# Significance of STEM-EDXS Analysis in the Characterization of Rechargeable Battery Components

Guest speaker: Michael Malaki

**Dr. Igor Németh**
Application Scientist EDS
Bruker Nano Analytics

**Michael Malaki**
phD candidate
Materials Sciences Center
Faculty of physics
Phillips University Marburg

# Outline

- EDS instrumentation for battery research

  **Igor Németh**
  Bruker Nano Analytics

- Significance of STEM-EDXS Analysis in the Characterization of Rechargeable Battery Components

  **Michael Malaki**
  Phillips University Marburg

- Comparison of STEM-EDS and SEM-EDS

  **Igor Németh**
  Bruker Nano Analytics

# Bruker Nano GmbH,
# EDS instrumentation for battery research

Dr. Igor Németh

# Requirements, tools and methods of EDS analysis for battery research

- High solid angle X-ray collection in SEM and in STEM

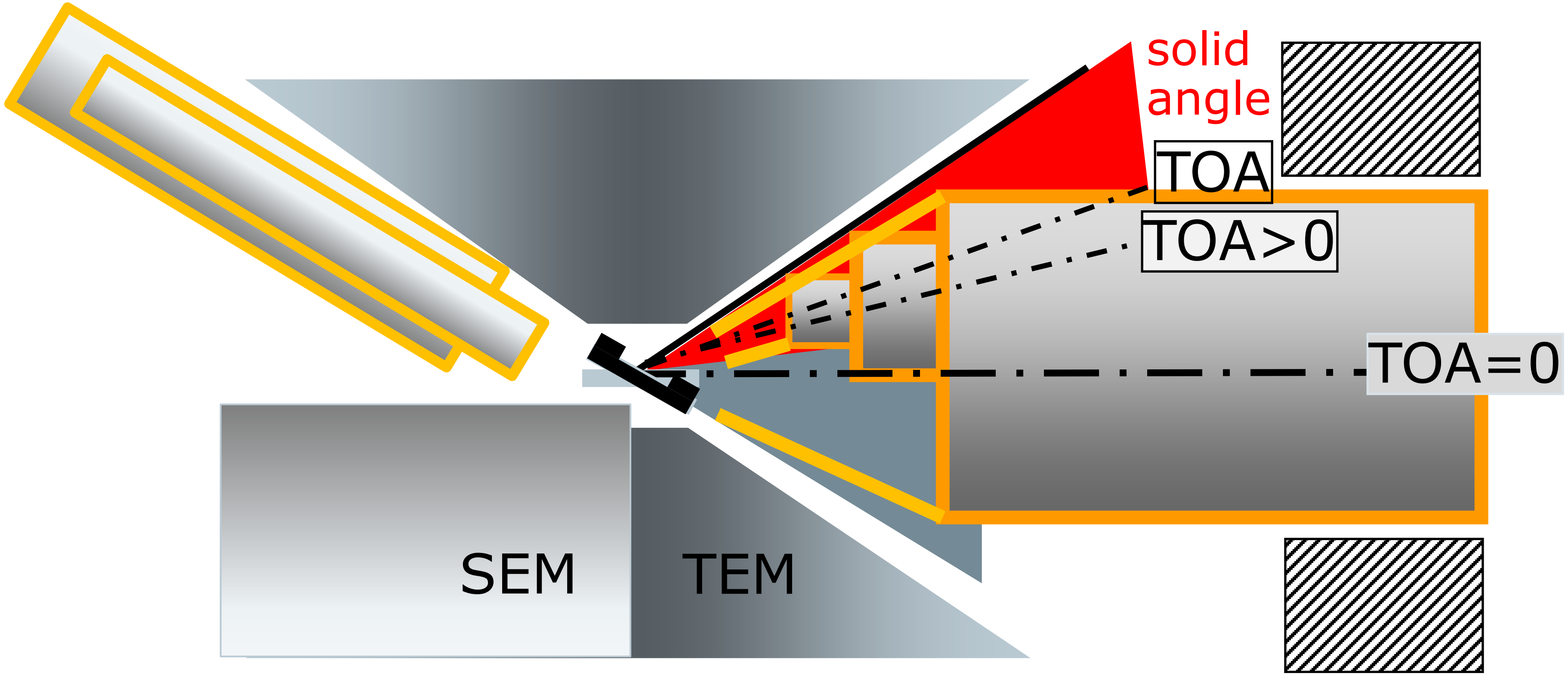
  -> sufficient data quantity for thin FIB lamellae samples
- Hypermap: measure data and process later

  -> element distribution maps, line profiles
- Deconvolution:

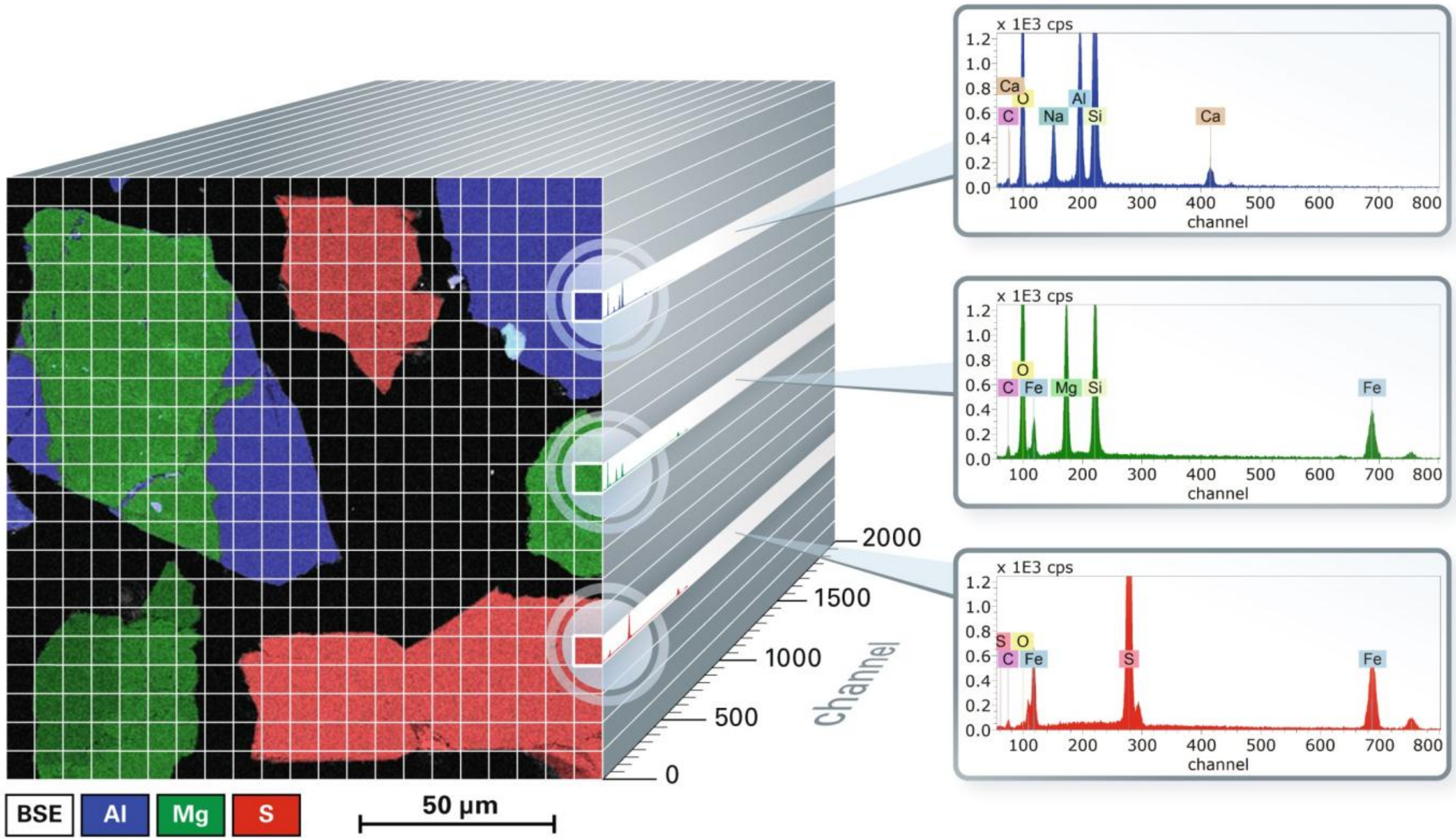
  -> Real distribution maps (also for overlapping peaks)

  -> Quantification of spectra and maps
- In situ measurements: EDS at elevated temperatures

# Geometric constraints in SEM and STEM:
## Solid and take-off angle are important to consider!



# Tools of EDS analysis: Hypermap




Save data as **Hypermap** and **process later**:

Extract spectra:

-> prove presence/absence of elements

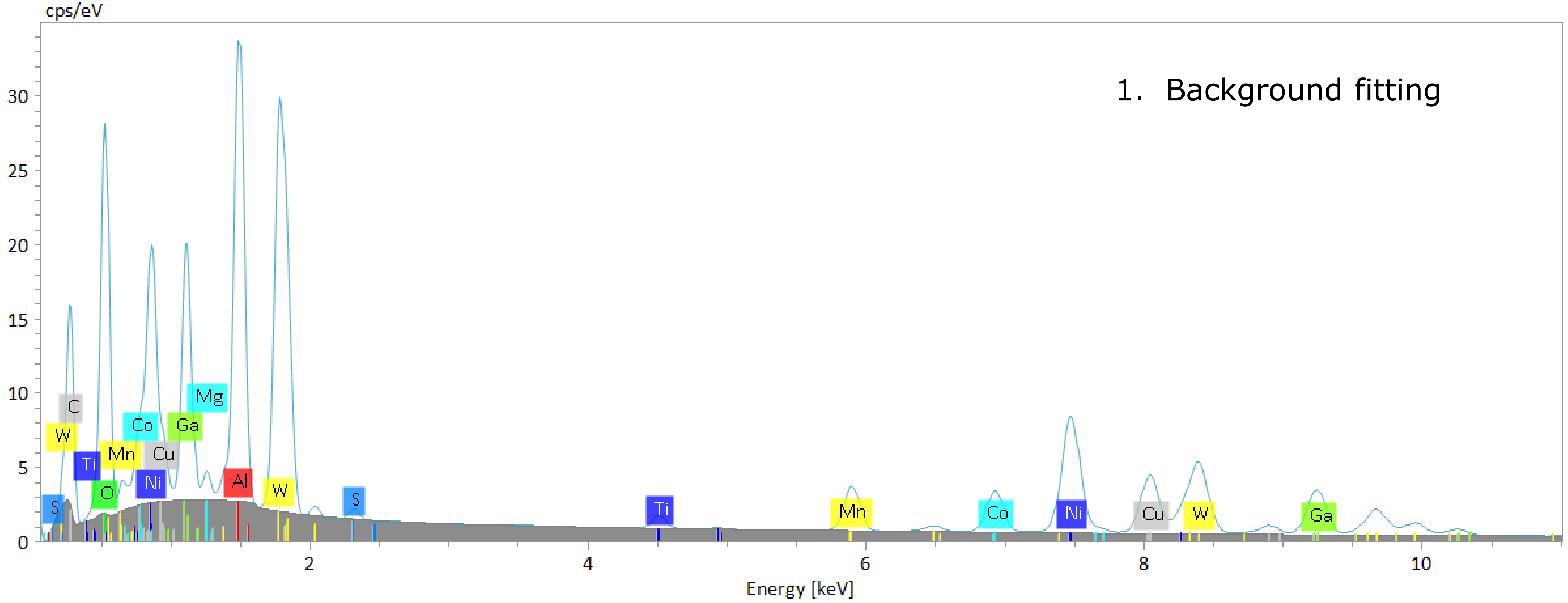
-> Calculate quantitative concentration values

Extract line profiles:

-> Quantitative line profiles

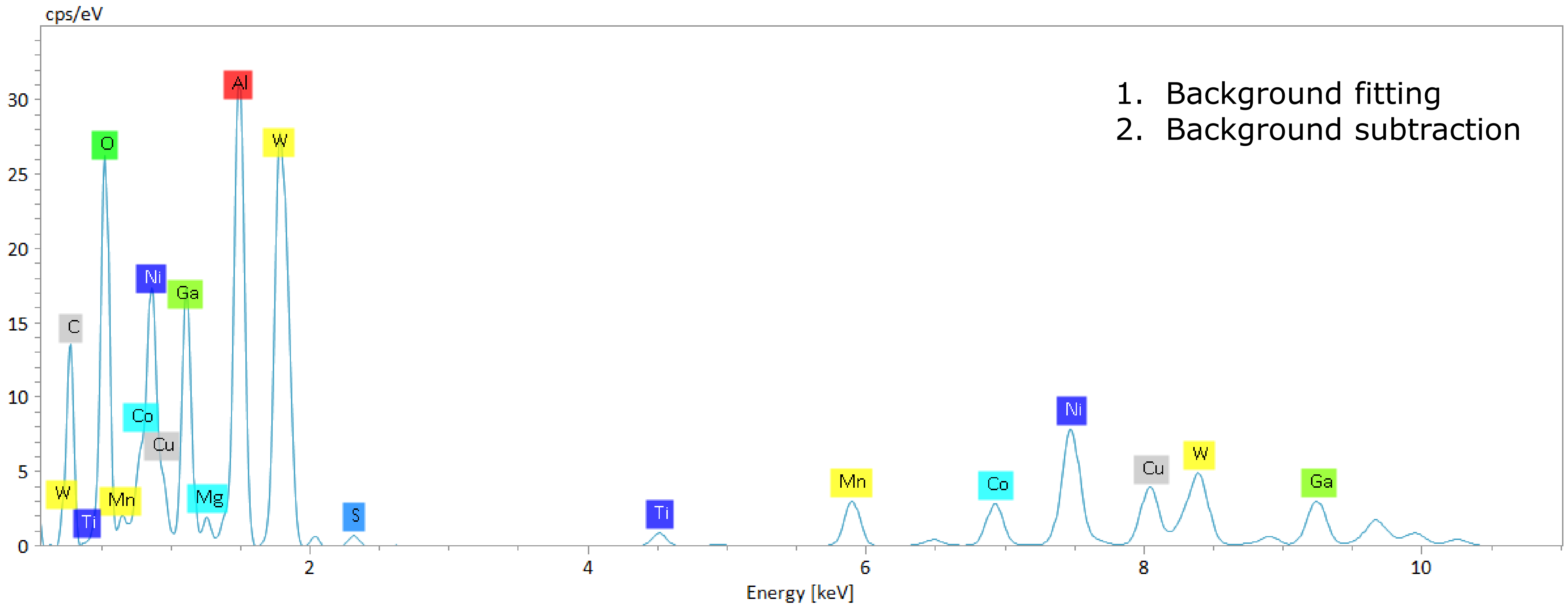
Quantitative element distribution maps

# Tools of EDS analysis: Deconvolution



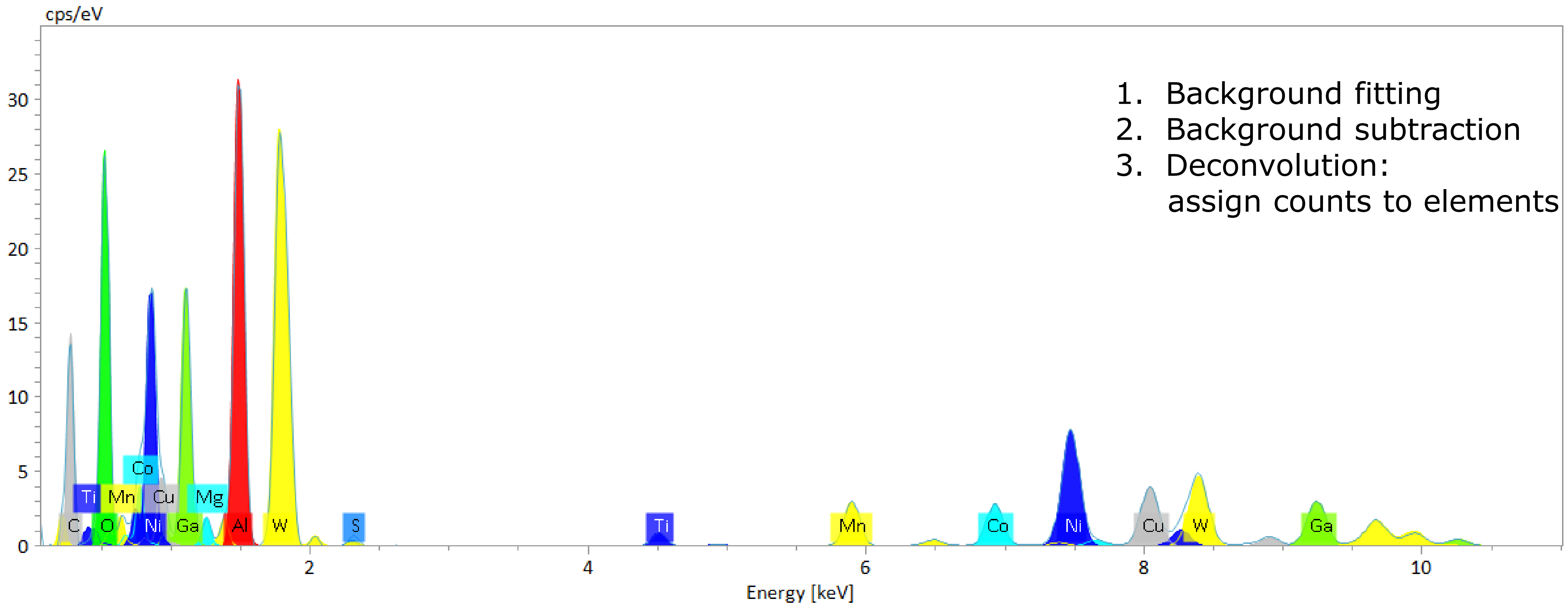

1. Background fitting

# Tools of EDS analysis: Deconvolution



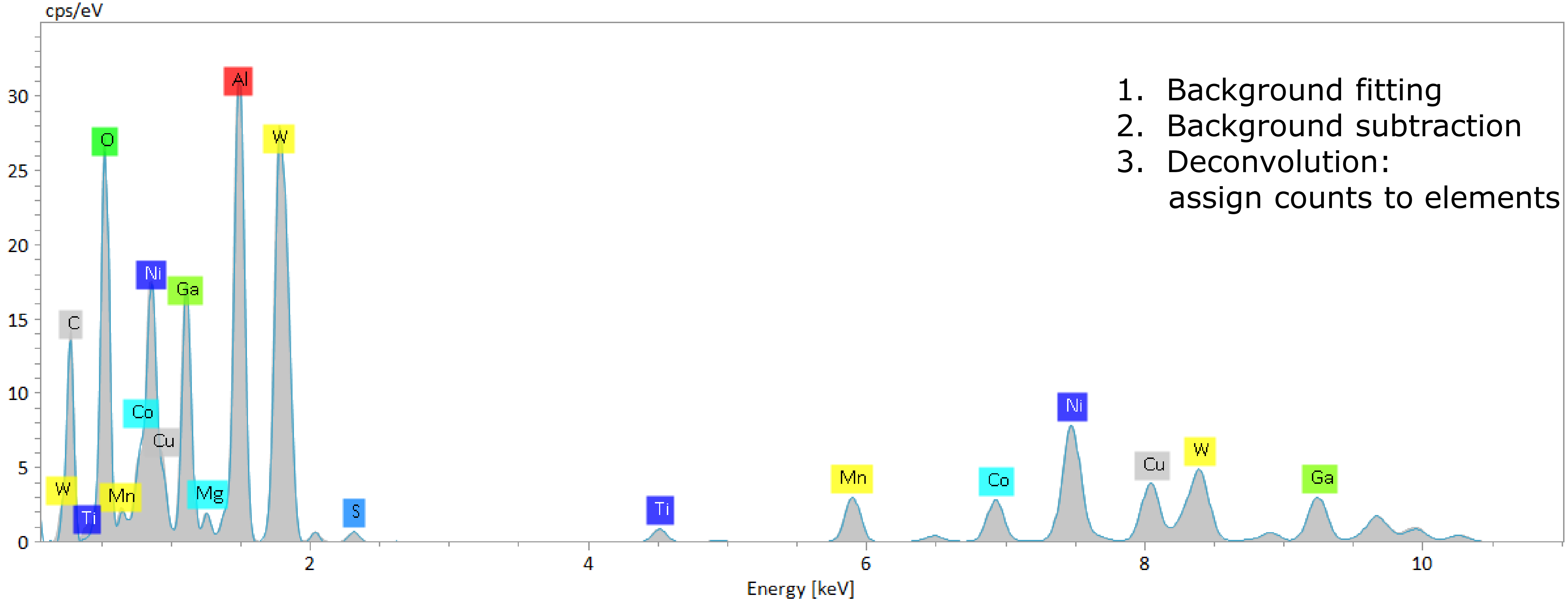

1. Background fitting
2. Background subtraction

# Tools of EDS analysis: Deconvolution



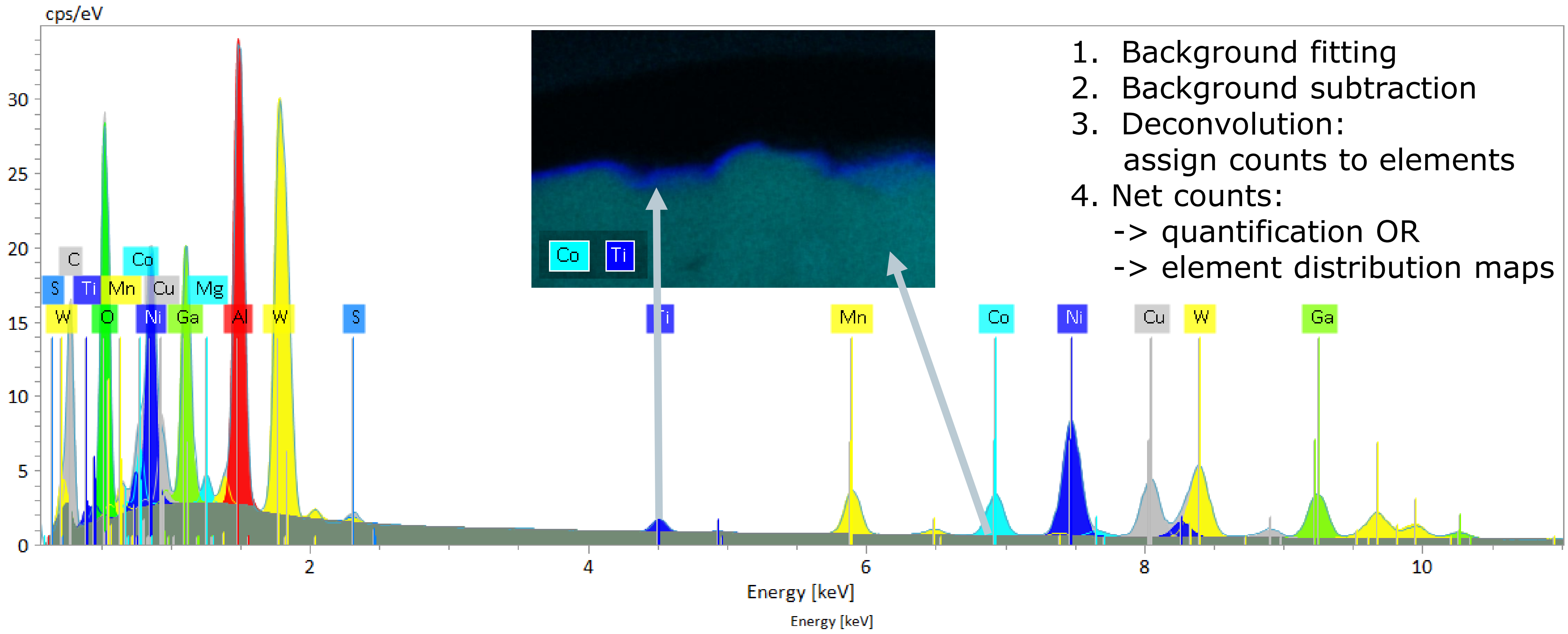

1. Background fitting
2. Background subtraction
3. Deconvolution:
   assign counts to elements

# Tools of EDS analysis: Deconvolution



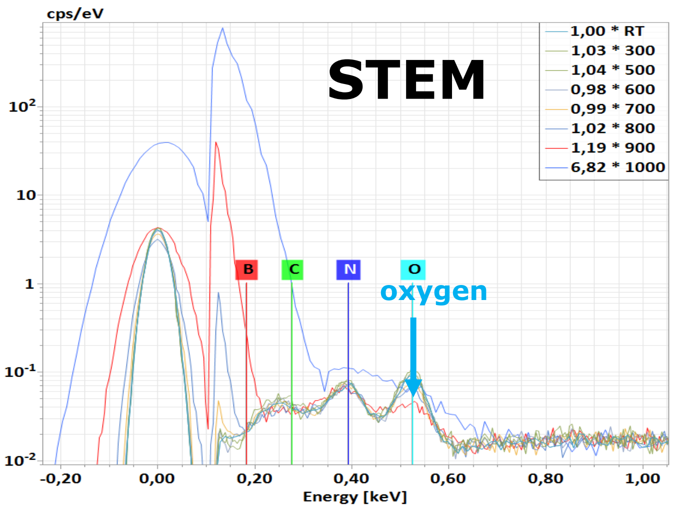

1. Background fitting
2. Background subtraction
3. Deconvolution:
   assign counts to elements

# Tools of EDS analysis: Deconvolution




1. Background fitting
2. Background subtraction
3. Deconvolution:
   assign counts to elements
4. Net counts:
   -> quantification OR
   -> element distribution maps

