

Application of FIB/SEM nanotomography to the study of electrical properties in lithium-ion batteries

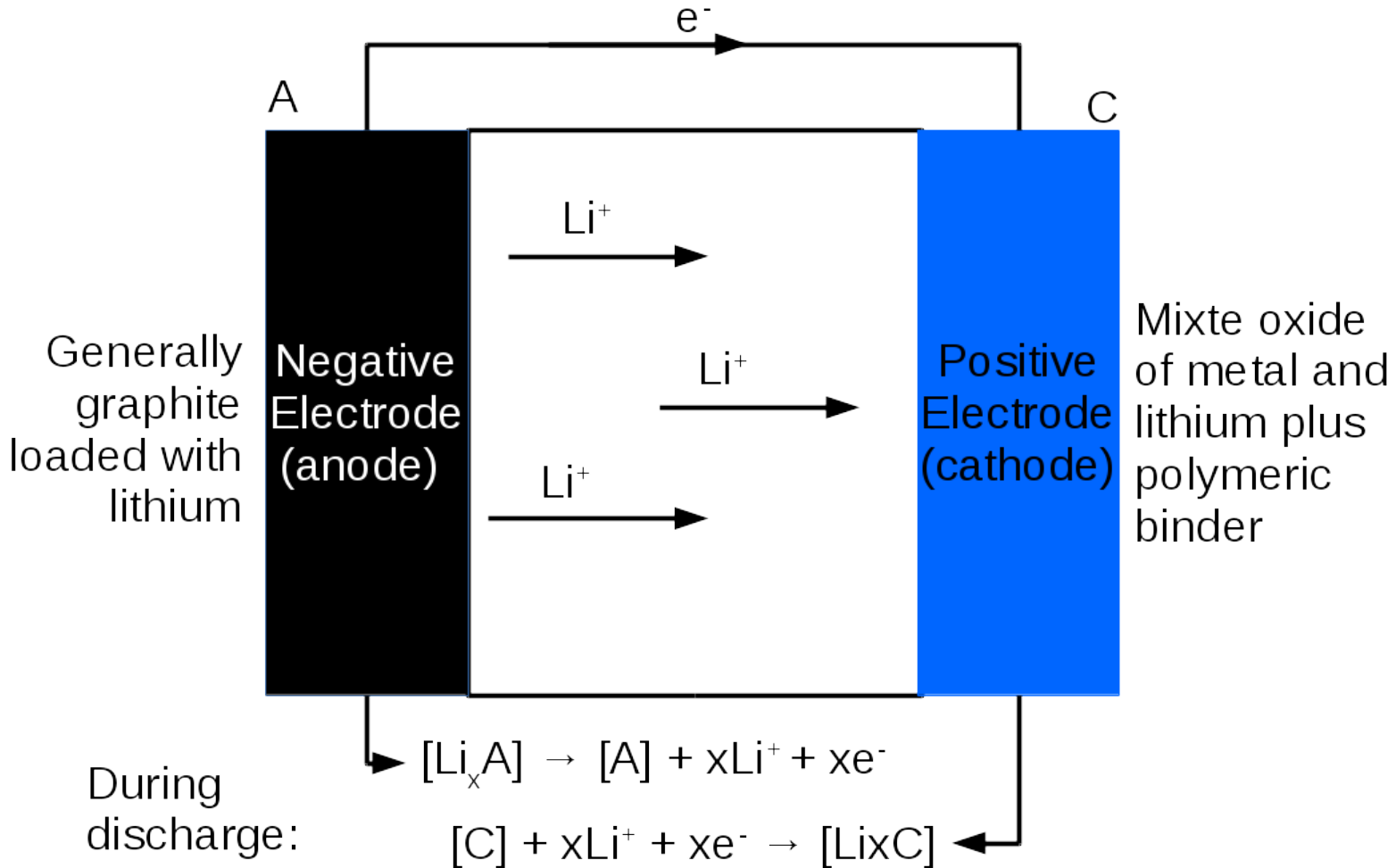
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GNMEBA - 06/06/2018

Introduction

- **Li-ion batteries**, an every day life technology:
 - Smartphones, laptops...
 - And **electric cars** (EV, HEV, plug-in HEV...)
- Advantages:
 - **High power density**
 - **High capacity**
- However the **autonomy** for vehicle applications still **need to be extended**



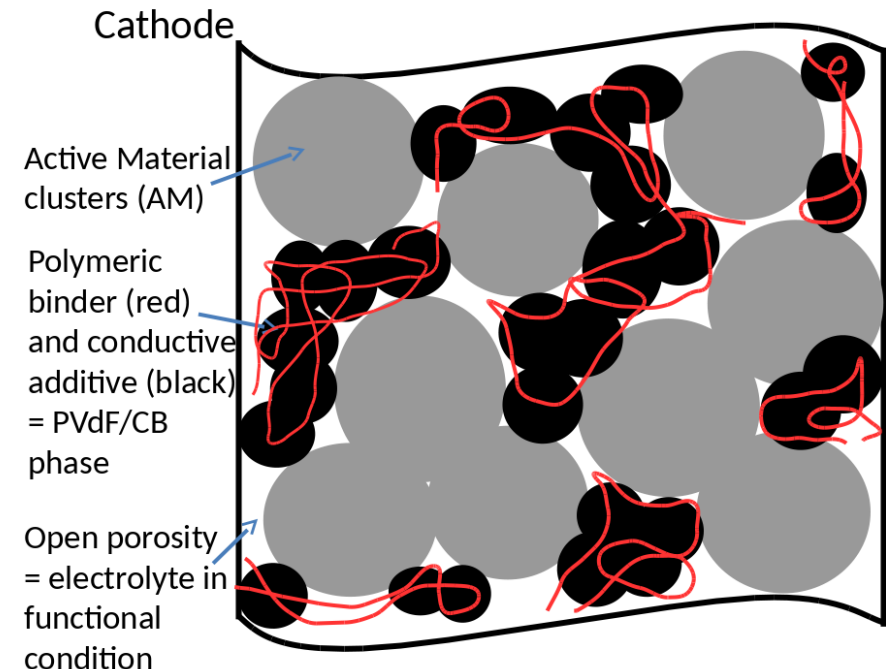
Generalities – Li-ion batteries



General concept of a Li-ion battery during discharge
Inverse reaction during charge

Generalities - Cathode microstructure

- The cathode:
 - Positive electrode
 - Complex material (3 phases)
 - **Complex microstructure**
 - **Huge impact on effective properties**
 - Need for a better understanding of this phenomenon



Schematic representation of a cathode microstructure

Overview

- Introduction
- Generalities (Lithium-ion batteries and cathodes)
- **Sample preparation**
- **Volume acquisition**
- Results obtained
- Segmentation process
- Parameters impacting volume quality
- Examples of simulations on segmented volumes

Advanced sample preparation for FIB/SEM tomography

- Ion polishing **before FIB/SEM**:
 - **Ilion II Gatan** ionic polisher
 - Titanium protection for **cross section**

