Operando diffraction mapping of commercial Li-ion batteries

Doing XRD with complex samples, difficult data, and spatial/temporal changes

Canadian Powder Diffraction Workshop – July 31, 2025

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Overview

Background

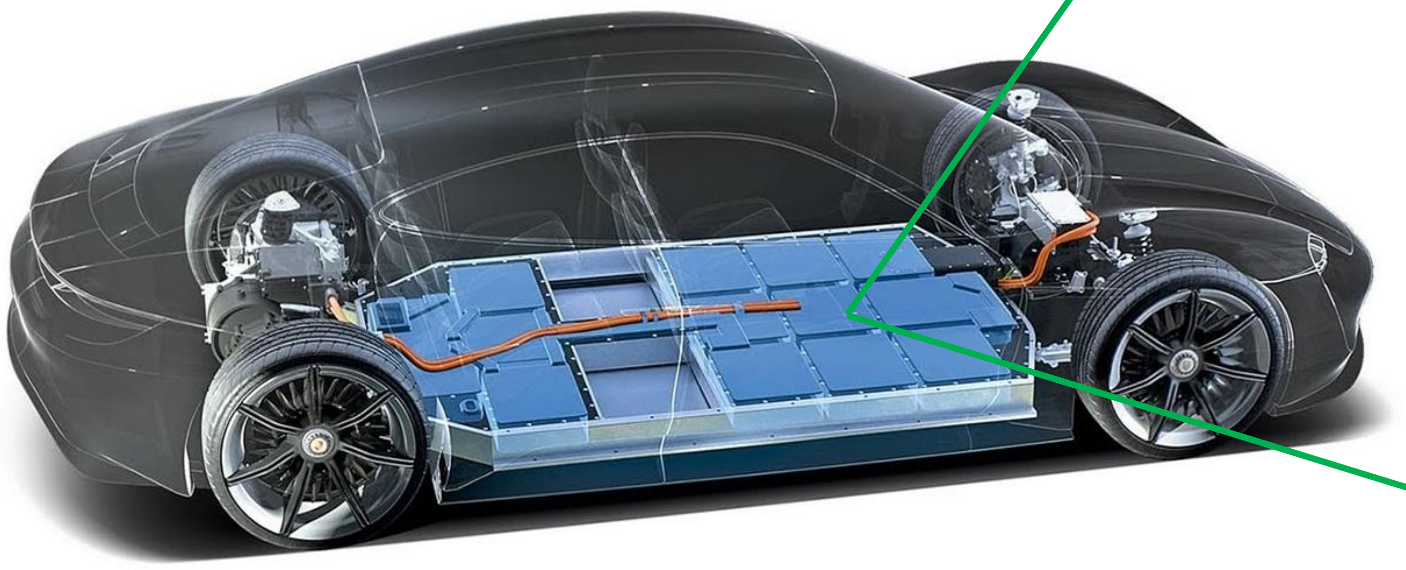
- Li-ion batteries: electrodes and cells
- Degradation and microcracking
- In-situ vs commercial cells

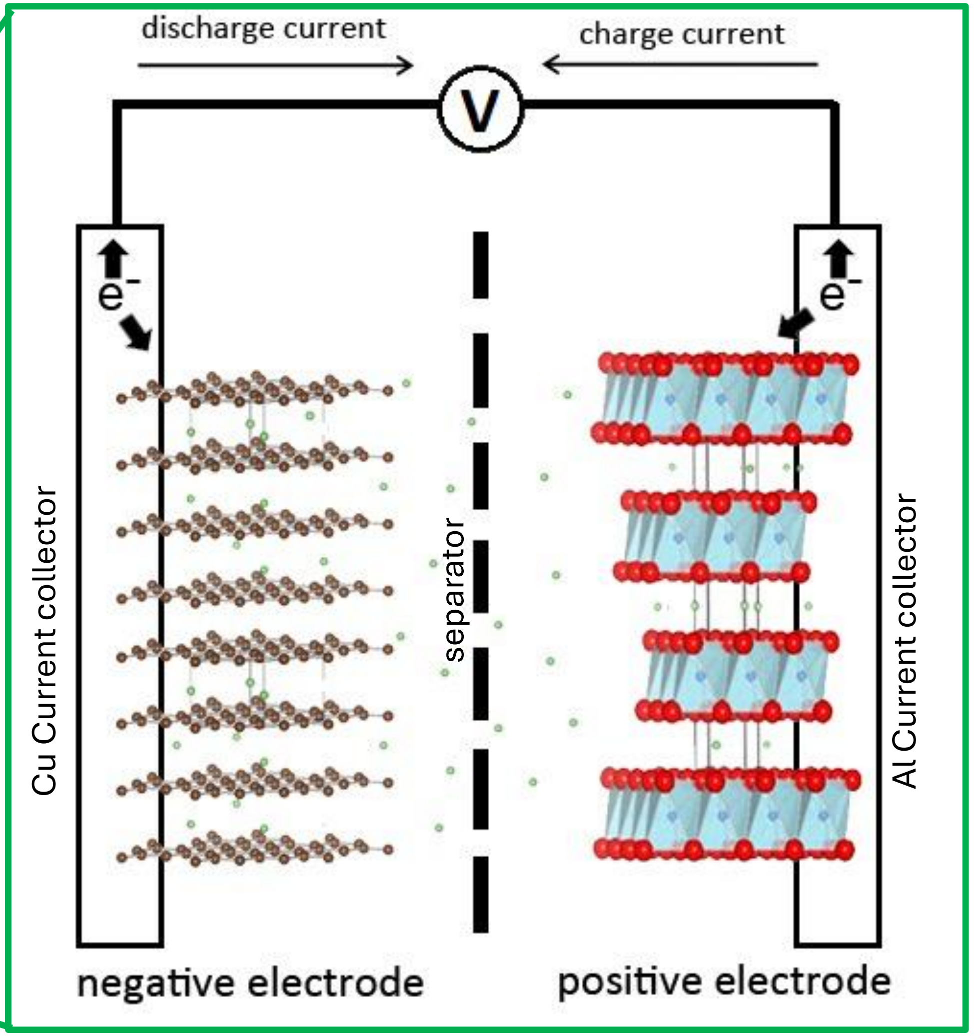
Time-resolved mapping with Synchrotron XRD