# EDS in situ / at elevated temperatures




TEM: 11mm sample – detector distance

## Challenges:

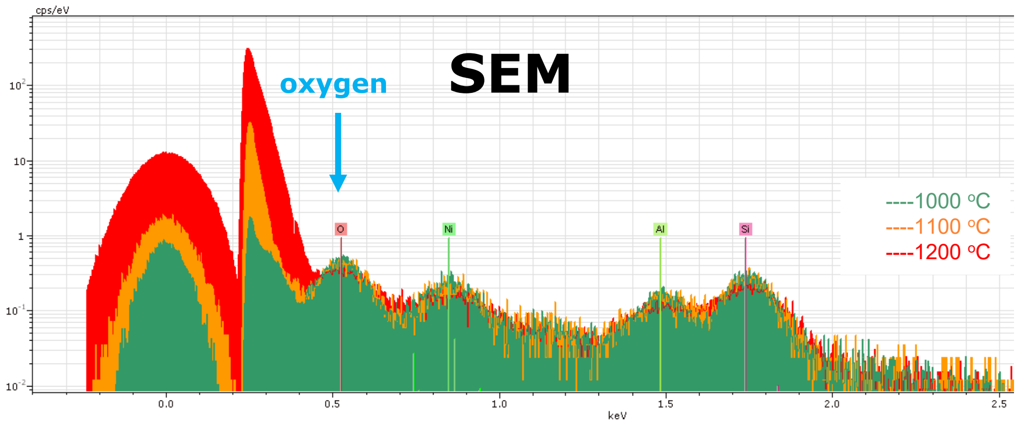
Thermal radiation -> noise -> high background below 2keV: detection of light elements affected

This effect depends on:

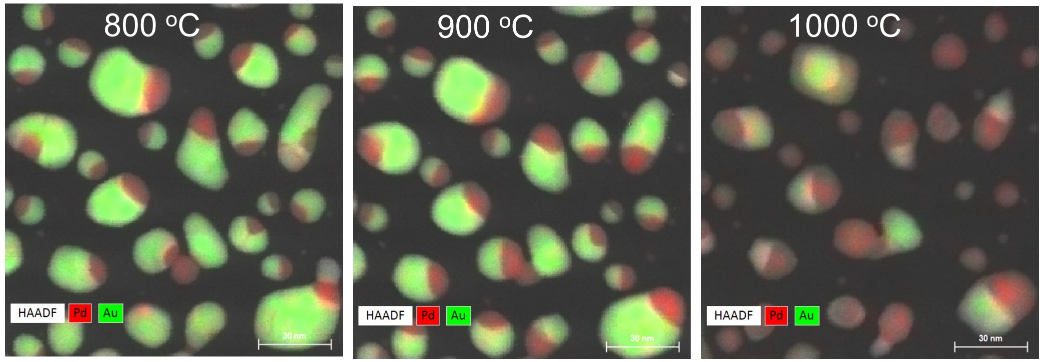
- sample-detector distance
- detector window material

## Possibilities:

- Spectra: monitoring of element lines
- Mapping: Phase changes, segregations

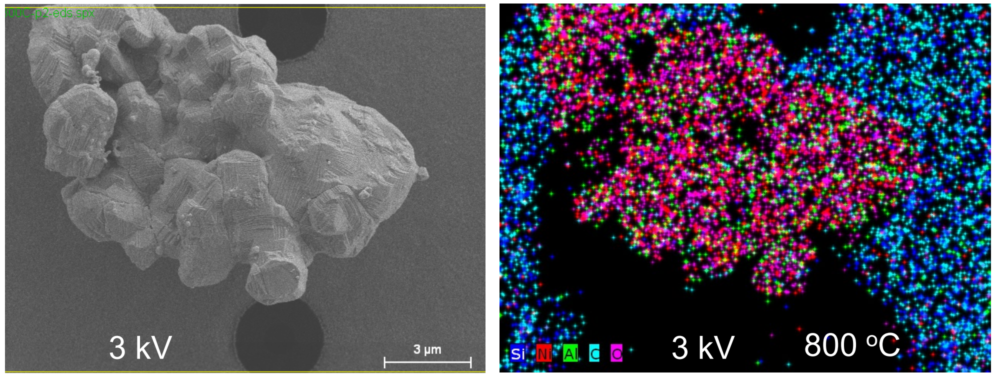



SEM: 25mm sample – detector distance




J. T. van Omme et al., Ultramicroscopy 192 (2018) 14–20

DENS solutions




Jane Y. Howe (ORNL), Christianne Beekman (Florida St. Uni)

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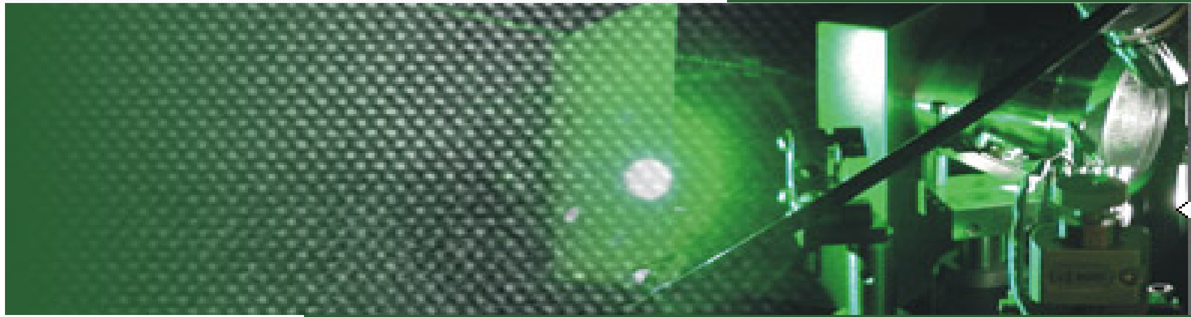
Structure & Technology Research Laboratory

# Significance of STEM-EDXS analysis in the characterization of rechargeable battery components



*Michael Malaki, Shamail Ahmed, Anuj Pokle*

*Material Science center, Faculty of physics*
*Philipps university Marburg*

# Contents

## Motivation

- Material
- Instrumentation and work-flow

## Nanopore Defects in NCM Cathodes

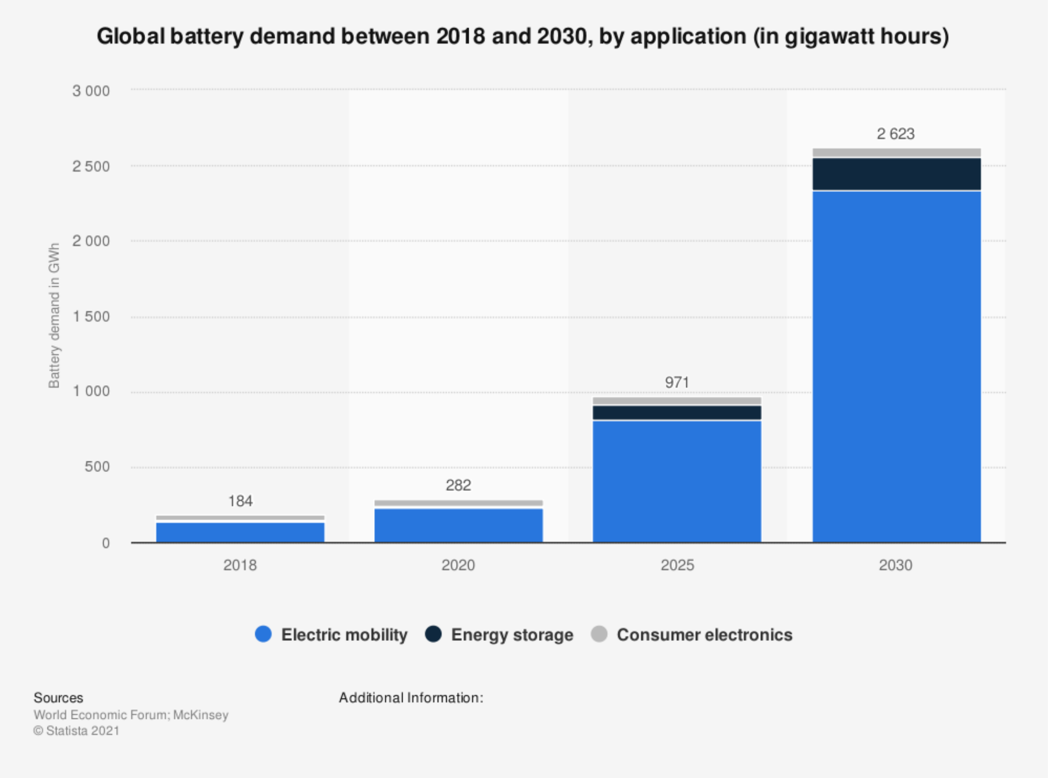
- HRSTEM and EDXS at Nanopores
- In-*situ* Evolution of Nanopores

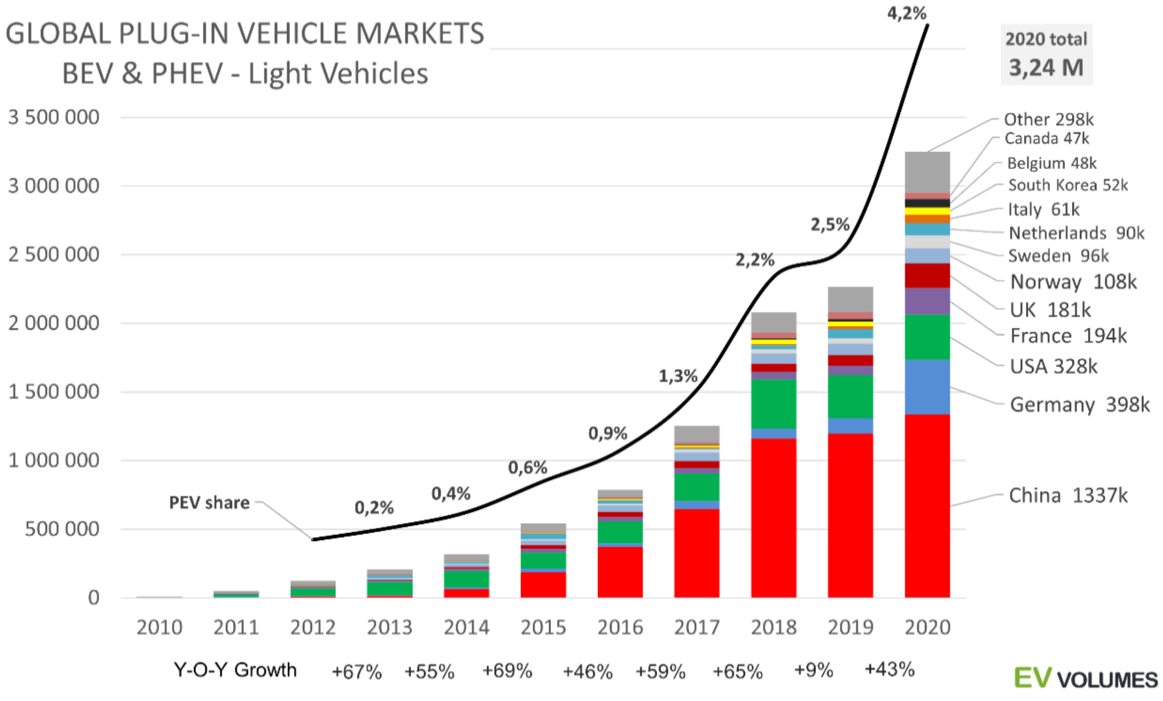
## Surface Coating and thin-films

- EDXS at Lithium-Cobalt oxide thin-films
- EDXS on NCM Surface Coatings

## Conclusion

# Motivation




- The global battery energy demand set to increase over 14x by 2030
- Global PEV sales of 3.24 million in 2020 compared to 2.26 million in 2019

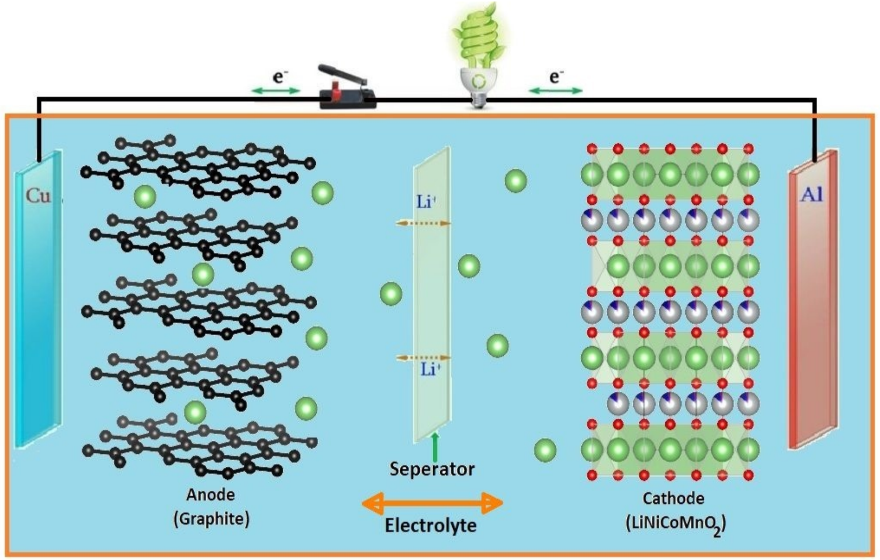


World Economic Forum, Global Battery Alliance; McKinsey analysis
http://www3.weforum.org/docs/WEF_A_Vision_for_a_Sustainable_Battery_Value_Chain_in_2030_Report.pdf



Roland Irle, https://www.ev-volumes.com/

# Material

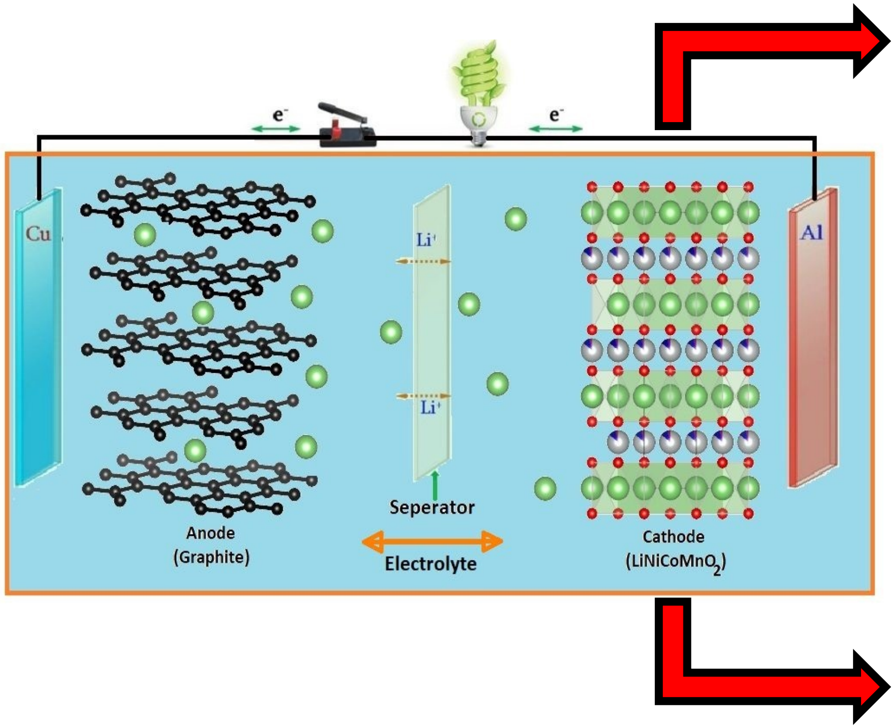


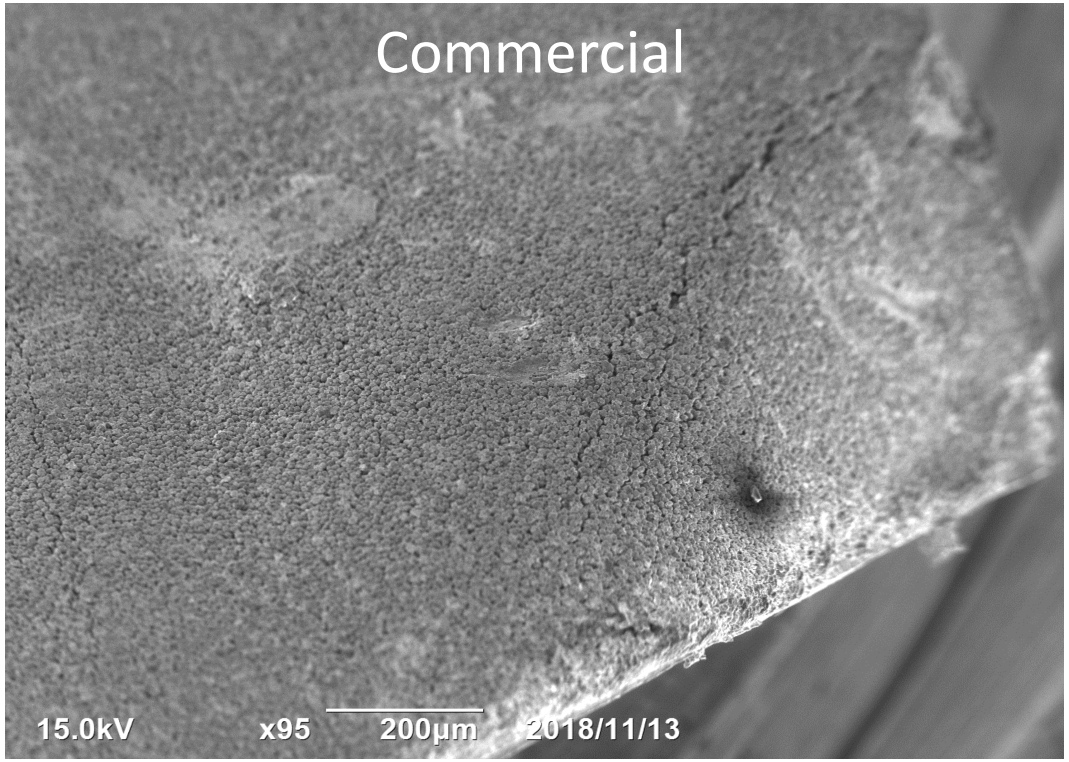



Modified from C. Liu, Z. G. Neale, and G. Cao, “Understanding electrochemical potentials of cathode materials in rechargeable batteries,” *Materials Today*, vol. 19, no. 2, pp. 109–123, Mar. 2016.

# Material

**Ni-rich NCM layered Cathode Material**
**(85% Ni, 10% Co & 5% Mn)**






Modified from C. Liu, Z. G. Neale, and G. Cao, "Understanding electrochemical potentials of cathode materials in rechargeable batteries," *Materials Today*, vol. 19, no. 2, pp. 109–123, Mar. 2016.

S. Ahmed, A. Pokle, S. Schweidler, A. Beyer, M. Bianchini, F. Walther, A. Mazilkin, P. Hartmann, T. Brezesinski, J. Janek, K. Volz, *ACS nano* 2019, *13*, 10694.

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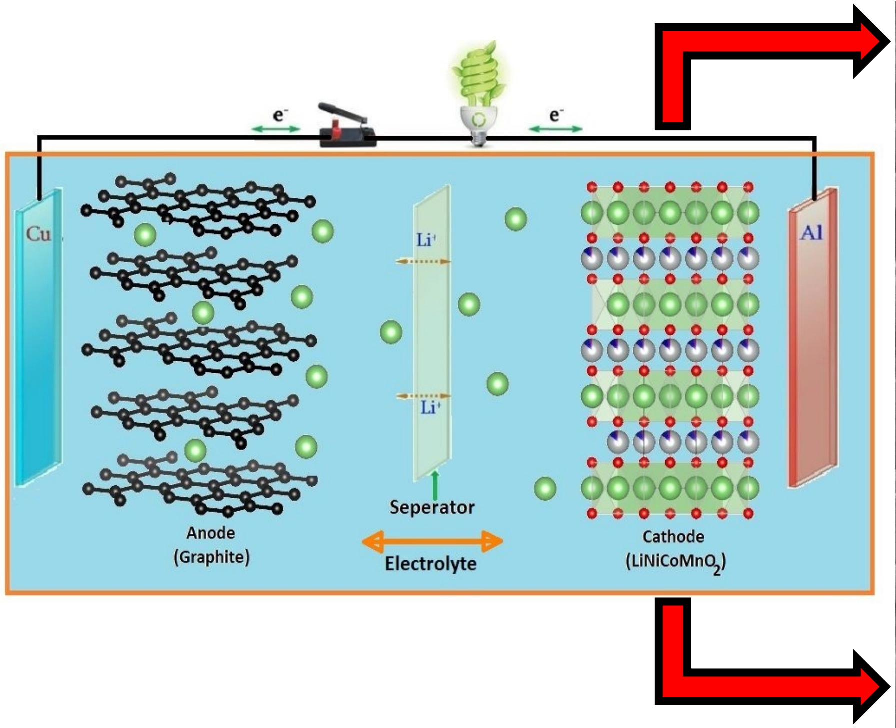


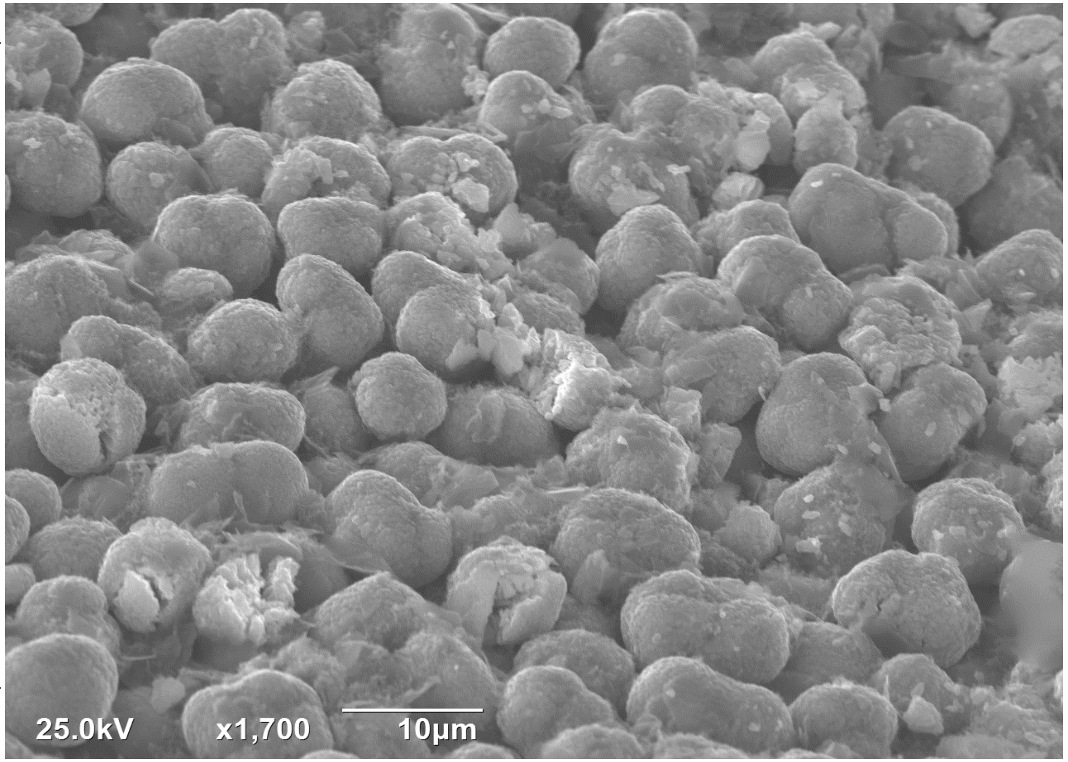




Modified from C. Liu, Z. G. Neale, and G. Cao, "Understanding electrochemical potentials of cathode materials in rechargeable batteries," *Materials Today*, vol. 19, no. 2, pp. 109–123, Mar. 2016.