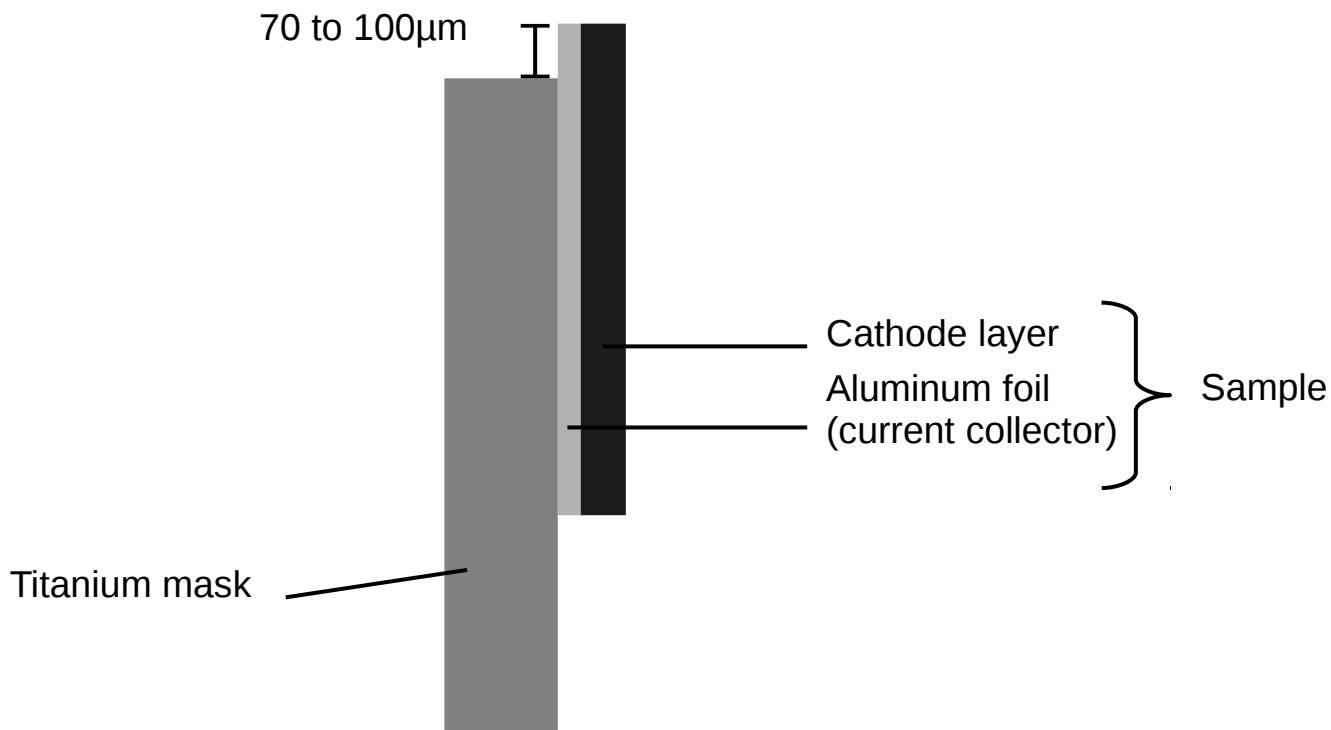
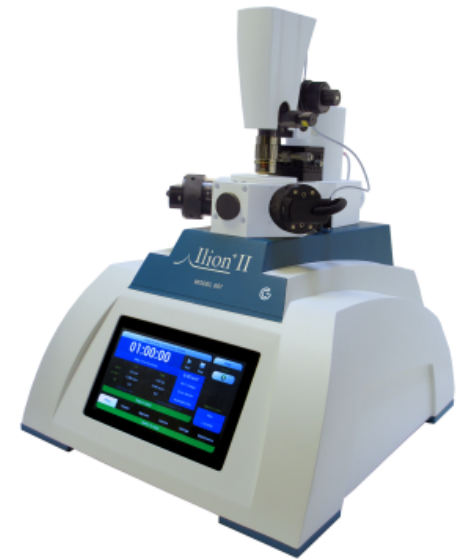


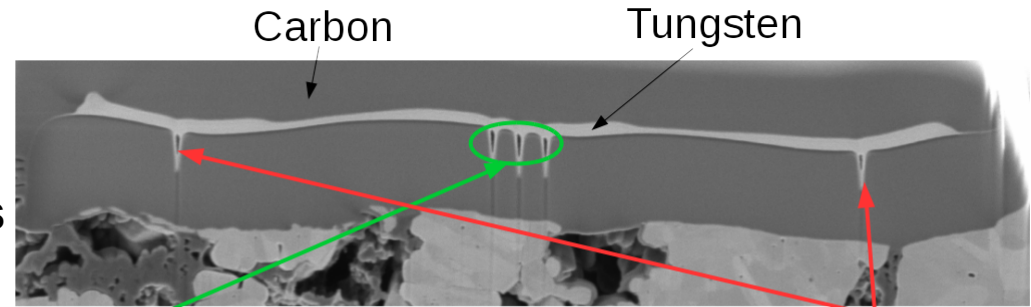
Illustration of sample preparation for Cross-section polishing



Ilion II system Gatan

Advanced sample preparation for FIB/SEM tomography

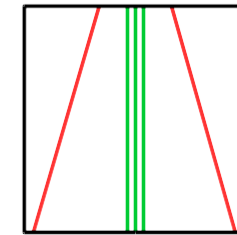
- **Advanced preparation inside FIB/SEM:**
 - Volume protection and **3D tracking marks**
 - Carbon and tungsten deposits
 - **Preparative milling**
 - Avoid shadowing effect and redeposition



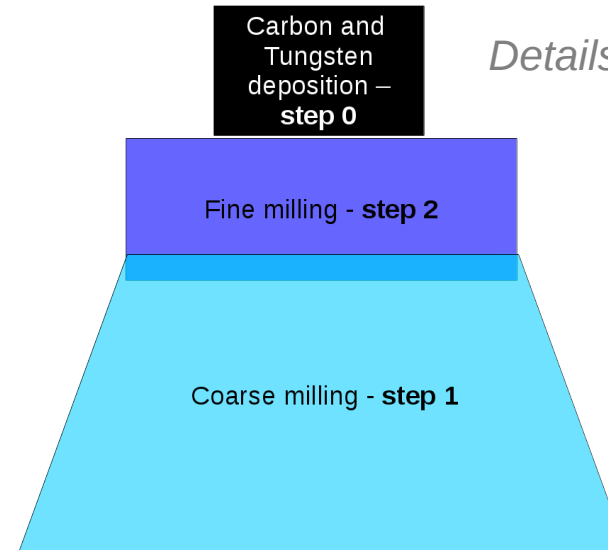
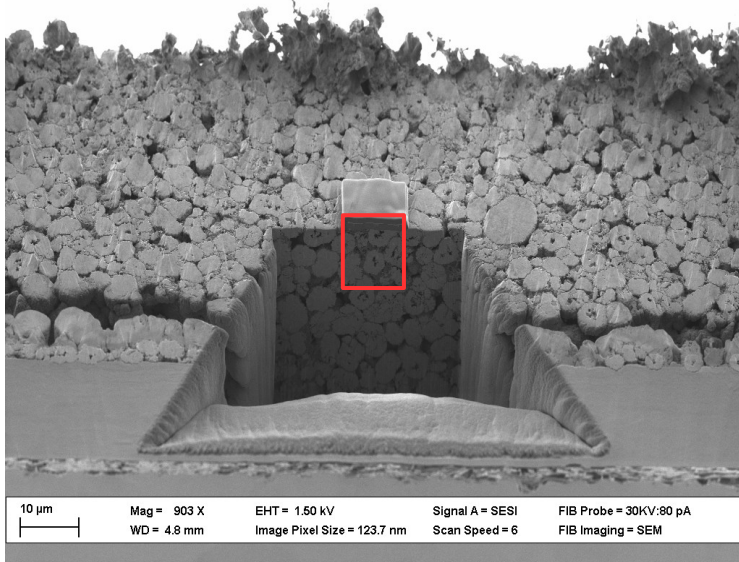
Marks for autofocus and autoastigmatism

Transversal view of the deposits

Control marks for switching and milling progression



Schematic top view of the mark depositions



Details of carbon and tungsten deposit utility

Illustration of the preparatory phase inside FIB/SEM prior to volume acquisition

Volume acquisition

- Zeiss Nvision 40 FIB/SEM
- ATLAS 3D (Fibics) software:
 - **Automation** of the acquisition
 - 3D tracking marks used (drift correction, auto focus and astigmatism correction)
 - FIB setup (milling time, Z resolution...)
 - SEM setup (exposition, x and y resolution...)
 - SE and BSE image acquisition
 - Simultaneous milling and image acquisition



