HZB Helmholtz Zentrum Berlin

4D Neutron Imaging of Lithium Batteries and Fuel Cells

Joint ESS ILL User Meeting 2022 (Lund, Sweden)

5th October 2022

Dr. Ralf F. Ziesche

@ESS/ILL 2022

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BACKGROUND INFORMATION

#HZB

#TheGroup

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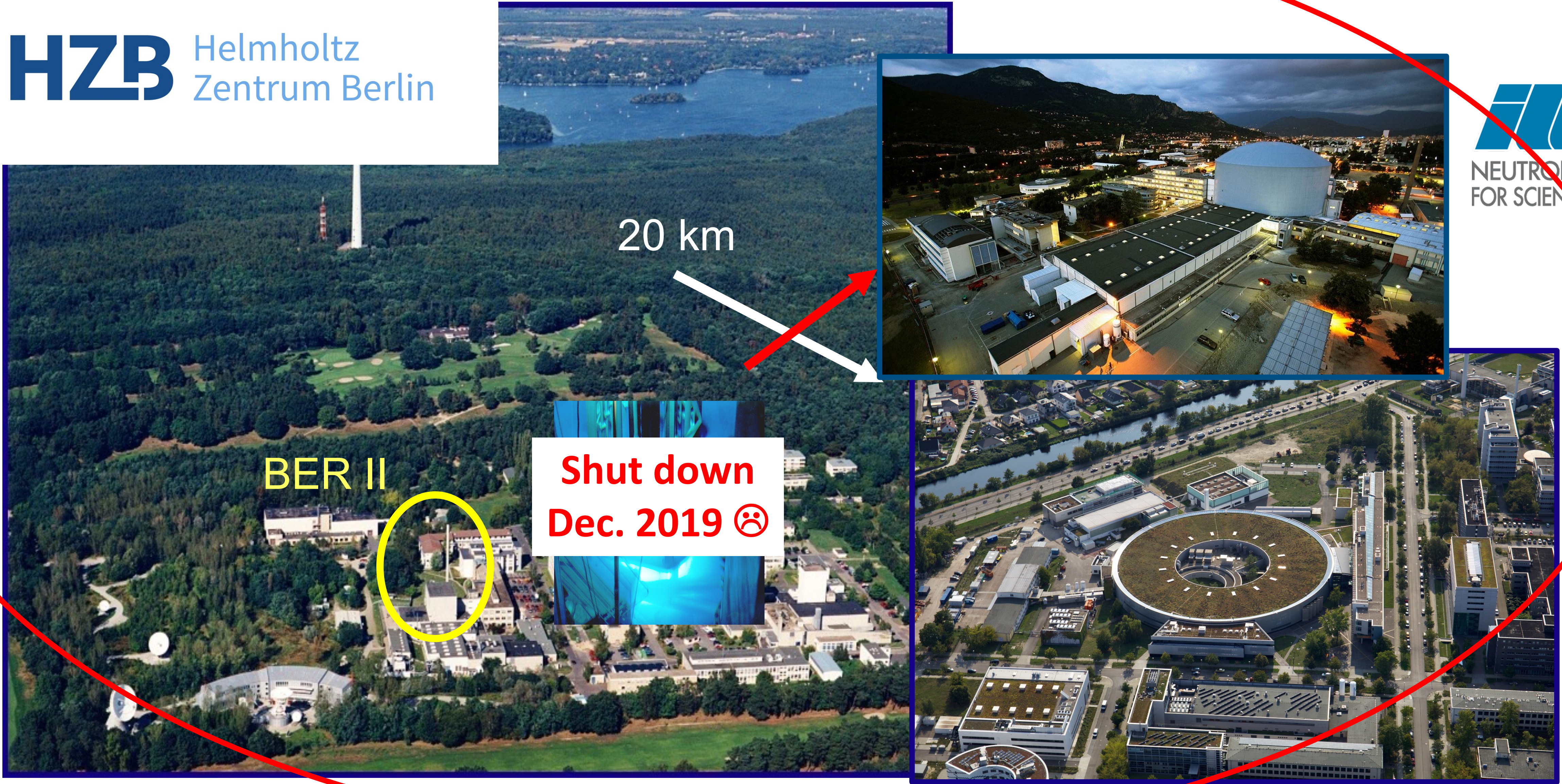


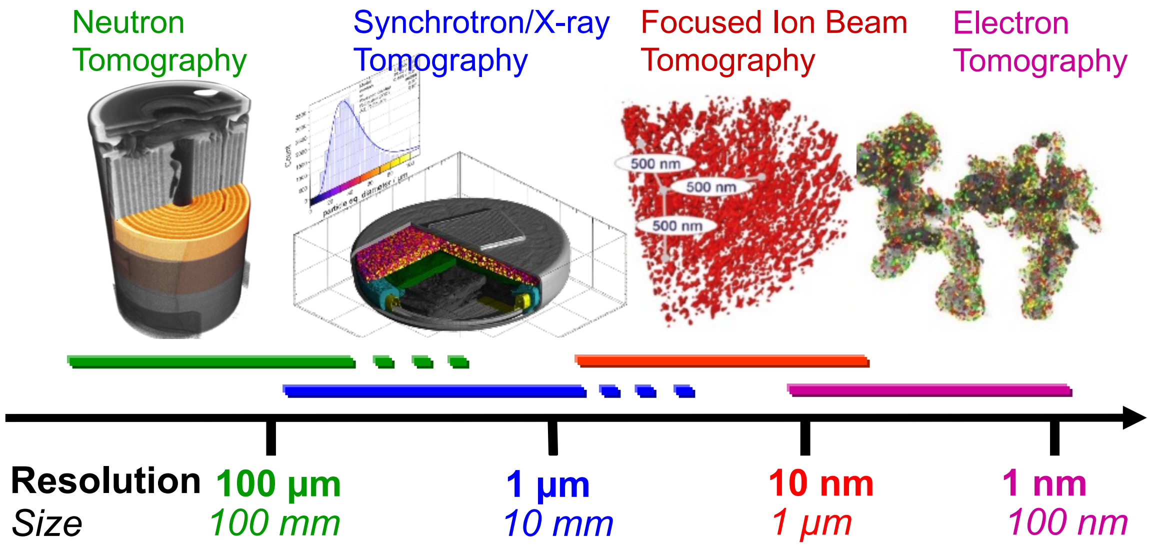
NEUTRONS FOR SCIENCE®

BESSY II

(Operando) Characterization of the 3D Structure and Morphology of Electrochemical Materials

Imaging Group, Institute of Applied Materials

- Investigation of 2D/3D structures and processes on different size scales
- 3D Structure-Properties Relationships
- In-situ/operando investigations
- Development of 3D materials



Partners:

ILL, UGA, HZB

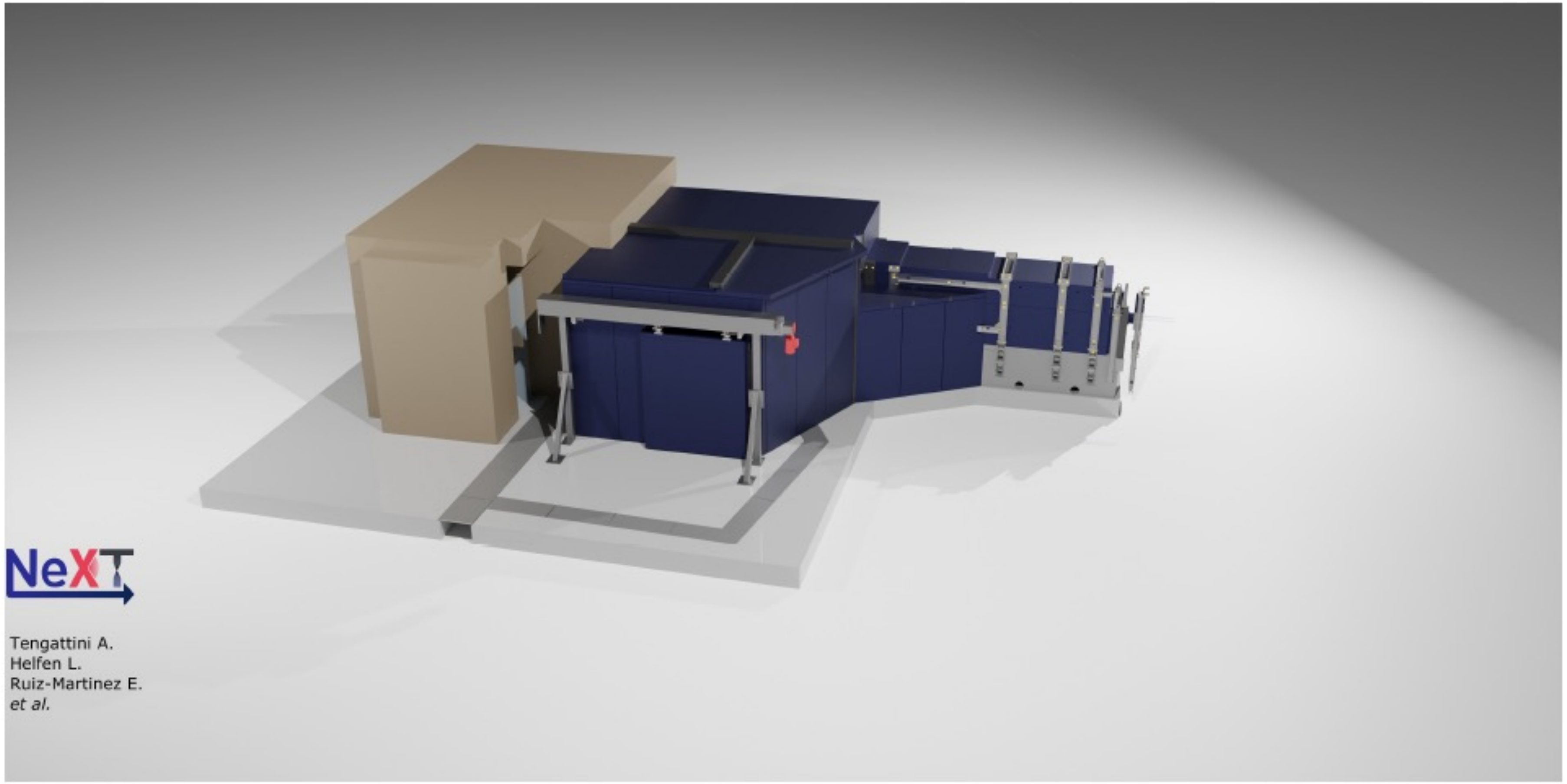
Topic:

Neutron Imaging for Materials and Energy Research.

Scope:

20 % of the beam time provided for experiments with outstanding scientific output.