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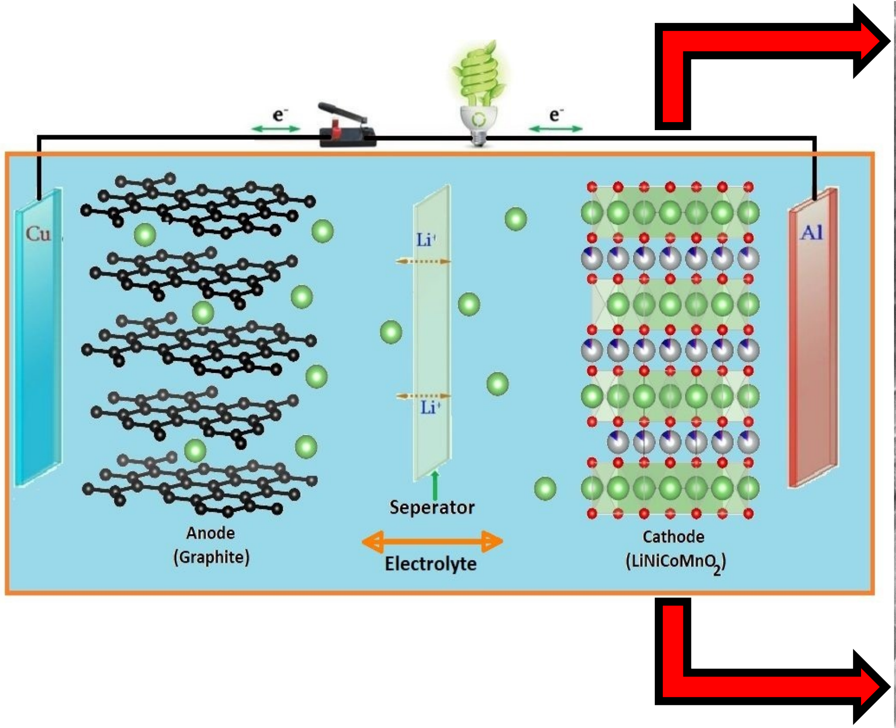


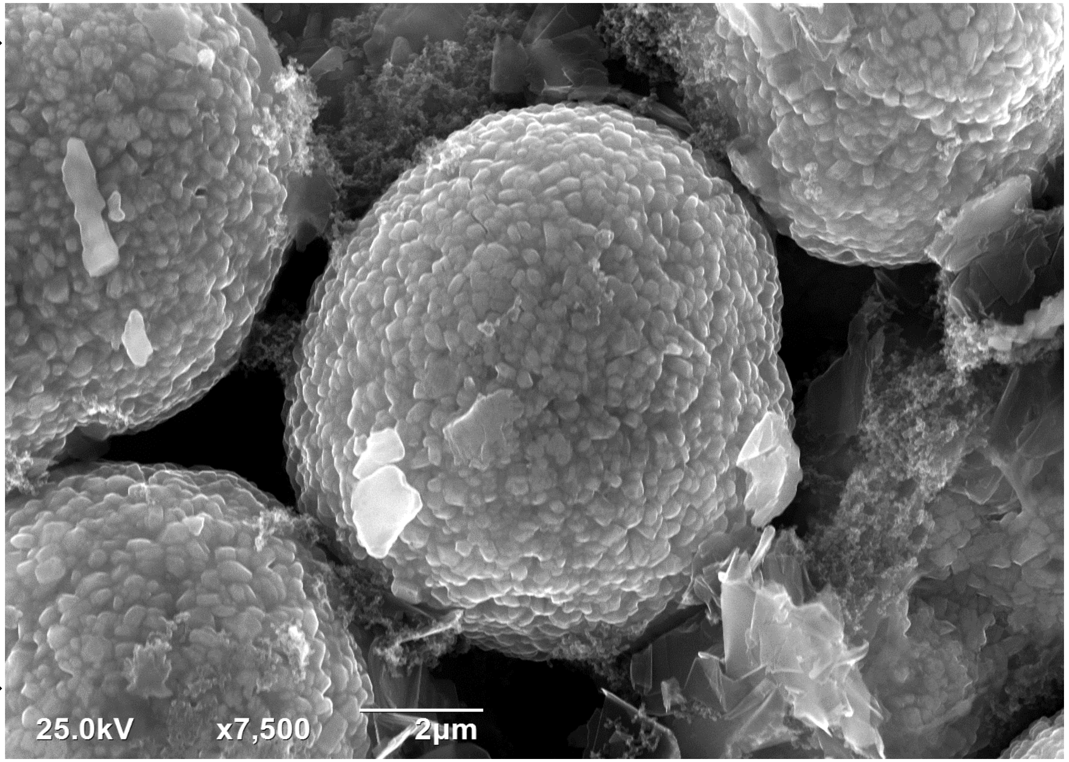




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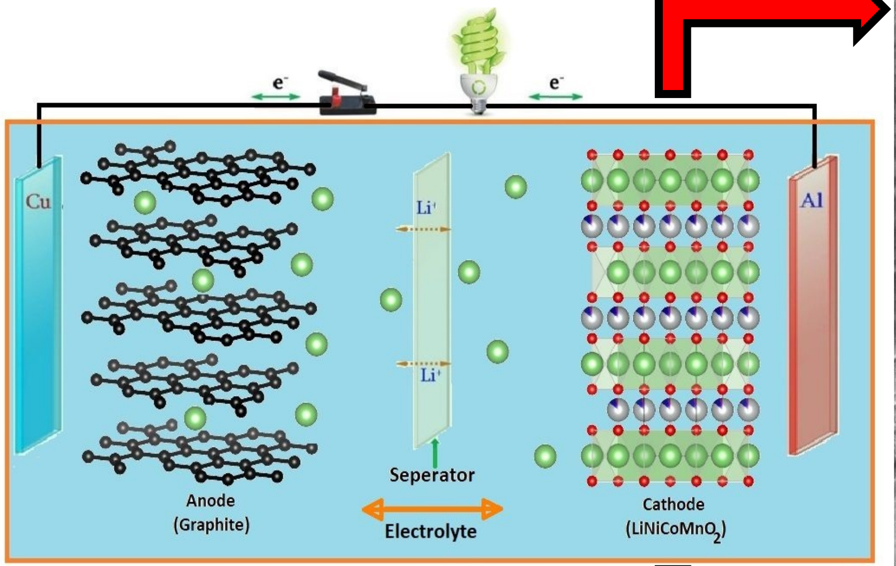


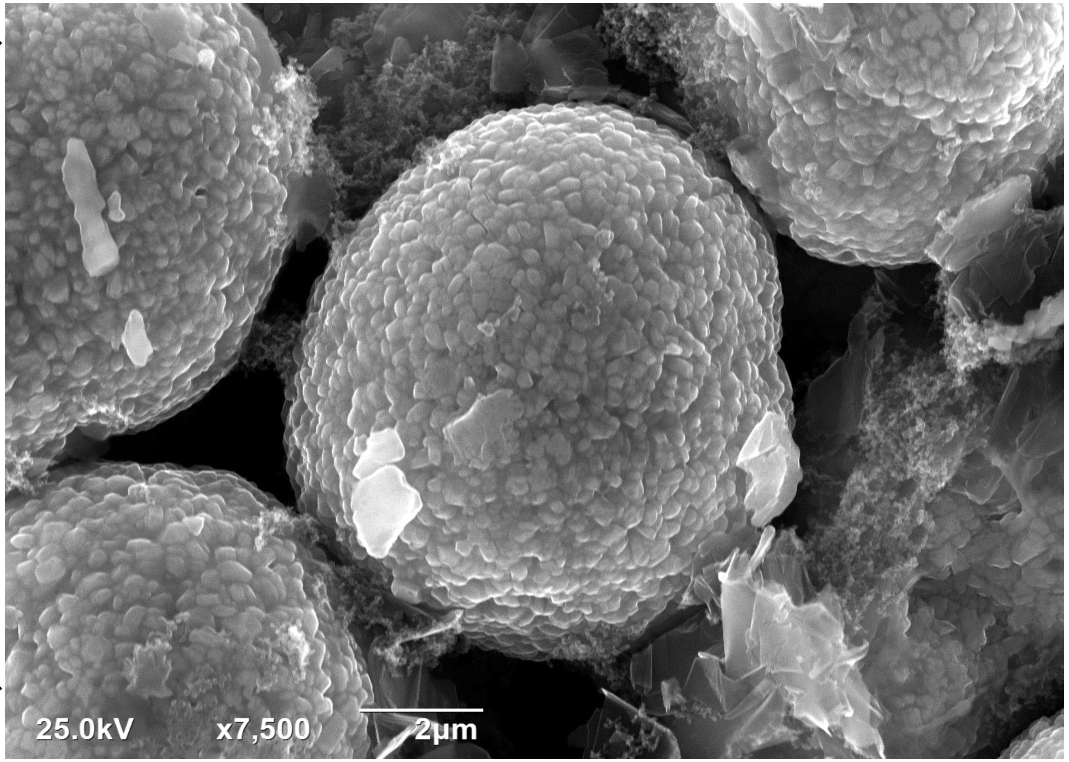


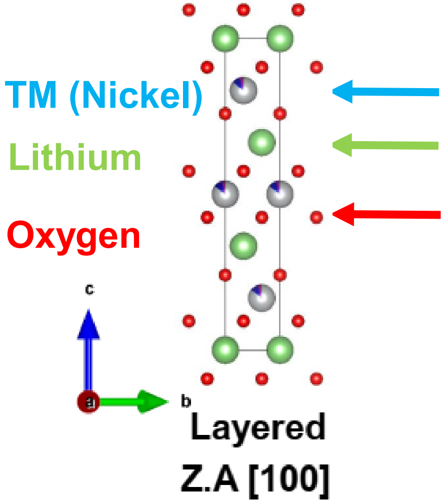


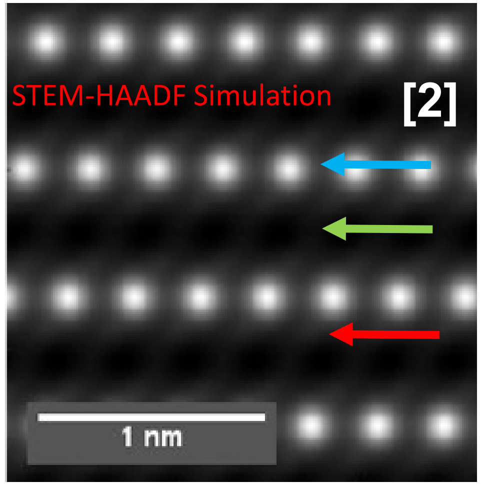





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*STEMsalabim — STEMsalabim 5.0.0 documentation.*" [Online]. Available: http://www.stemsalabim.de/en/latest/

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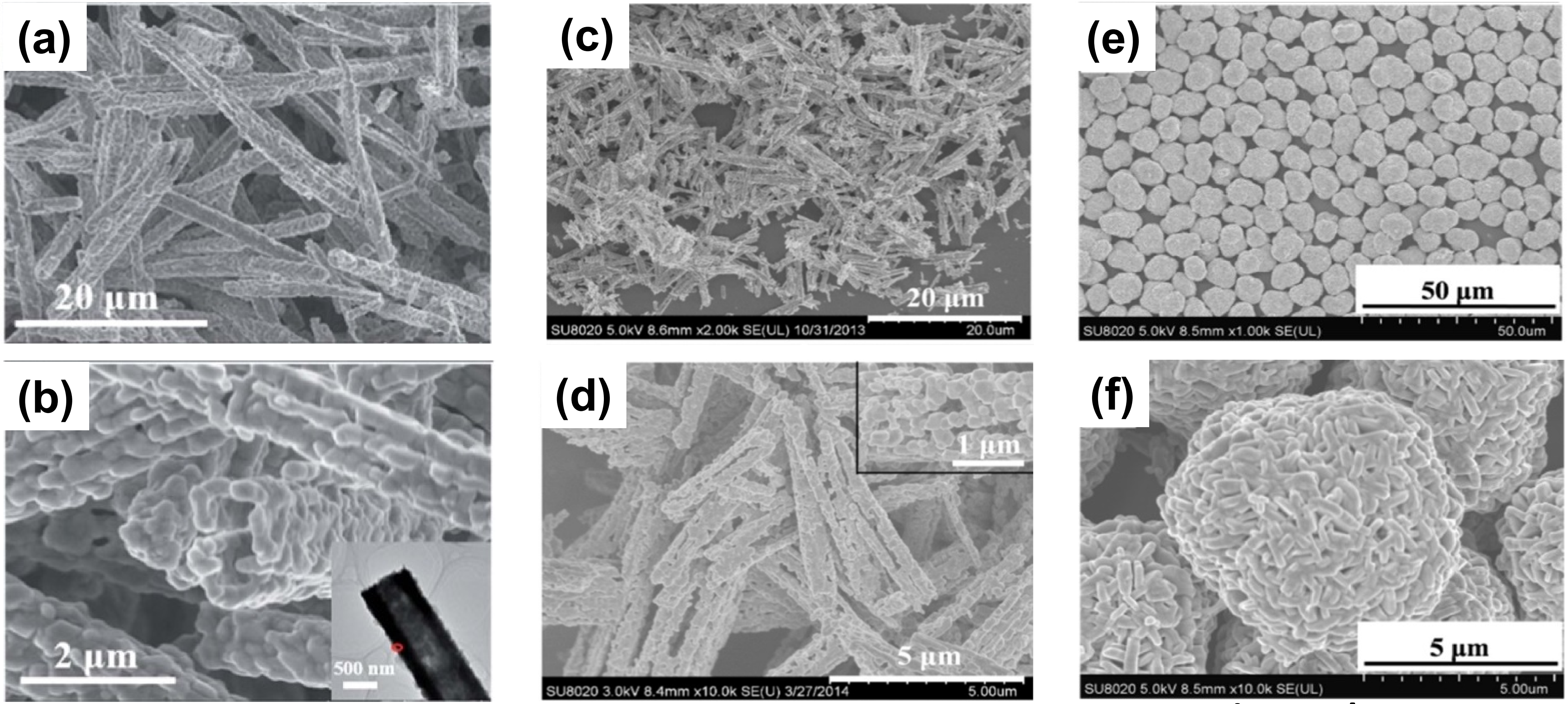
# Morphology of NCM Cathodes in SEM

Low Mag

High Mag

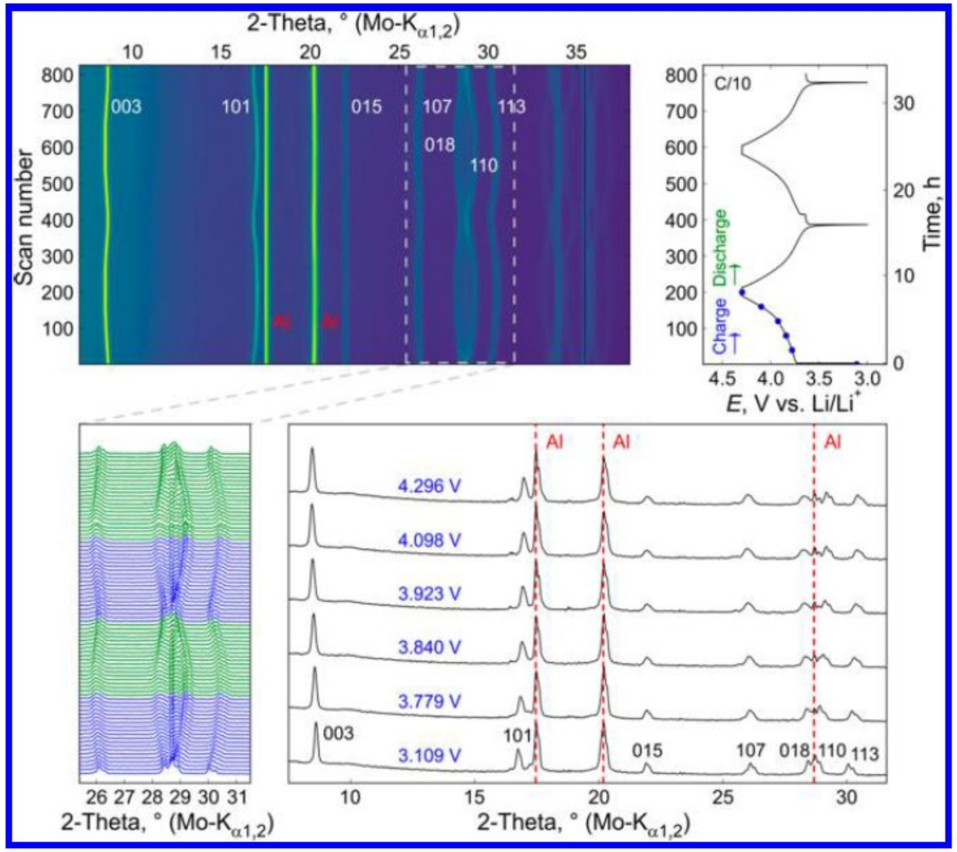



**Micro-tubes** **Micro-rods** **Micro-spheres**

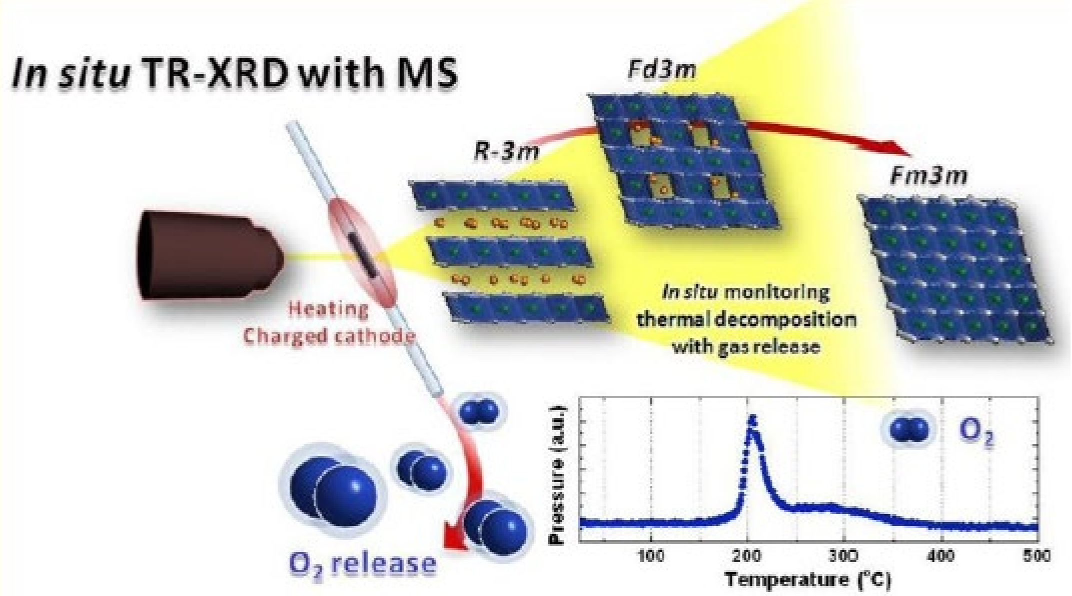


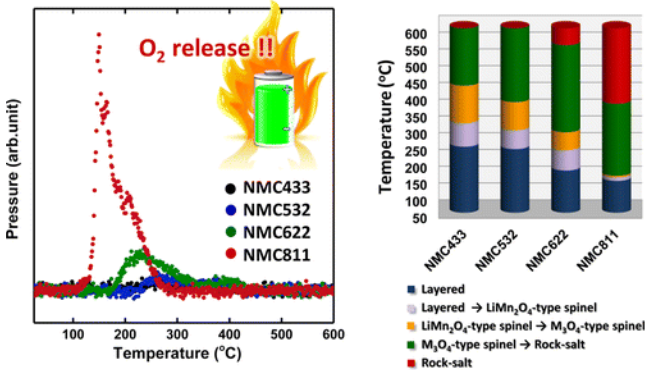
Zhangxian Chen, Weixin Zhang, Zeheng Yang, "A review on cathode materials for advanced lithium-ion batteries: microstructure designs and performance regulations" 2020 *Nanotechnology* 31 012001

# Complimentary Instrumentation




S.-M. Bak, E. Hu, Y. Zhou, X. Yu, S. D. Senanayake, S.-J. Cho, K.-B. Kim, K. Y. Chung, X.-Q. Yang, K.-W. Nam, *ACS applied materials & interfaces* 2014, *6*, 22594.



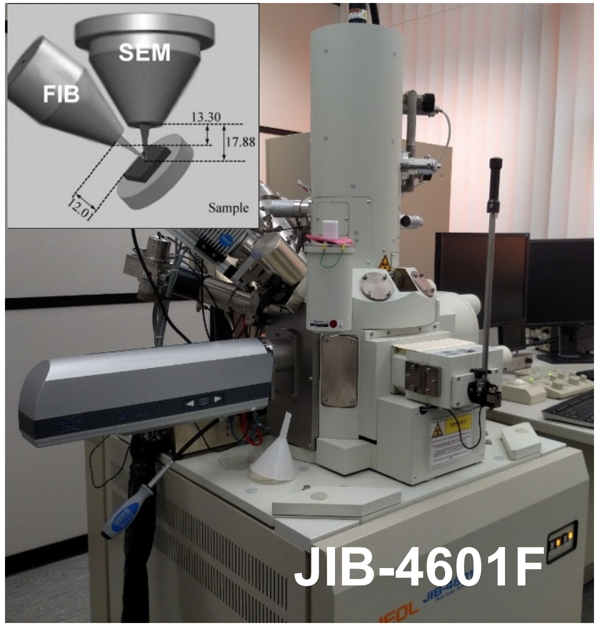

- XRD (In-*situ*)
- Mass Spectroscopy (MS)
- Auger Electron Spectroscpy (AES)
- X-ray Photoelectron Spectroscopy (XPS)



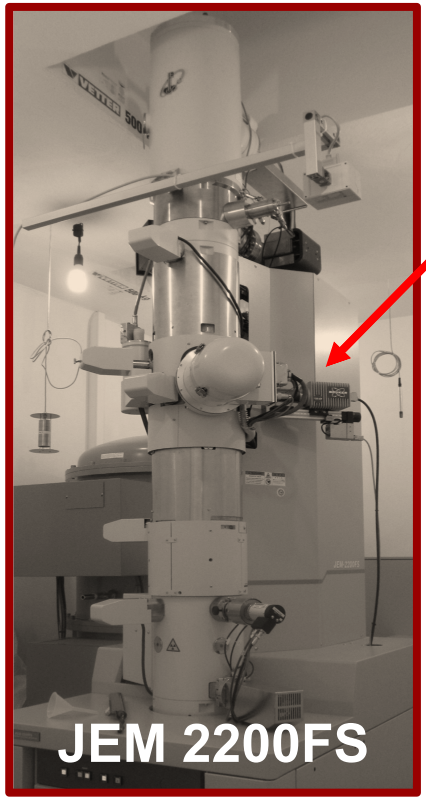
Kondrakov, A., Schmidt, A., Xu, J., Geßwein, H., Mönig, R., & Hartmann, P. et al. (2017). *The Journal Of Physical Chemistry C*, *121*(6), 3286-3294. doi: 10.1021/acs.jpcc.6b12885

S.-M. Bak, K.-W. Nam, W. Chang, X. Yu, E. Hu, S. Hwang, E. A. Stach, K.-B. Kim, K. Y. Chung, X.-Q. Yang, *Chem. Mater.* 2013, *25*, 337