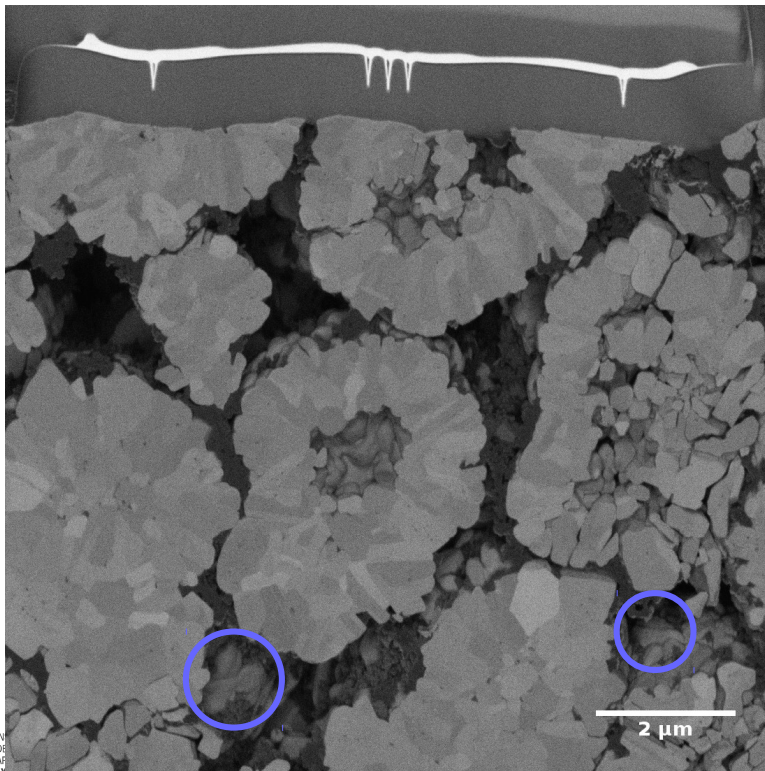
Zeiss Nvision 40 System

Overview

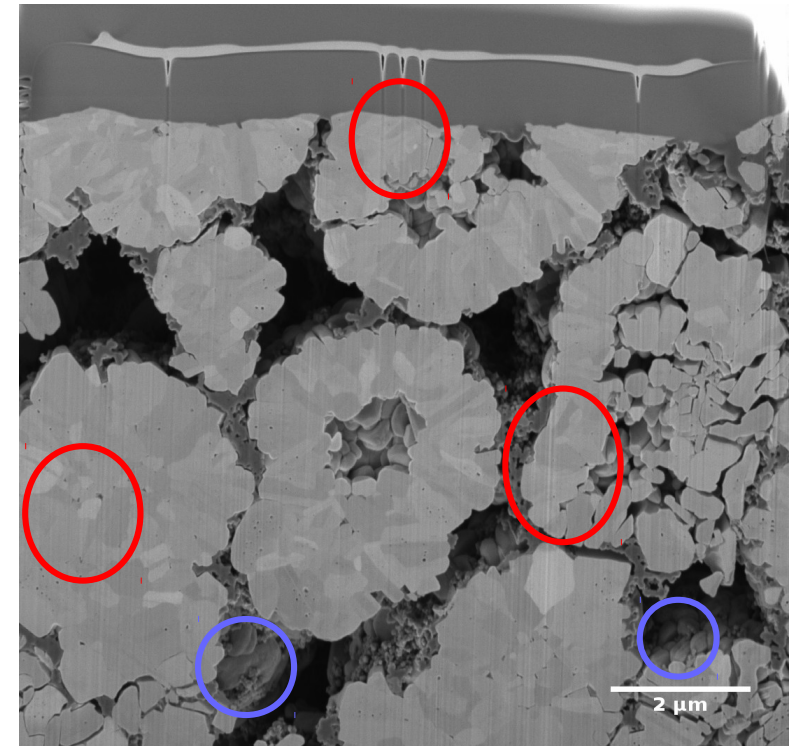
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Result of FIB/SEM acquisition

- 2 stacks of images: SE and BSE
 - Marks included (picture realignment necessary)
 - 10nm pixel resolution – 2 days acquisition
 - 2 types of artifacts:
 - Curtaining effect (Ion beam)
 - “Shine through” effect (SEM imaging)



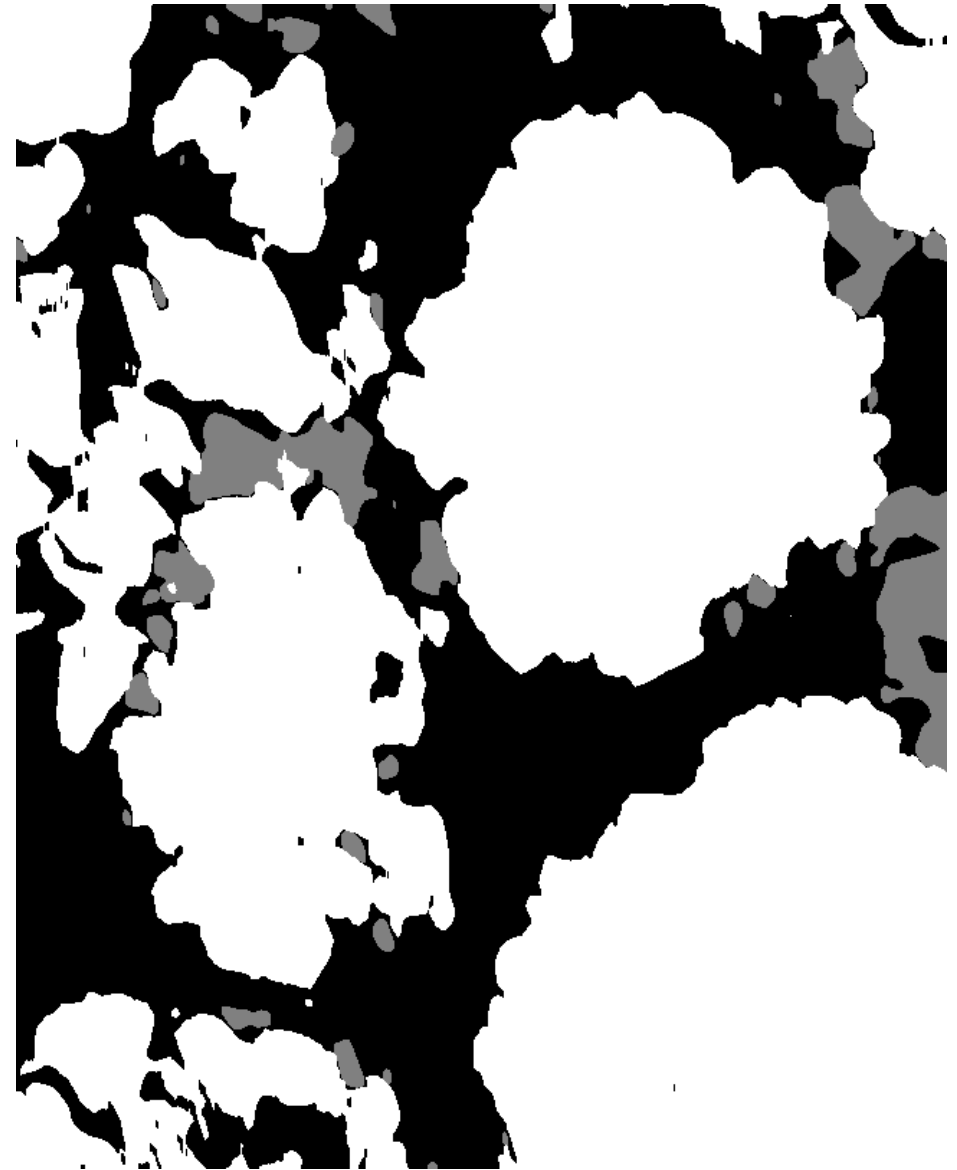
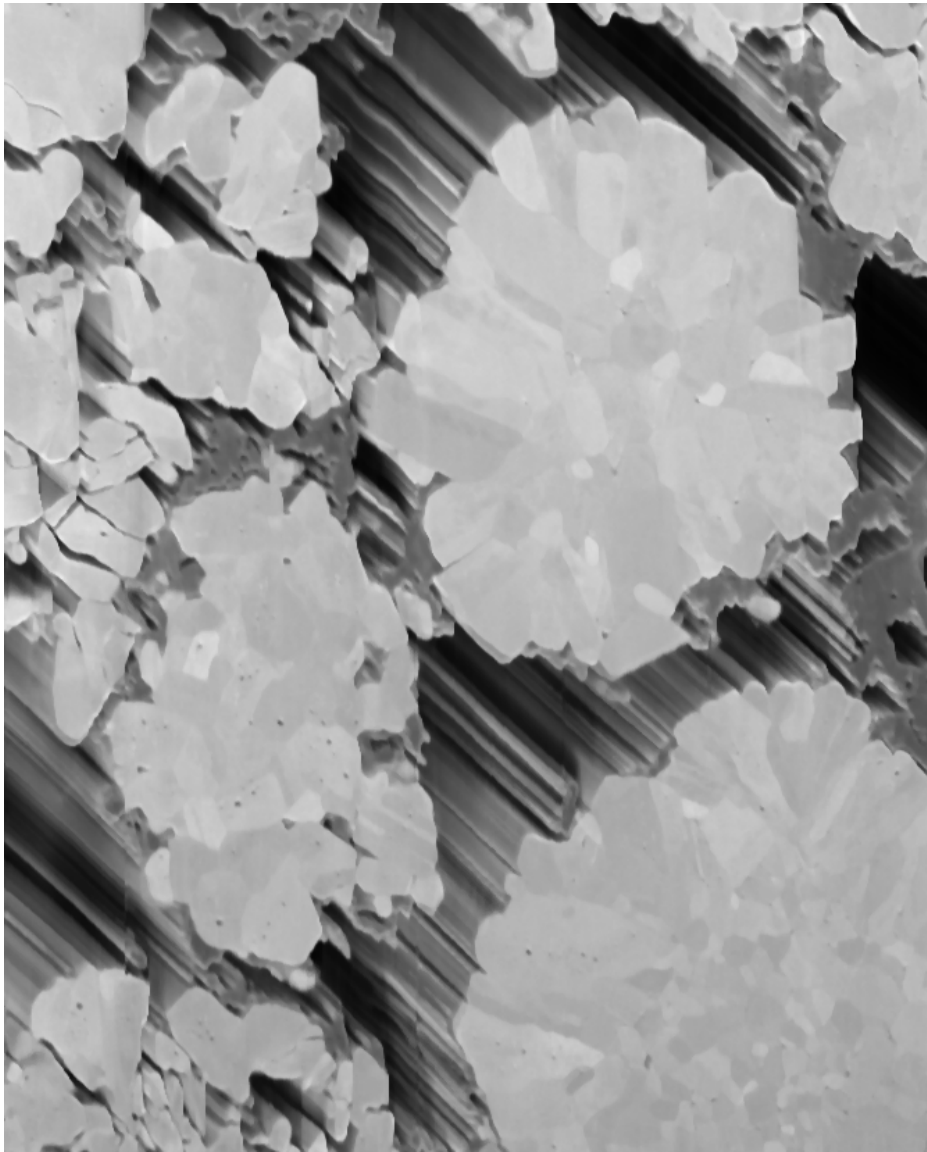
BSE image