- Experimental considerations
- Data analysis

Li-ion batteries: Overview

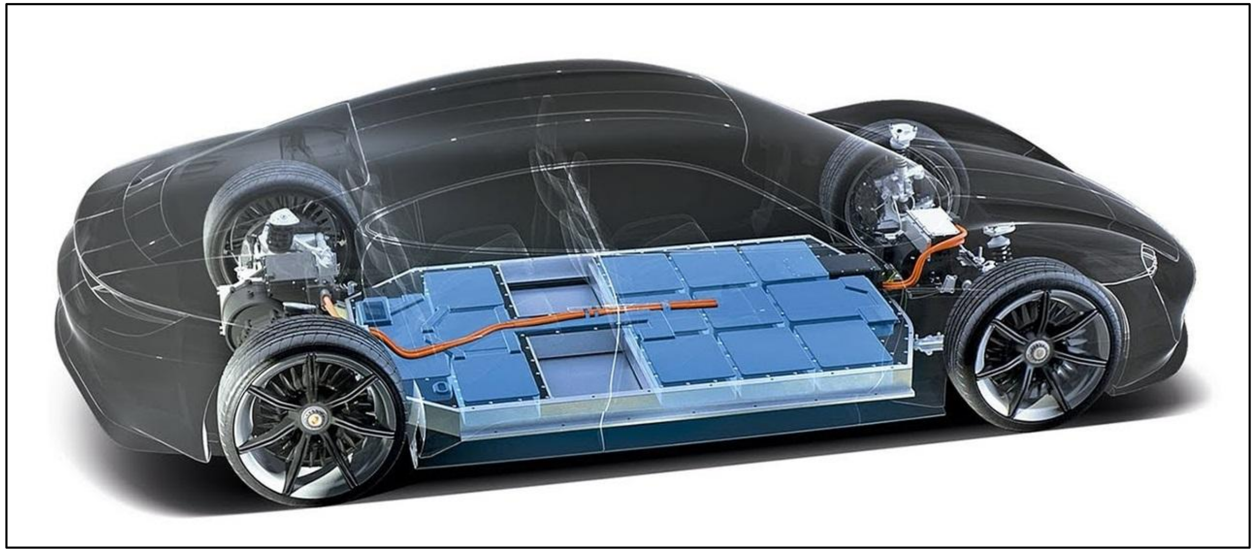
- Most common negative electrode is graphite
- Many different positive electrodes – here we only consider NMC (Nickel Manganese Cobalt oxide) in particular, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)