# Instrumentation & Workflow

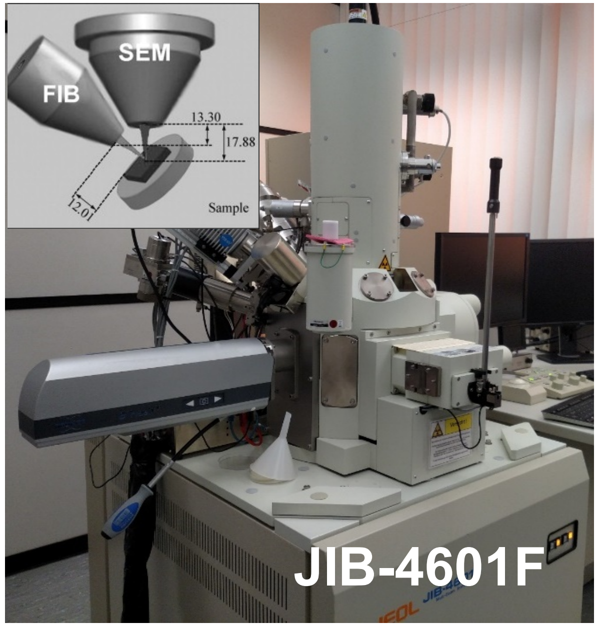




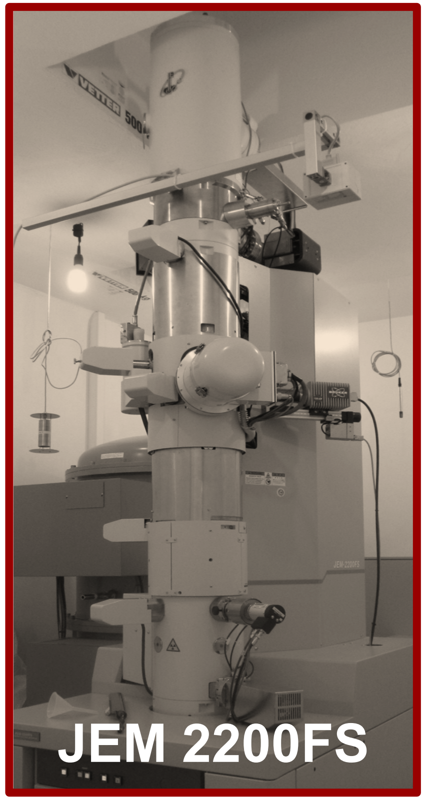


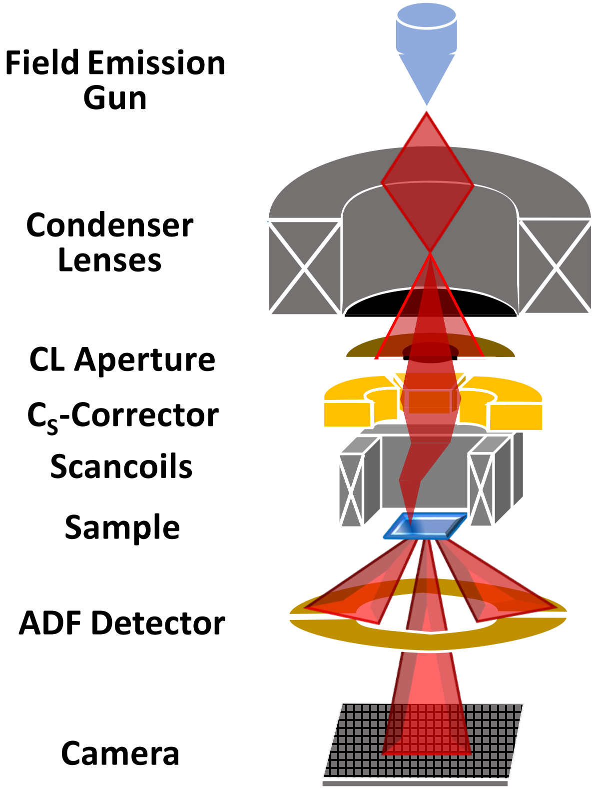

EDX Detector

# Instrumentation & Workflow







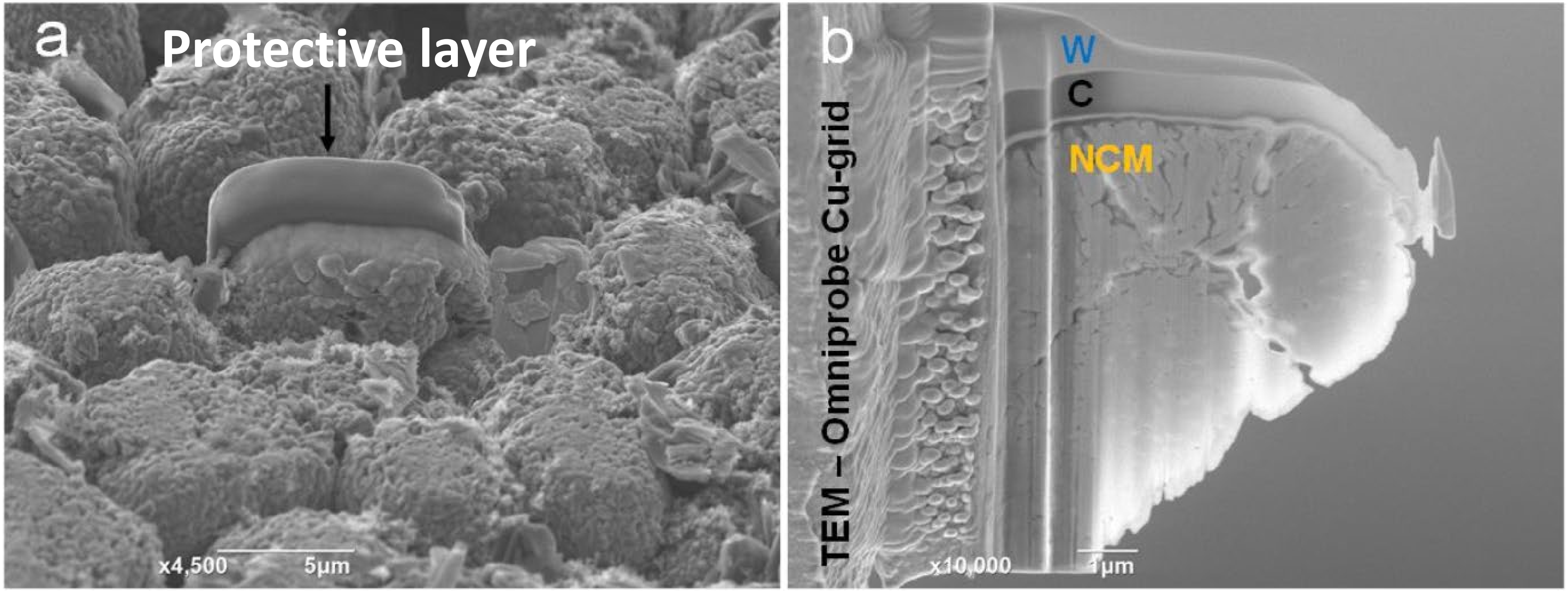




$$I \propto Z^{1.7}$$



R. Brydson, *Aberration-corrected analytical transmission electron microscopy*, RMS-Wiley, Chichester West Sussex U.K. 2011

# FIB Lamella

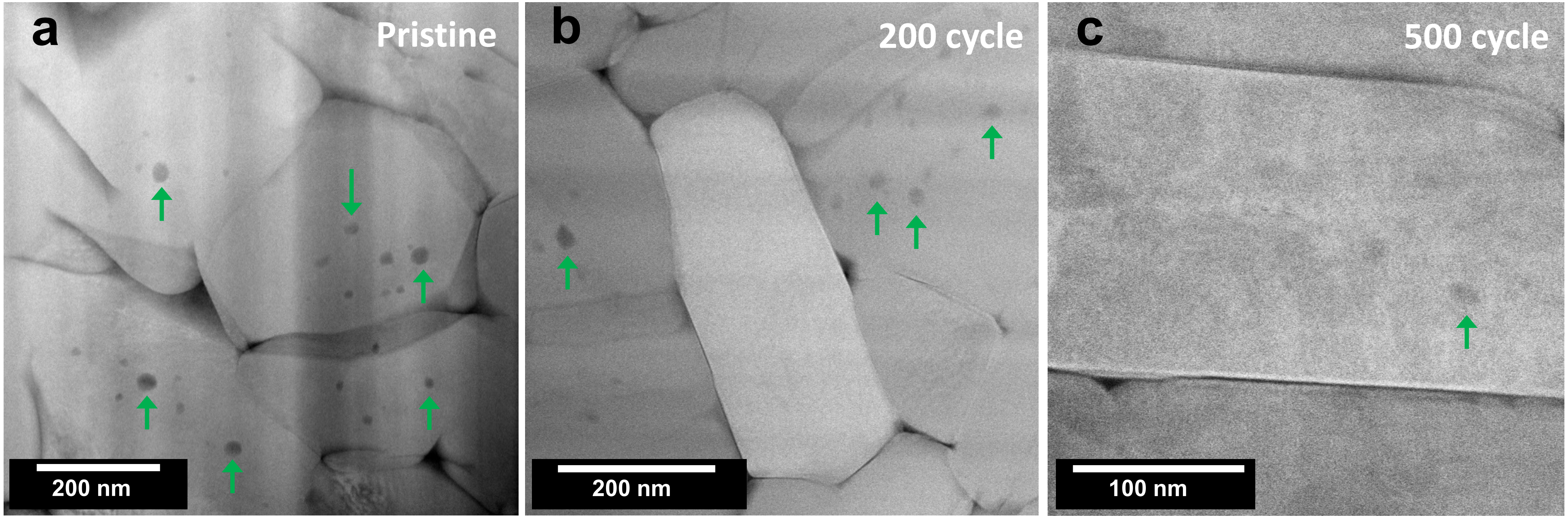





**[1]** S. Ahmed, A. Pokle, S. Schweidler, A. Beyer, M. Bianchini, F. Walther, A. Mazilkin, P. Hartmann, T. Brezesinski, J. Janek, K. Volz, *ACS nano* 2019, *13*, 10694.

# Contents

# Nanopore Defects in NCM Cathodes

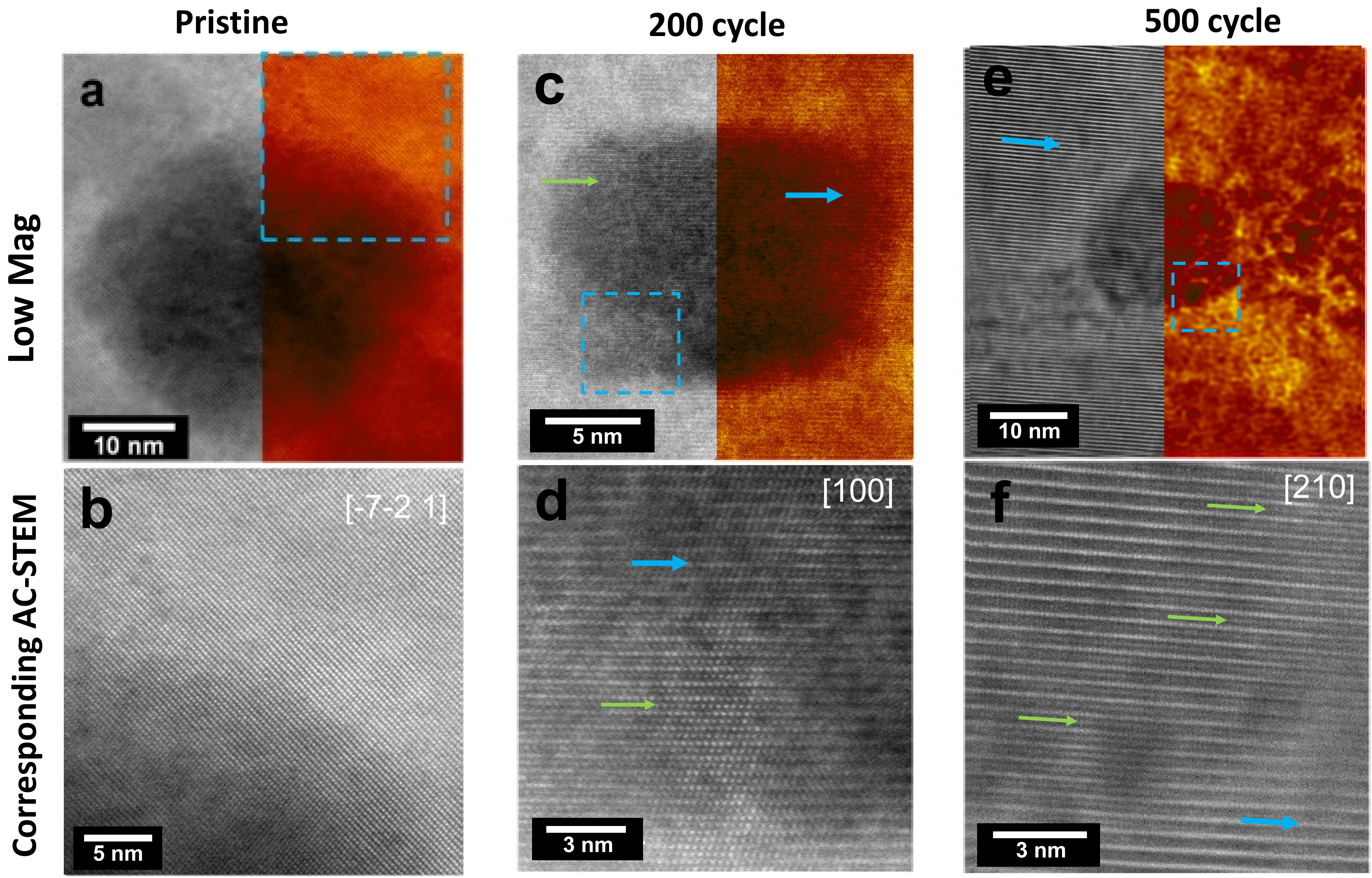



STEM-HAADF of Primary grains

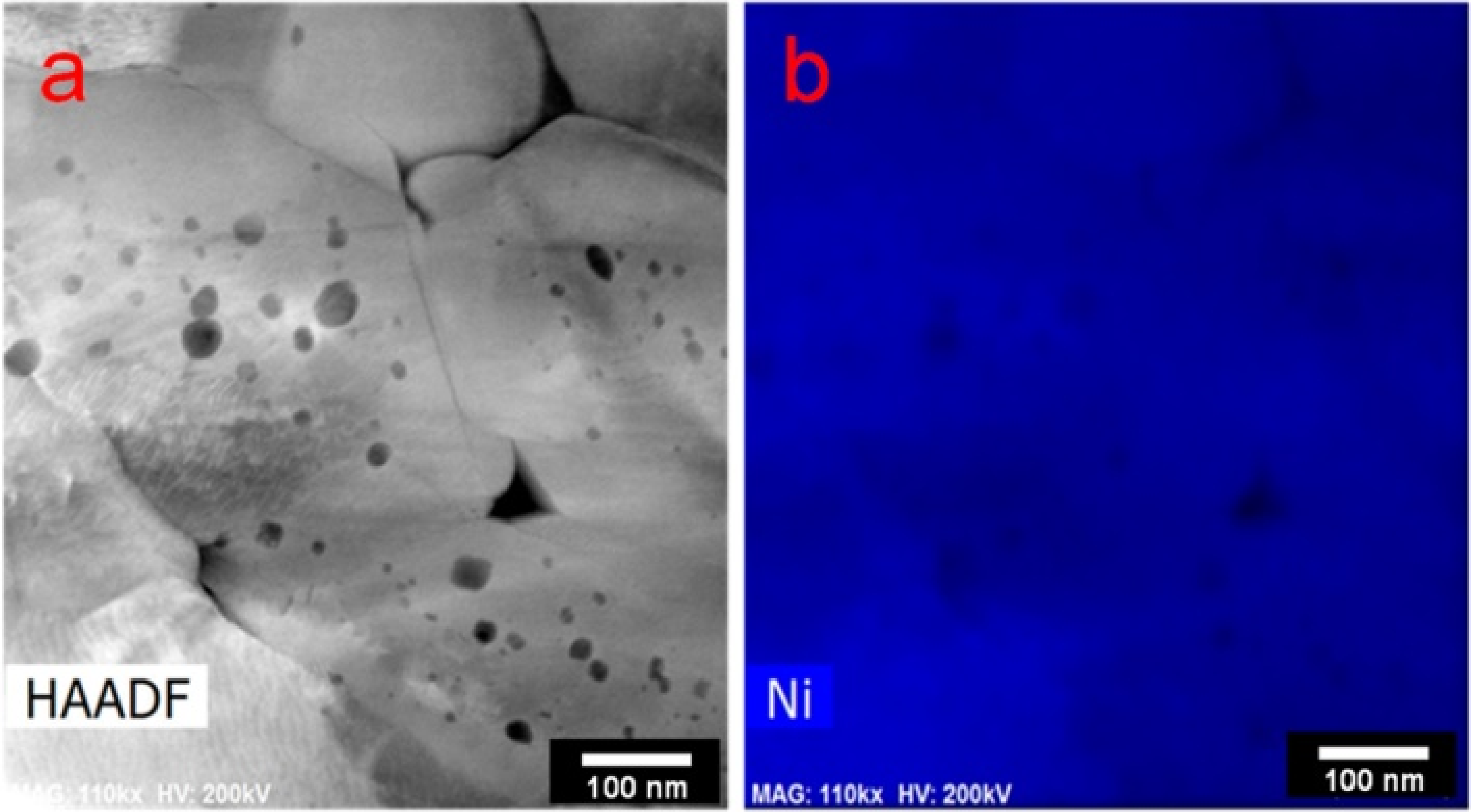
- Nanopores have distinct dark contrast in HAADF images
- Inherent, cycling and/or thermal induced?



**[1]** S. Ahmed, A. Pokle, S. Schweidler, A. Beyer, M. Bianchini, F. Walther, A. Mazilkin, P. Hartmann, T. Brezesinski, J. Janek, K. Volz, *ACS nano* 2019, *13*, 10694.


Pristine
200 cycle
500 cycle
Low Mag
Corresponding AC-STEM
a
10 nm
c
5 nm
e
10 nm
b
[-7-2 1]
5 nm
d
[100]
3 nm
f
[210]
3 nm

# EDX Mapping at Nanopores



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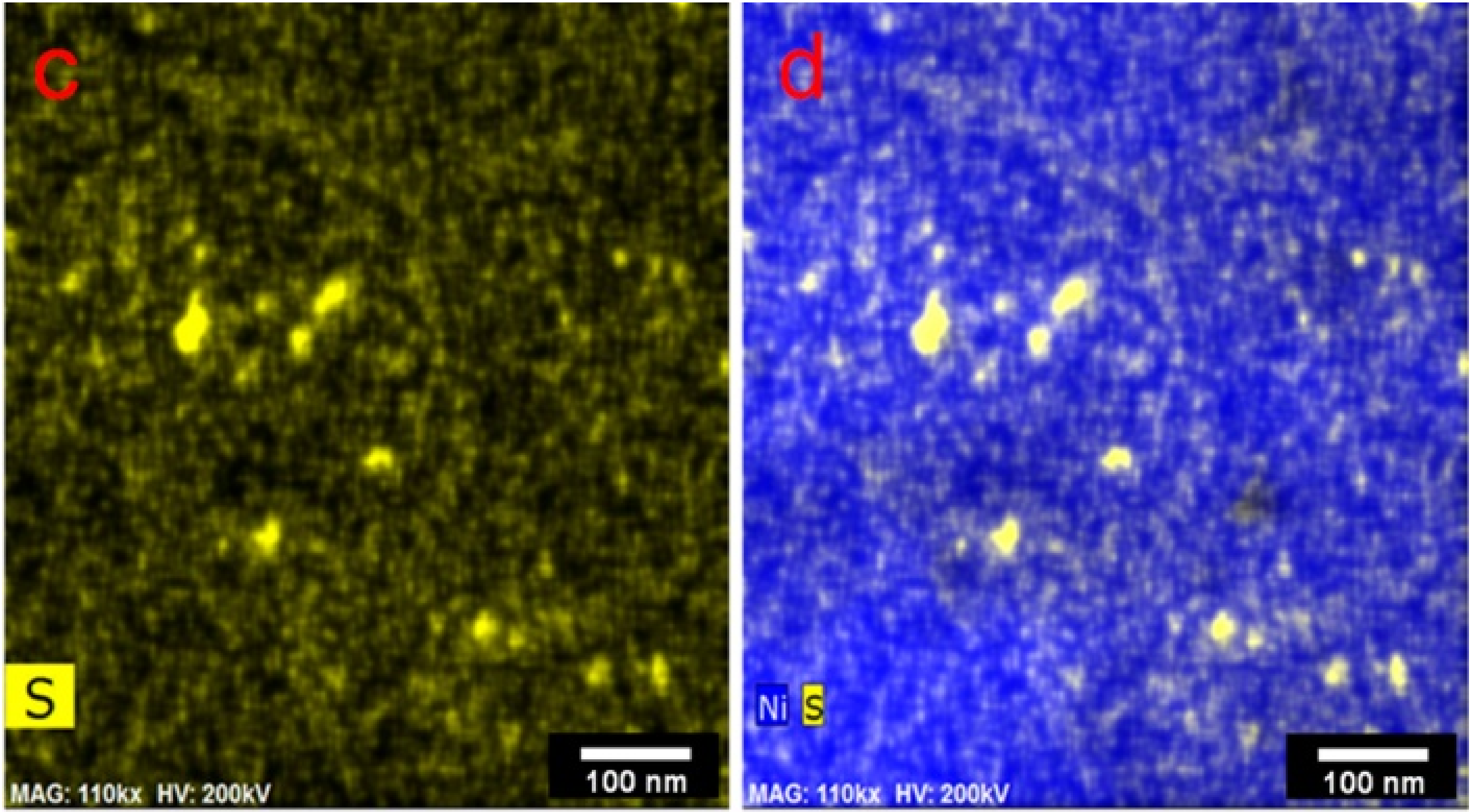
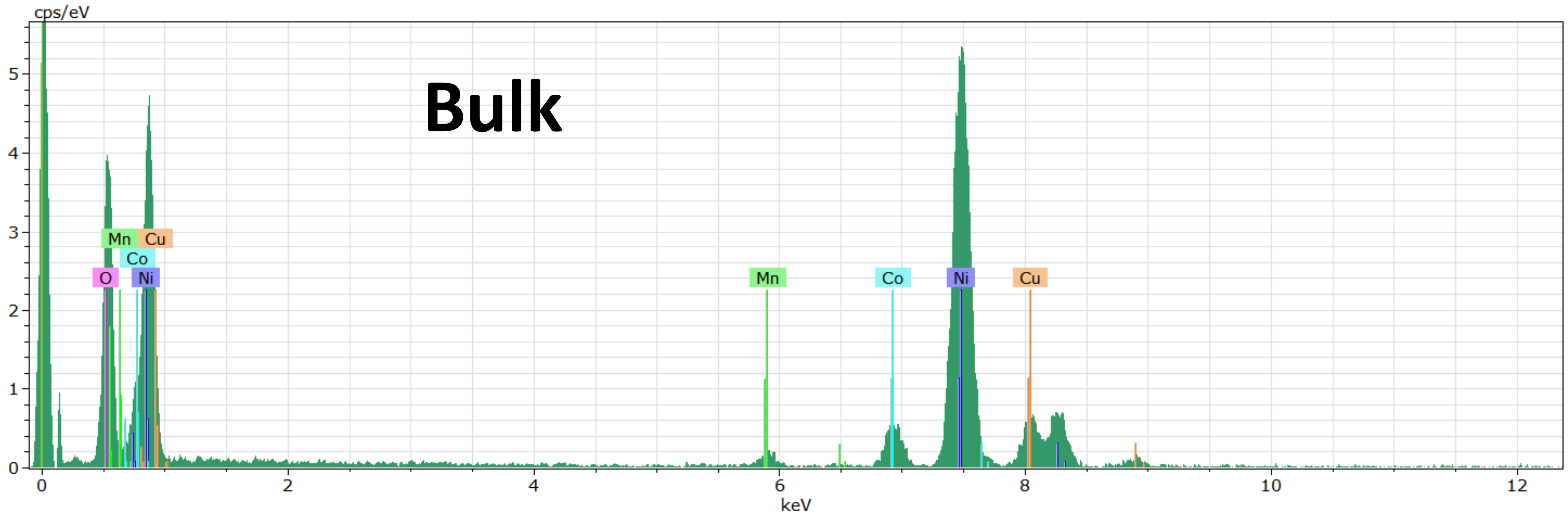
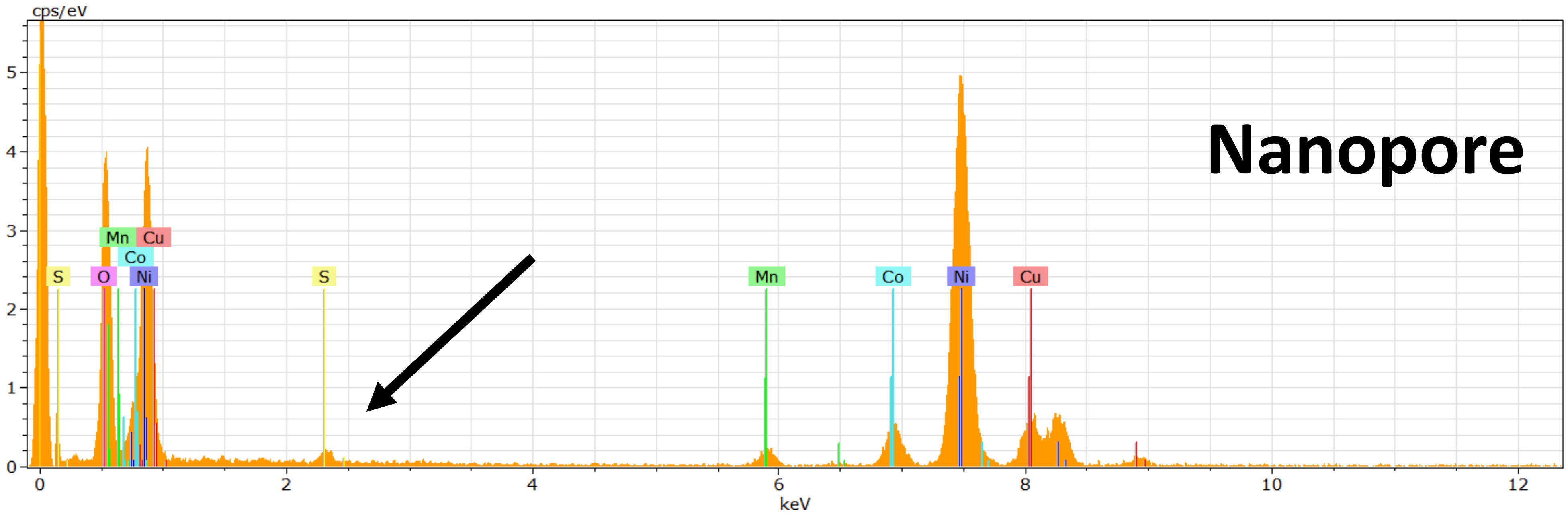
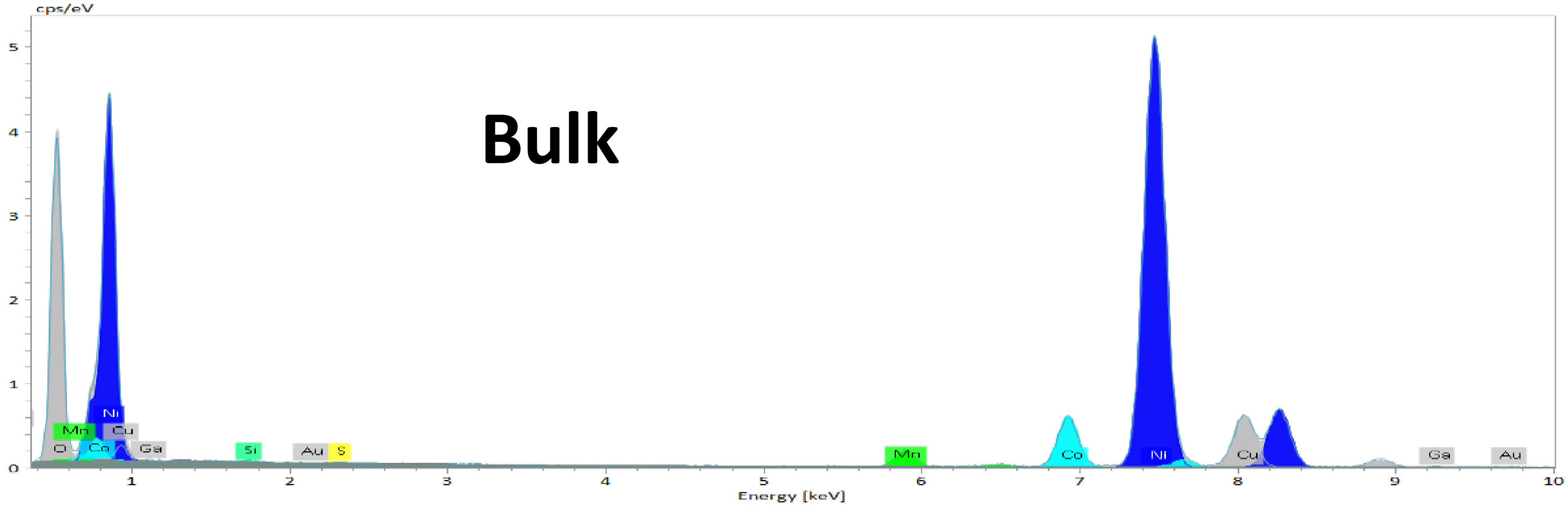