SE image

Shine through effect
Curtaining effect

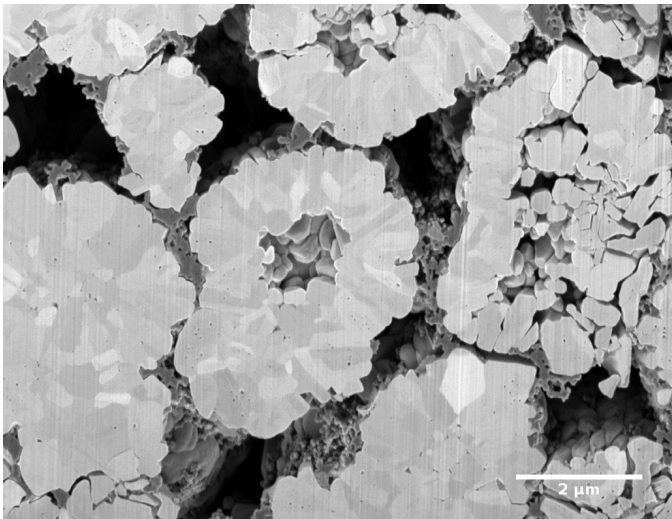
View of the “shine through” artifacts on transverse view



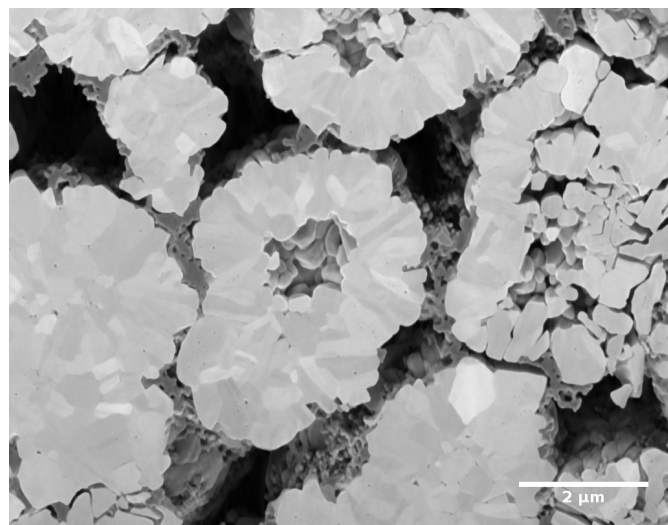
Volume segmentation - Summary

- Fiji software:
 - Stack realignment: MultiStackReg
 - Curtaining effect correction: VSNR2 plugin
 - Segmentation with “shine through” effect correction (Fiji macro, A. Etienne)

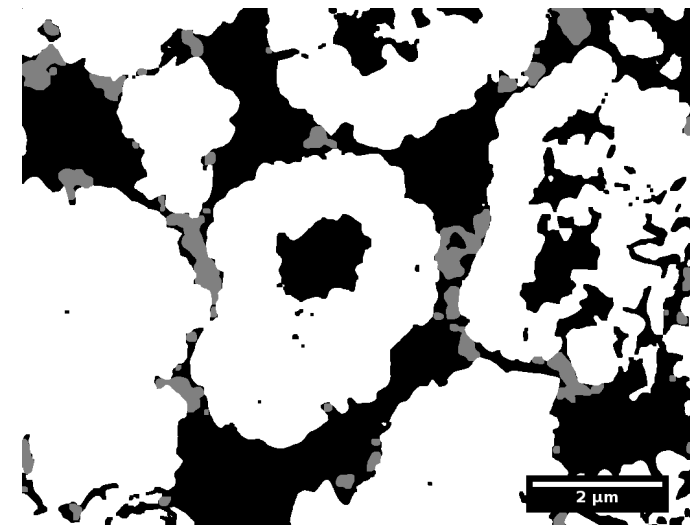
Stack processing



*Raw image after
realignment and crop*



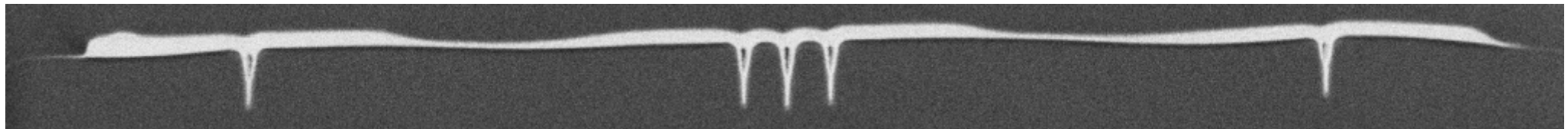
*Image after curtaining
effect removal*



*Image after segmentation
with the Fiji macro*

Volume segmentation - Registration

- **Stack realignment:**
 - Fiji Plugin **MultiStackReg**
 - Using only a **translation matrix**
 - **Calculated on a cropped volume** concentrating on the registration marks
 - BSE volume seems to give better results

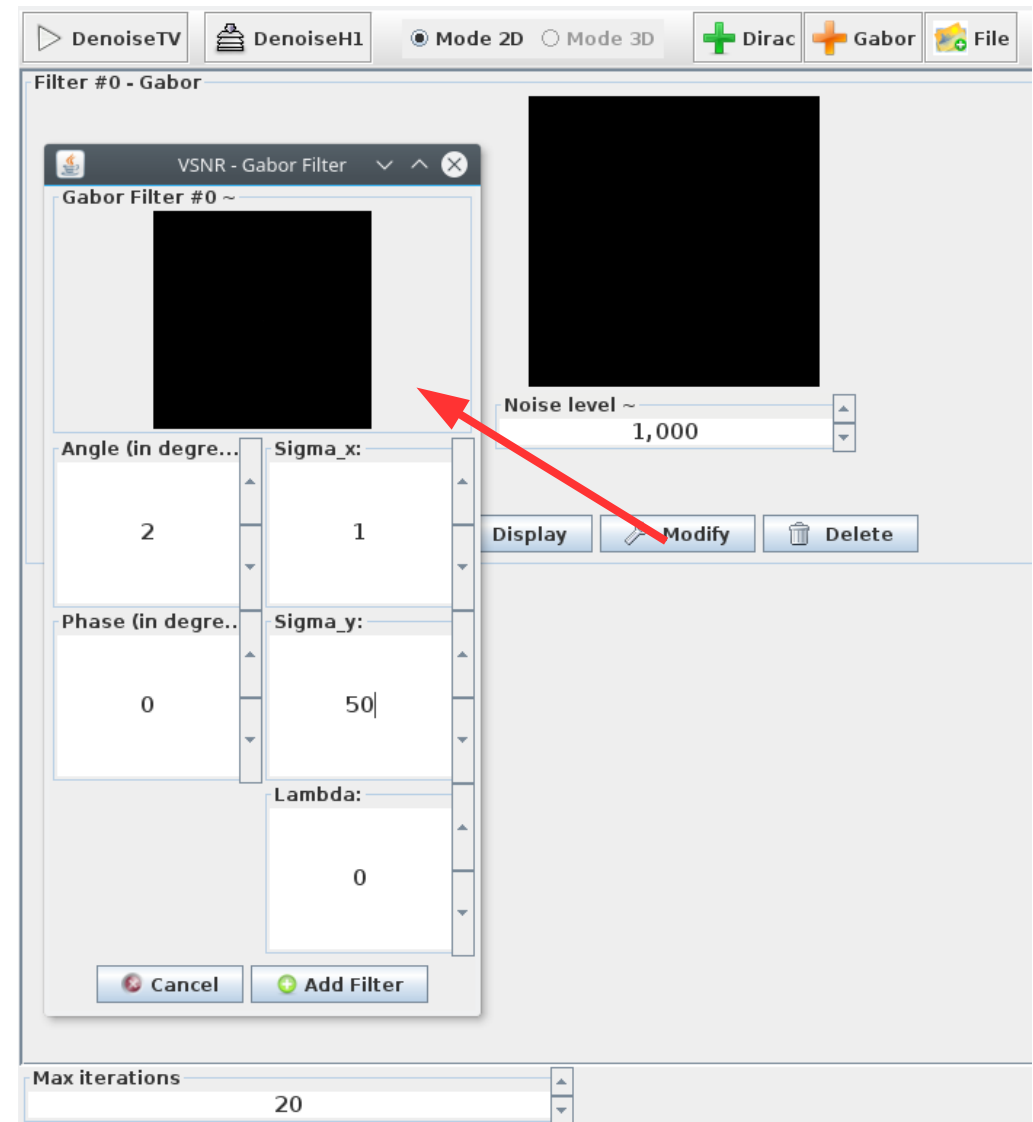


Extract from cropped stack used to compute the translation matrix

- Translation matrix is **applied to both BSE and SESI volumes**
- Final crop

Volume segmentation – Image improvement

- Removing the curtaining effect:
 - Fiji Plugin **VSNR_V2**
 - **Gabor filter:**
 - 2D mode
 - Curtain angle
 - Curtain width
 - Curtain length
 - Quite a long process over an entire stack