Neutron Imaging Instrument NeXT @ ILL



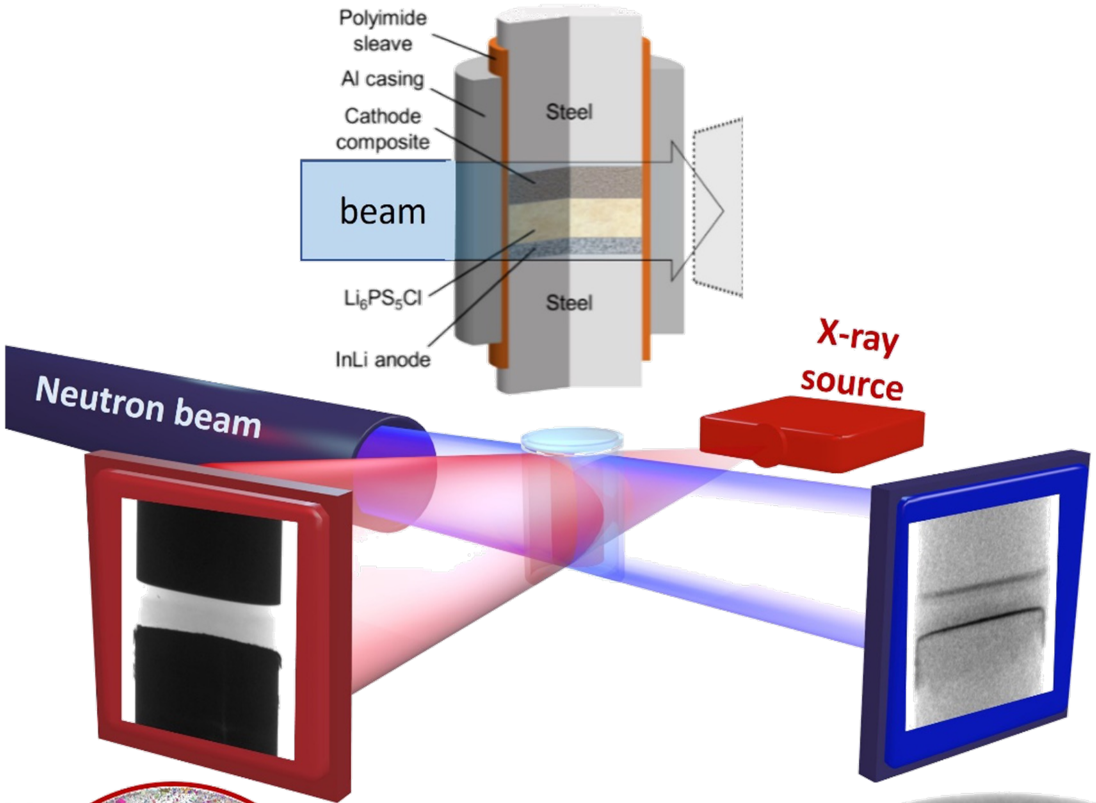
Spatial resolution:
better than 3 µm

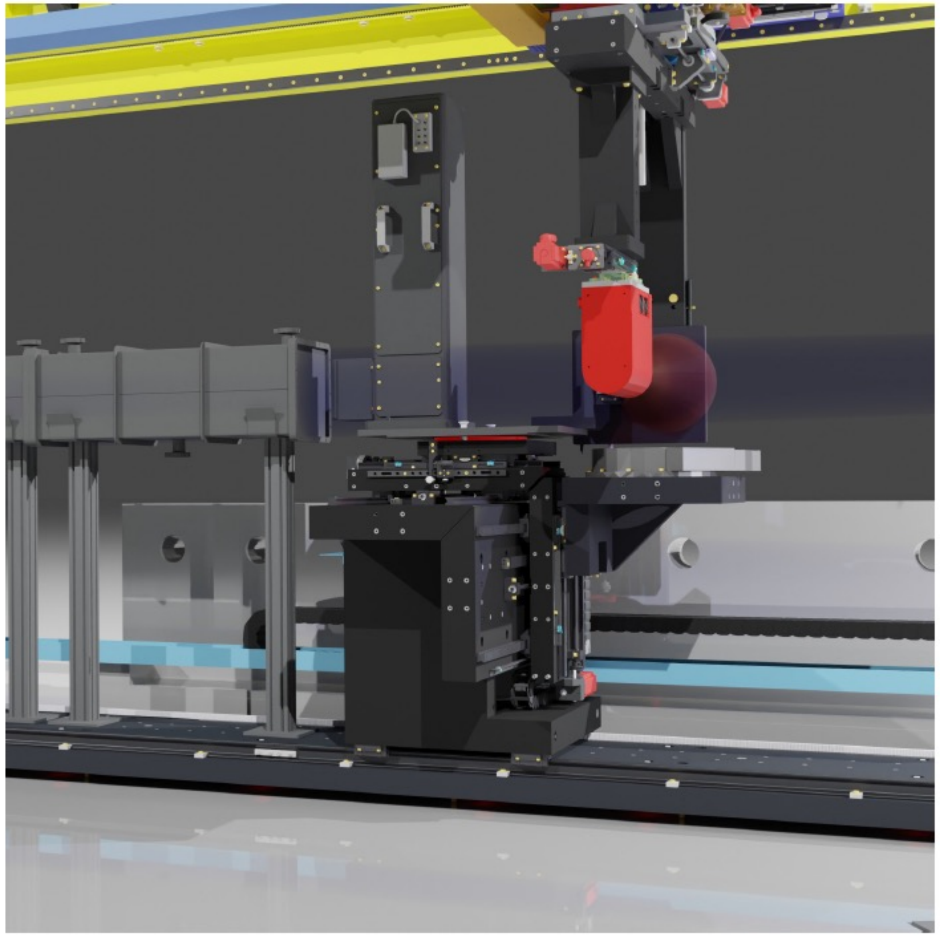
Temporal resolution:
1 ms / single image
1 s / 3D tomography

Characteristics:
Cold neutron beam
High flux
Low background

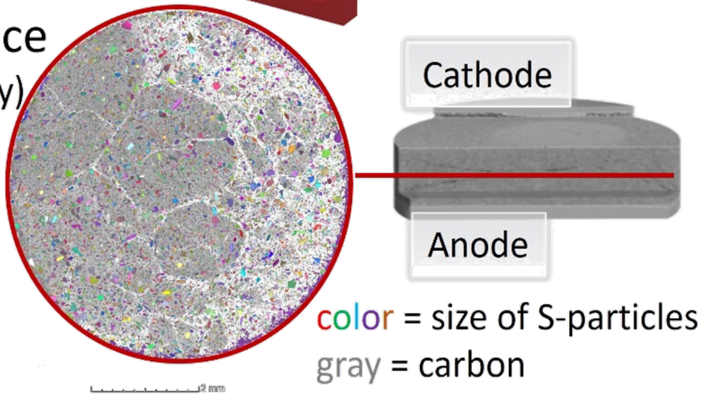
An upgraded facility by the end of 2022
Expanded range of options

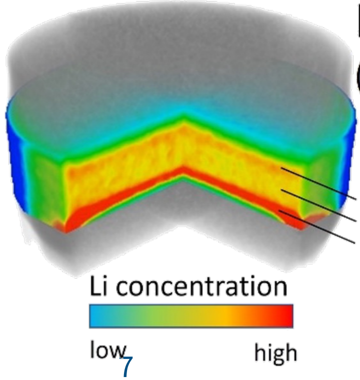
Dual-mode X/N imaging





Electrolyte slice
(X-ray tomography)



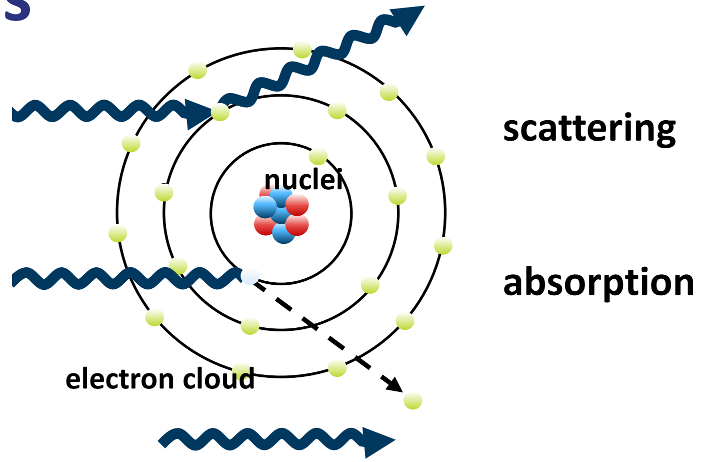


Lithium distribution
(Neutron tomography)
Discharged state
Cathode
Solid-state electrolyte
Anode