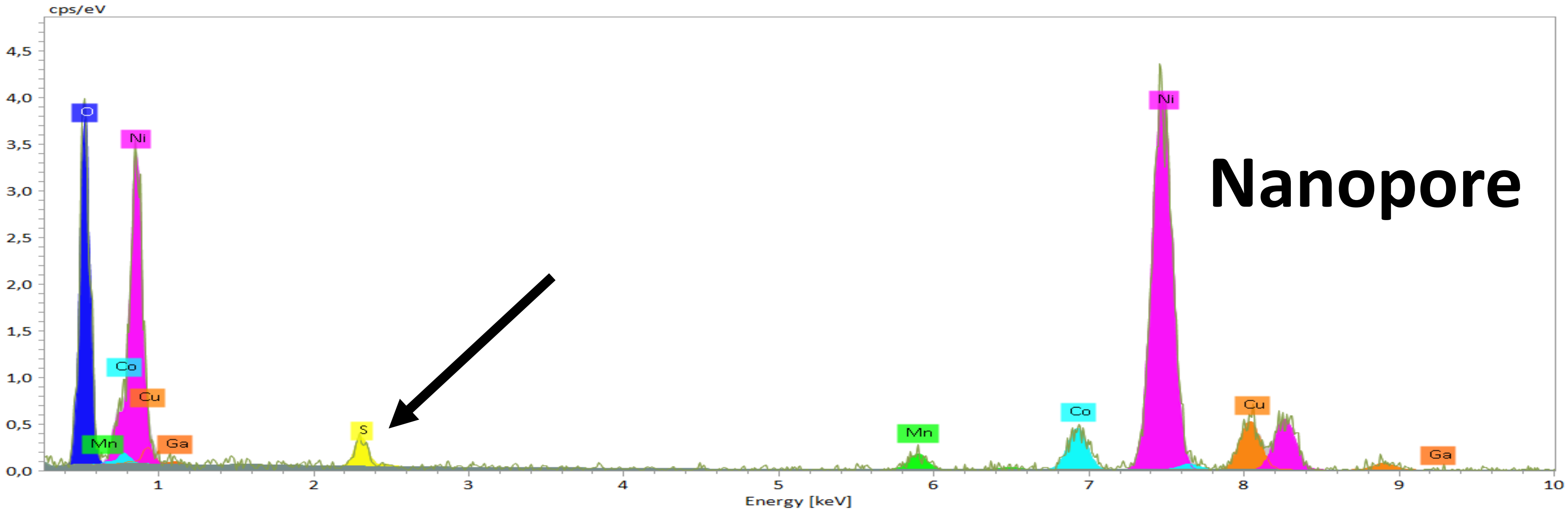

cps/eV
Bulk
Mn
Cu
Co
O
Ni
Mn
Co
Ni
Cu
keV
0
2
4
6
8
10
12
0
1
2
3
4
5

## Raw Spectra

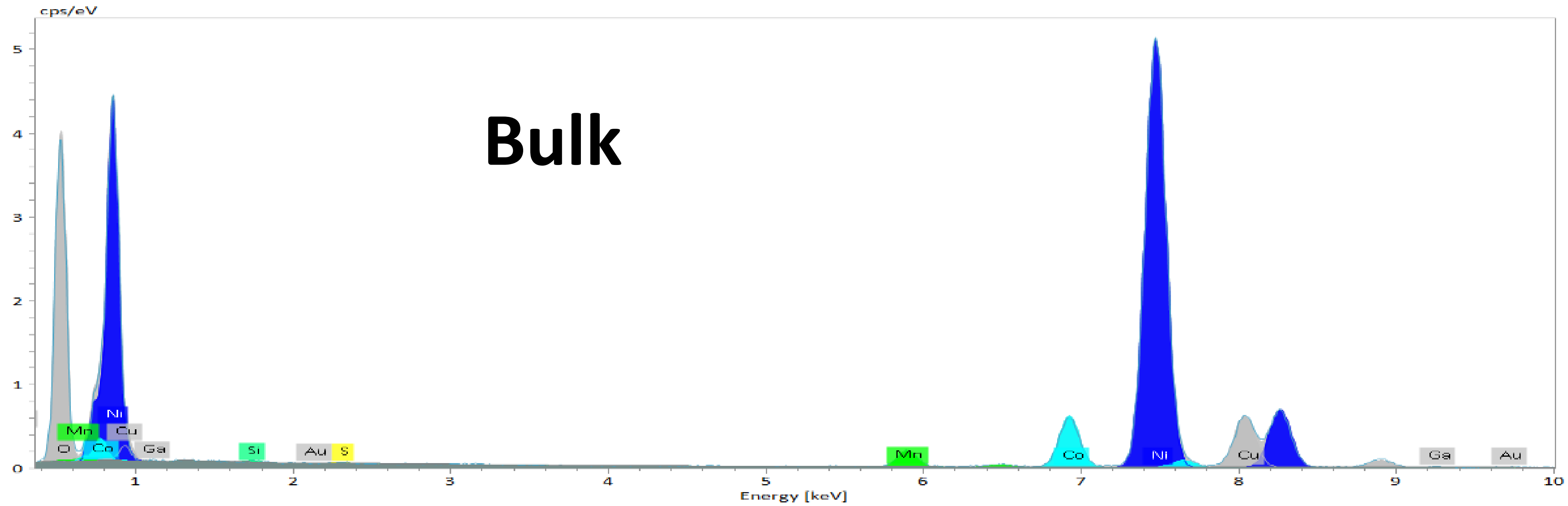

cps/eV
Nanopore
Mn
Cu
Co
S
O
Ni
S
Mn
Co
Ni
Cu
keV
0
2
4
6
8
10
12
0
1
2
3
4
5

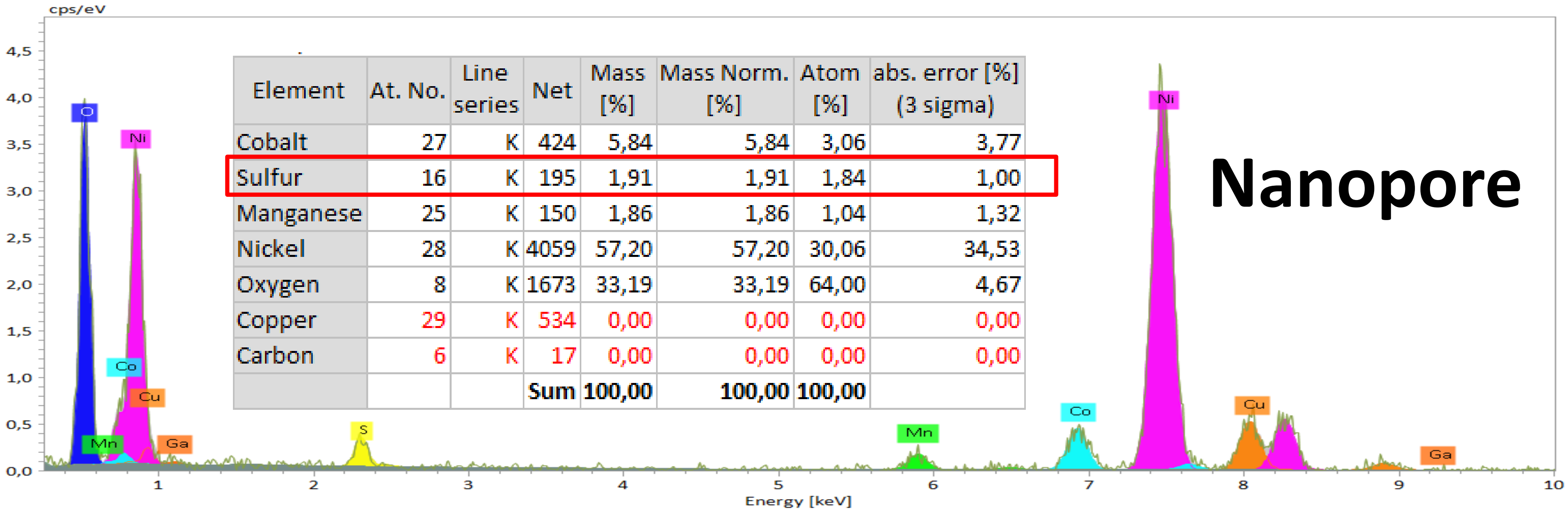
## Deconvoluted Spectra



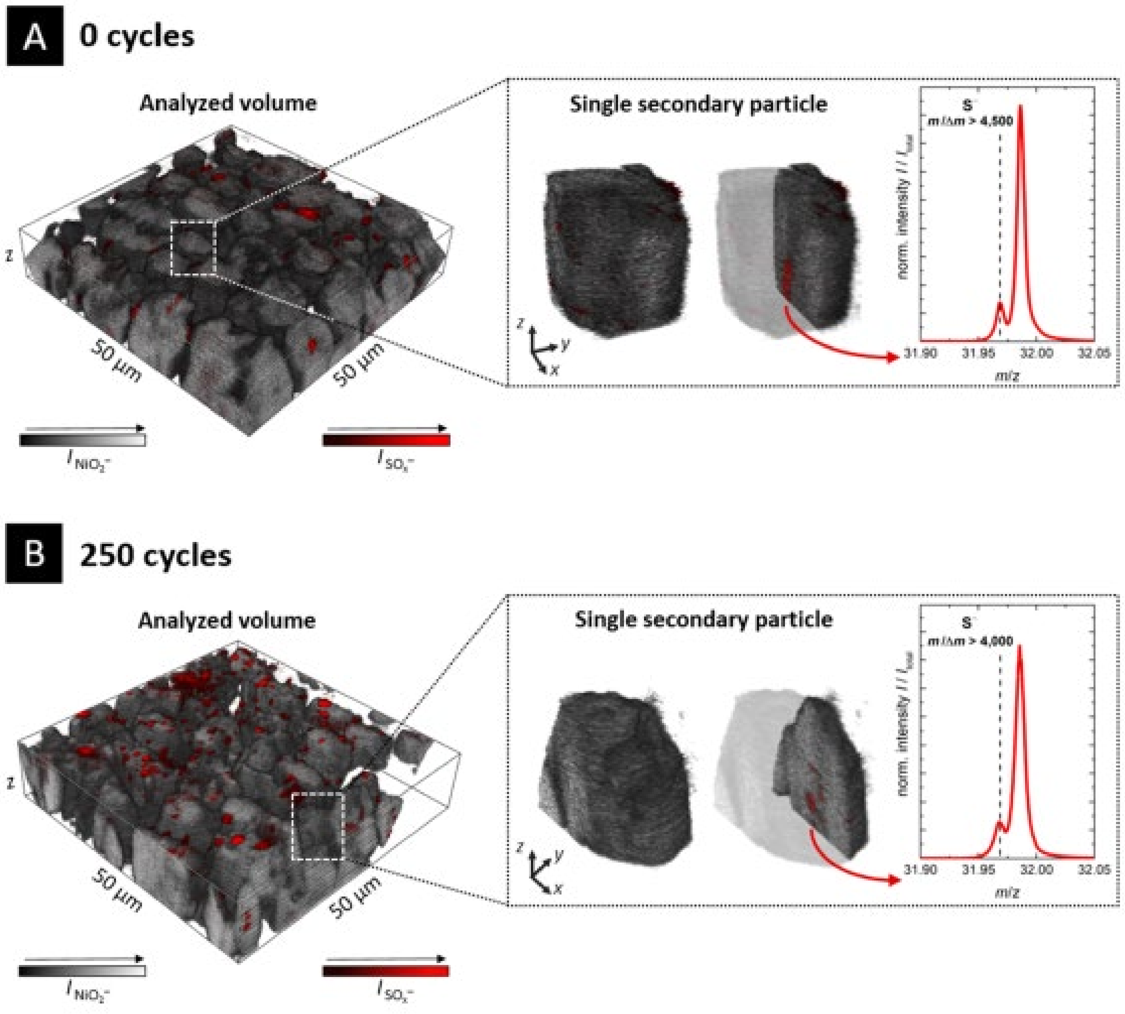
# Deconvoluted Spectra

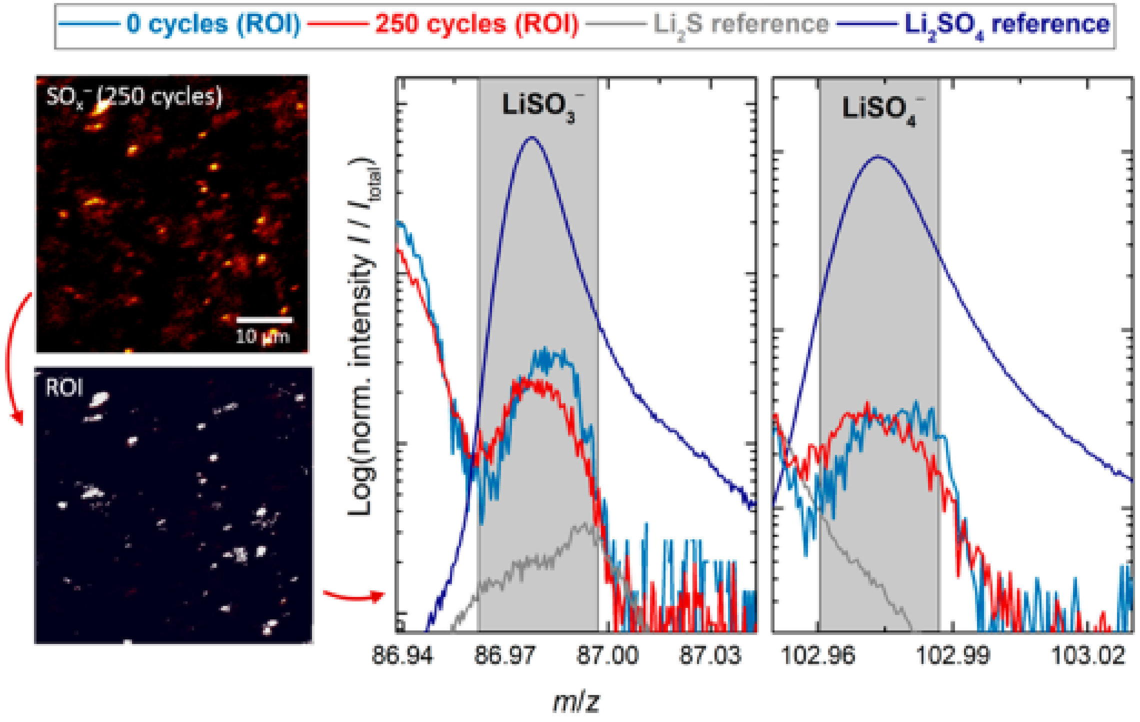



| Element | At. No. | Line series | Net | Mass [%] | Mass Norm. [%] | Atom [%] | abs. error [%] (3 sigma) |
|---|---|---|---|---|---|---|---|
| Cobalt | 27 | K | 424 | 5,84 | 5,84 | 3,06 | 3,77 |
| Sulfur | 16 | K | 195 | 1,91 | 1,91 | 1,84 | 1,00 |
| Manganese | 25 | K | 150 | 1,86 | 1,86 | 1,04 | 1,32 |
| Nickel | 28 | K | 4059 | 57,20 | 57,20 | 30,06 | 34,53 |
| Oxygen | 8 | K | 1673 | 33,19 | 33,19 | 64,00 | 4,67 |
| Copper | 29 | K | 534 | 0,00 | 0,00 | 0,00 | 0,00 |
| Carbon | 6 | K | 17 | 0,00 | 0,00 | 0,00 | 0,00 |
| | | | Sum | 100,00 | 100,00 | 100,00 | |

# Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) on NCM85



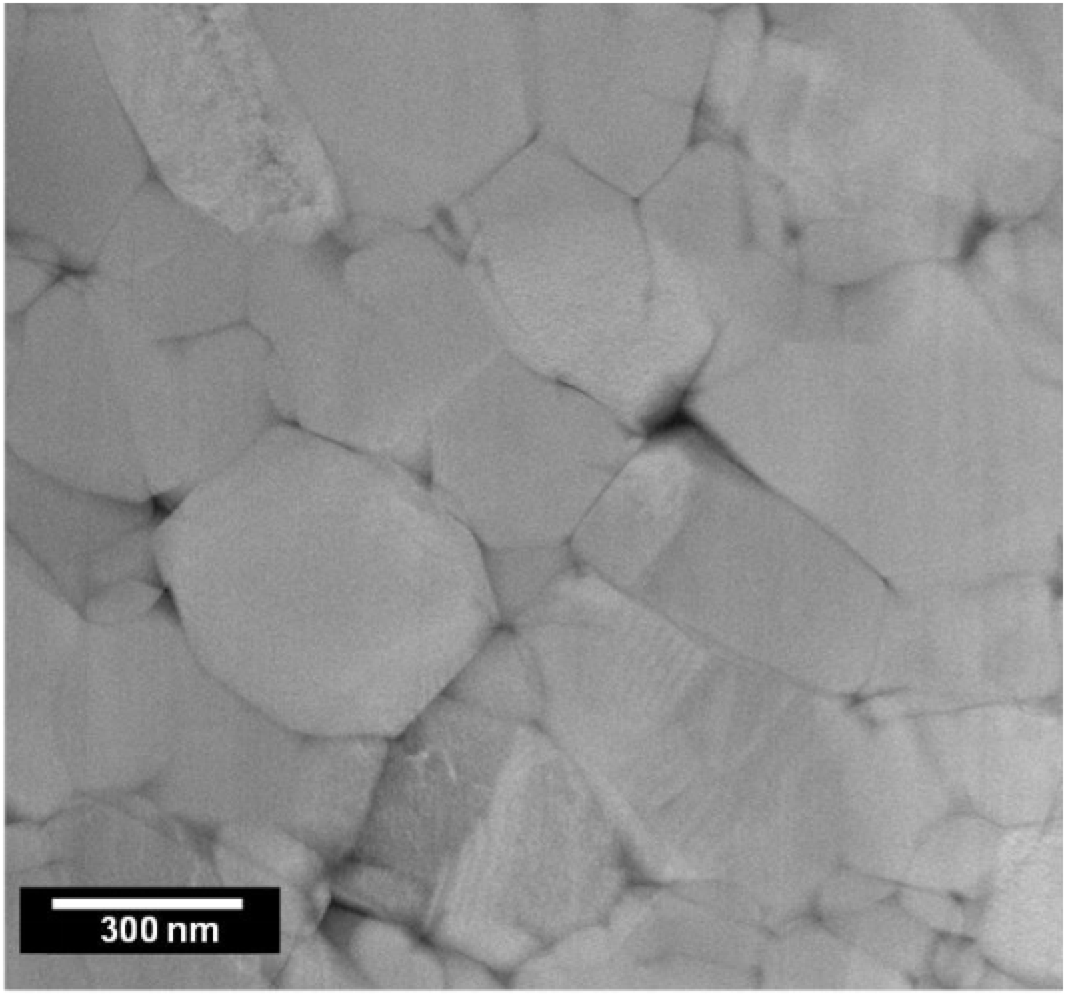




ToF-SIMs show that sulfur contaminants exist as $Li_2SO_4$

# Implications for synthesis

- Synthesis involves co-precipitation of TM sulfates $NiSO_4$, $CoSO_4$ and $MnSO_4$ into metal hydroxides $Ni(OH)_2$, $Co(OH)_2$, and $Mn(OH)_2$

- LiNiO2 (LNO) prepared using commercial NiO precursor does not exhibit intragranular nanopores

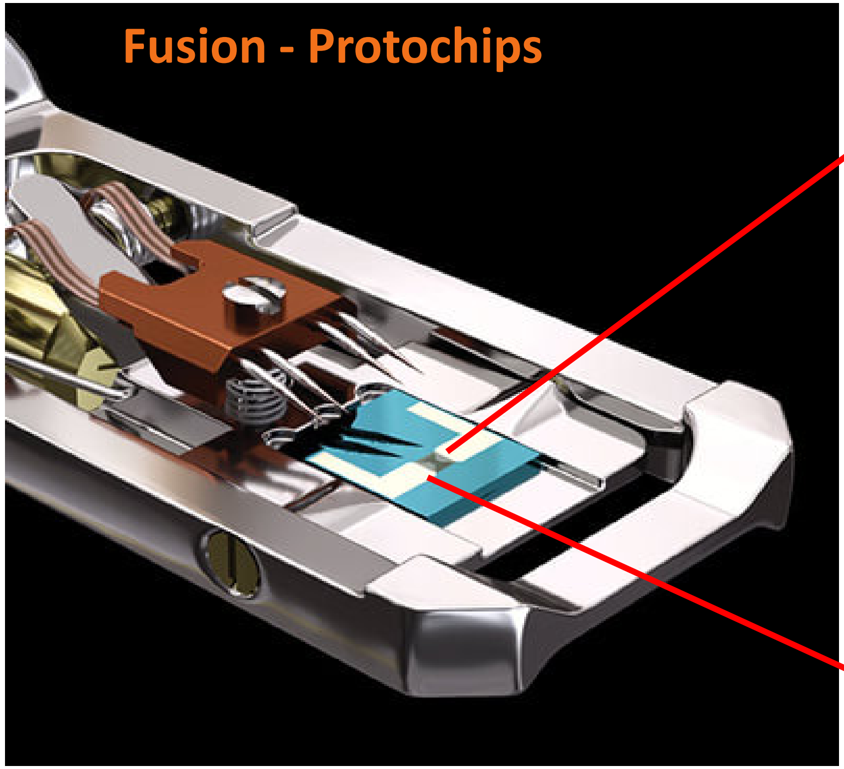


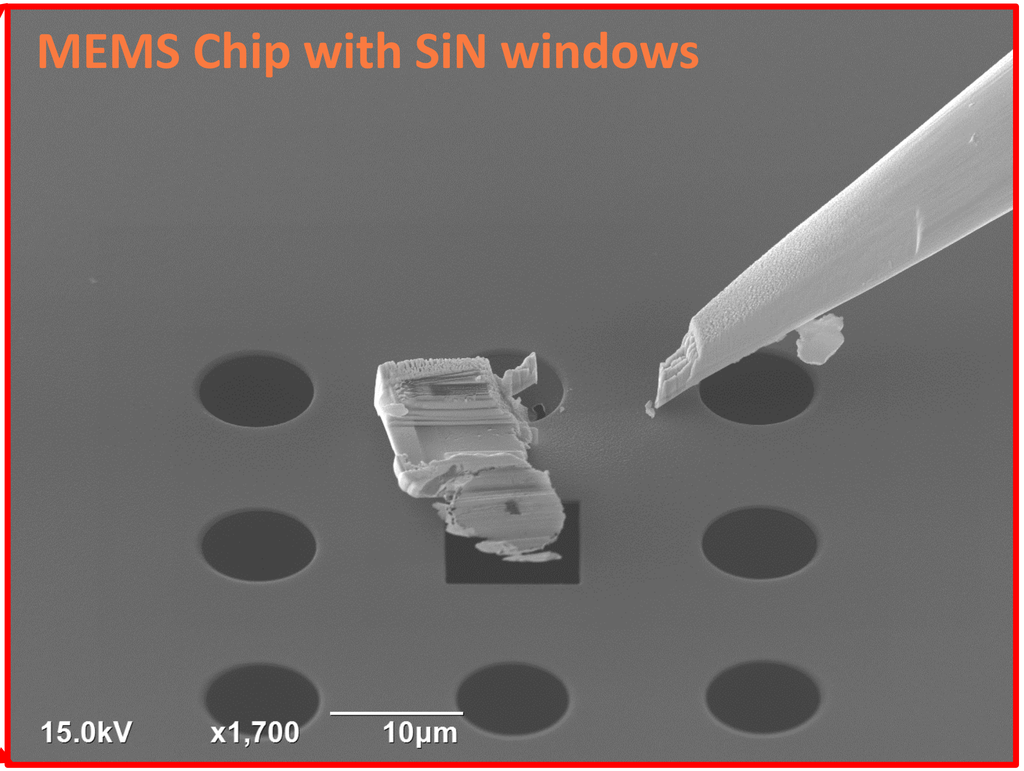



S. Ahmed, A. Pokle, S. Schweidler, A. Beyer, M. Bianchini, F. Walther, A. Mazilkin, P. Hartmann, T. Brezesinski, J. Janek, K. Volz, *ACS nano* 2019, *13*, 10694.