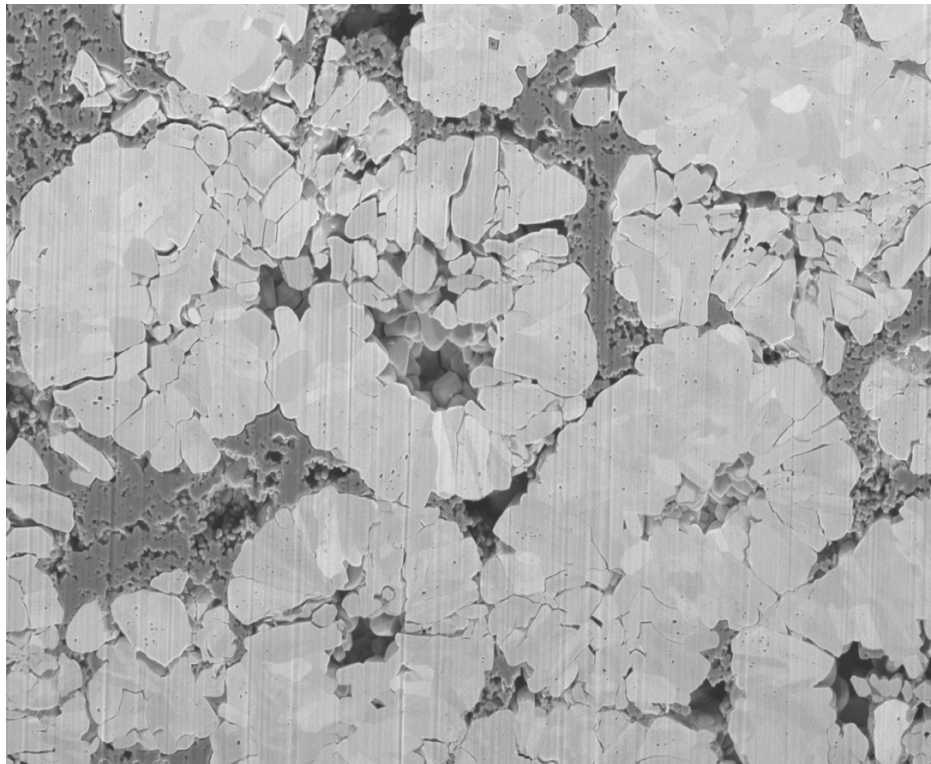


Extract from VSNR_V2 for Gabor filter configuration

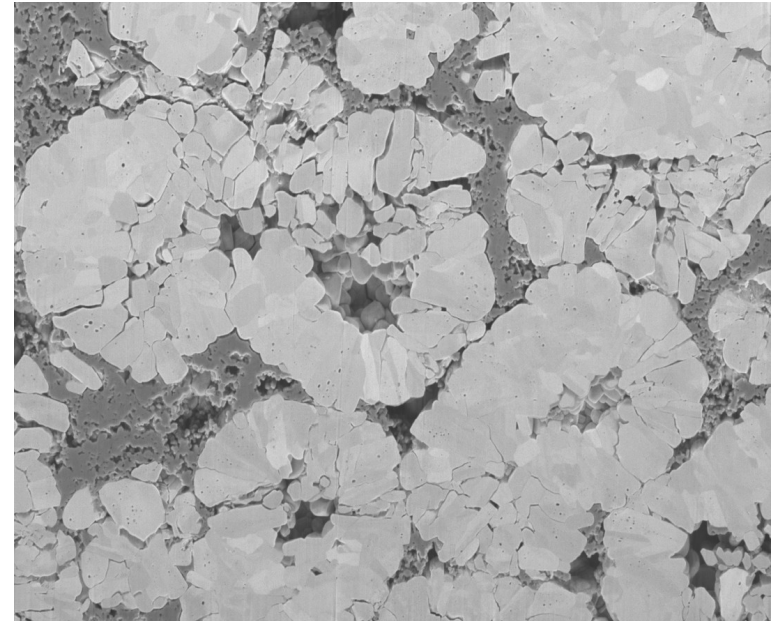
Volume segmentation – Image improvement

- Example of the Gabor filter action:

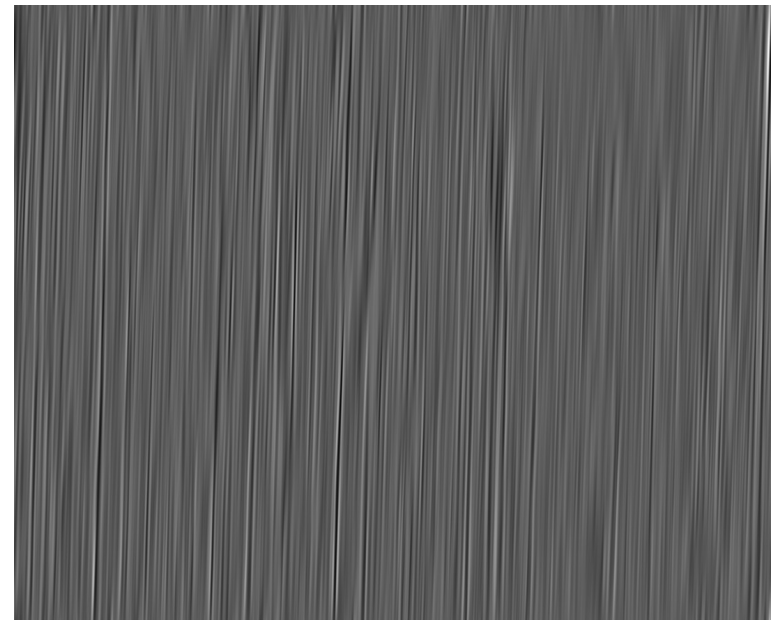
Raw data



Result

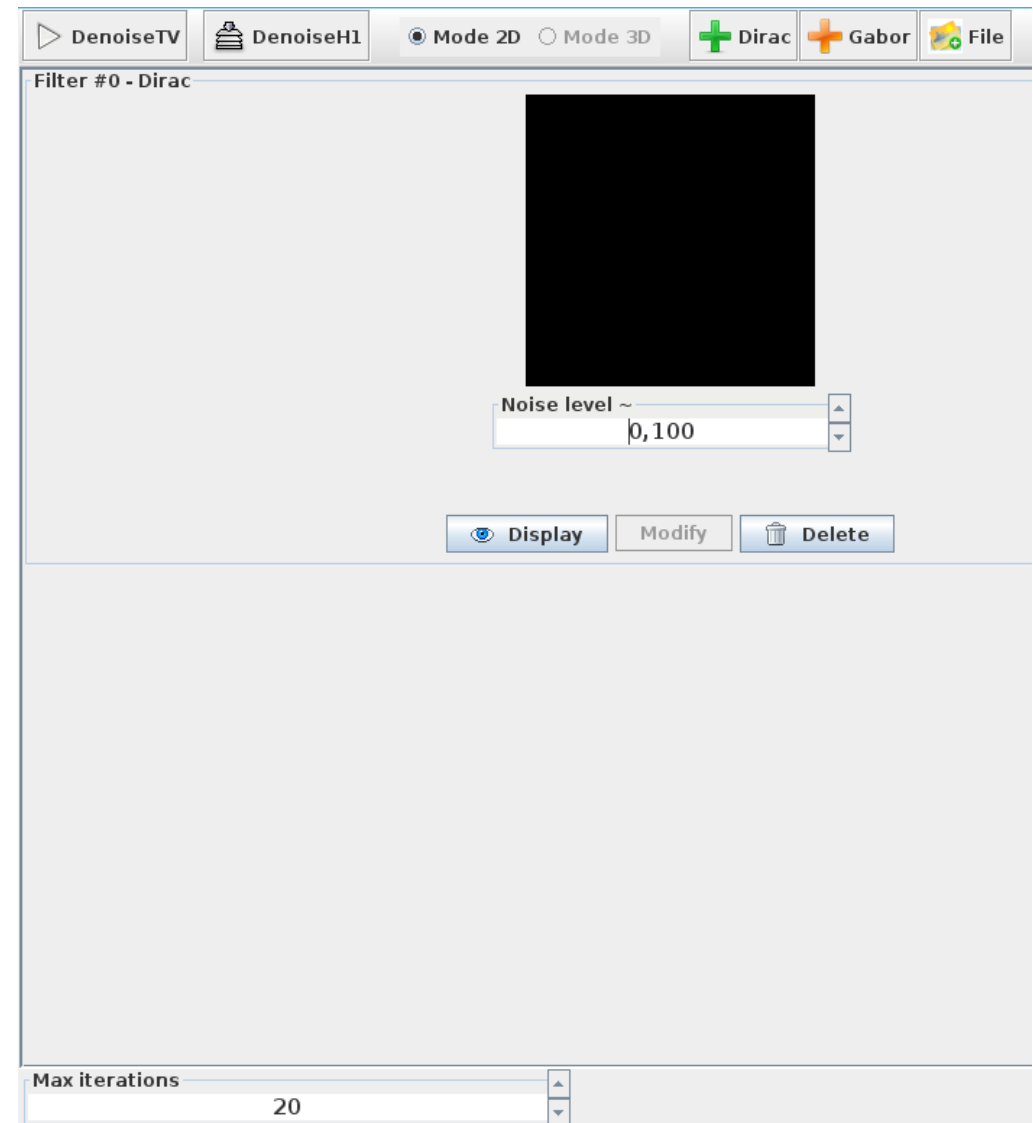


Noise



Volume segmentation – Image improvement

- **Enhancing BSE images:**
 - Noise reduction
 - Fiji Plugin **VSNR_V2**
 - **Dirac filter:**
 - 2D mode
 - Specify noise level
 - Quite a long process over an entire stack