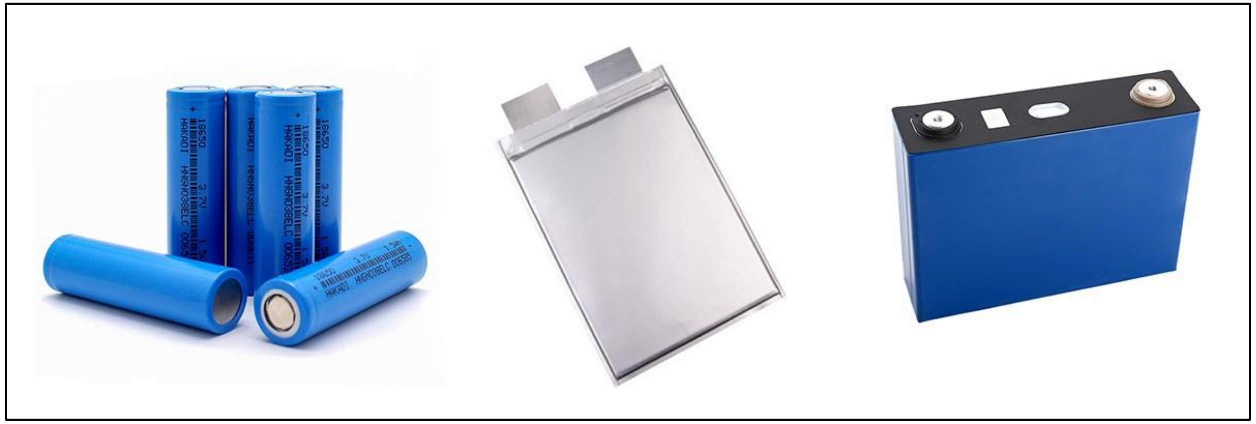


Li-ion batteries: packs, cells, and electrodes

Battery packs and modules



Cylindrical cell | Pouch cell | Prismatic cell



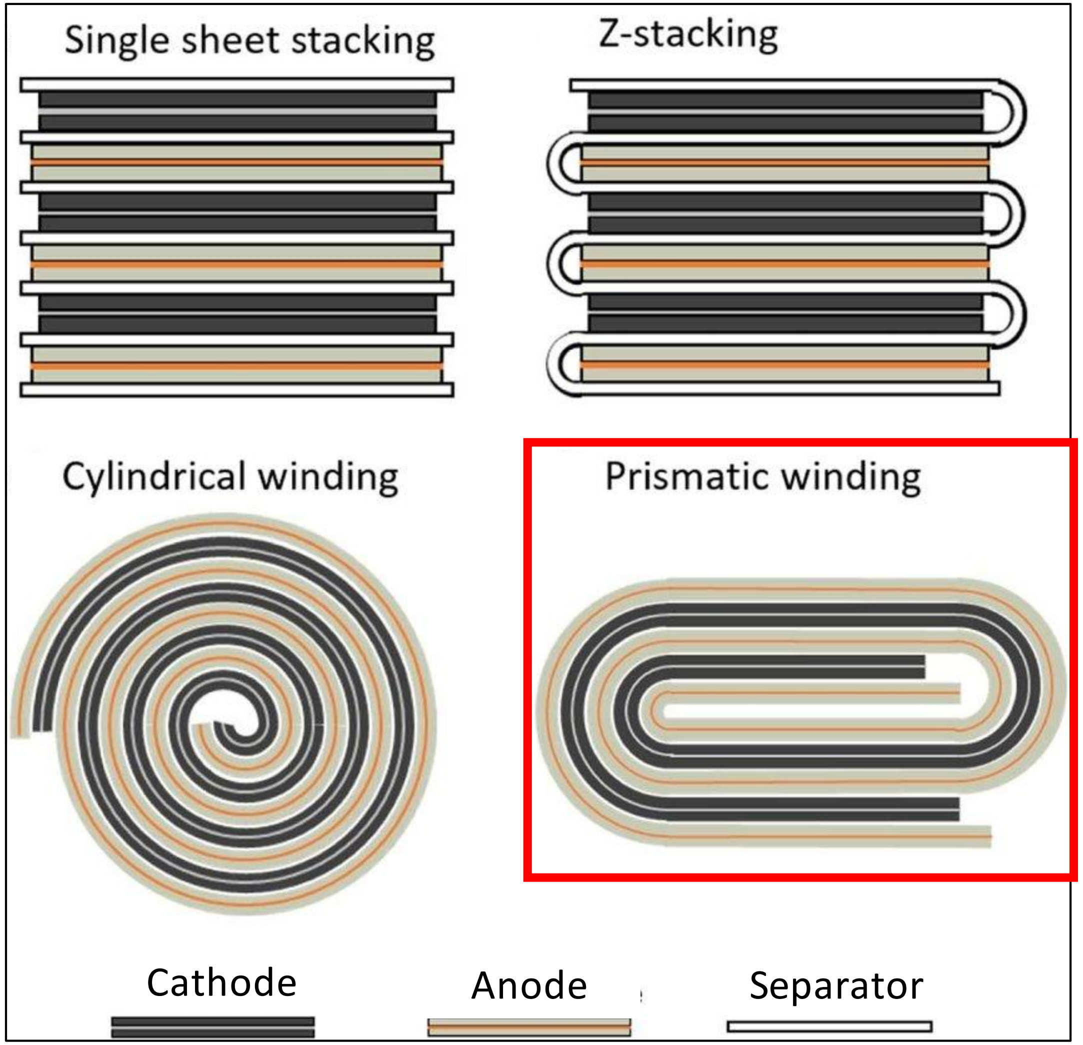
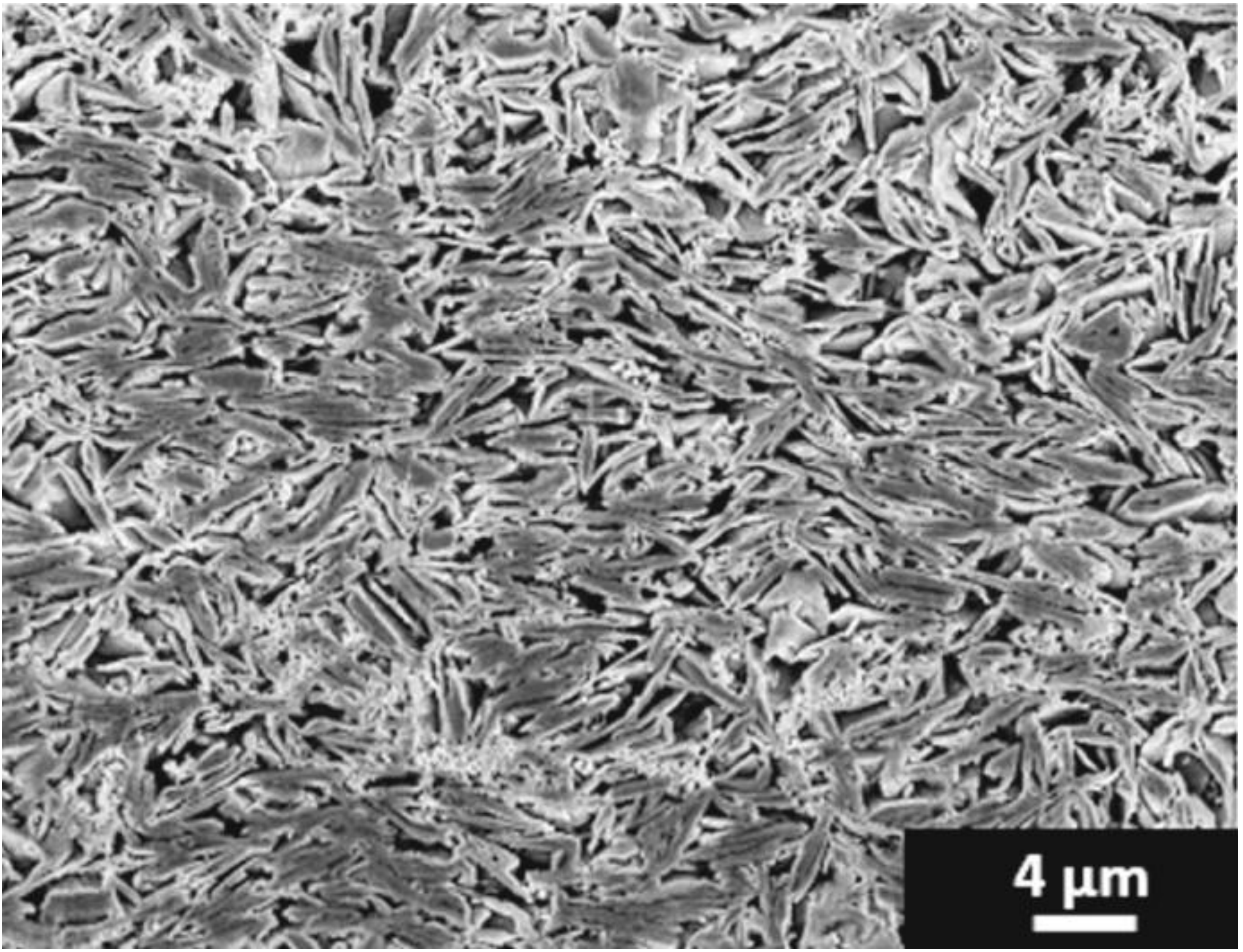


Image sources: https://www.flickr.com/photos/argonne/14547144640, https://iopscience.iop.org/article/10.1149/2.0691916jes