# Contents

# In-*situ* Heating of Nanopores



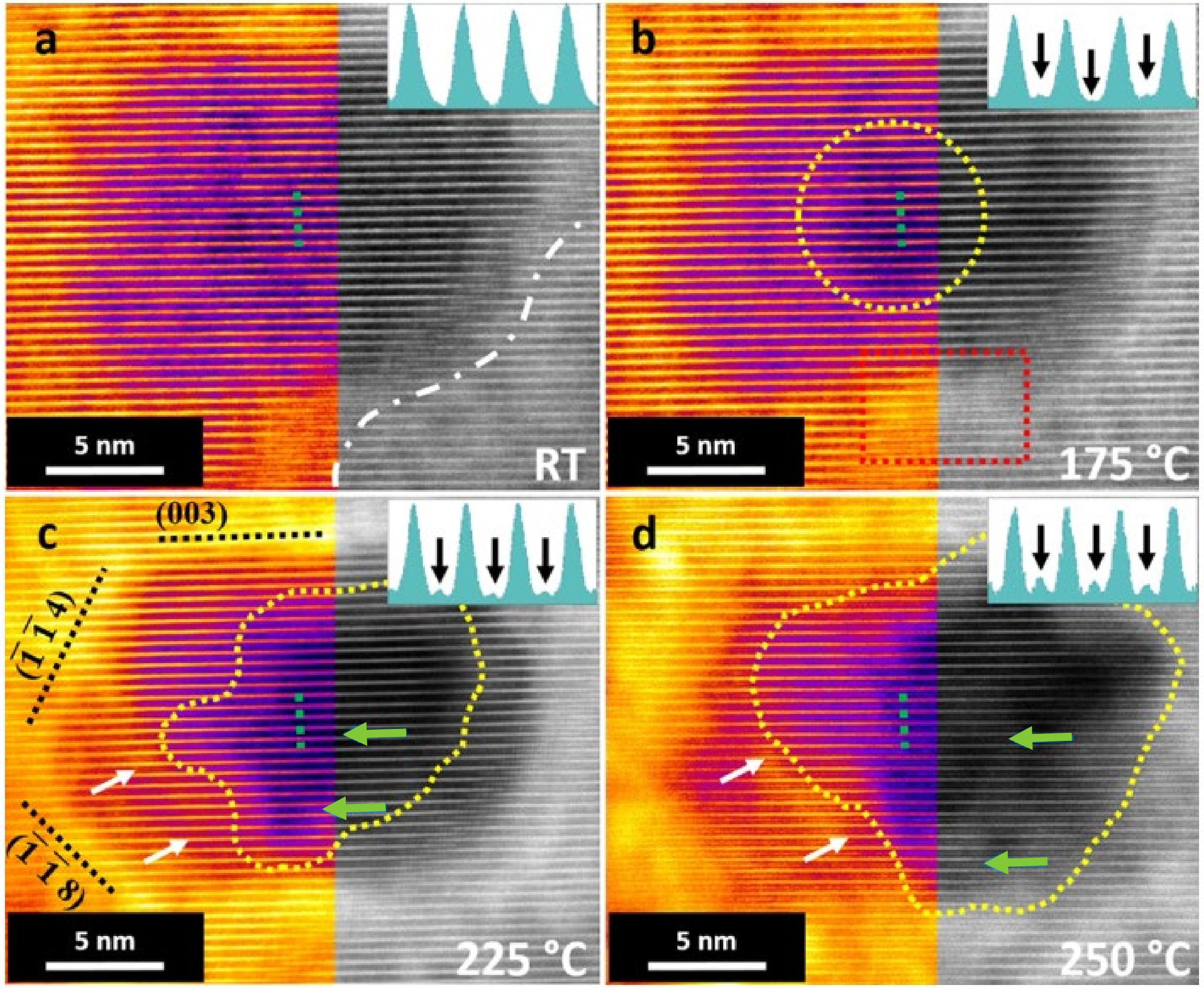




- Is heating intragranular nanopores similar to cycling?
- What happens to NCM85 during thermal runway?



A. Pokle, S. Ahmed, S. Schweidler, M. Bianchini, T. Brezesinski, A. Beyer, J. Janek, K. Volz, *ACS applied materials & interfaces* 2020, *12*, 57047

# In-*situ* Heating of Nanopores



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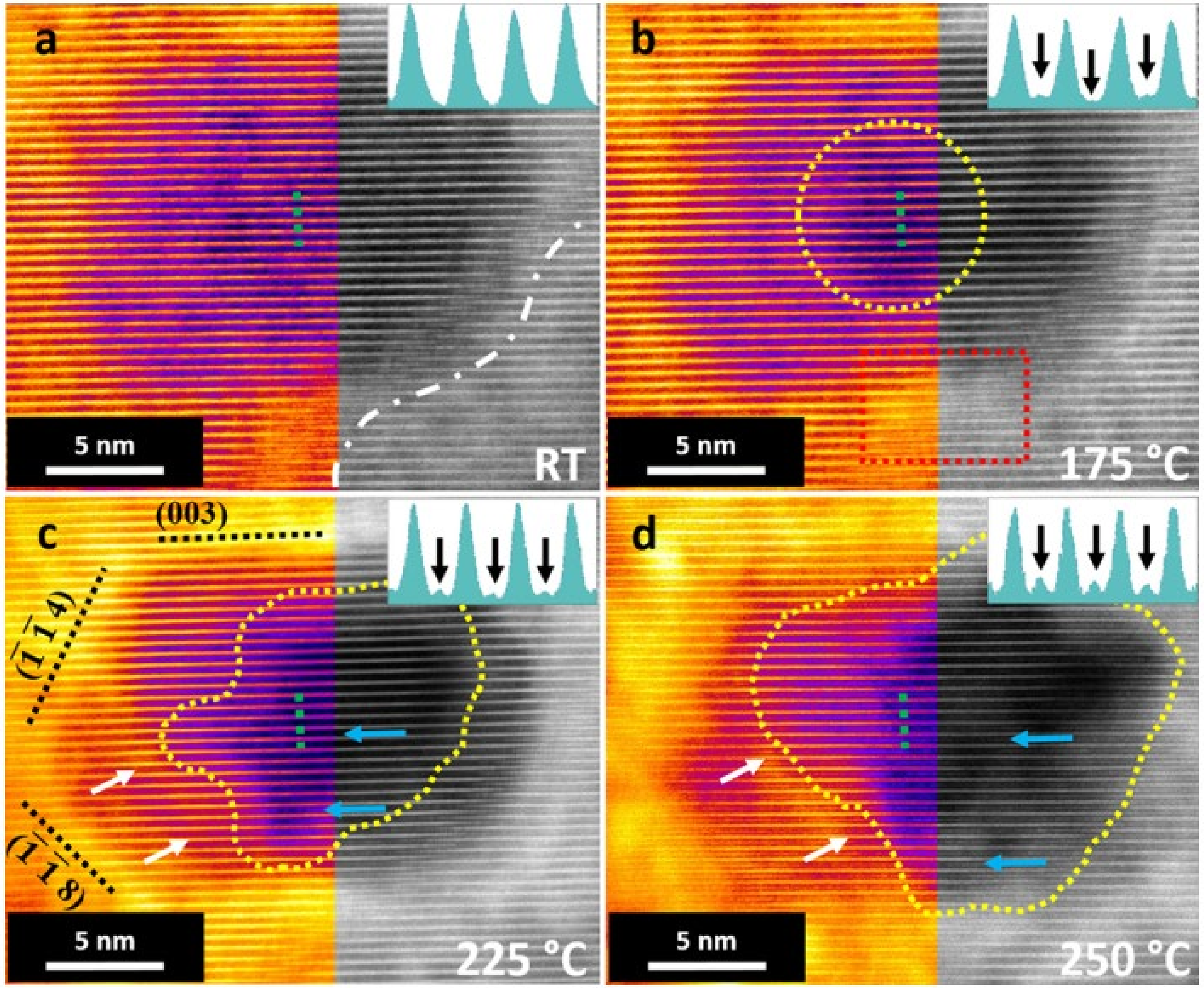
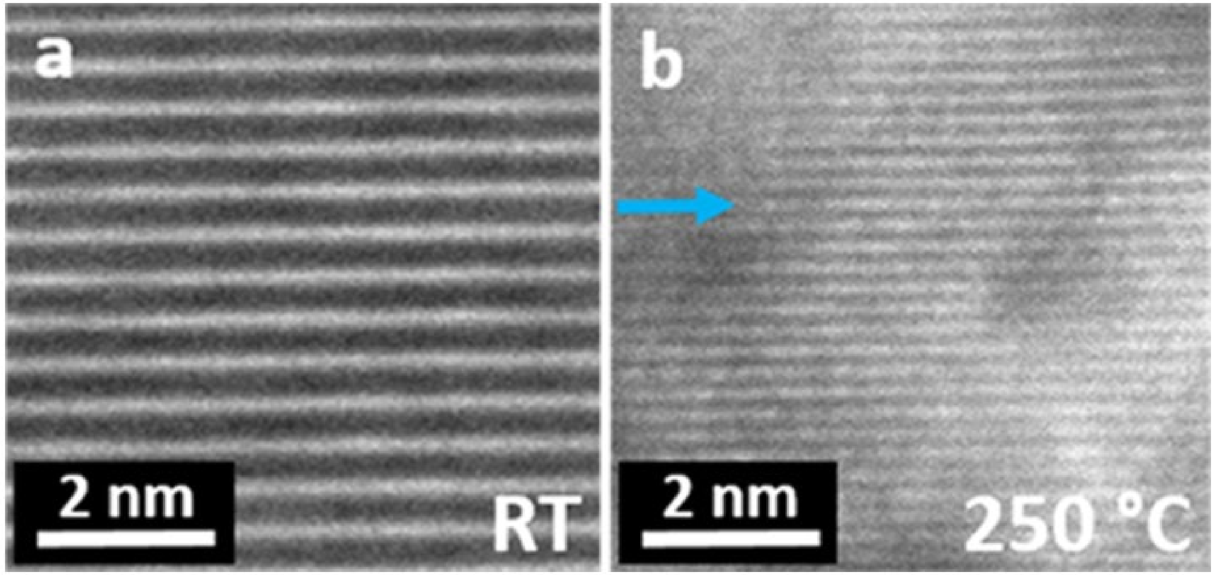
# In-*situ* Heating of Nanopores



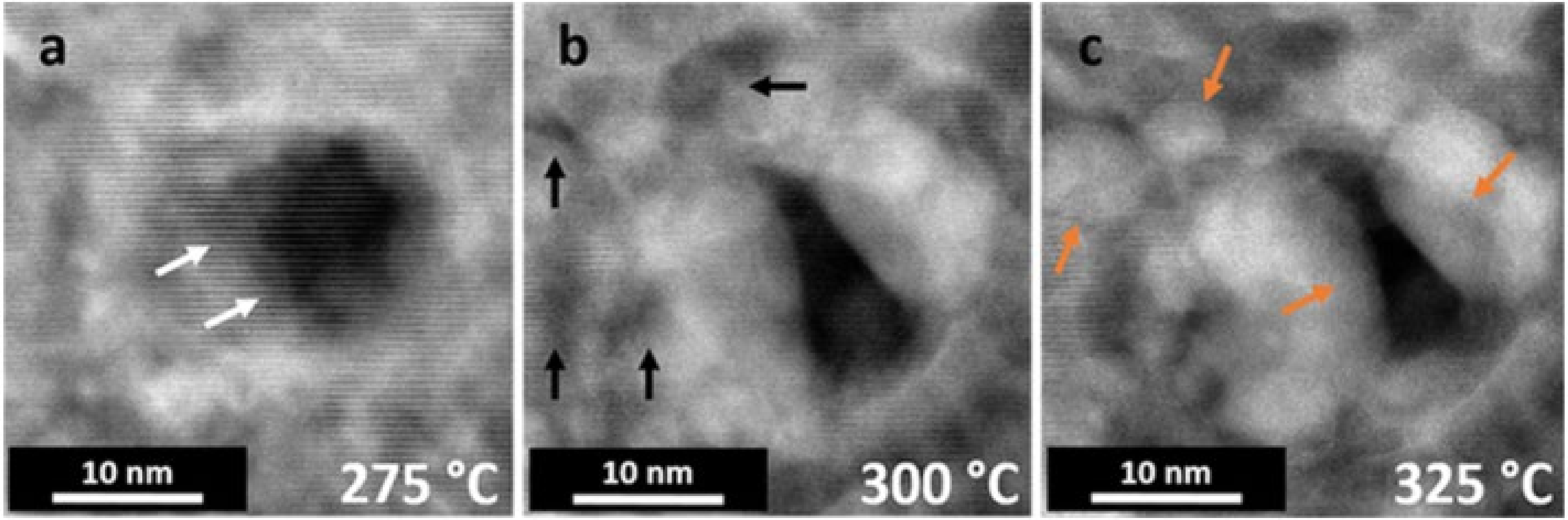




- Transition metals (mostly Nickel) migrate into the Li-slabs.
- The pore boundary densification with sharp facets at high temperature.



A. Pokle, S. Ahmed, S. Schweidler, M. Bianchini, T. Brezesinski, A. Beyer, J. Janek, K. Volz, *ACS applied materials & interfaces* 2020, *12*, 57047

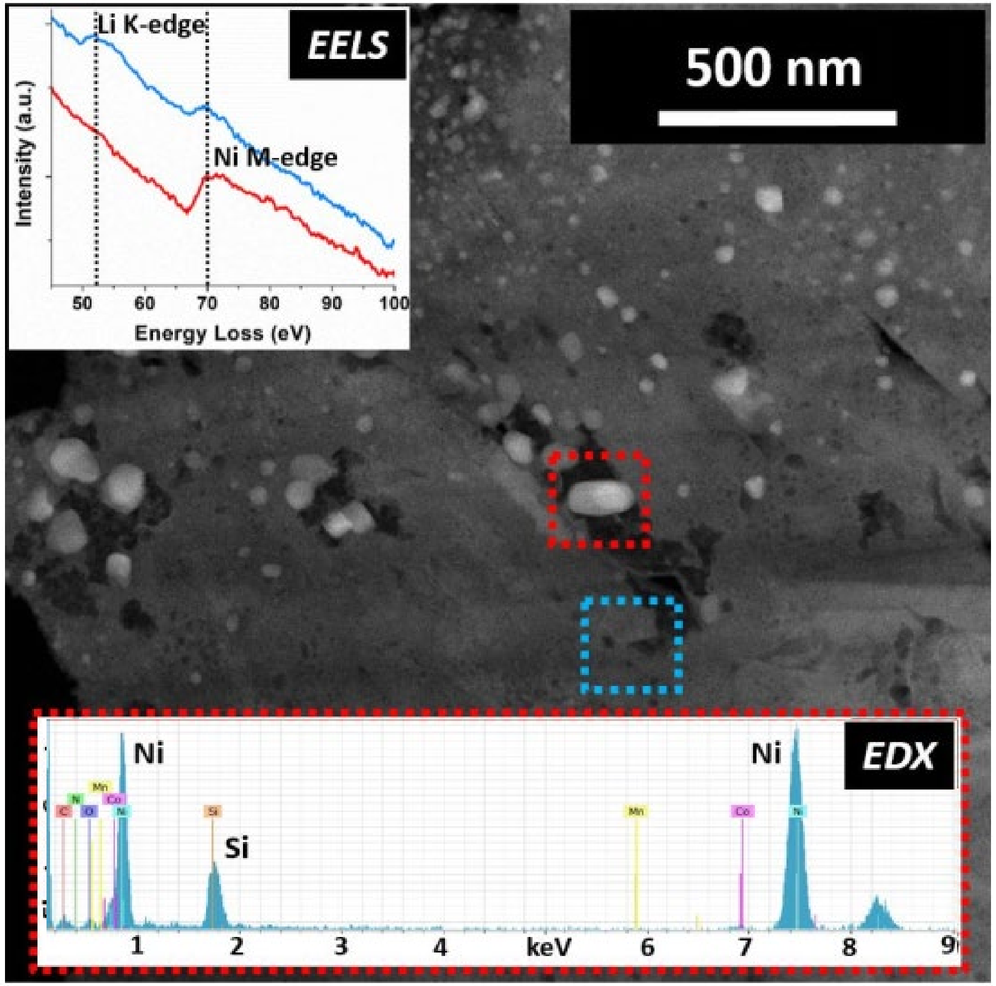
# Formation of Nanodomains

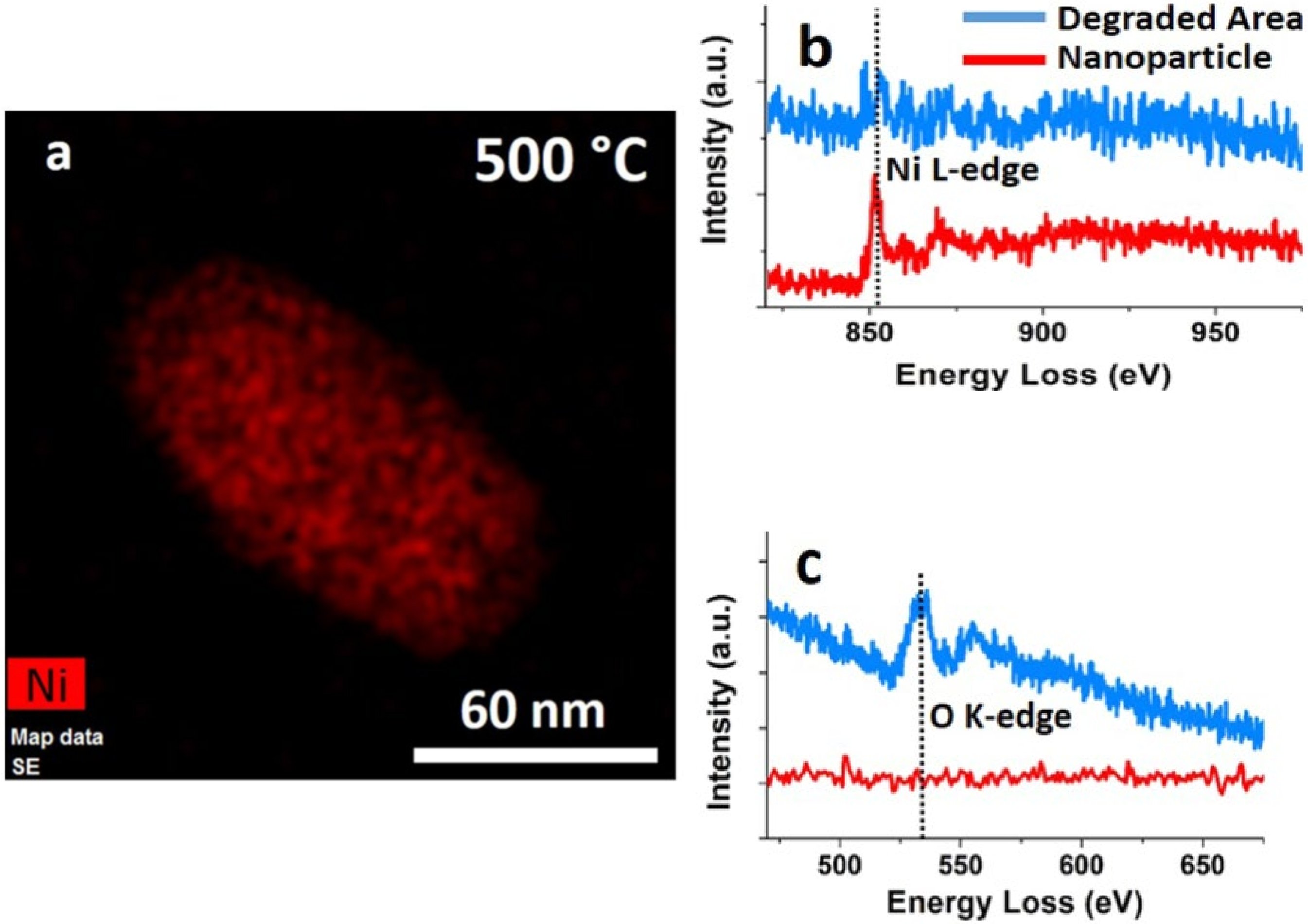





A. Pokle, S. Ahmed, S. Schweidler, M. Bianchini, T. Brezesinski, A. Beyer, J. Janek, K. Volz, *ACS applied materials & interfaces* 2020, *12*, 57047

# EDX and EELS on Nanodomains



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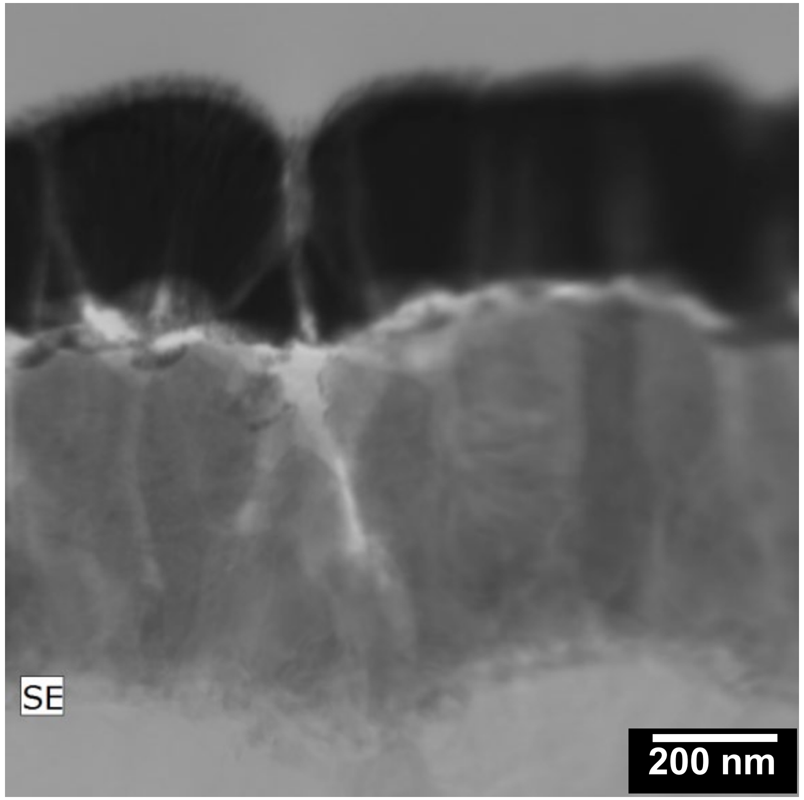
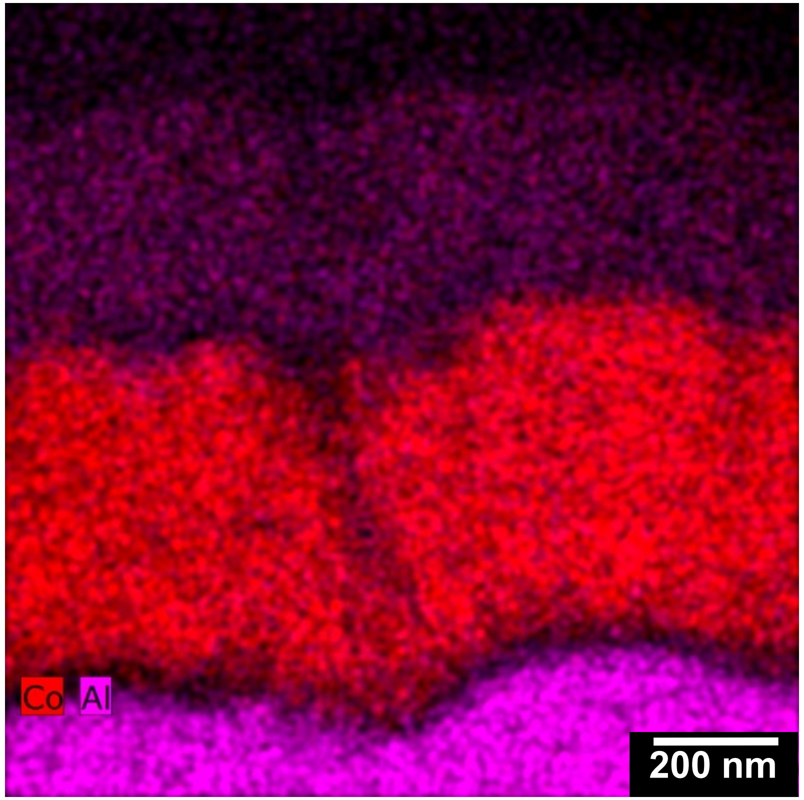
# Contents

