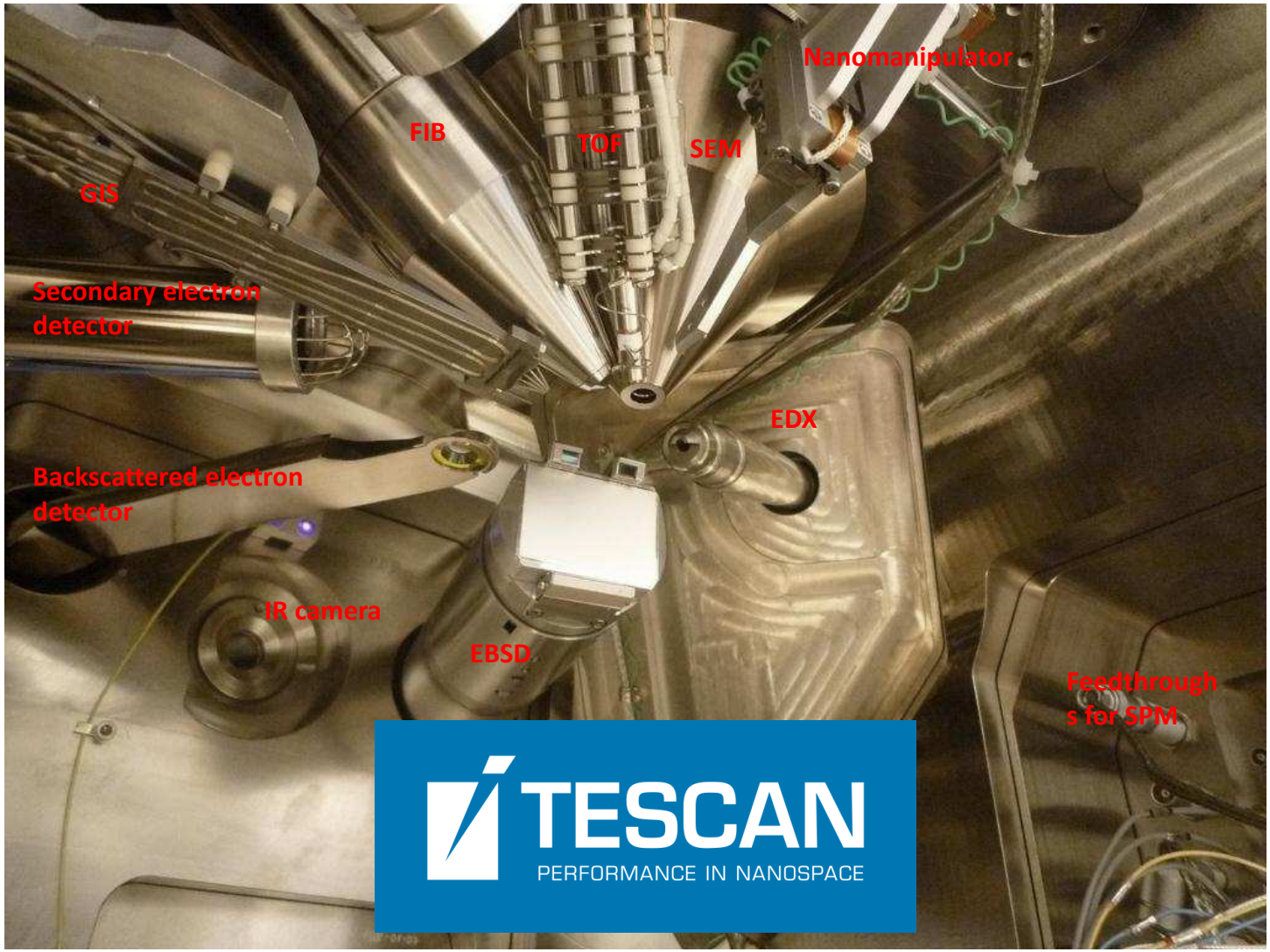
Summary

FIB-SEM and TOF-SIMS provide opportunities to improve our understanding of battery performance

- FIB-SEM imaging and TOF-SIMS reveal the global and local distribution of Li in addition to the distribution of particle cracking and concomitant electrolyte penetration into cathode particles

- Inhomogeneities revealed from particle to particle as well as local variations within individual particles suggest the evolution of reaction products leads to high-impedance areas that can reduce the performance and life of lithium-ion cells

Summary


Nanomanipulator
FIB
TOF
SEM
GIS
Secondary electron detector
EDX
Backscattered electron detector
IR camera
EBSD
Feedthroughs for SPM
TESCAN
PERFORMANCE IN NANOSPACE

TESCAN ORSAY HOLDING
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TESCAN FRANCE
13710 Fuveau, France

David BARRESI
Responsable TESCAN France