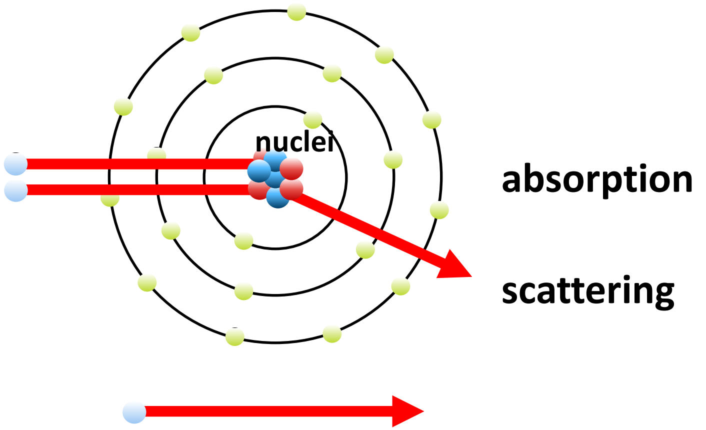
ANISSA
granted RAC project

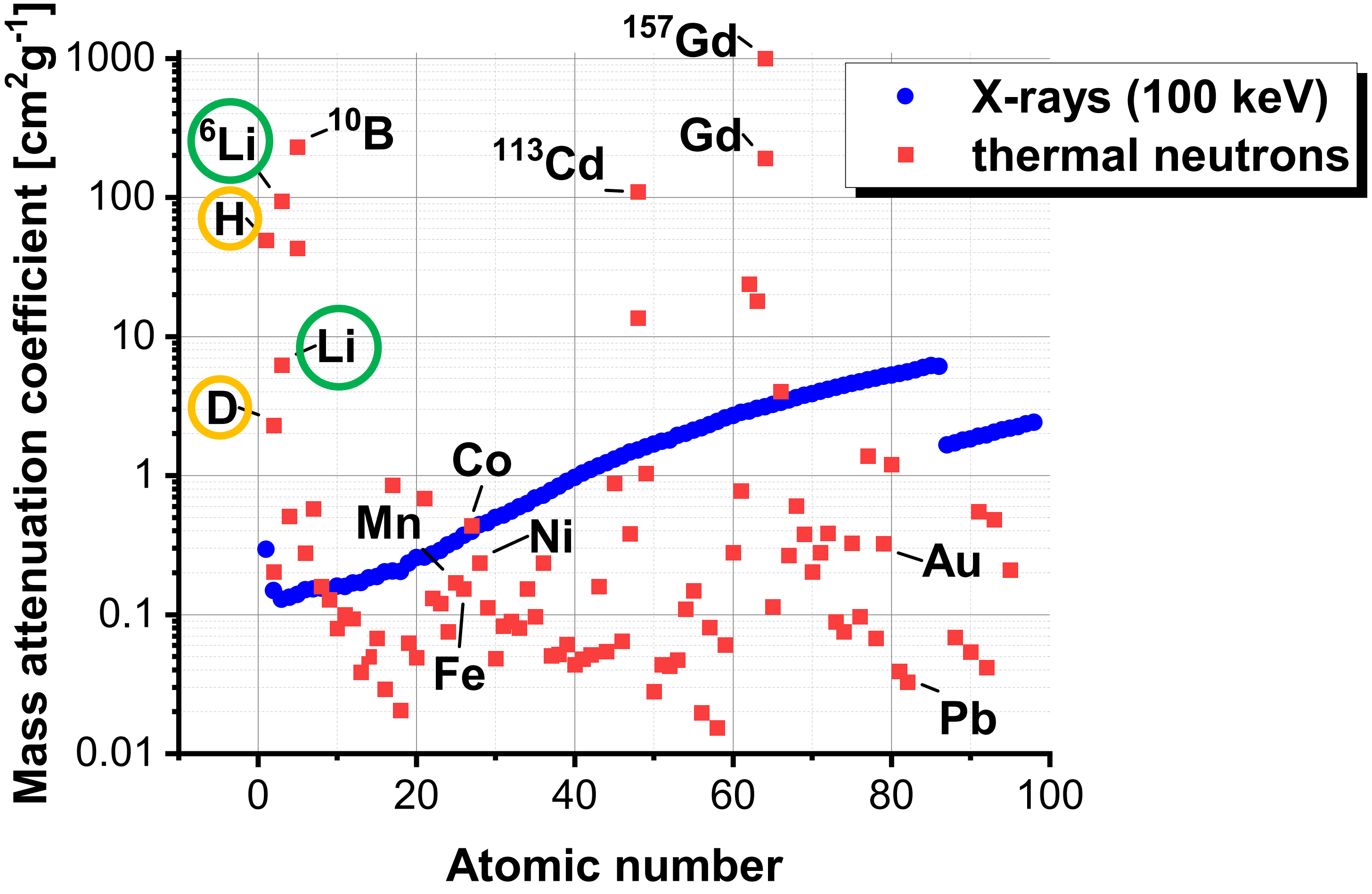
Dual-mode X/N imaging

X-rays

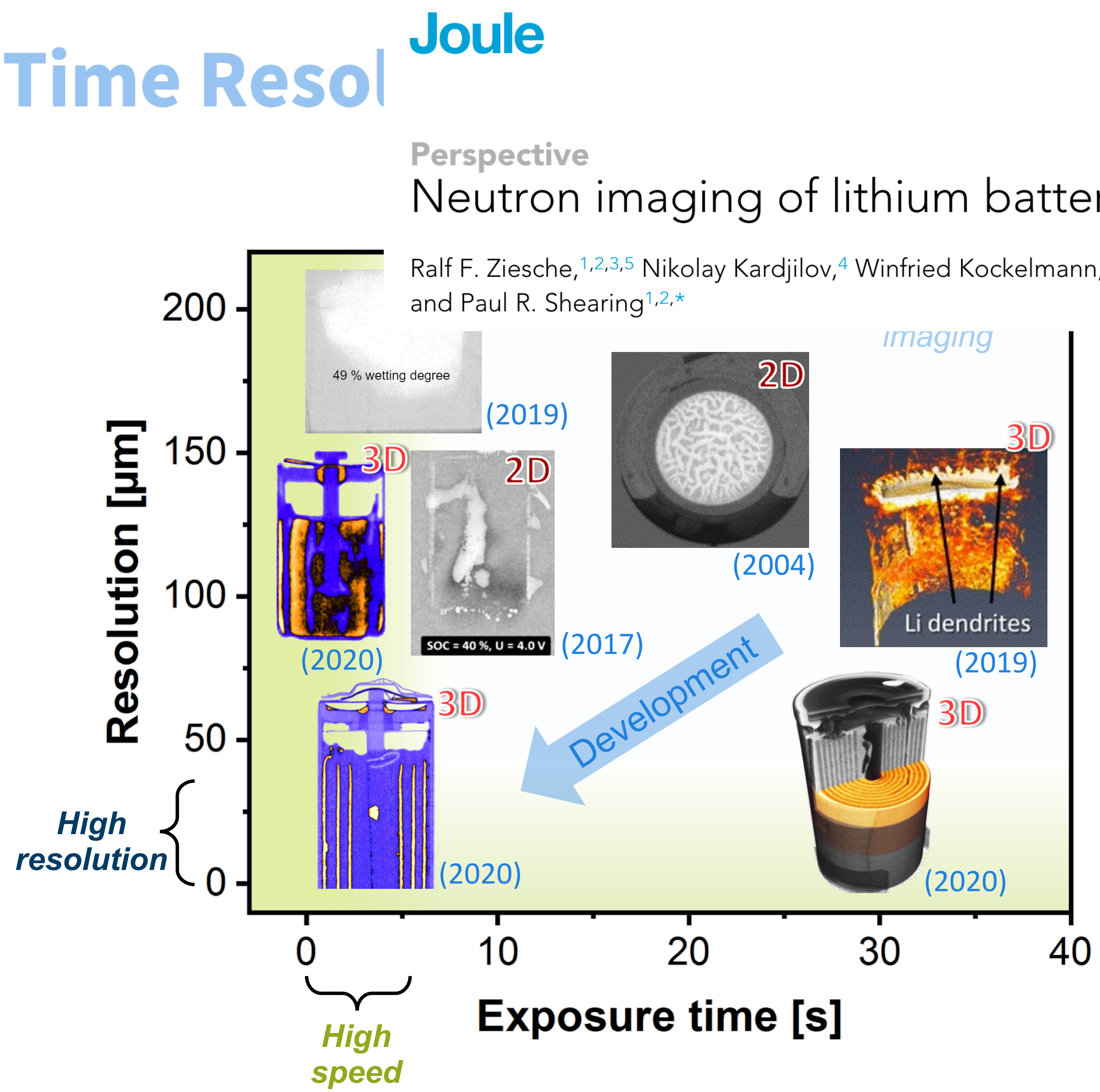


Neutrons





Spatial vs. Time Resol



Ziesche et al. (2022) *Joule*, *6*(1), 35–52.

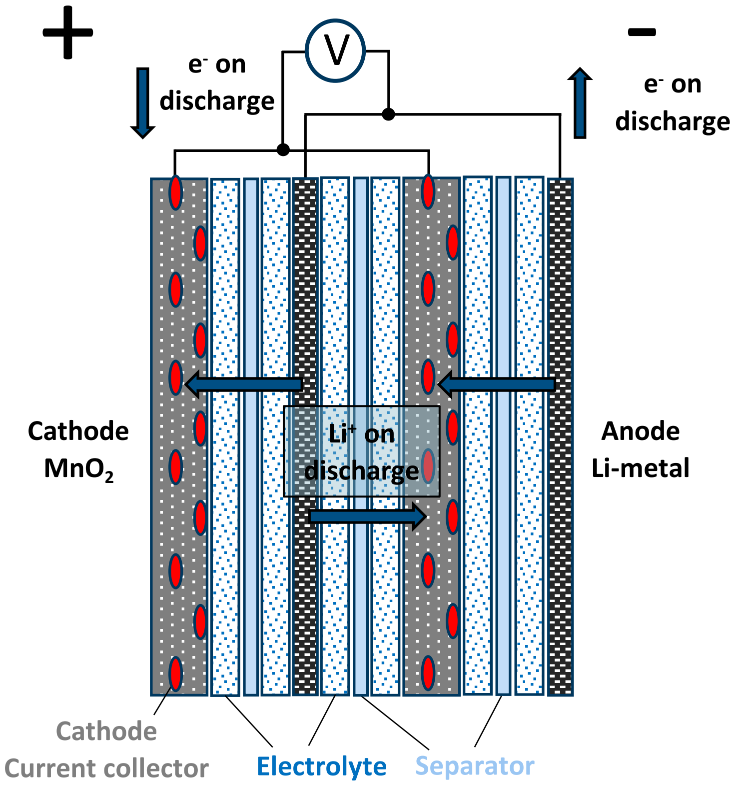
4D IMAGING OF LITHIUM BATTERIES

#Lithium-Batteries

Experimental – CR2 Lithium/Manganese Dioxide

CR2 - Duracell

Li-metal / MnO_2
normal voltage: 3.0 V
cut-off voltage: 1.6 V
capacity: 800 mAh
max. dc: >1000 mA
operating temp.: -20°C/+70°C



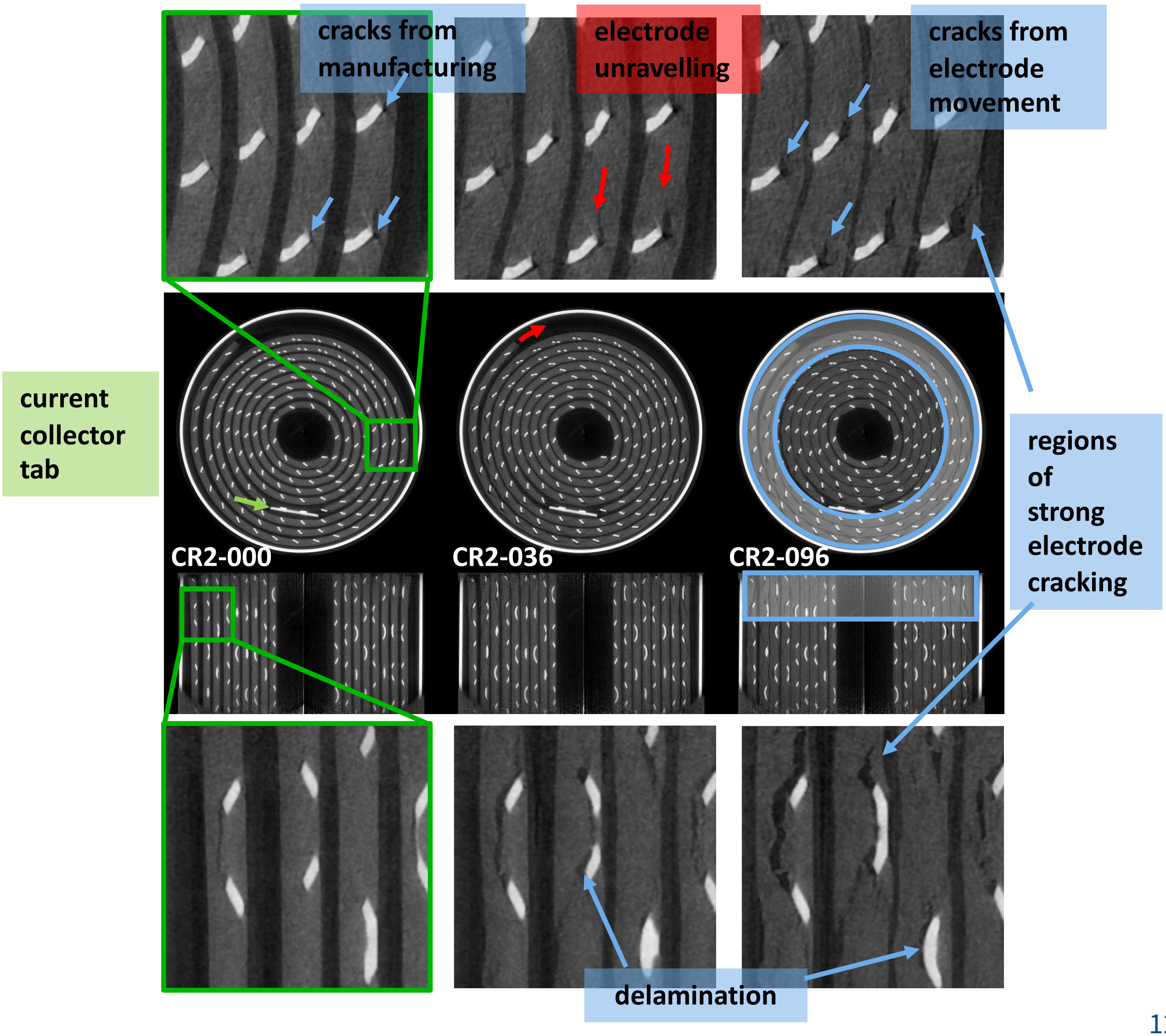
X-ray in operando tomography

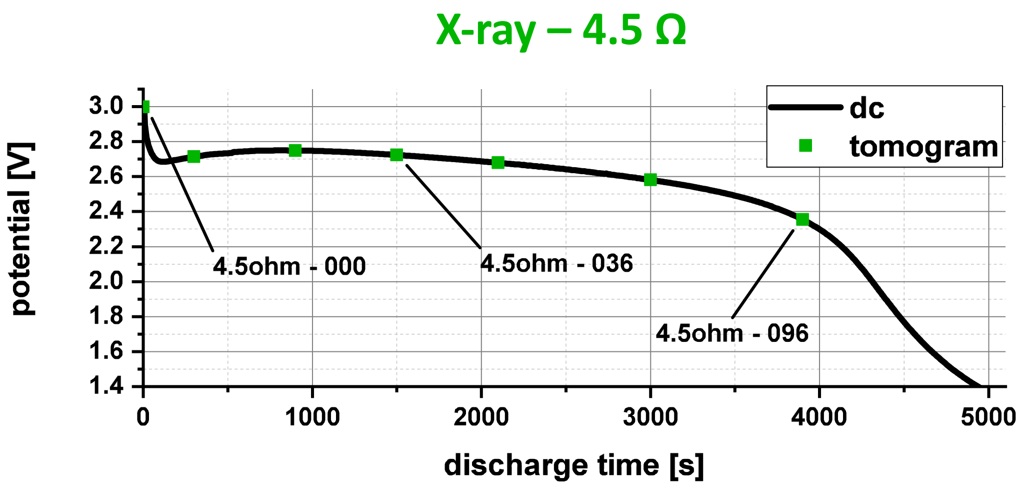
- ESRF
- scan time: 2.8 s (every 40 s)
- pixel size: 10.89 µm
- discharge over 2.75 Ω and 4.5 Ω
- 76 keV