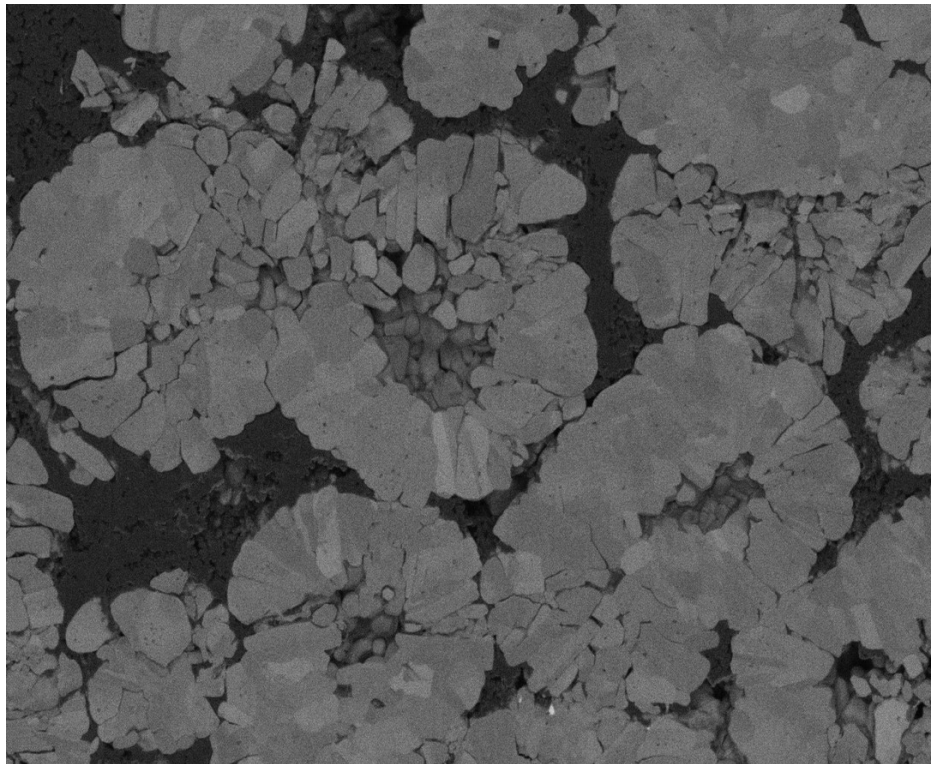


Extract from VSNR_V2 for Dirac filter configuration

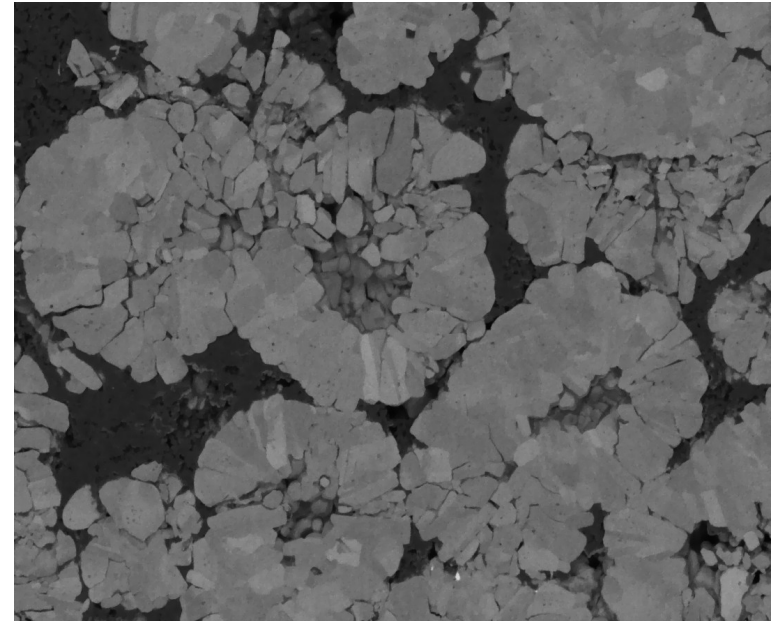
Volume segmentation – Image improvement

- Example of the Dirac filter action:

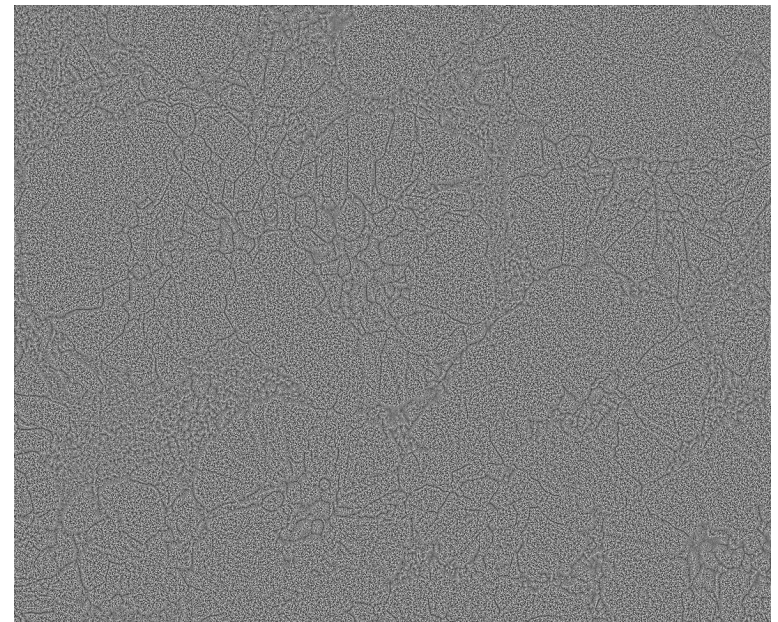
Raw data



Result



Noise



Segmentation process

- Use of a **Fiji macro** originally made by A. Etienne and based on an algorithm described in [1]
 - **Separate the material from the porosity**
- **Separation of the AM and binder mixture phases** using the macro result and simple thresholds from SESI and BSE volumes
- **Optimization** with simple morphological operations such as erosion and dilatation
- Theoretically works fine but imperfections in the volumes make a **manual cleaning** still necessary