Li-ion batteries: cells and electrode microstructure

Graphite anode



NMC cathode

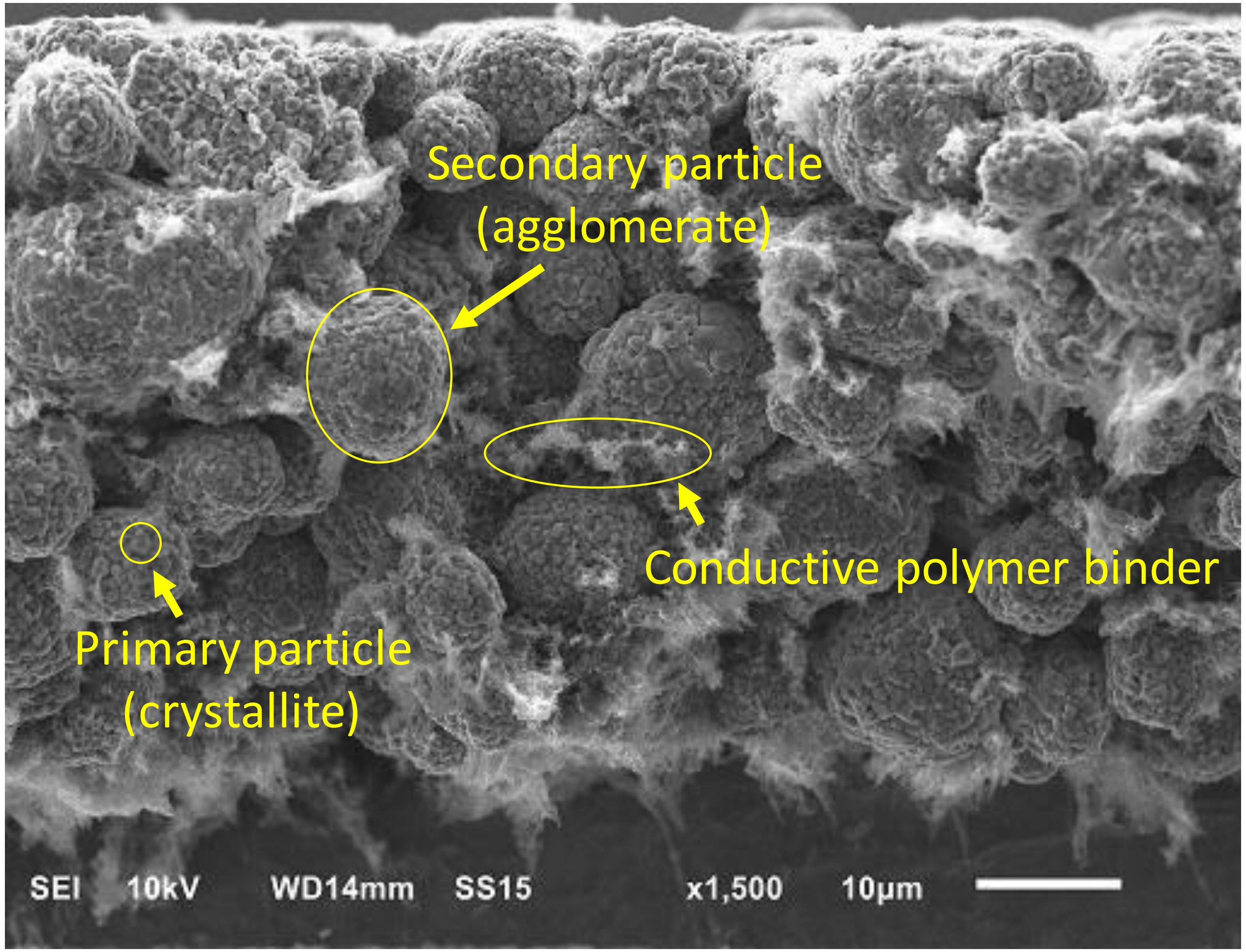
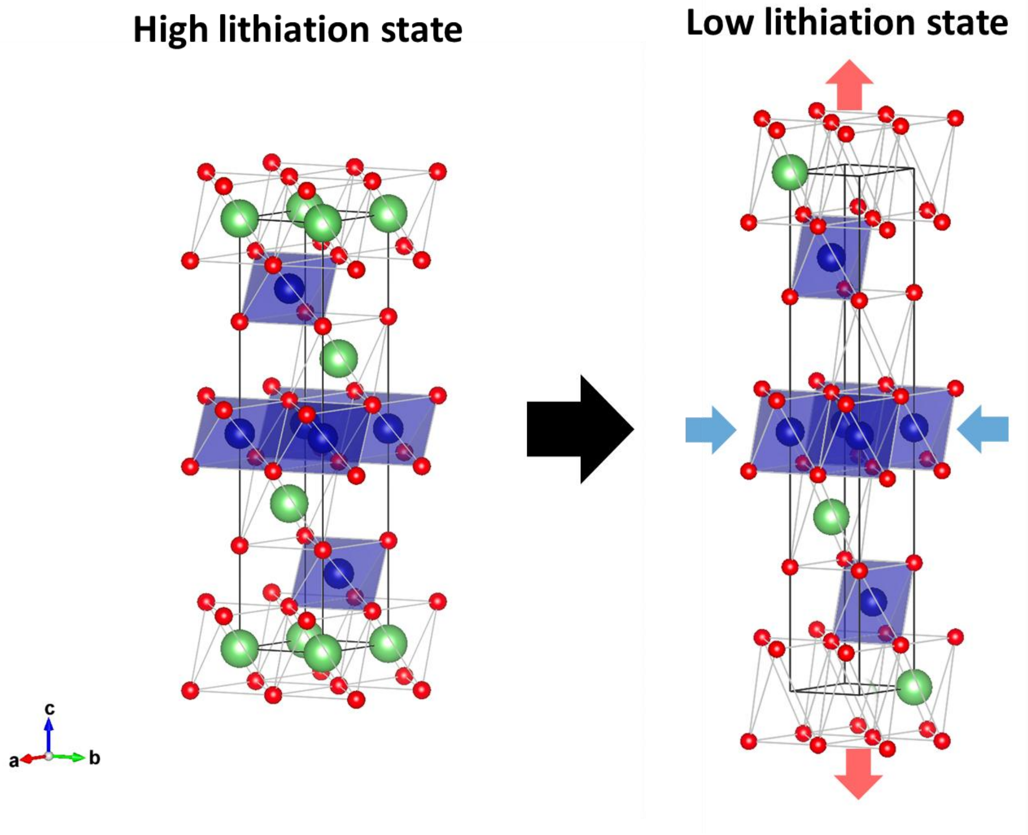
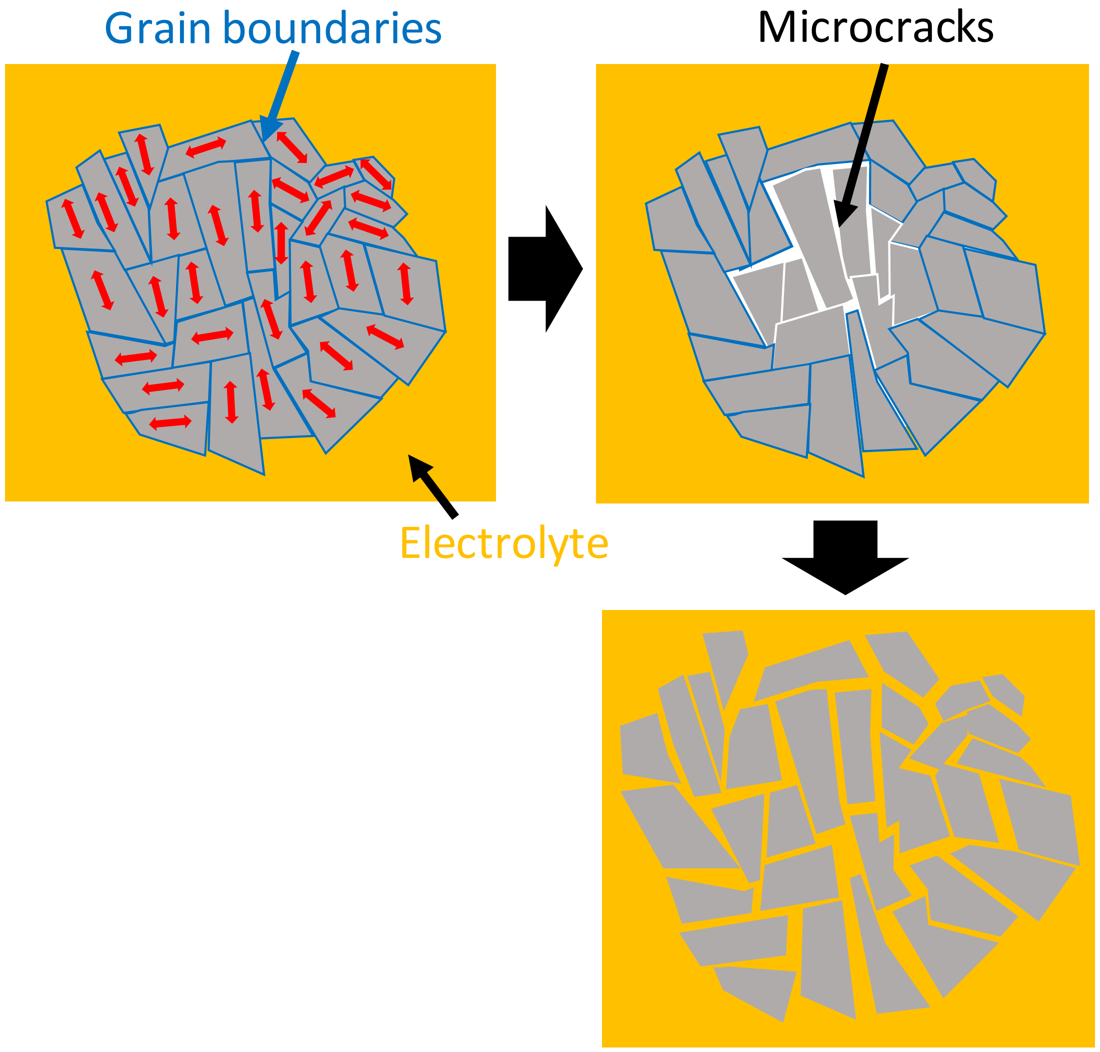