Neutron in situ tomography

- HZB
- scan time: ca. 8 h
- pixel size: 12.9 µm
- discharge: -200 mA and over 4.7 Ω
- cold neutron spectra

X-ray Tomography - 4.5 Ω





X-ray scan:

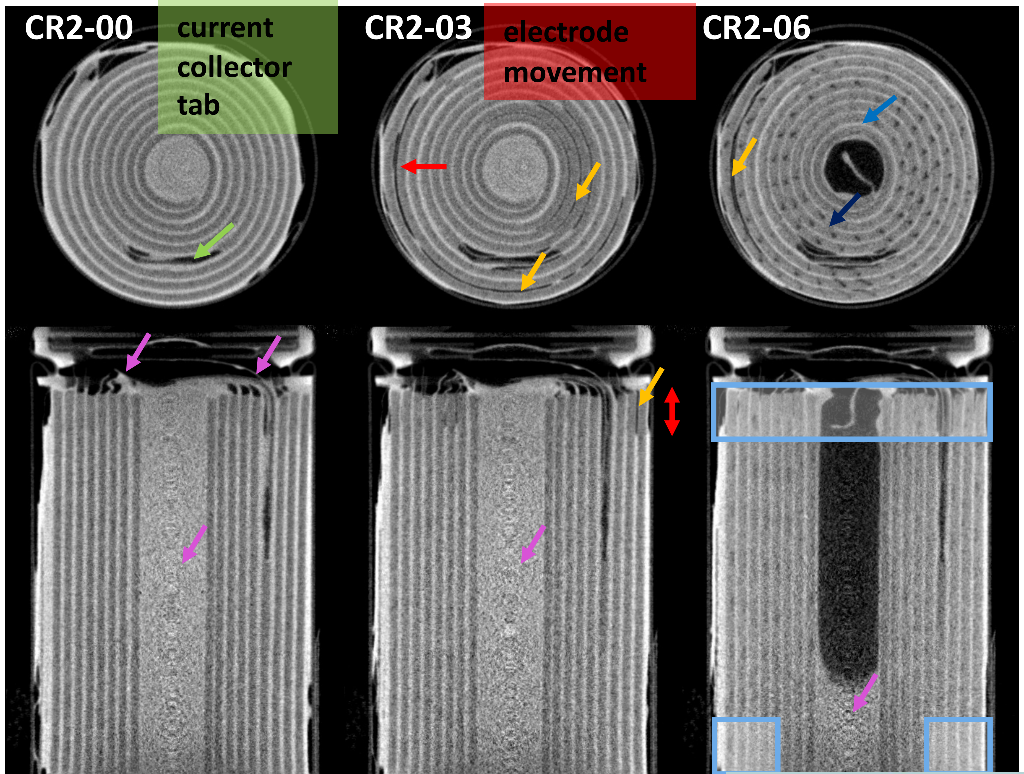
- 10.87 µm pixel size
- capacity (2.0V): 658 mAh
- 2.8 s per Tomogram every 40 s
- total time: ca. 4900 s
- # tomograms: 103

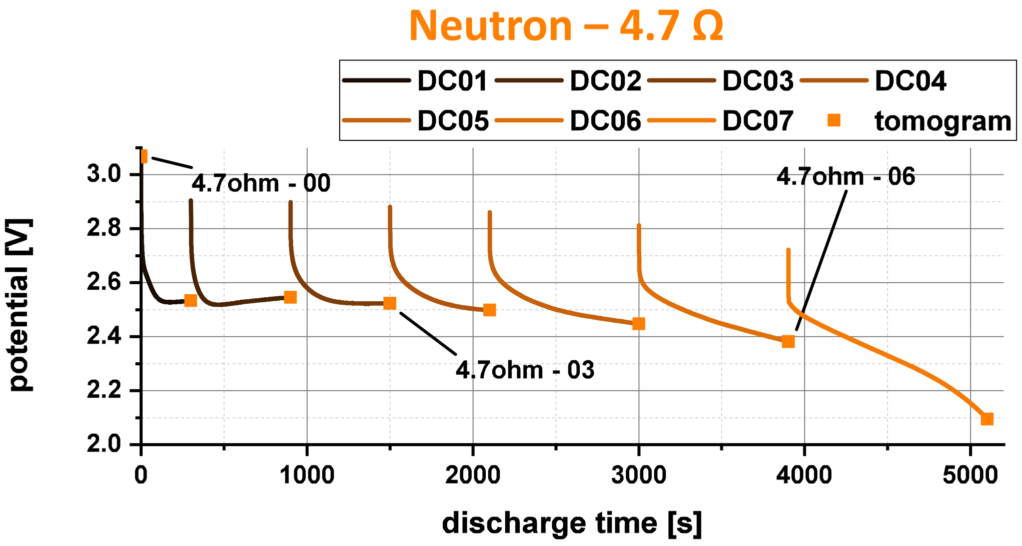
Results - Structure

- Cracking
- expansion of MnO_2 electrode

ID15A @ESRF

Neutron Tomography – 4.7 Ω





Neutron

- 12.9 µm pixel size
- capacity (2.0 V): 746mAh
- ca. 8 h per tomogram
- total time: ca. 65.5 h
- # tomograms: 8

Results – Electro-chemistry

- shows Li consumption from Li-metal anode and
- ...calation in MnO_2 electrode
- ...trolyte consumption during discharge

Ziesche et al. (2020) *Nature Communications*, *11:777*(1), 11.

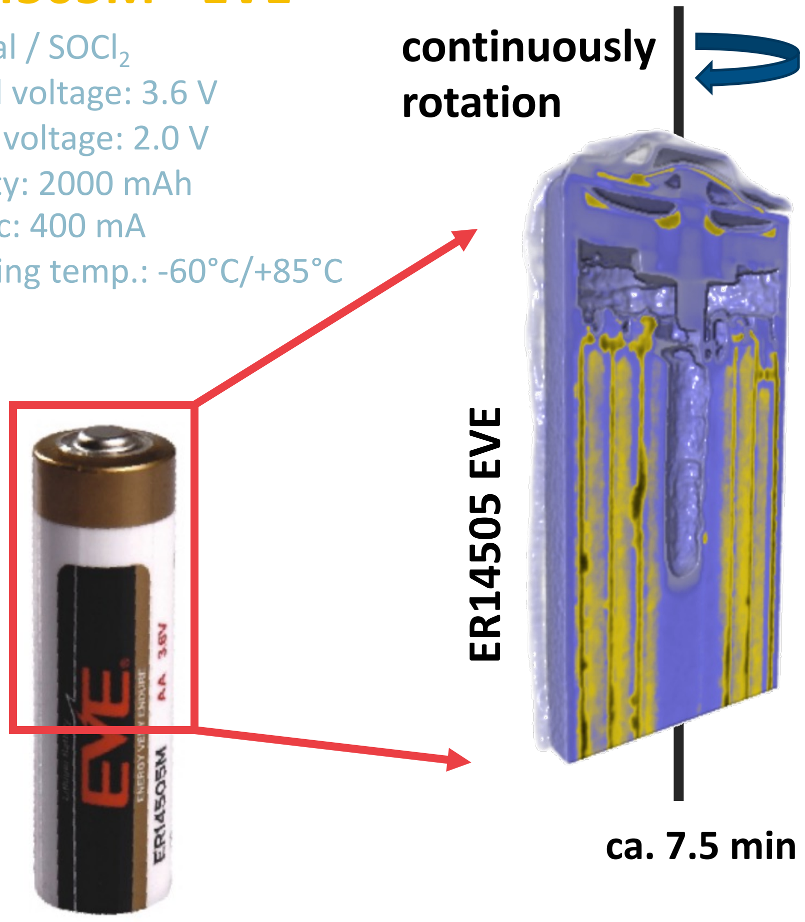
Experimental – ER14505M Lithium/Thionyl Chloride

ER14505M - EVE

Li-metal / $SOCl_2$
normal voltage: 3.6 V
cut-off voltage: 2.0 V
capacity: 2000 mAh
max. dc: 400 mA
operating temp.: -60°C/+85°C

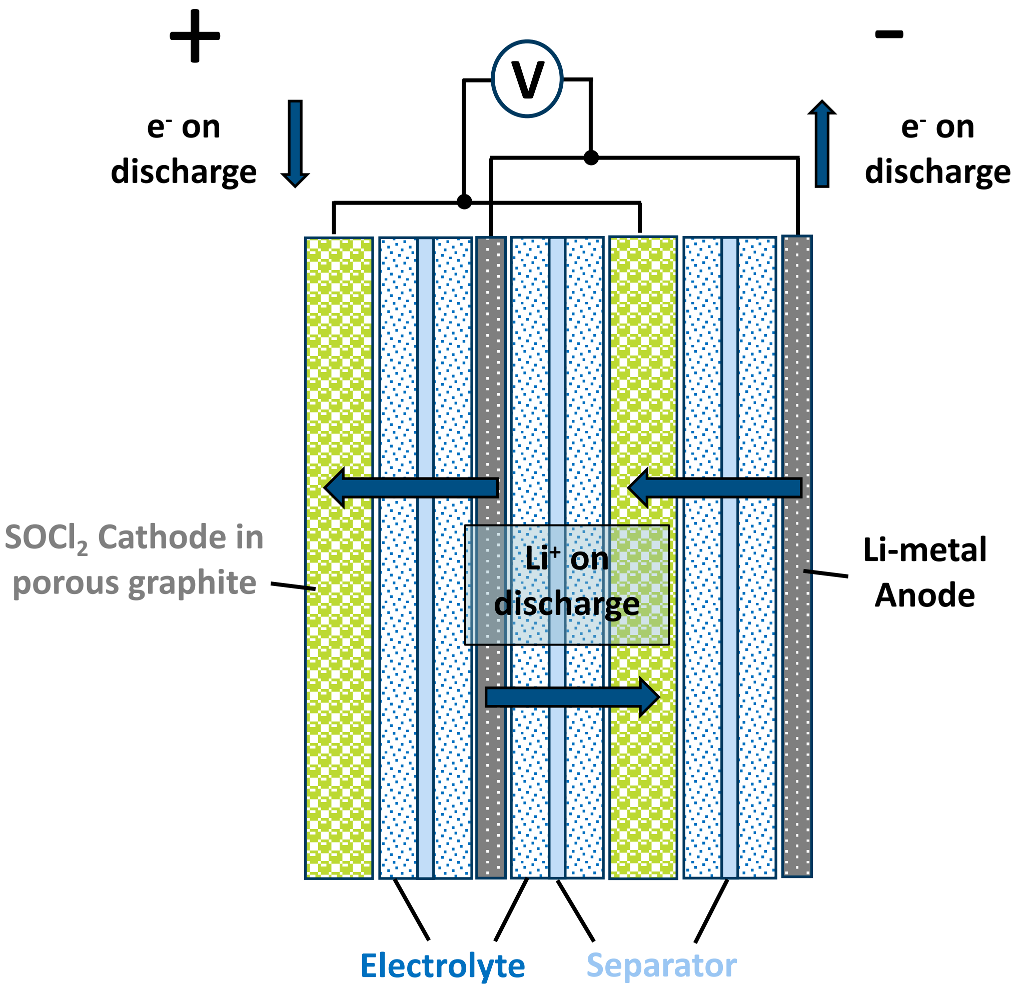
continuously rotation

360 ° CT reconstruction every 90 °



-300 mA and -100 mA discharge NeXT (ILL)