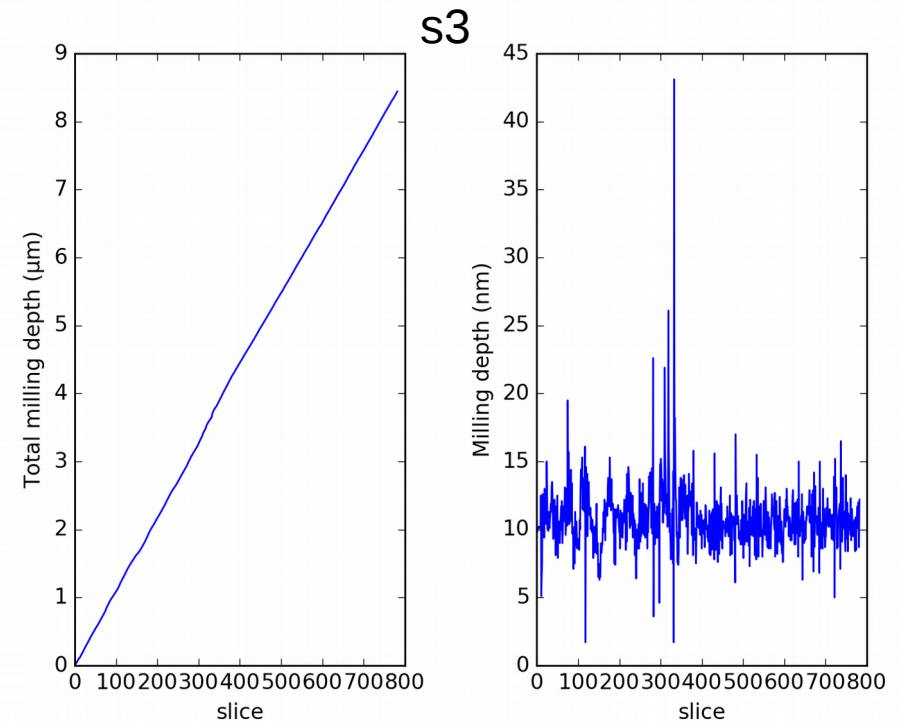
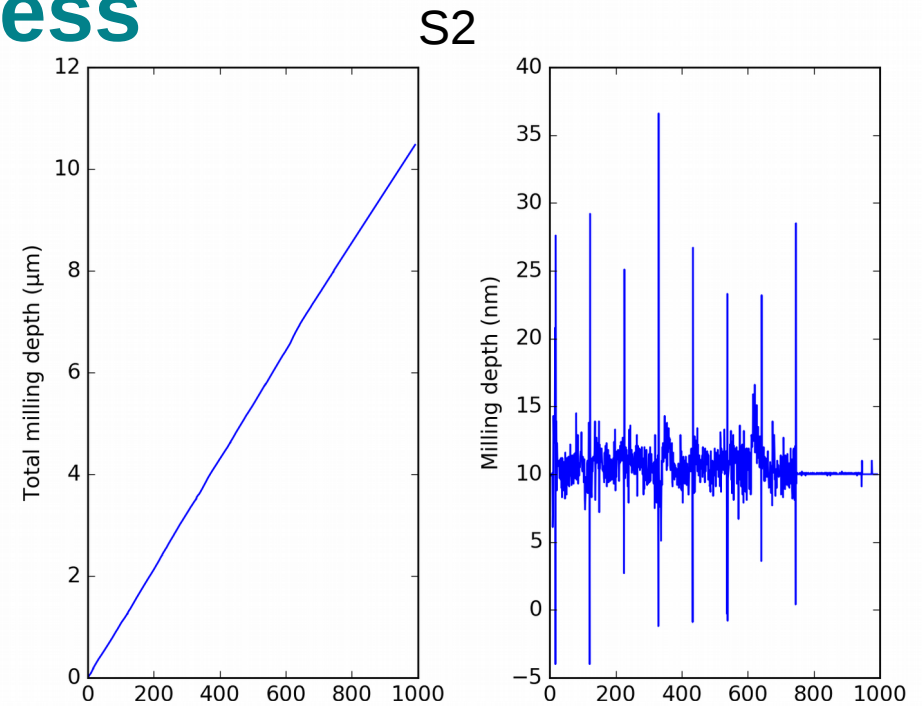
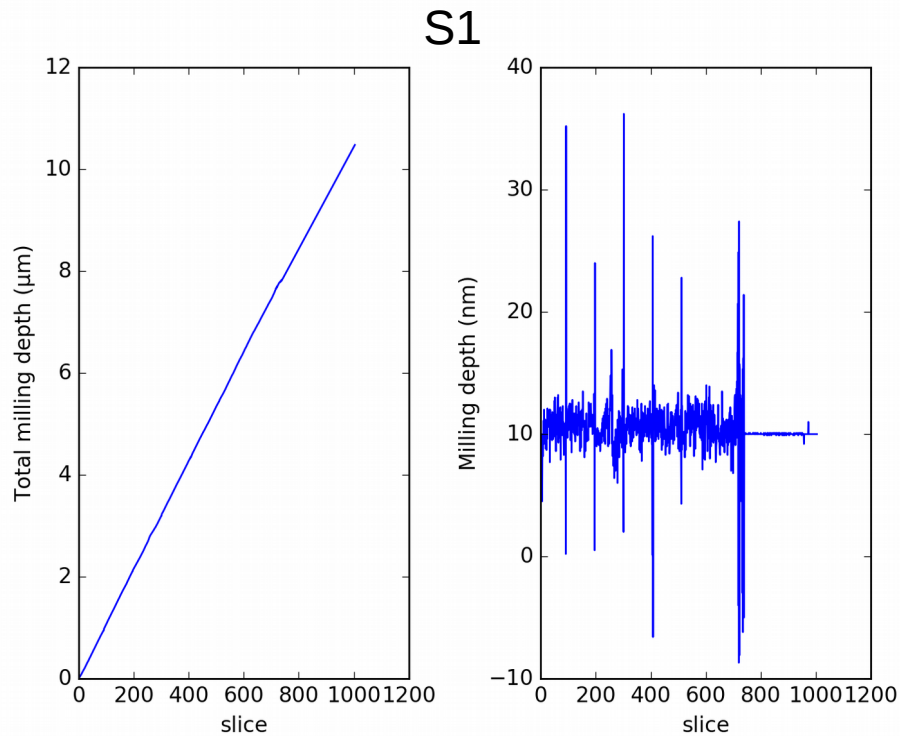
[1] T. Prill *et al*, Morphological segmentation of FIB/SEM data highly porous media, J. of Microscopy, 2013, 250, pp.77 – 87

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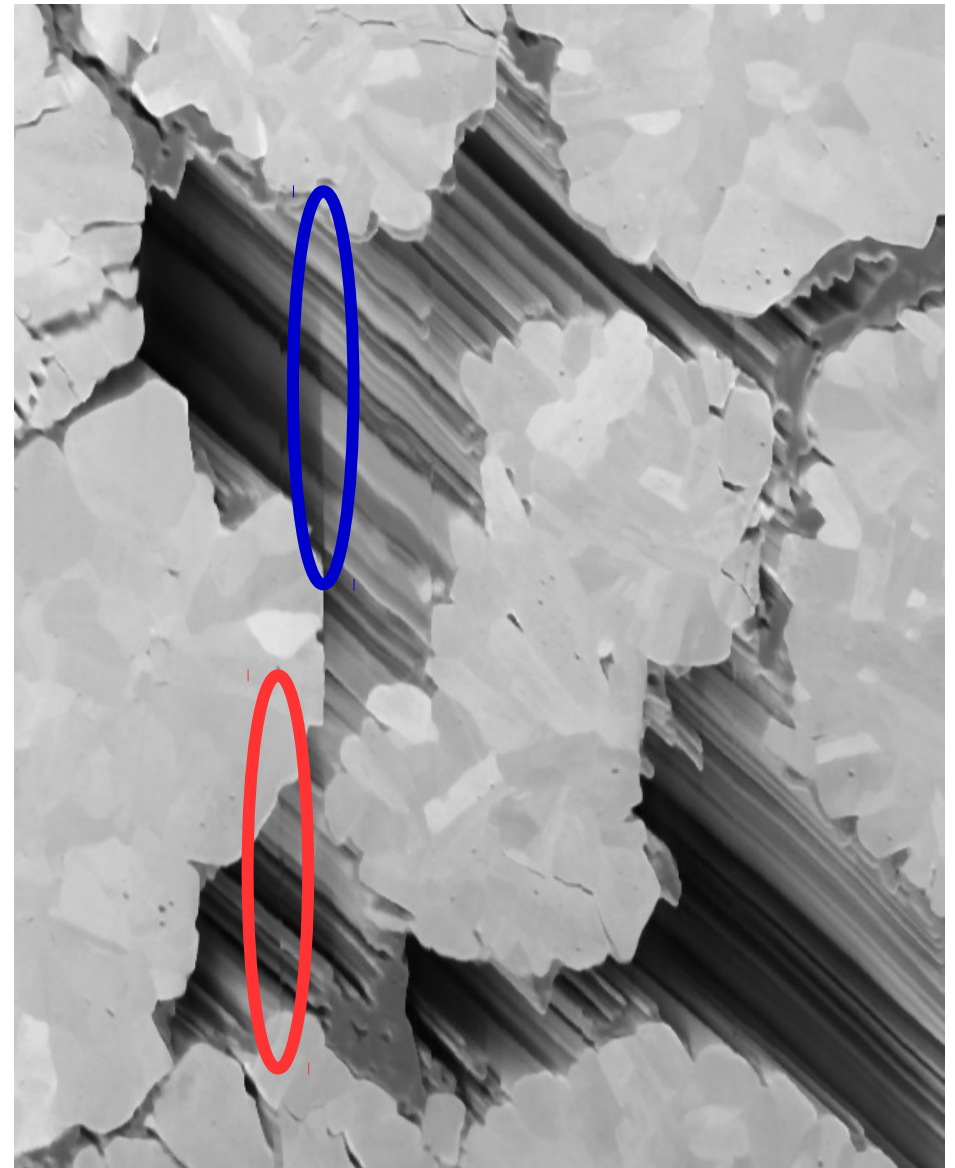
Variation of slice thickness

- **Set to be 10nm** but **variations** that seems important for some instabilities



Other artifacts

- **Other artifacts** in images:
 - Interfaces jagged (realignment or SEM drifting)
 - **Instability due to autofocus/stig (always or each)**
 - **Unknown, probably a brutal particle ejection during milling**