Image sources: https://www.flickr.com/photos/argonne/14547144640, Jeschull et al., J. Electrochem. Soc., 167, 100535 (2020)

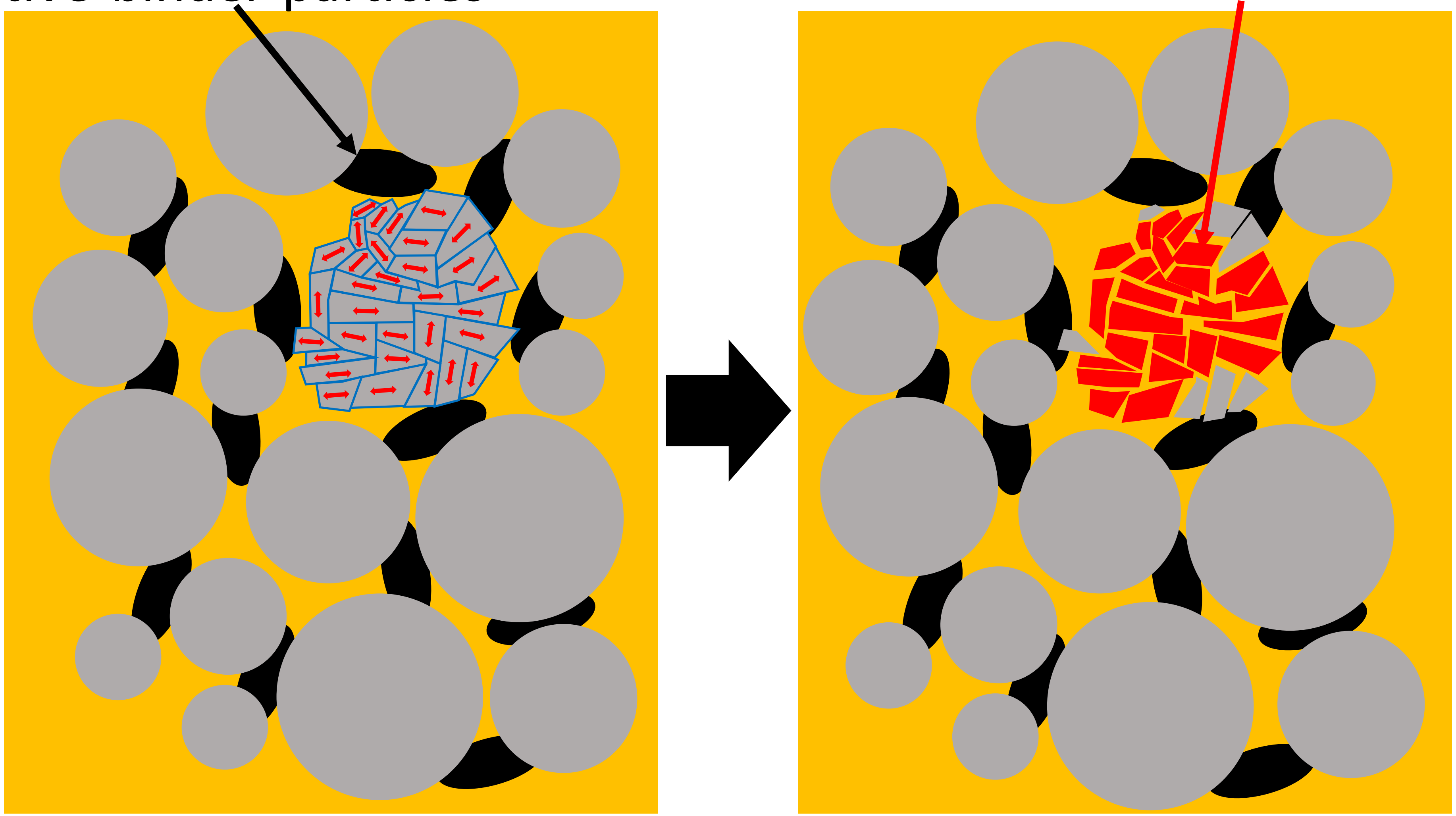
Cathode microcracking

- Anisotropic volume change in NMC and NCA causes significant stress at grain boundaries



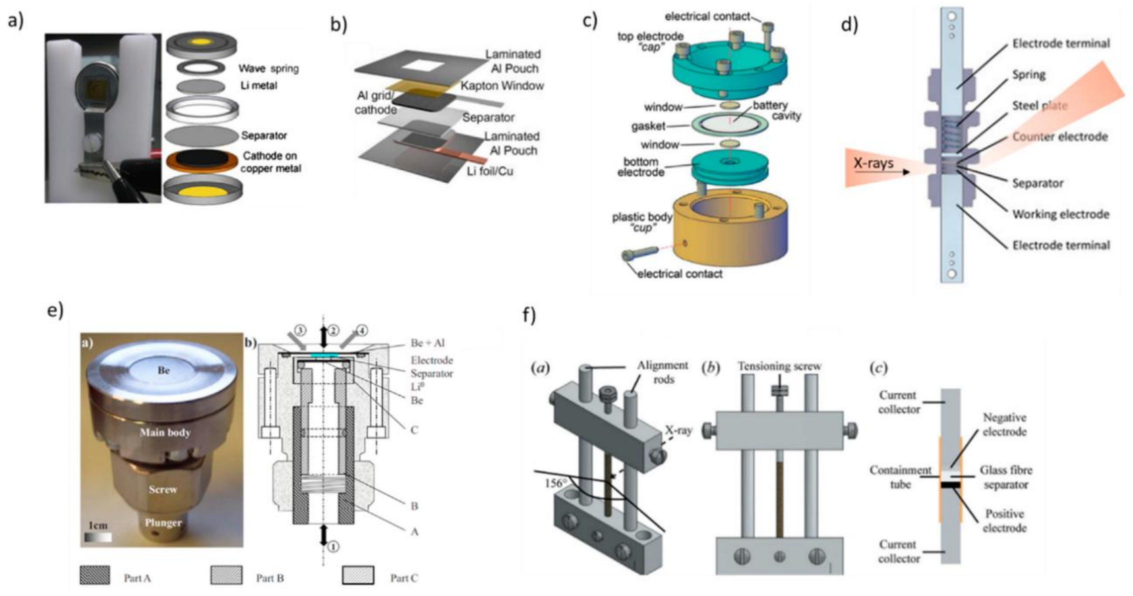


Cathode microcracking: electrical disconnection



In-situ cells vs commercial cells

In-situ cells



Pros:

- Optimized for x-ray experiments
- can be made in house
- Well suited to short, simple experiments

Cons:

- Not fully representative of real-world conditions
- Not built for long-term cycling
- Sensitive to alignment
- Can have poor reproducibility

Commercial cells

Pros:

- Real-world form factor
- Built for long-term cycling
- Highly reproducible
- Can test cells from the field

Cons:

- Not optimized for x-ray experiments
- Non-active components can interfere with data collection
- Need high x-ray energy to penetrate cells (especially steel casings)

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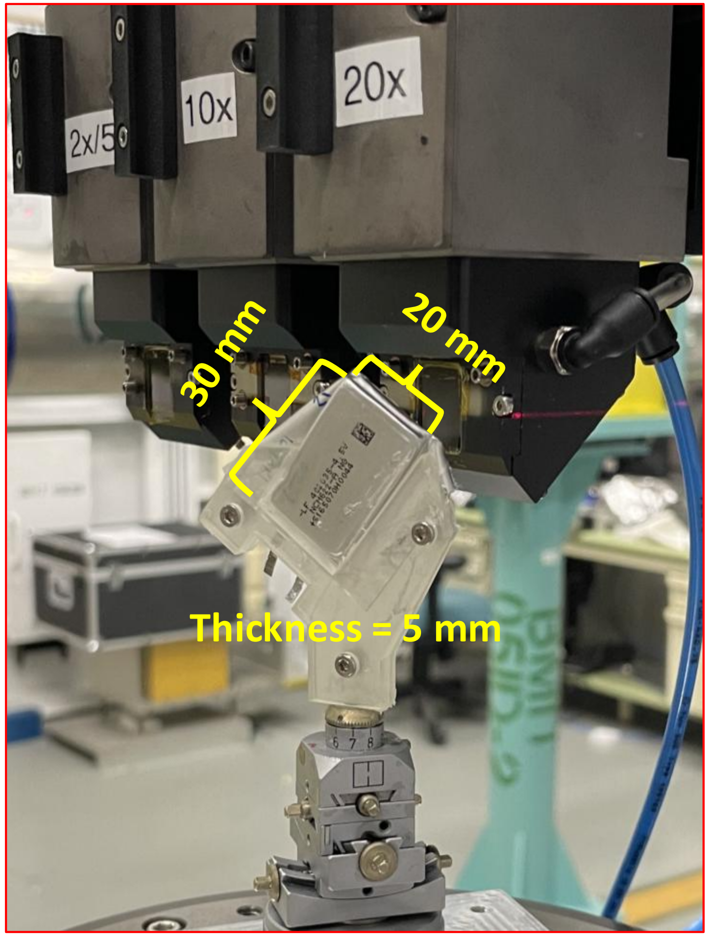
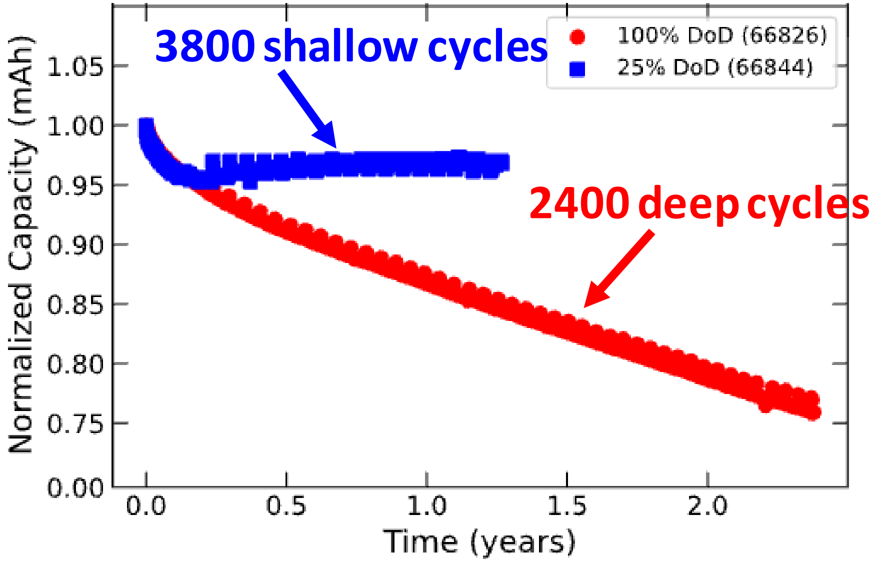
Figure by: A Llewellyn et al., Condens. Matter, 5(4), 75 (2020)

Long-Term Cycling of NMC622/NG Pouch Cells



- **NMC622** battery cells were cycled from 0% to 100% for 2.5 years
  - **Heavily cycled cell: deep cycling (0%-100%) for 2400 cycles (960k km) over 2.5 years**
  - **Lightly cycled cell: shallow cycling (75%-100%) for 3800 cycles (380k kms) over 1.5 years**
- A "fresh" cell was also used as a control