ca. 7.5 min per tomography

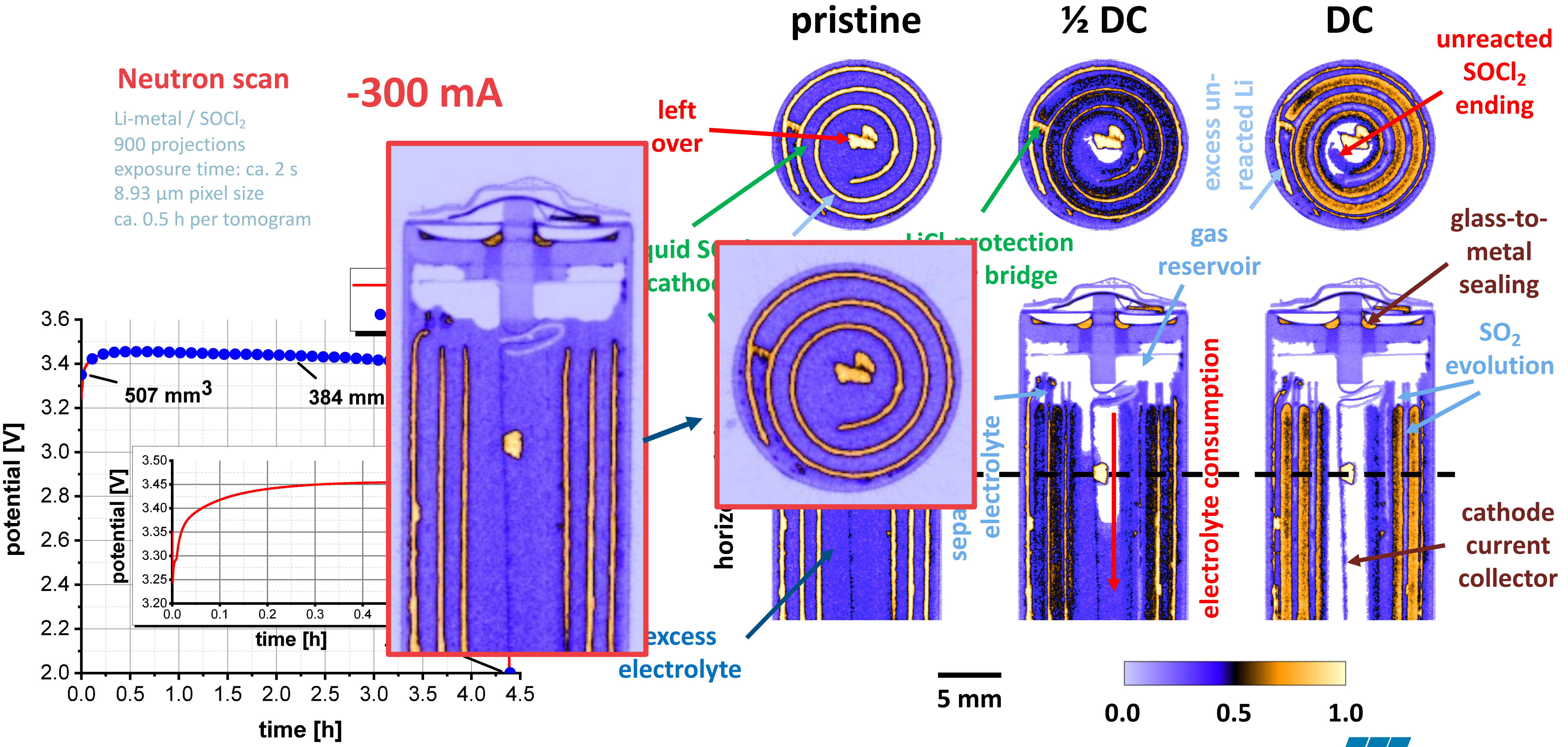


Ziesche et al. (2020). *Journal of The Electrochemical Society*, *167*(14), 140509.

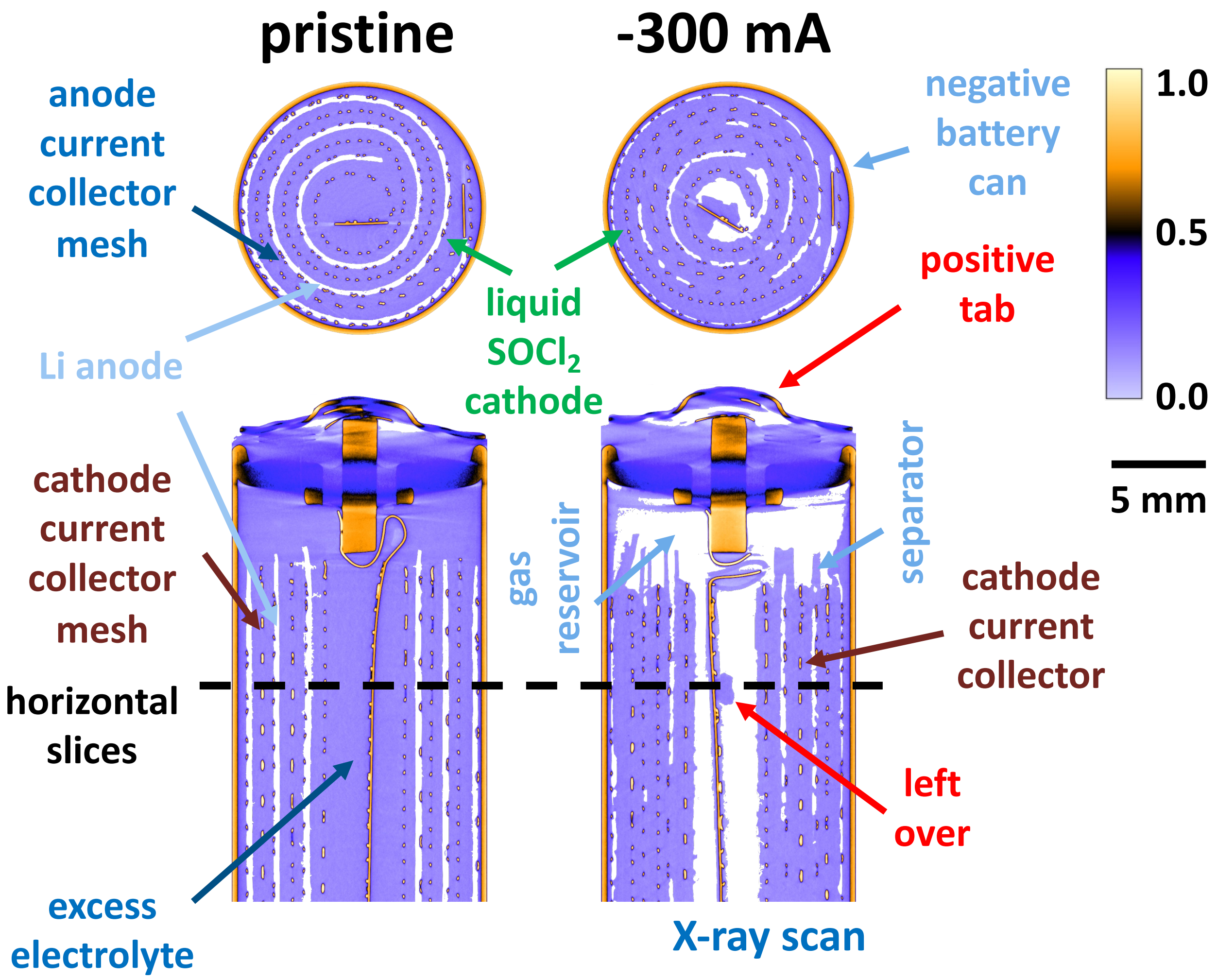
Neutron Computed Tomography -300 mA discharge

Neutron scan

Li-metal / $SOCl_2$
900 projections
exposure time: ca. 2 s
8.93 µm pixel size
ca. 0.5 h per tomogram

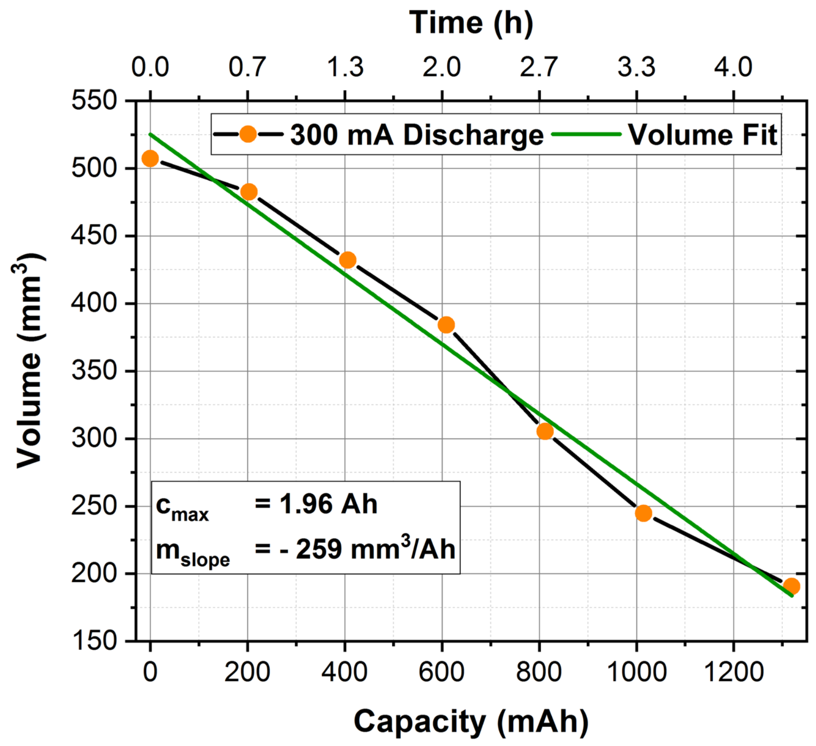


X-ray CT & Li-Volume Quantification

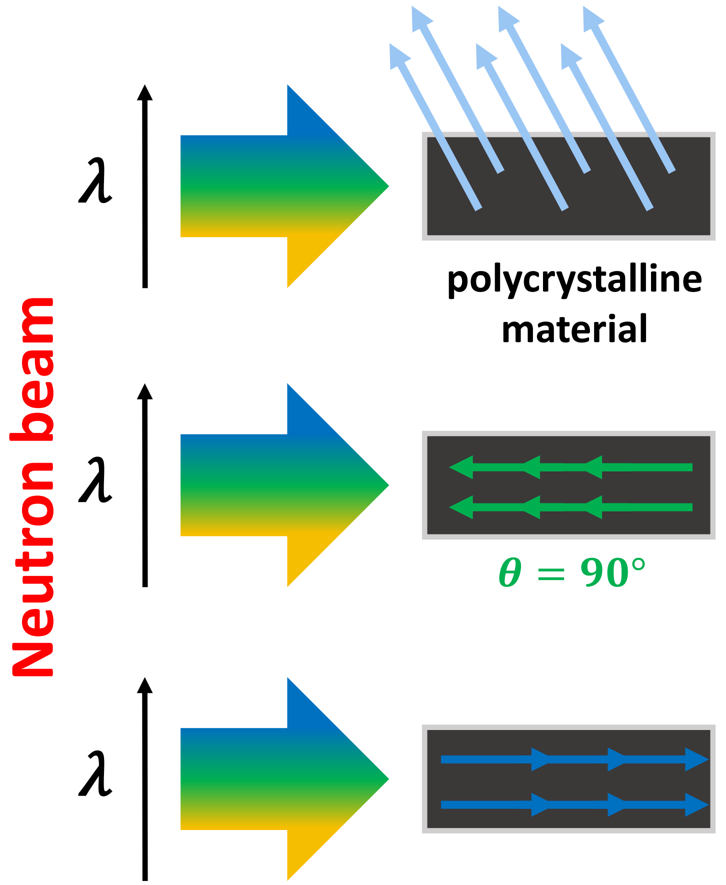


X-ray scan

Li-metal / $SOCl_2$
1600 projections
exposure time: ca. 0.33 s
19.8 µm pixel size
ca. 0.75 h per tomogram