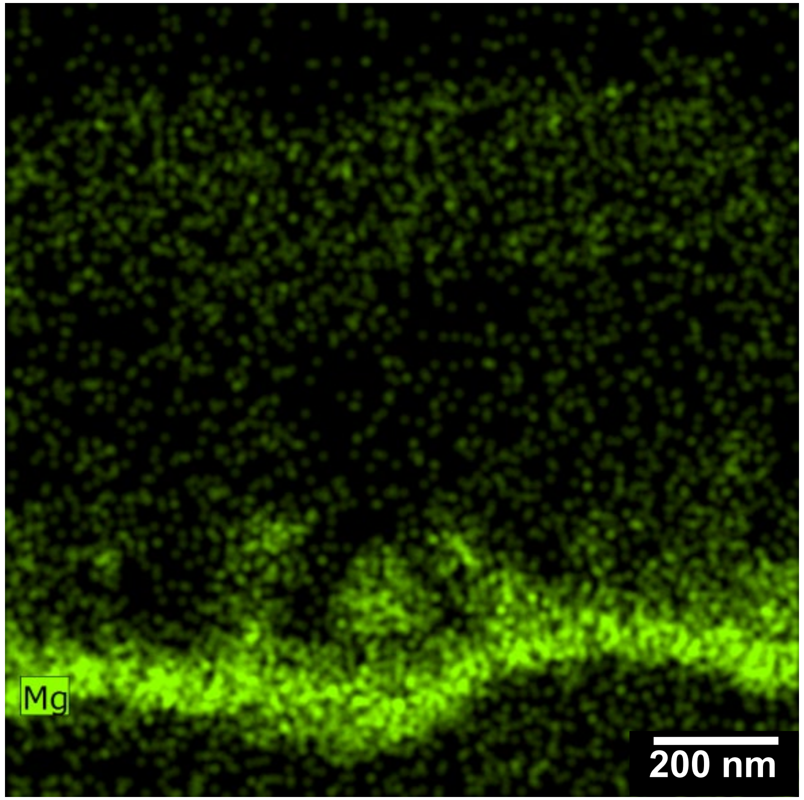
# Lithium Cobalt Oxide thin-film on $Al_2O_3$ Substrate




STEM-BF

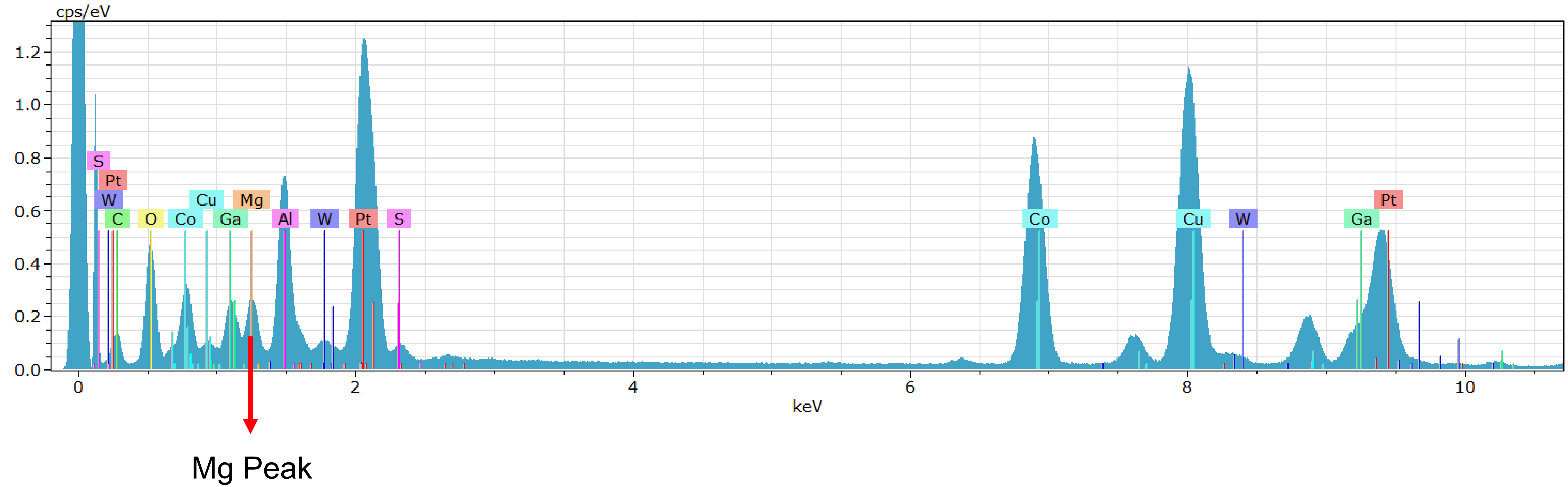



Co-Al Overlay

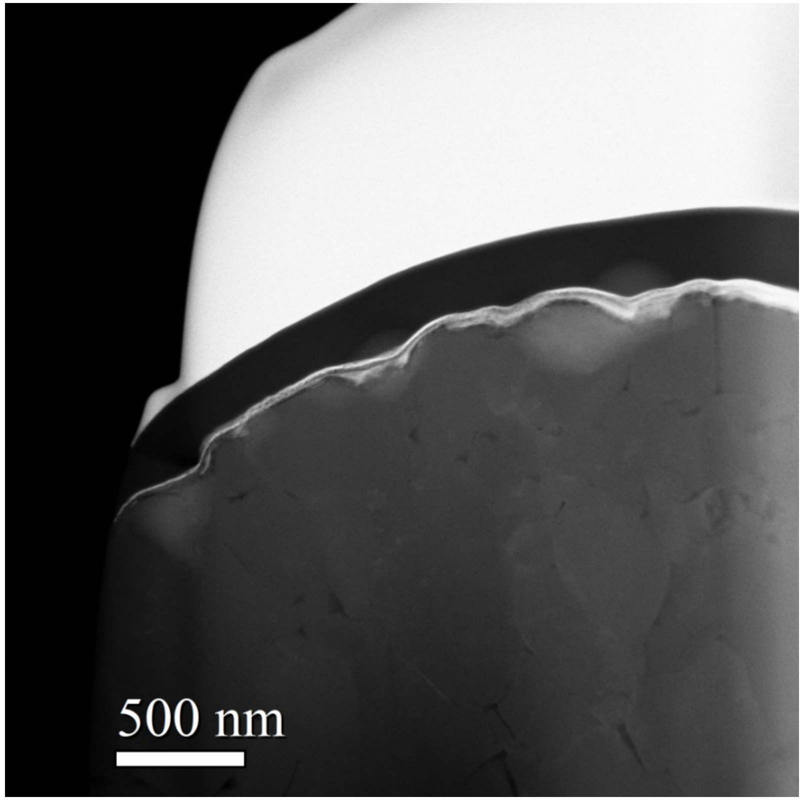



Mg EDX

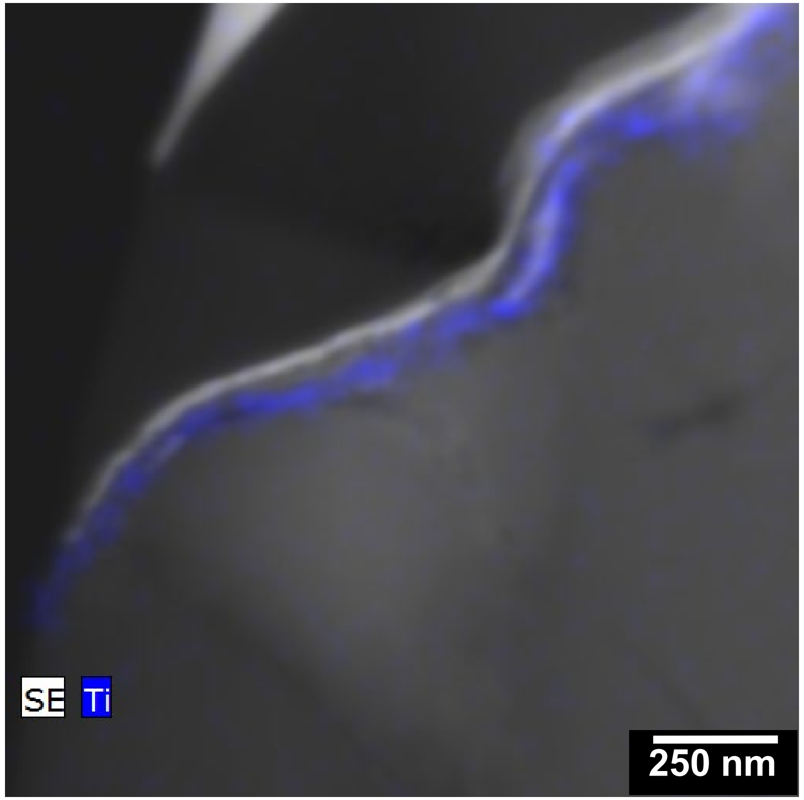
# EDX Spectrum of Lithium Cobalt Oxide thin-film on $Al_2O_3$ Substrate



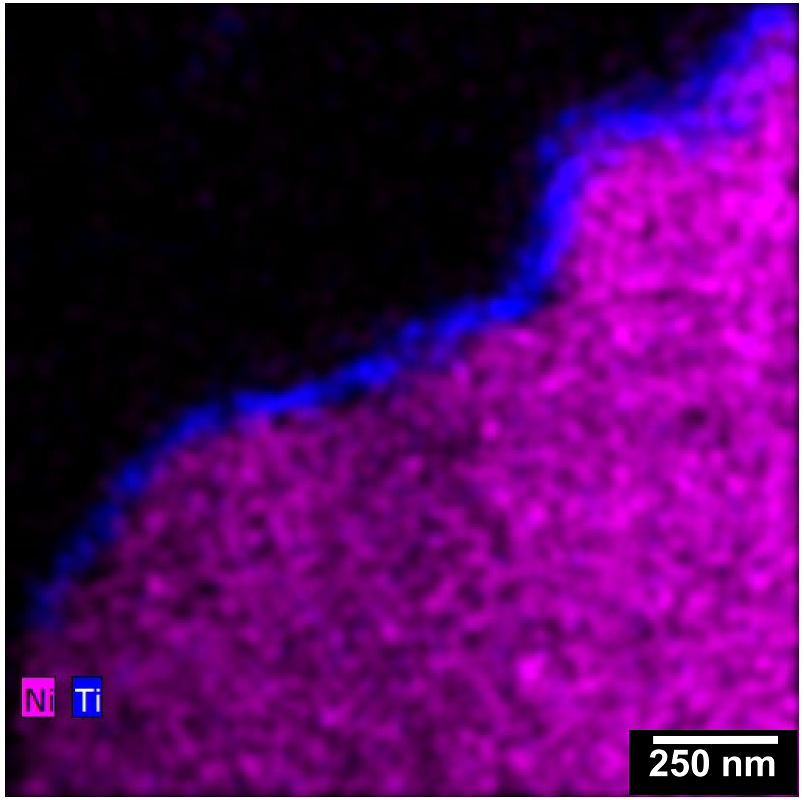
# Titanium Oxide (TiO) coating on NCM




HAADF

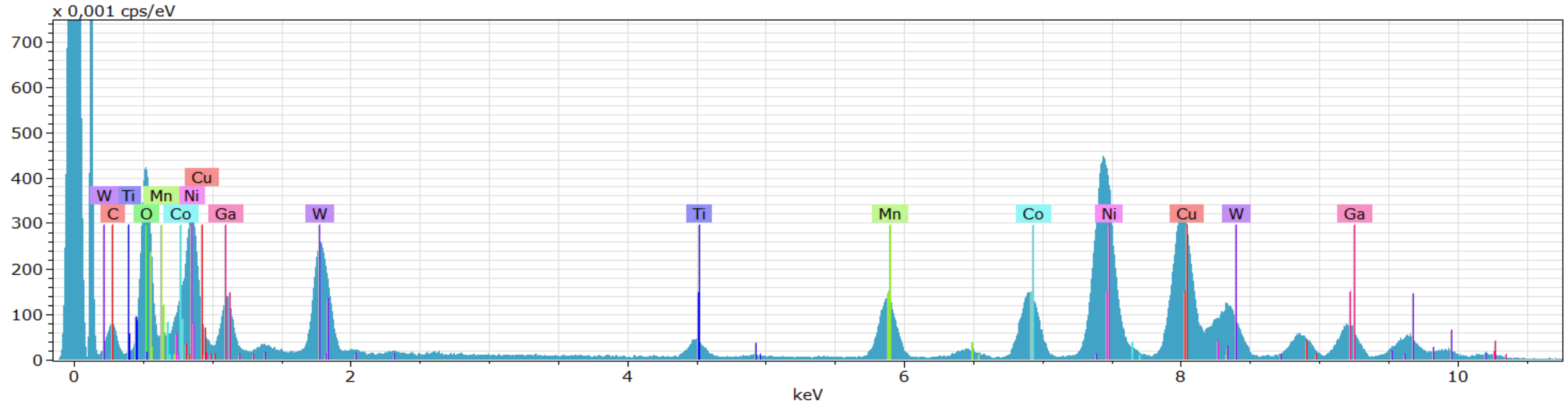



Ti EDX



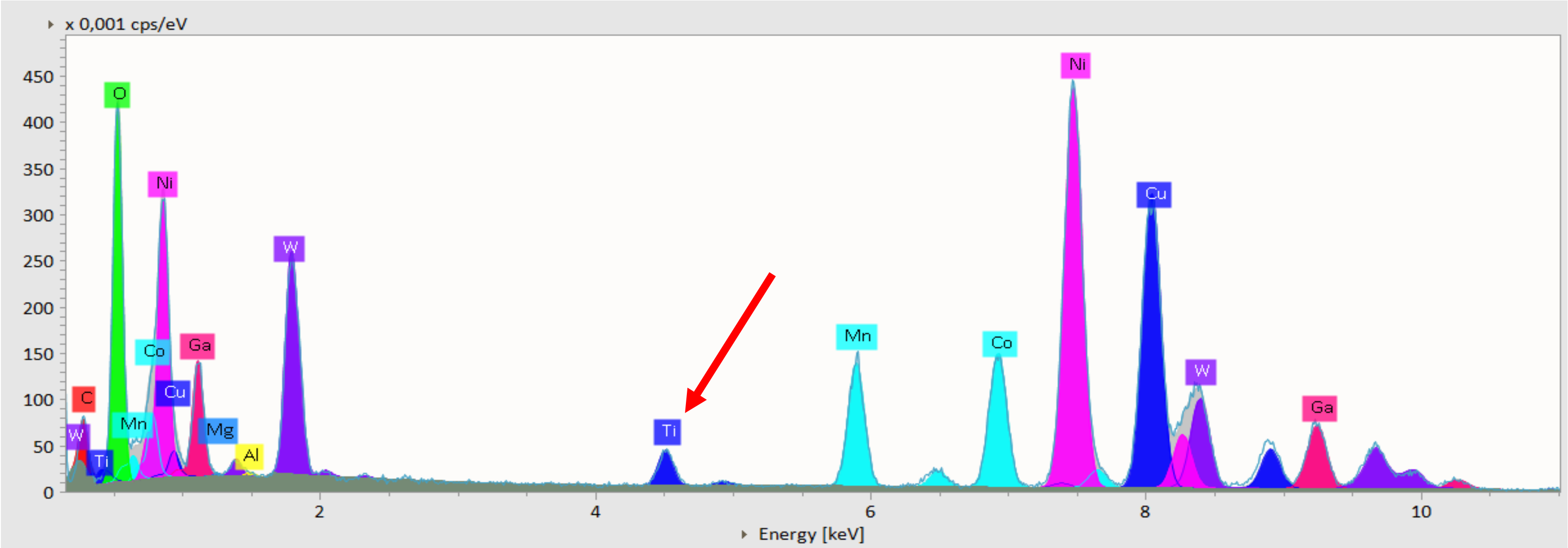

Ni-Ti Overlay

# EDX spectrum from TiO coated NCM



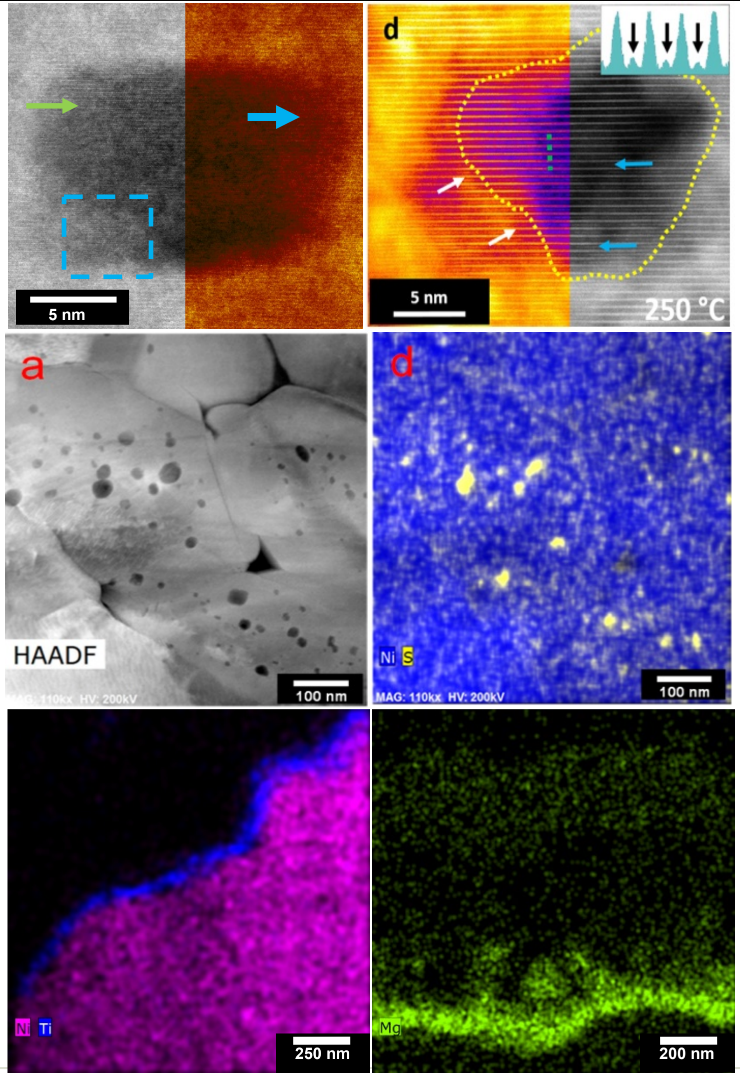

**Raw Spectrum**

**Deconvoluted Spectrum**



# Conclusions

- The intragranular nanopores evolve with cycling and temperatures.
- Sulfur species identified with STEM-EDX
- Thin coatings and contaminant layers detected.
- Contaminations can be introduced at any stage of synthesis.



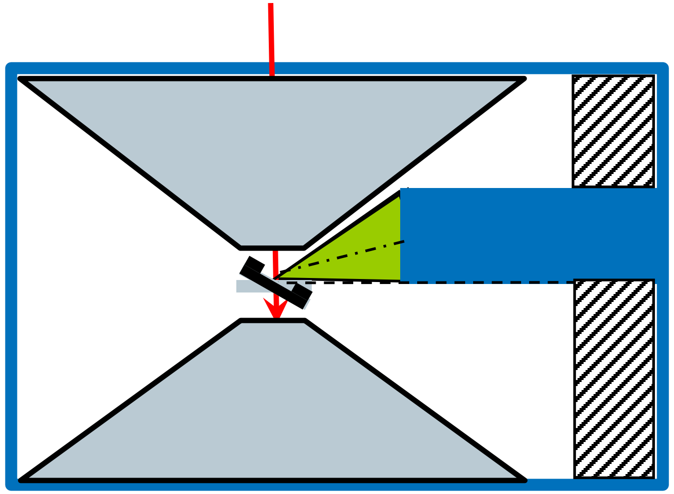
# Thank you for your attention!

**Dr. Igor Németh**
Application Scientist EDS
Bruker Nano Analytics

**Michael Malaki**
phD candidate
Materials Sciences Center
Faculty of Physics
Phillips University Marburg

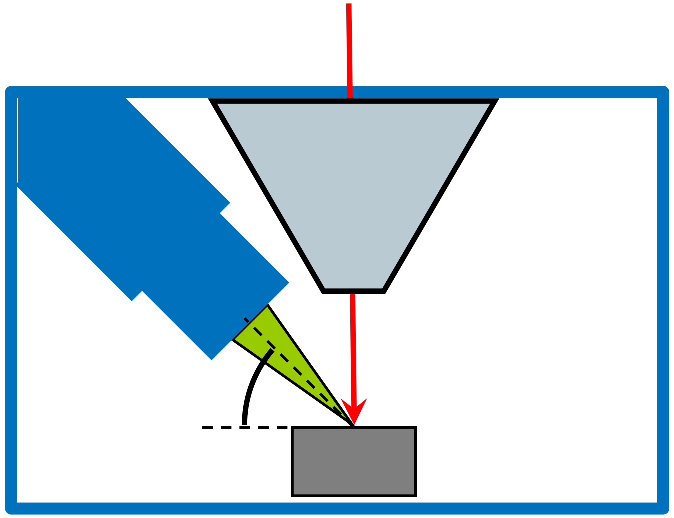
# Comparison of the same sample STEM - SEM

**STEM 200kV**
**60 mm² EDS detector**



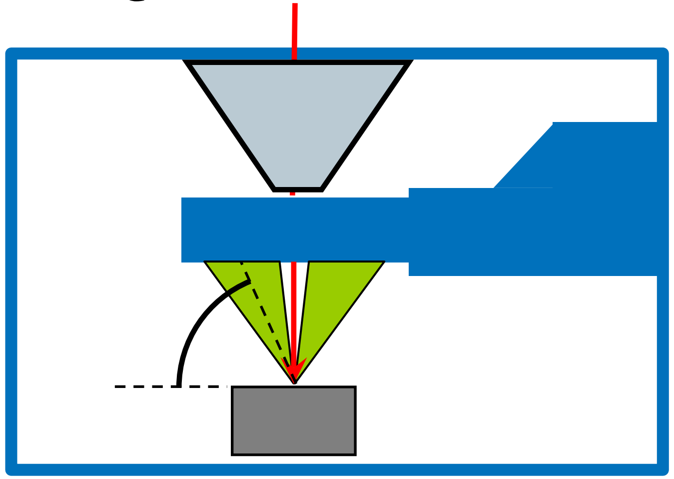
take off angle=22°
solid angle~0.26sr
beam current~0.05 nA