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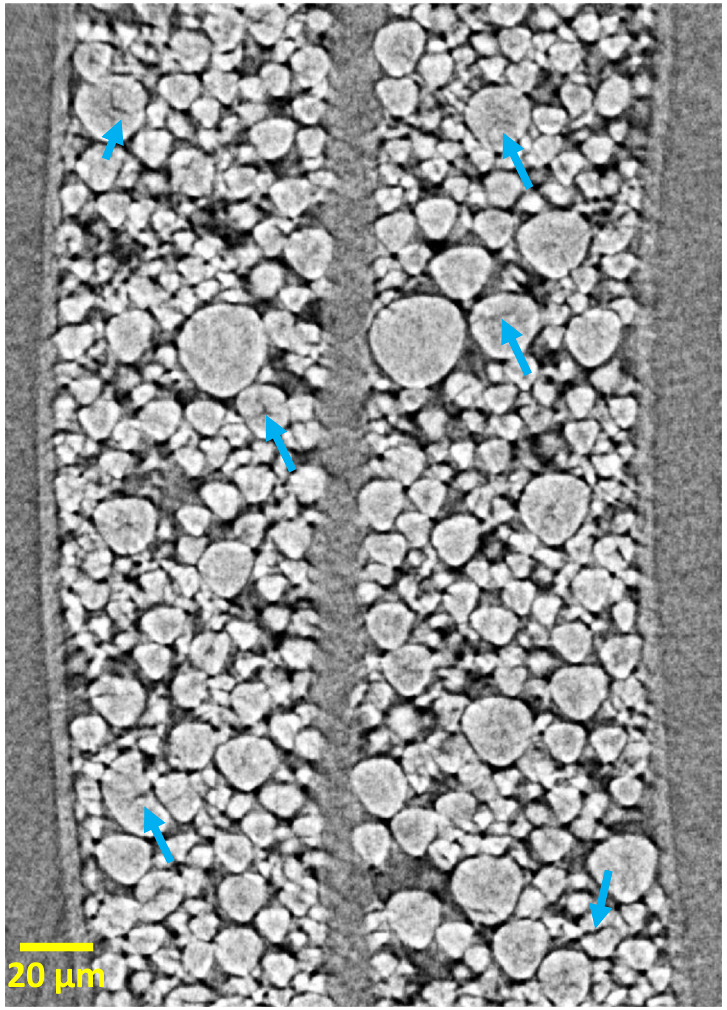
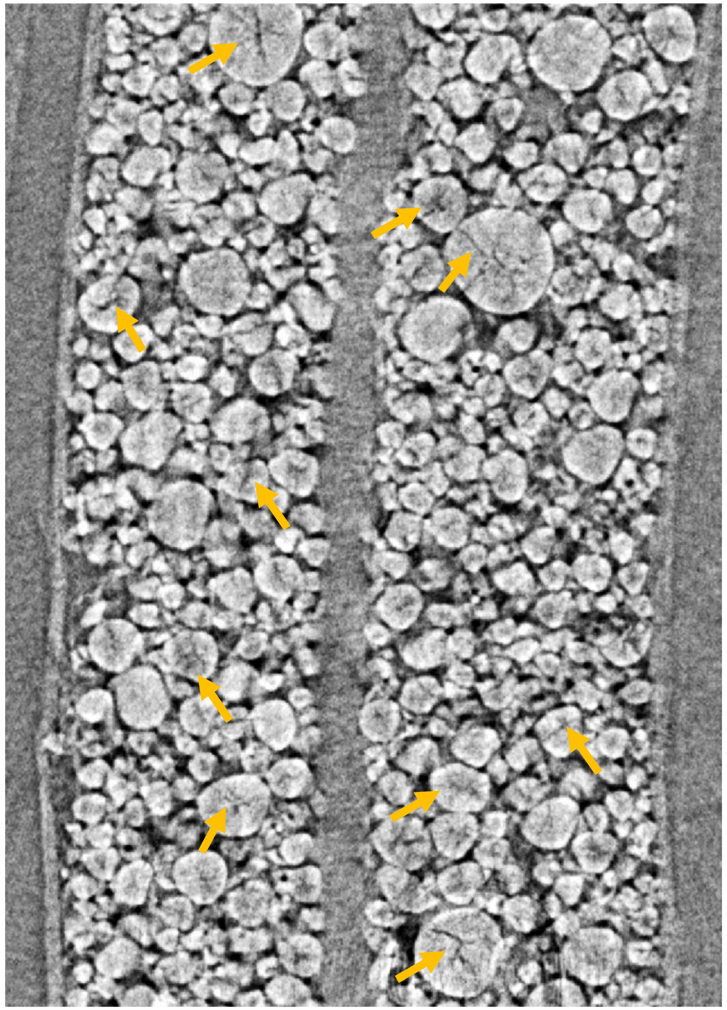
T. Bond et al., J. Electrochem. Soc. 169, 080531 (2022)

Microcracking after heavy cycling

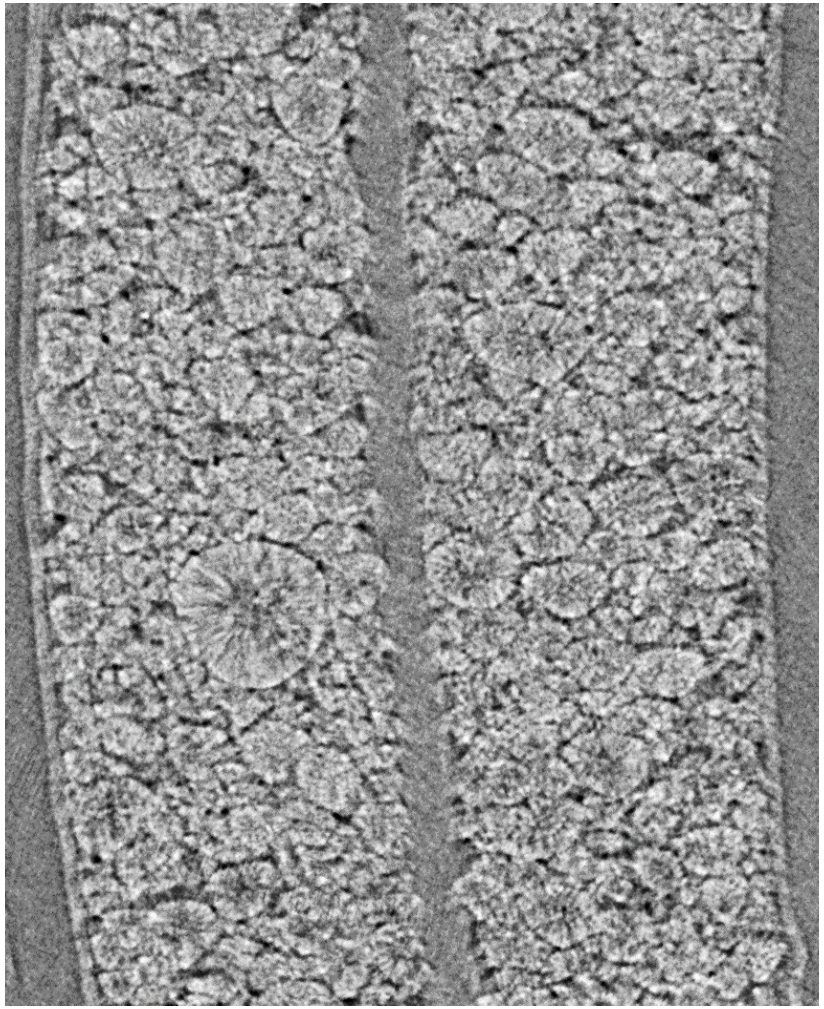
Control cell



Lightly cycled cell



Heavily cycled cell



T. Bond et al., J. Electrochem. Soc. 169, 080531 (2022)

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Time-resolved mapping with Synchrotron XRD