Bragg Edge Imaging



$\lambda < 2d_{hkl}$

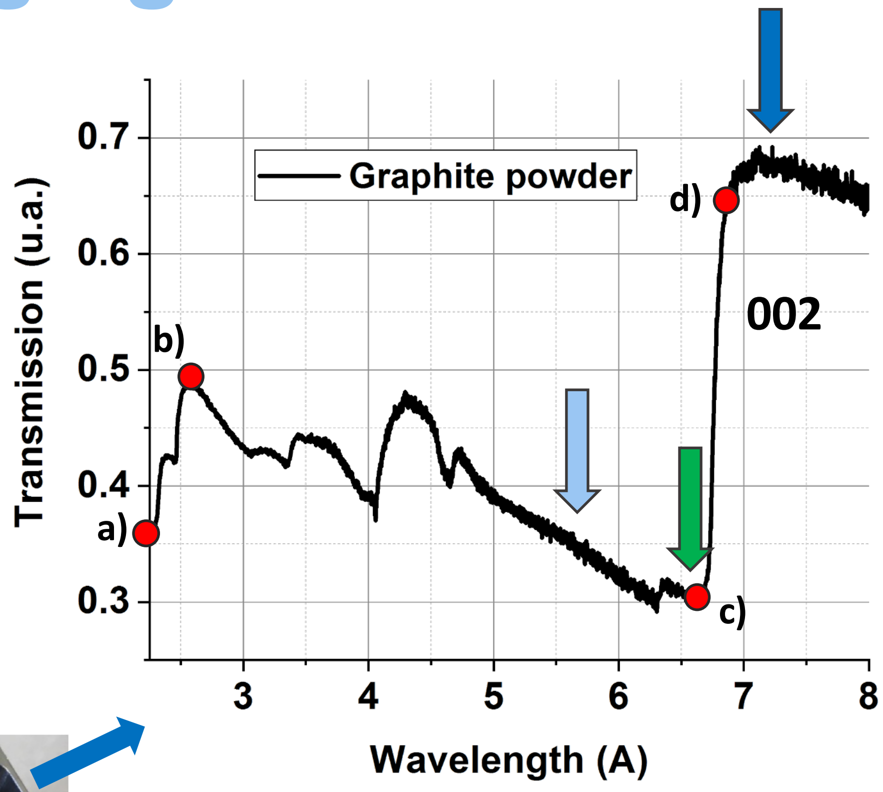
Bragg law

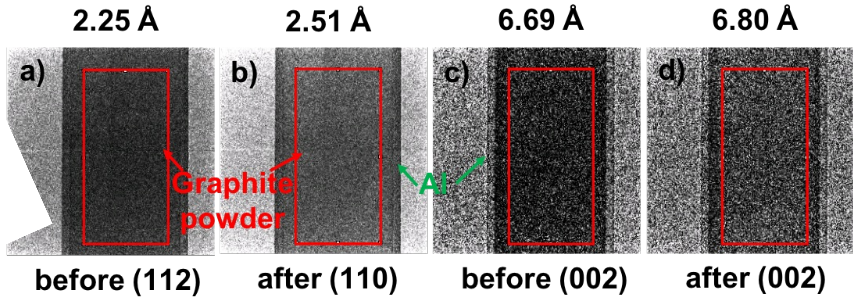
$$2d_{hkl} sin\theta = \lambda$$

$\lambda = 2d_{hkl}$

$\lambda > 2d_{hkl}$

no more scattering from same hkl plane





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Science & Technology Facilities Council ISIS

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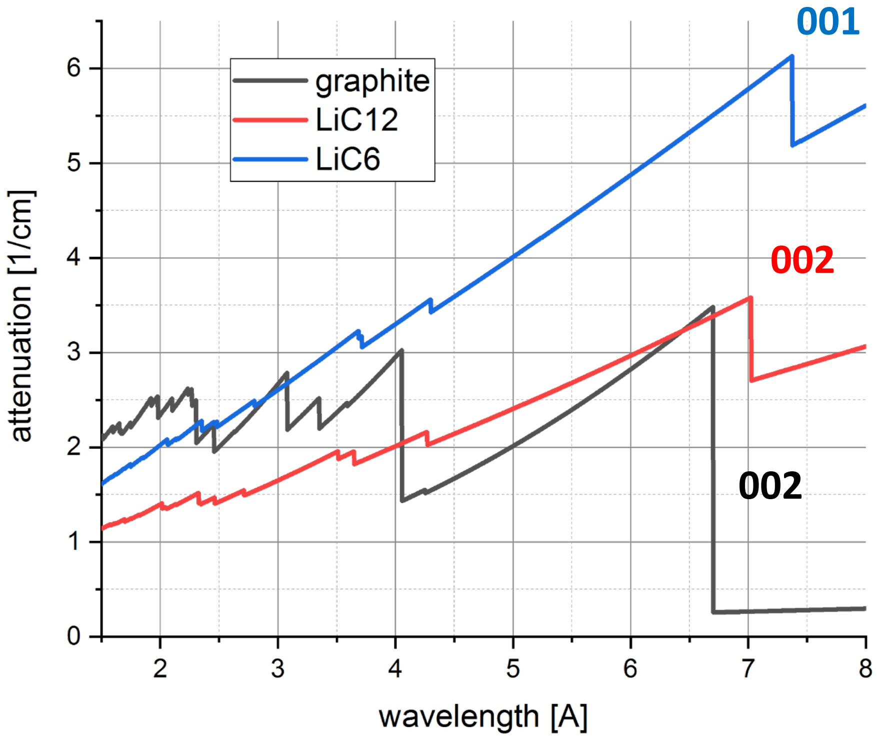
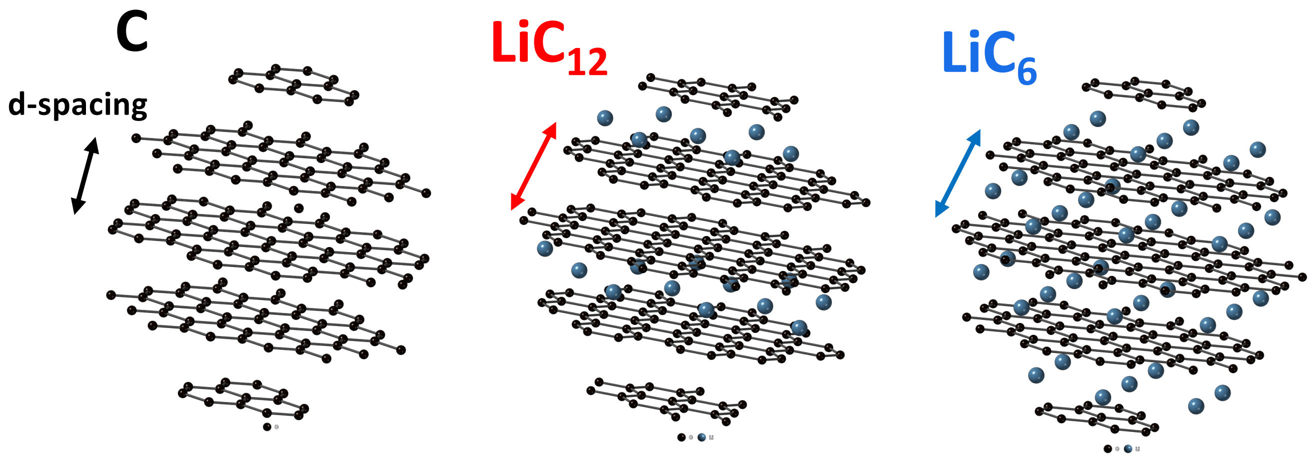
Lithiation of Graphite