**SEM 20kV**
**60 mm² EDS detector**
**@WD= 8mm**



take off angle=35°
solid angle=0.043 sr
beam current~ 2nA

**SEM 20kV**
**60 mm² 4x15mm²**
**FlatQUAD detector**
**@WD=16mm**



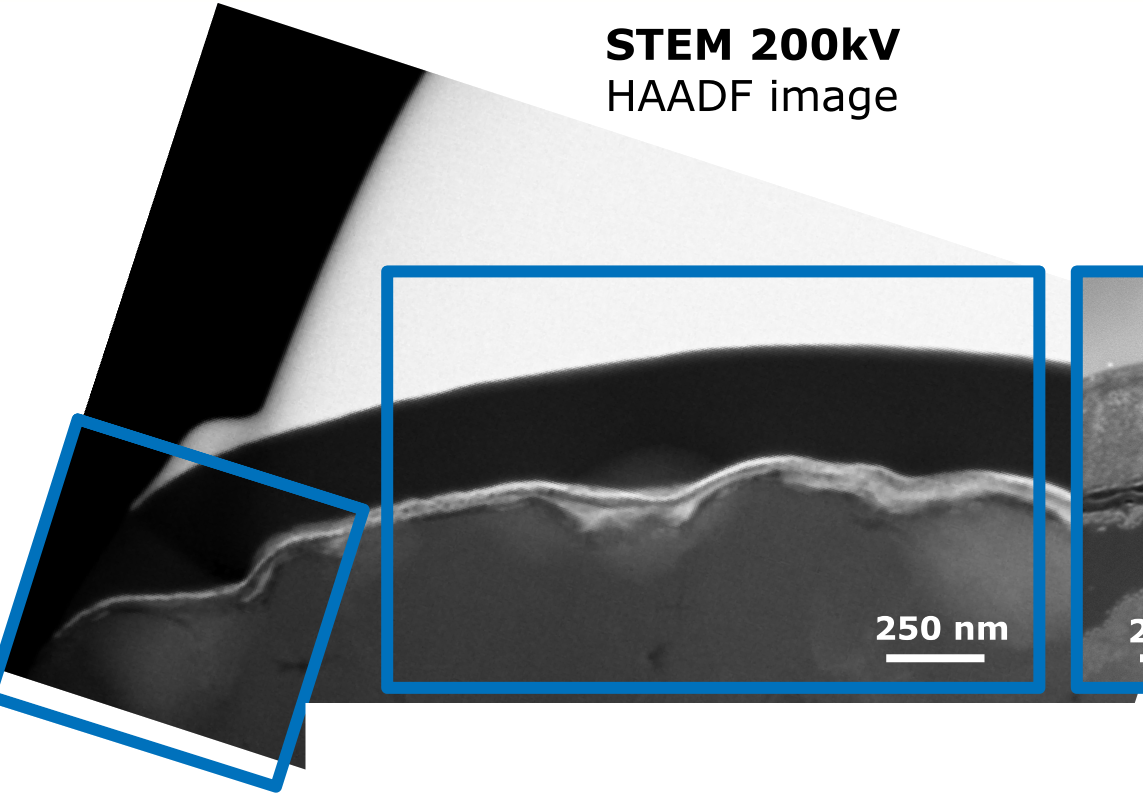
take off angle=60-70°
solid angle= 0.7-1 sr
beam current~ 2nA

x7 more X-ray signal

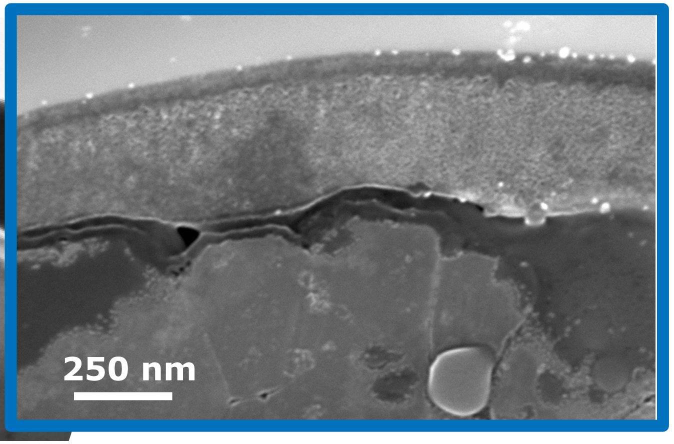
x15-20 more X-ray signal

# Comparison of the same sample  STEM - SEM

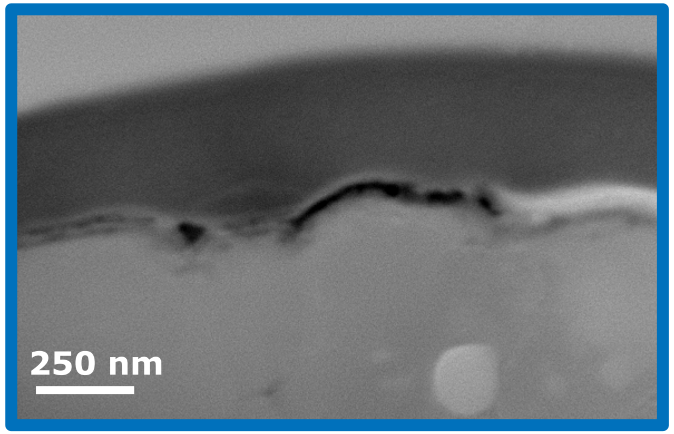
**STEM 200kV**
HAADF image



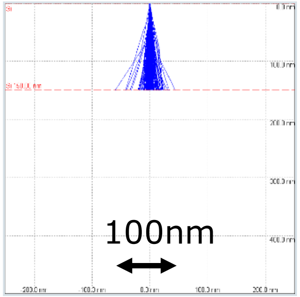

**SEM 20kV**
In-lens image
WD=8mm




**SEM 20kV**
SE image with
inserted FlatQUAD
WD=16mm

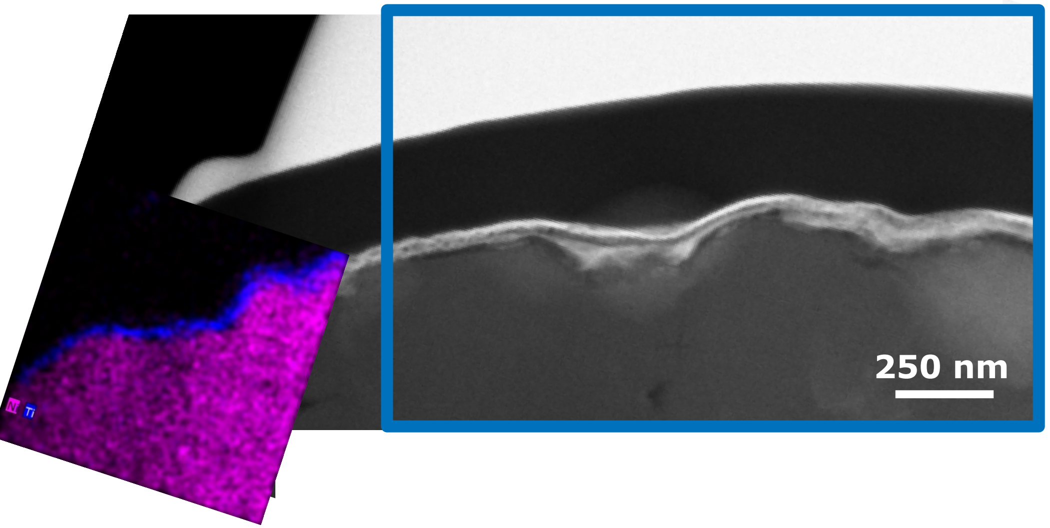



Images taken under measurement conditions optimized for EDS analysis
Image quality does not affect EDS resolution on this scale!



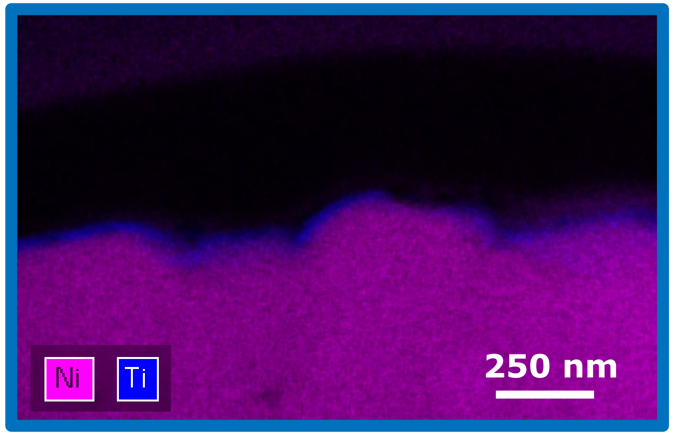
# Comparison of the same sample  STEM - SEM

**STEM 200kV**
**60 mm² EDS detector**



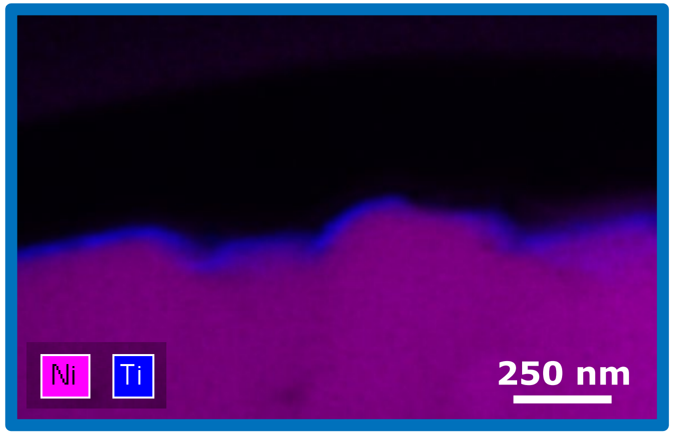

Total measurement time= 8 mins
Beam current= 0.2 nA
Input count rate ~  1 kcps

**SEM 20kV**
**60 mm² EDS detector**




Total measurement time= 34 mins
Beam current=2 nA
Input count rate ~ 30 kcps

**SEM 20kV**
**FlatQuad detector**




Total measurement time= 34 mins
Beam current= 2 nA
Input count rate ~ 460 kcps

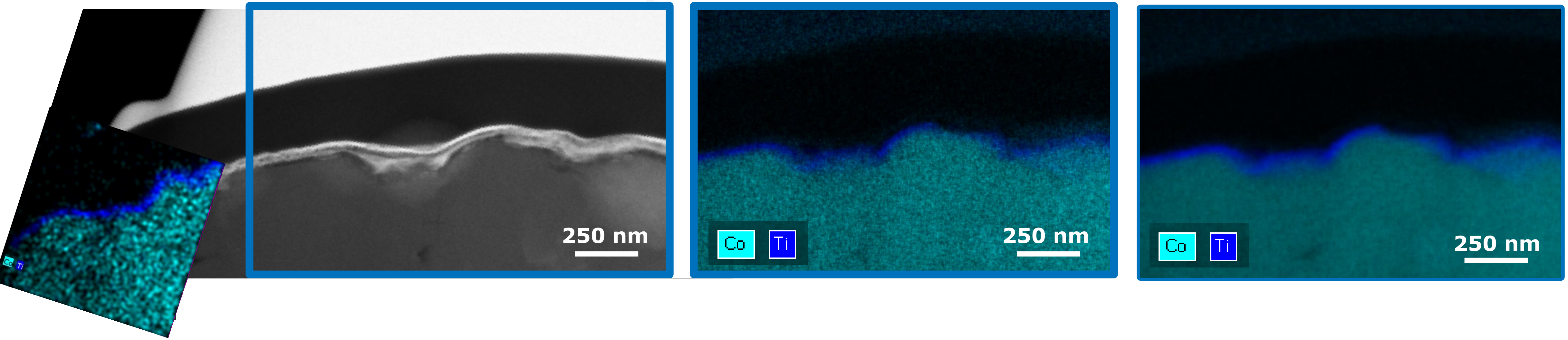
Sample and data courtesy: Michael Malaki, Shamail Ahmed, Materials Sciences Center, Philipps University Marburg

# Comparison of the same sample STEM - SEM

**STEM 200kV**
**60 mm² EDS detector**

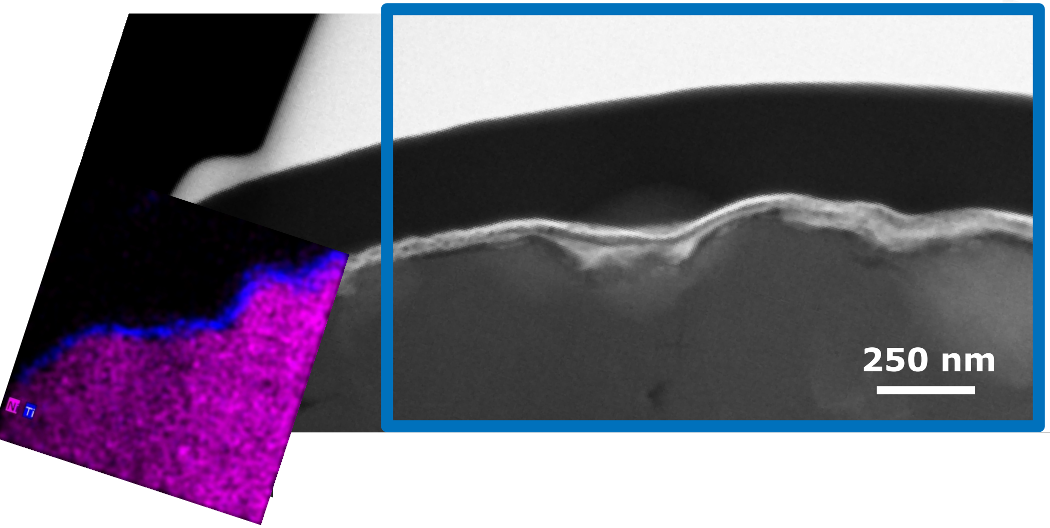
**SEM 20kV**
**60 mm² EDS detector**

**SEM 20kV**
**FlatQuad detector**

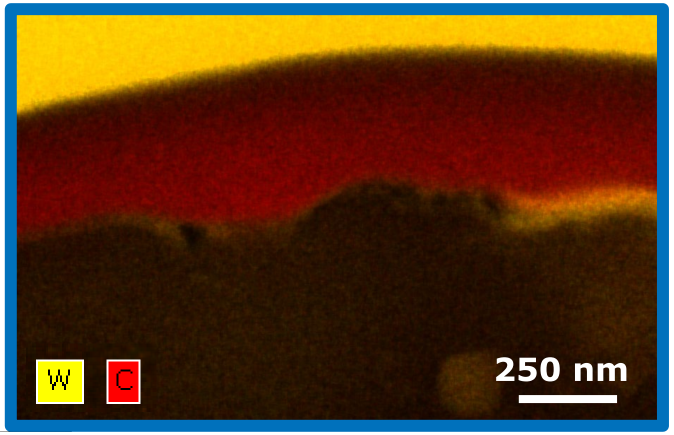


# Comparison of the same sample  STEM - SEM

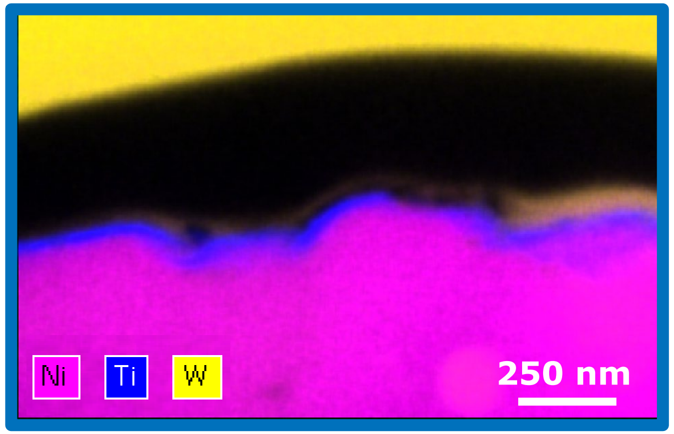
**STEM 200kV**
**60 mm² EDS detector**




**SEM 20kV**
**60 mm² EDS detector**



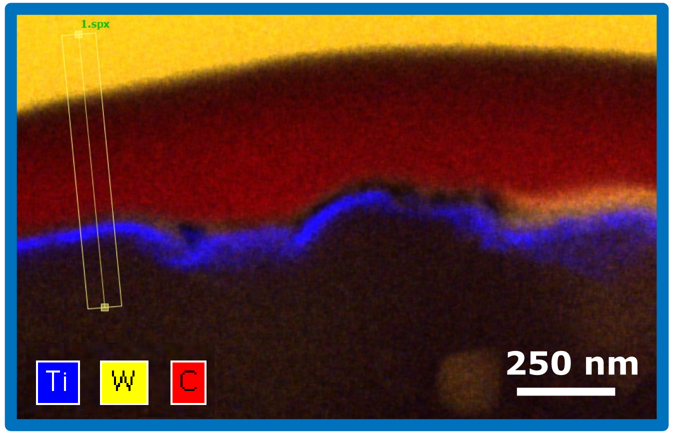

**SEM 20kV**
**FlatQuad detector**

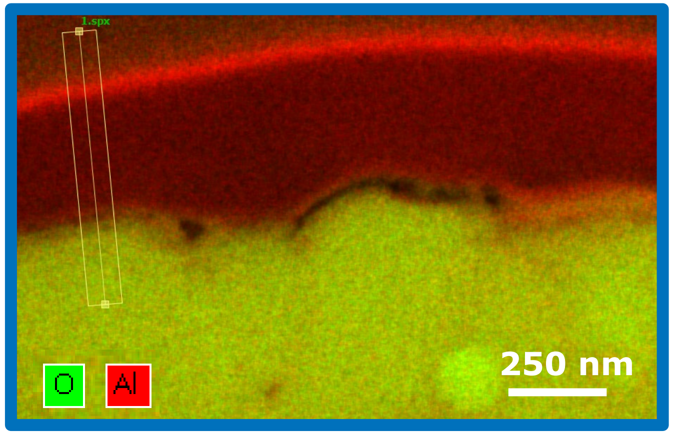



Sample and data courtesy: Michael Malaki, Shamail Ahmed, Materials Sciences Center, Philipps University Marburg

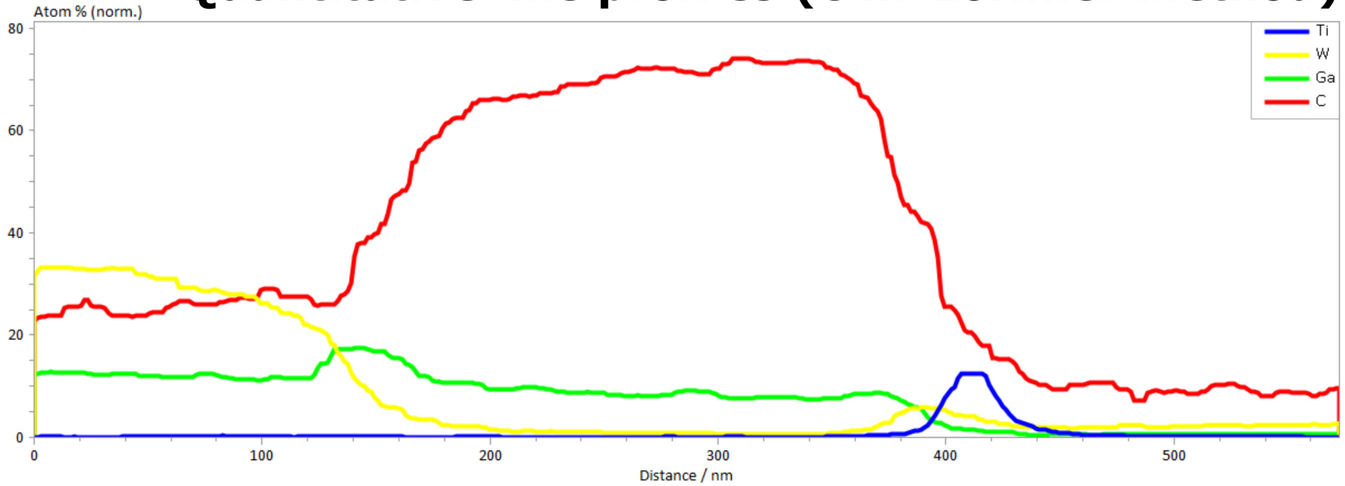
# What additional information EDS reveals

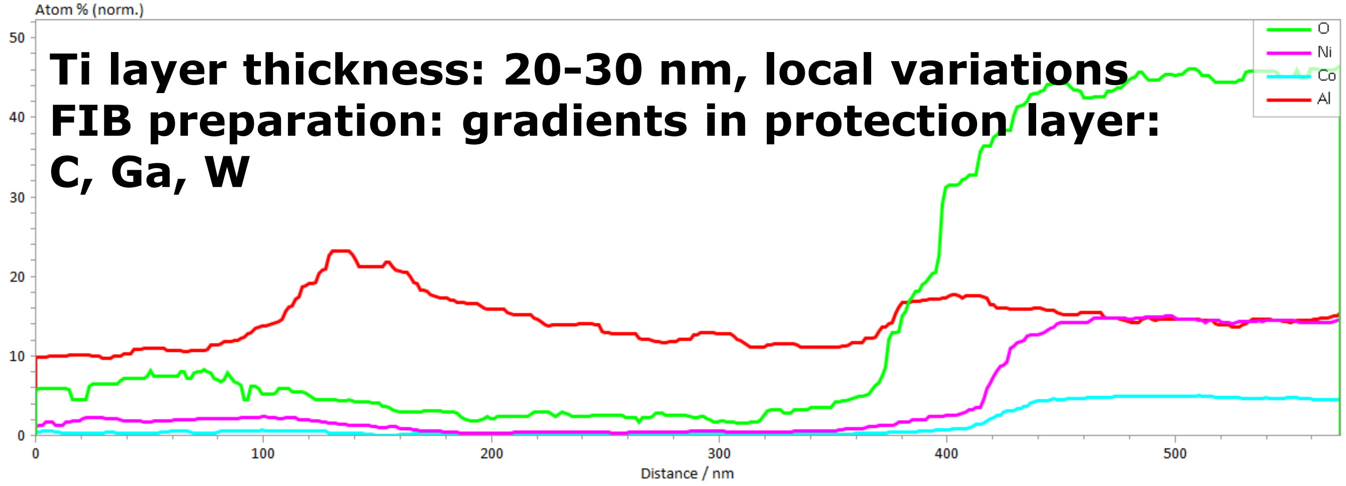
**SEM 20kV**
**60 mm² EDS detector**




## Quantitative line profiles (Cliff-Lorimer method)

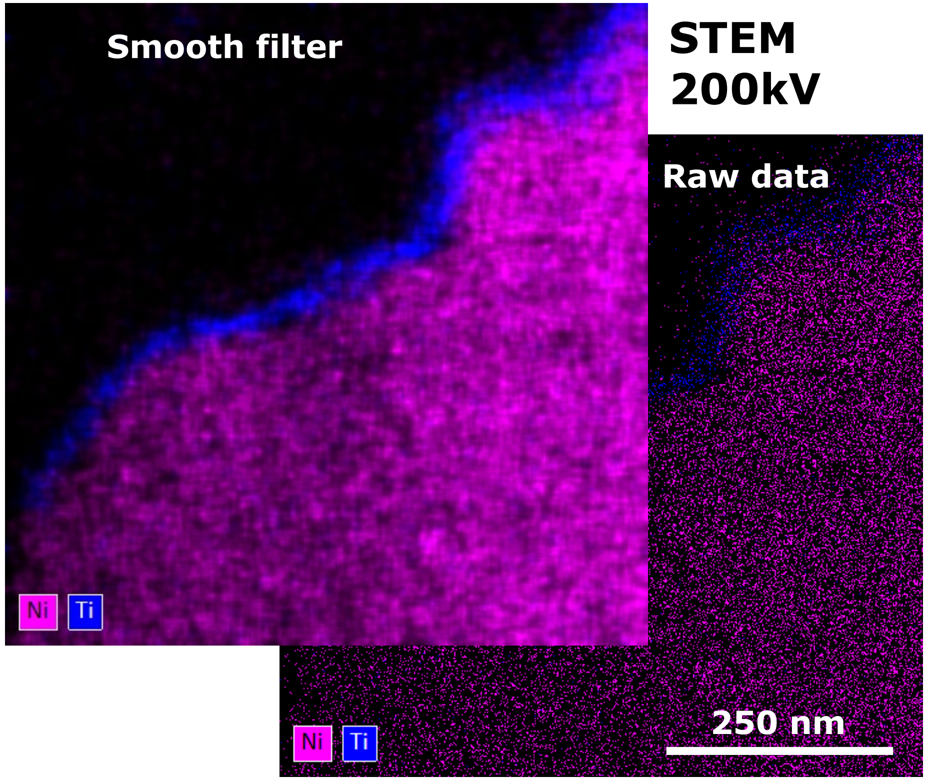



**Ti layer thickness: 20-30 nm, local variations**
**FIB preparation: gradients in protection layer: C, Ga, W**

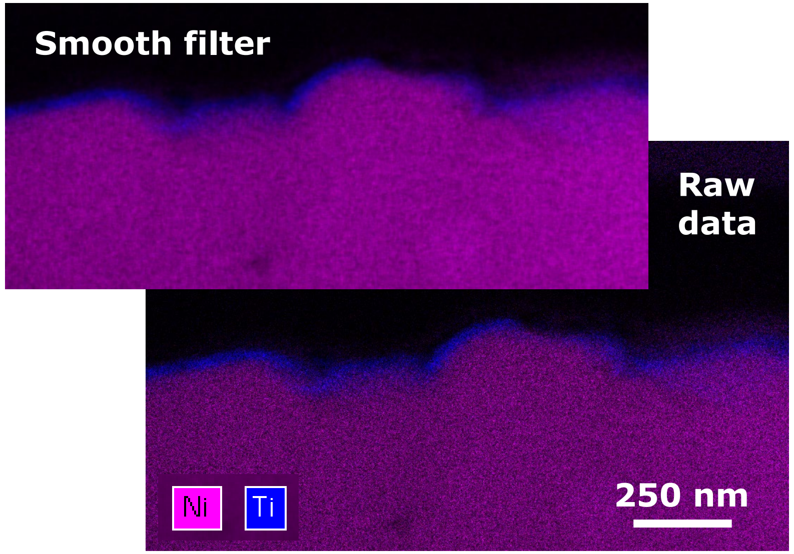
# STEM-EDS vs. SEM-EDS vs. SEM-FlatQuad EDS

**STEM 200kV**



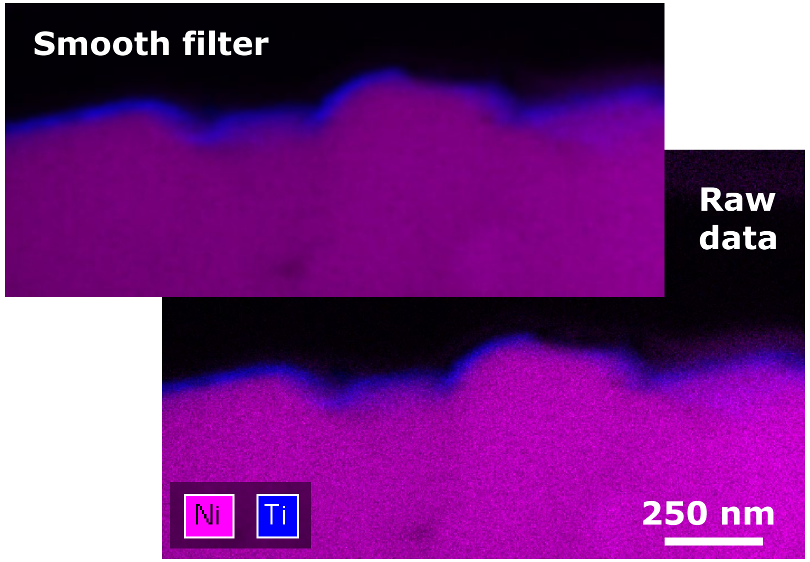

Higher spatial resolution
Lower beam currents
-> less signal (filtering needed) or longer measurements

**SEM 20kV conventional EDS**




Lower spatial resolution due to lower kV
Lower solid angle due to larger sample-detector distance
Higher beam currents -> more signal or shorter measurements

**SEM 20kV FlatQUAD EDS**




Maps with very high statistics
EDS spatial resolution not affected due to longer WD

Sample and data courtesy: Michael Malaki, Shamail Ahmed, Materials Sciences Center, Philipps University Marburg

Innovation with Integrity