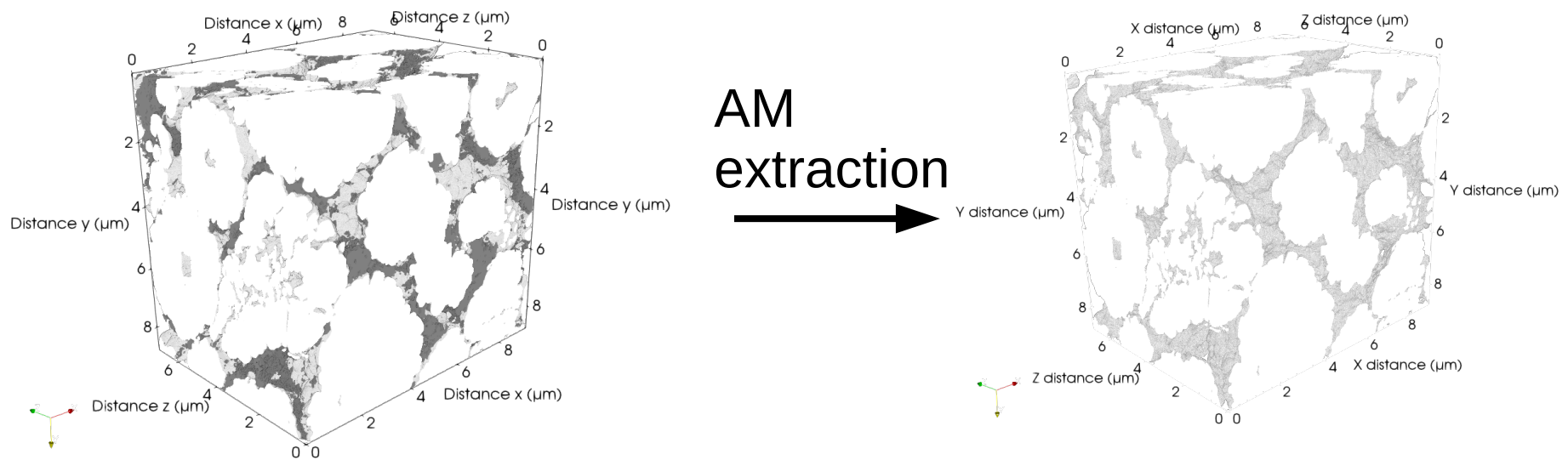


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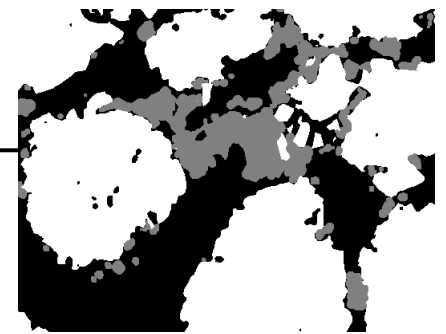
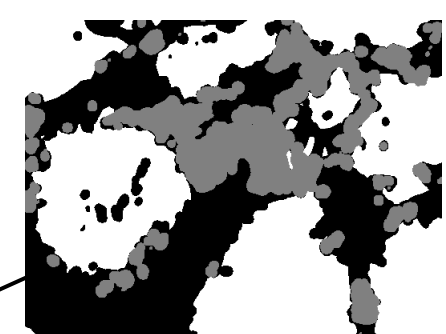
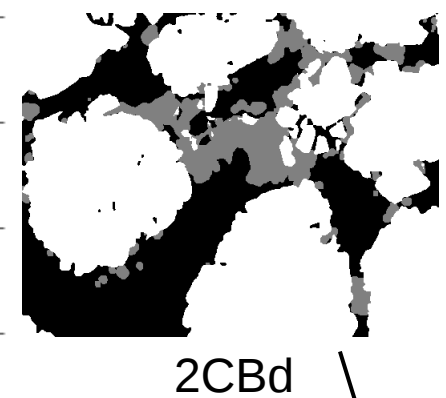
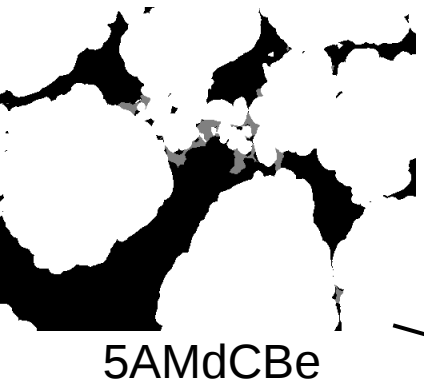
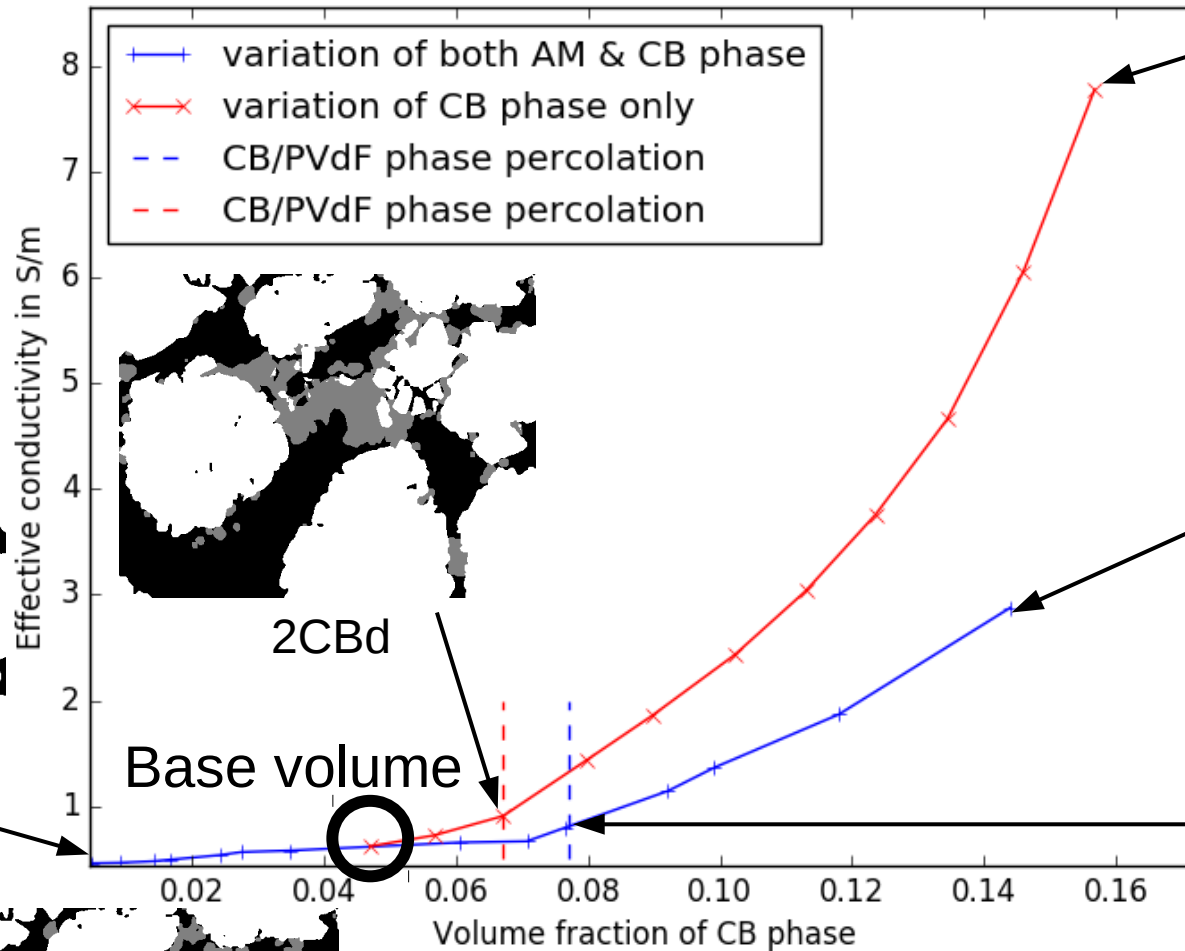
AM conductivity

- **Extracting AM phase** from segmented volumes allows to have an **AM packing**
 - With **experimental measurements of the effective conductivity**, it is possible to **back calculate the AM phase conductivity** (with the adequate volume fraction)



Impact of phase volume fractions

Evolution of the effective conductivity as a function of the CB/PVdF volume fraction - FFT



Conclusion

- **FIB/SEM nanotomography** is a complex and precise way to **image the 3D microstructure of Li-ion cathodes at a small scale**
- The **segmentation of porous 3D volume** is an important part of the process and contributes to its complexity
- Segmented images and FFT simulation method allows to perform studies on the electrical (and mechanical) behavior of the cathodes
 - Questions have to be asked, the most important one is the representativity of the volumes captured by FIB/SEM

Thank you for your attention !

Any questions ?