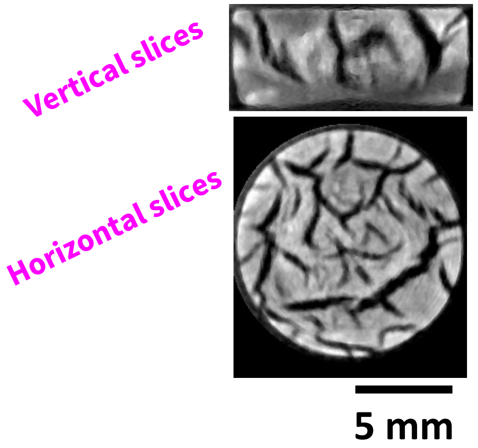
Theoretical Attenuation Coefficient



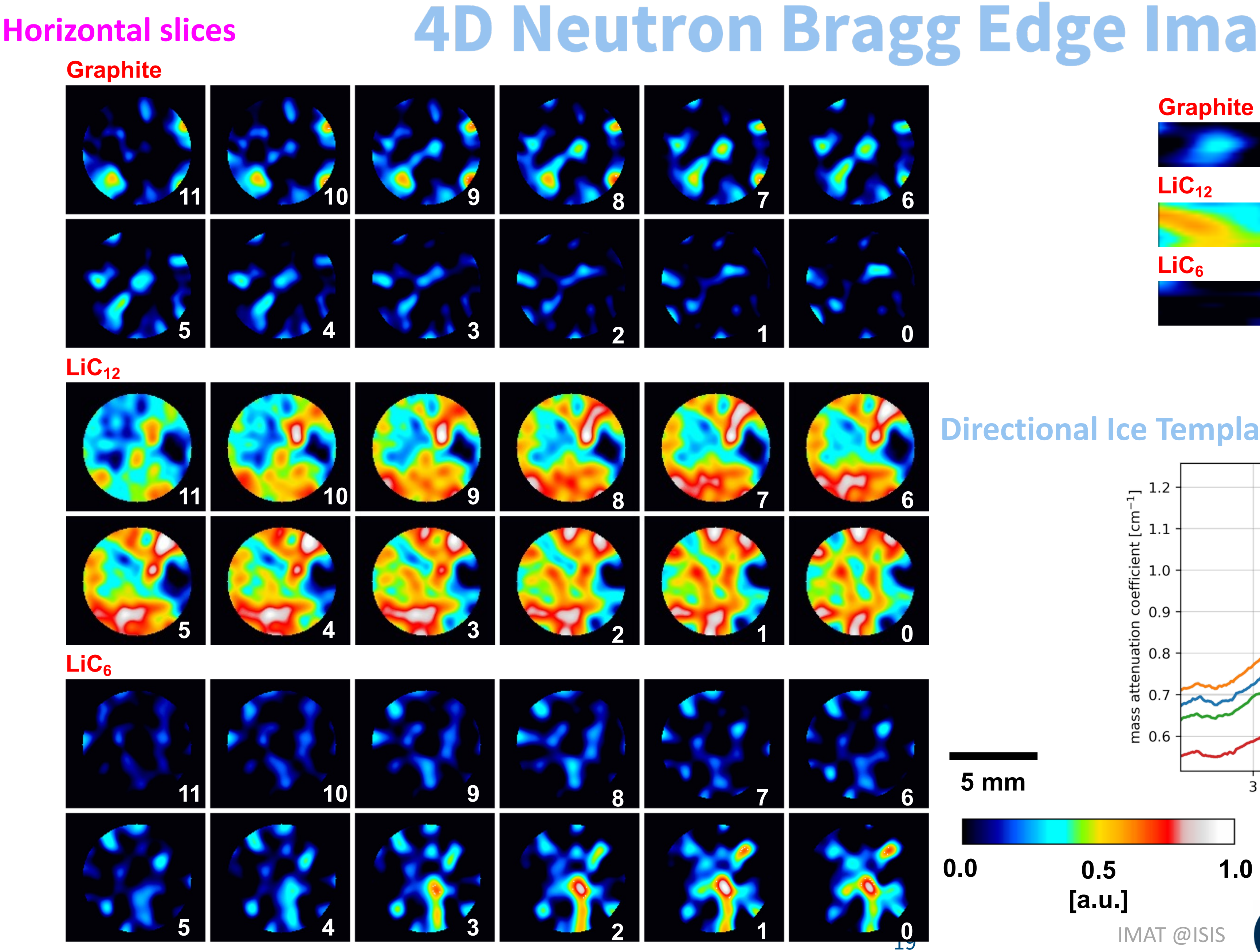


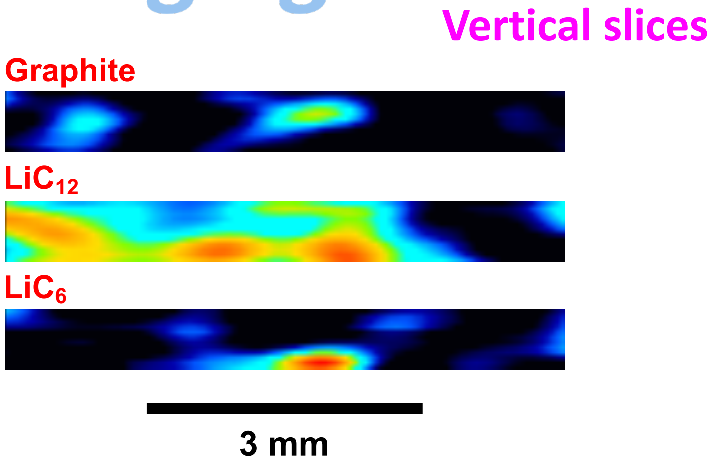
	crystal orientation	d-spacing [Å]	Bragg-λ [Å]
C	002	3.36	6.71
LiC12	002	3.51	7.02
LiC6	001	3.69	7.37

thick porous Ice Templated Graphite Electrode - partly lithiated

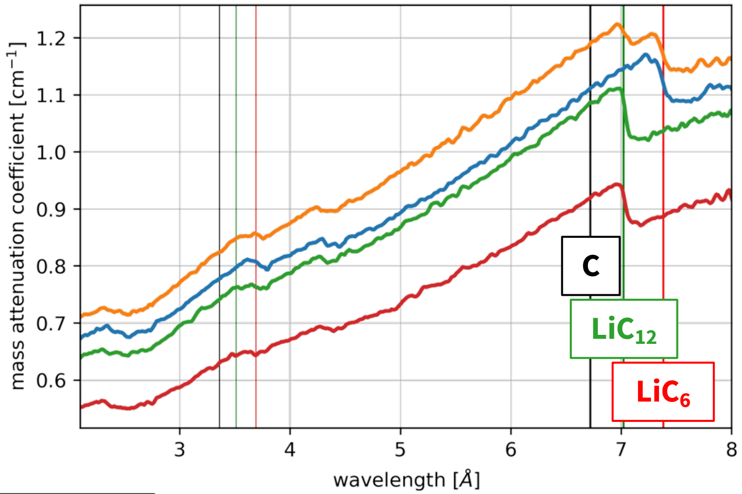


4D Neutron Bragg Edge Imaging





Directional Ice Templated Graphite Electrode @ ca. 33 % SoC



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Ziesche, R. F et al. (2020),. *Journal of Imaging*, *6*(12), 136.

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4D IMAGING OF FUEL CELLS

#FuelCells

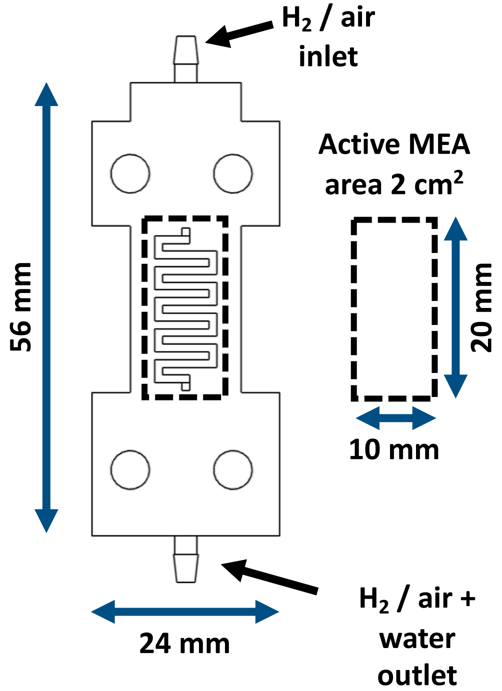
Water Management

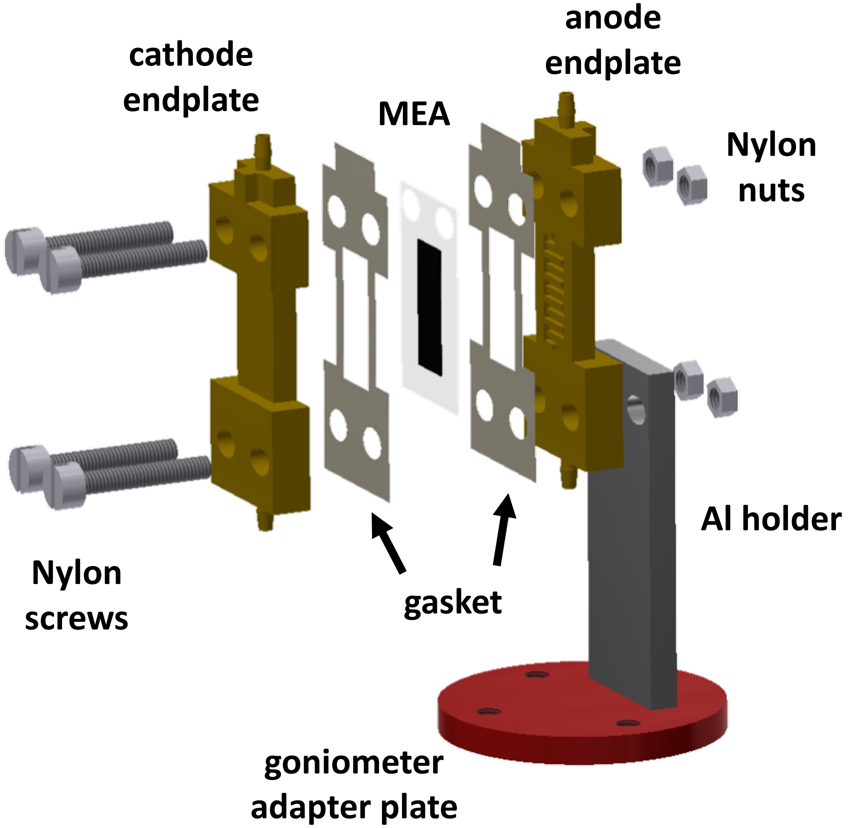
High-speed 4D Neutron CT of Polymer Electrolyte Fuel Cells

Miniature Fuel Cell

Polymer Electrolyte Fuel Cell
Max. voltage: ca. 1 V
Max. current: 700 mA cm^{-1}
operating temp.: no heating
Flow field design: single serpentine

Anode / Cathode flow field and endplate

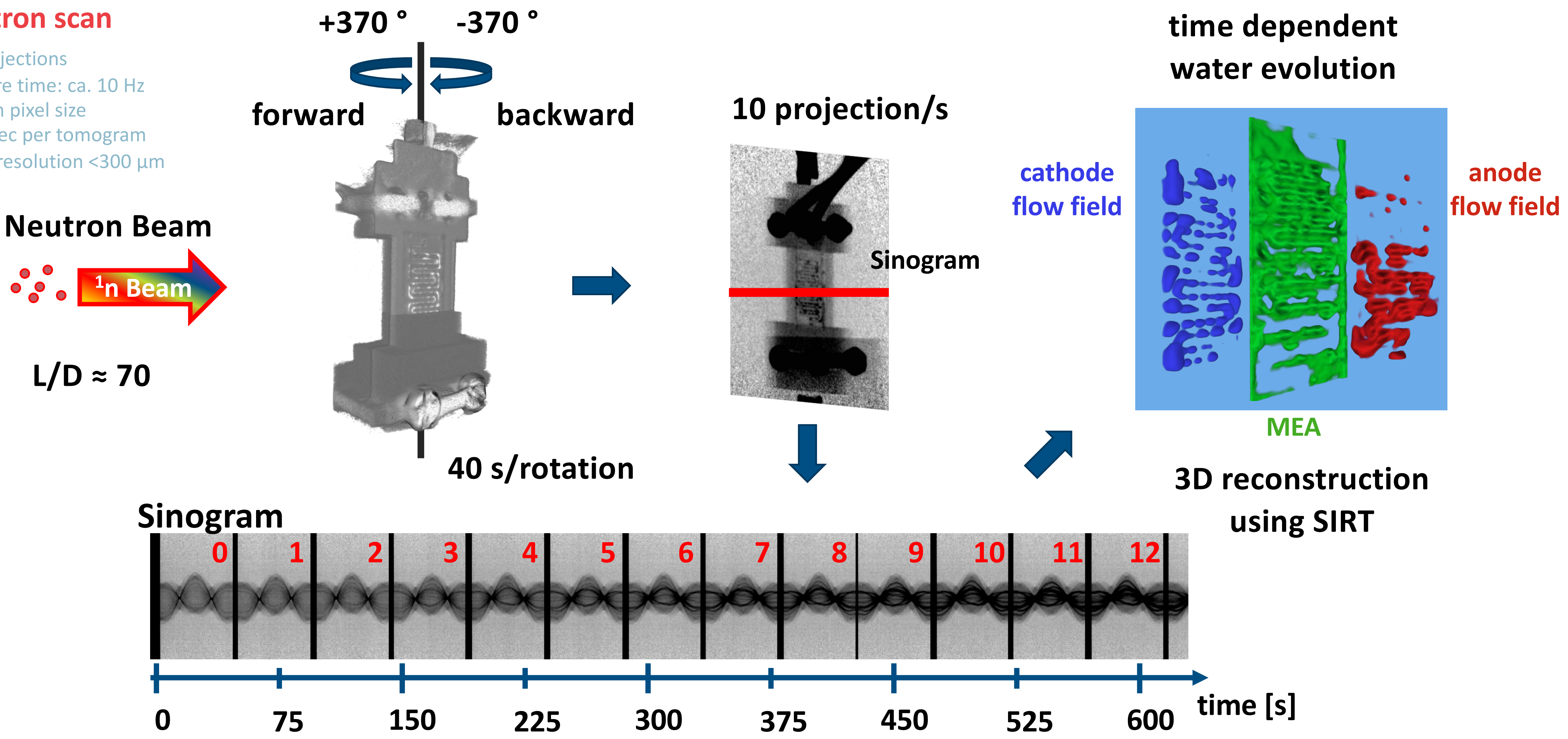




4D High-Speed Imaging – Work Flow

Neutron scan

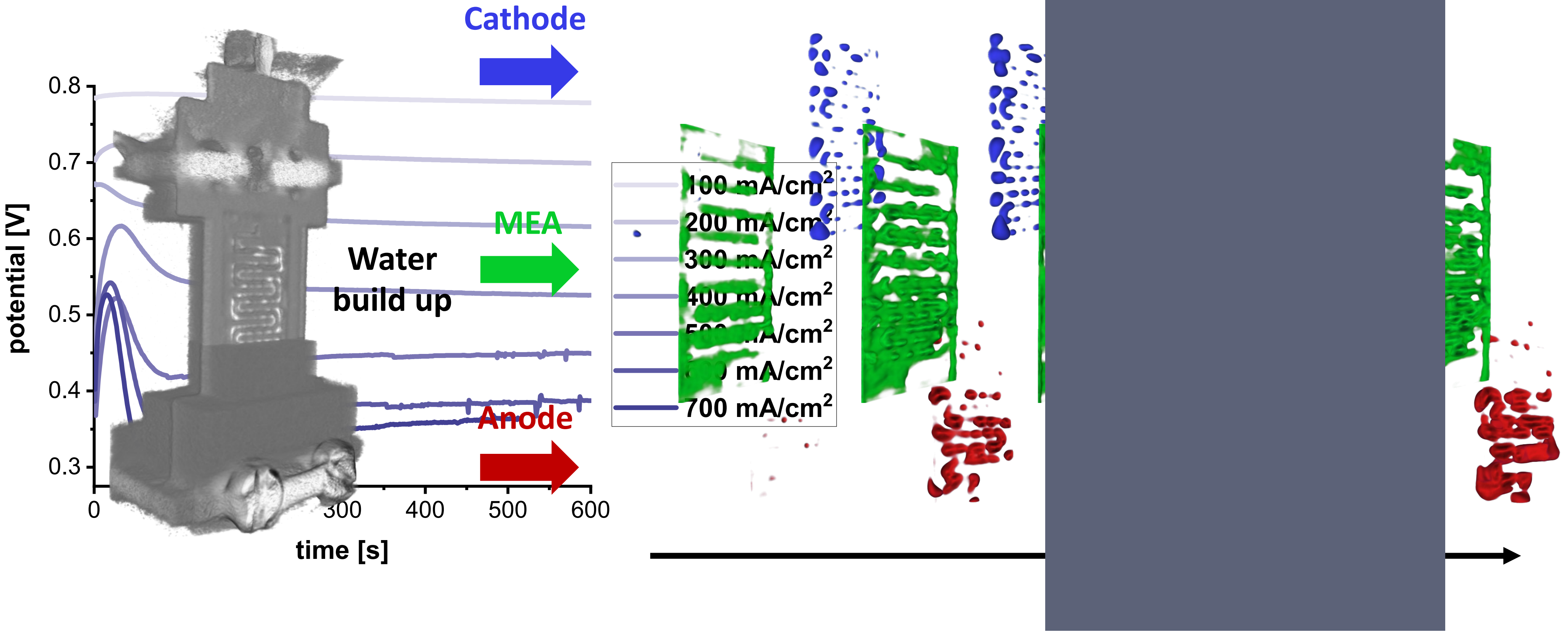
394 projections
exposure time: ca. 10 Hz
63.6 µm pixel size
ca. 40 sec per tomogram
Spatial resolution <300 µm



Water evolution – Current Hold

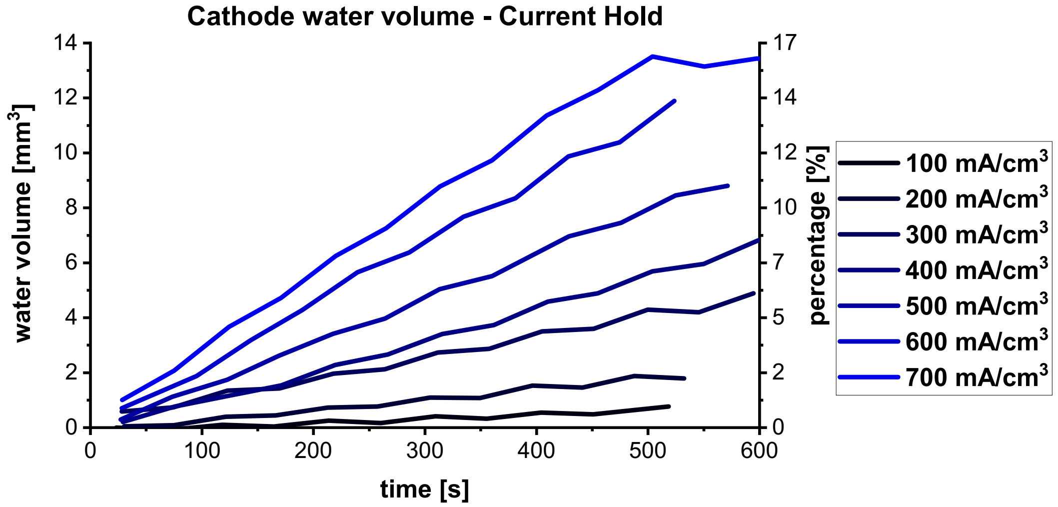
current hold
400 mA cm^{-2}

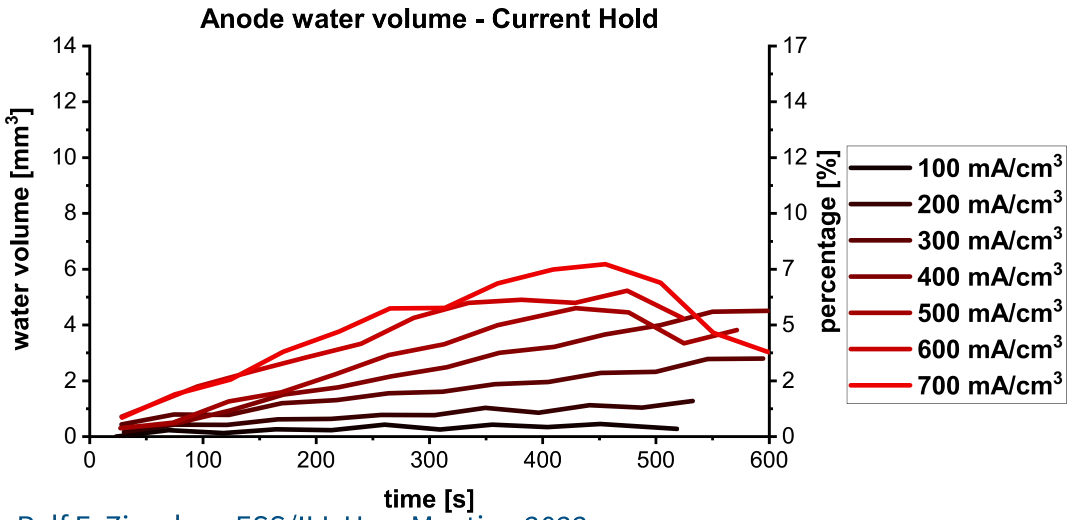
Cathode



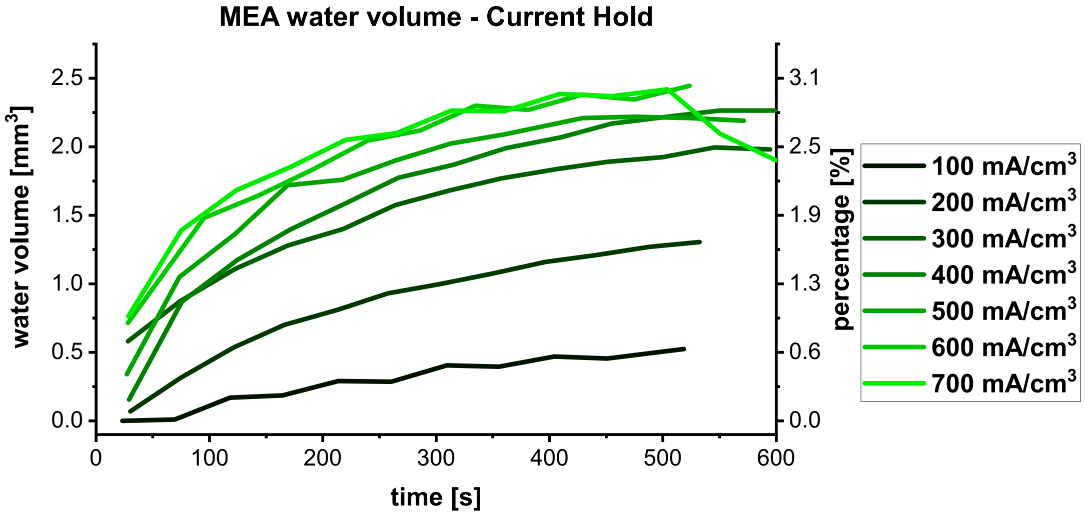
Quantification of Water Volume – Flow Fields

Cathode / Anode Water





MEA Water



nature COMMUNICATIONS

Ziesche et al. (2022) *Nature Communications*, *13*(1), 1616.

Preliminary Results ILL: 4D Fuel Cell Imaging

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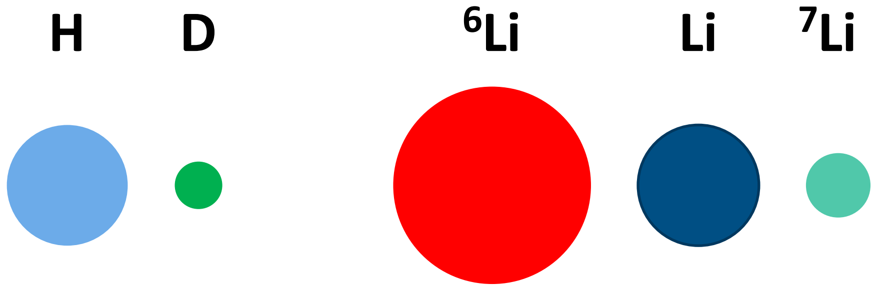
CONCLUSION

#Neutron Imaging

Conclusion

Why Neutron Imaging?

- **High sensitivity to Li and H (Contrast)**
- **Different attenuation coefficient for Isotopes**



- **dynamic imaging**
- **time resolved tomography**
- **quantitative data analysis**
- **phase information**

- **Similar length scale as X-rays (cm to µm)**

Complementarity

X-rays
Information about structural changes

Neutrons
Information about the electrochemistry

- **Useful in a width field of Energy System:**
  - **Li Batteries**
  - **Fuel Cells**
  - **Electrolysers**
  - **H-Storage**

Outlook

- **Instruments and Detector getting more optimised**
  → Higher spatial and temporal resolution

Thank You

For Your Attention!

HZB BESSY

#NI-Matters