- Experimental considerations
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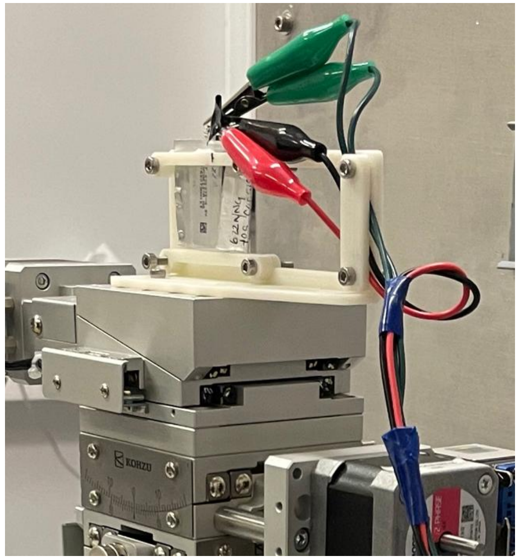
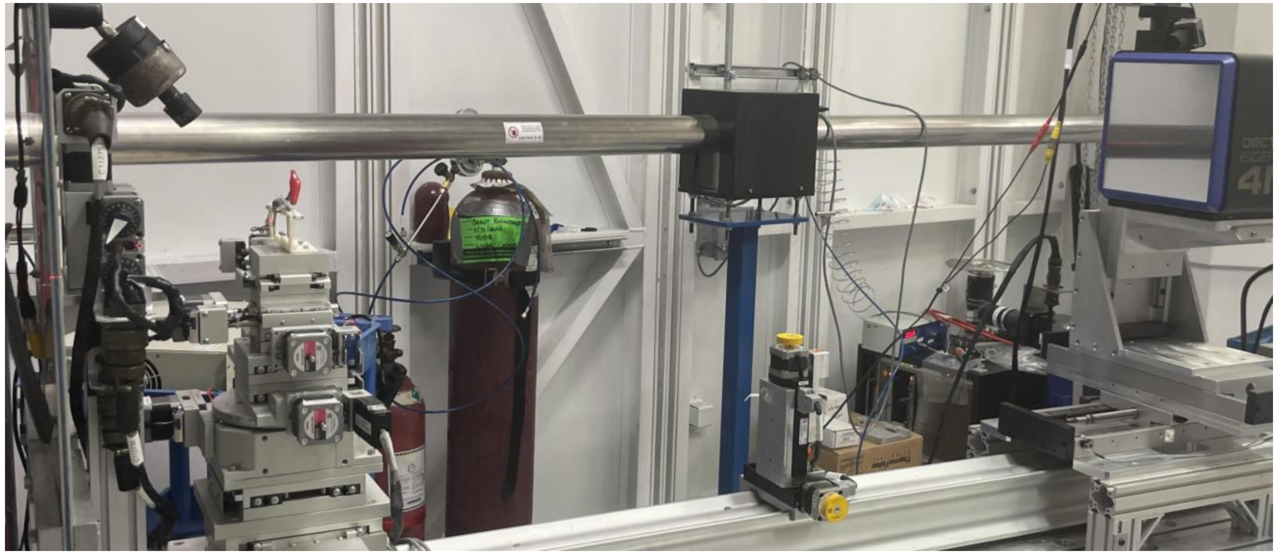
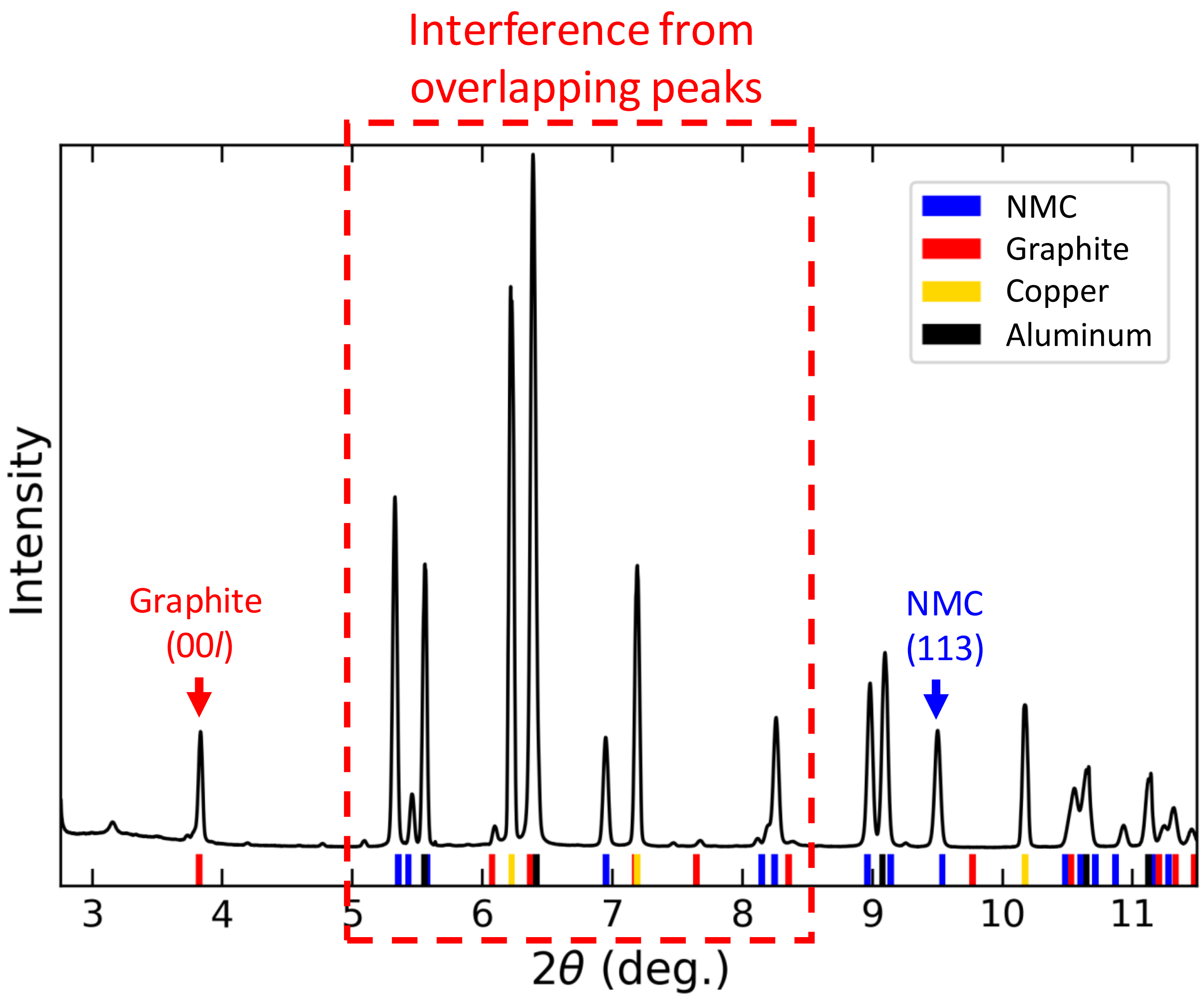
Synchrotron XRD of cycled pouch cells

- Flat pouch cells are great for transmission XRD
- This work was done on the BXDS high-energy wiggler beamline
- Beam width ~200 µm







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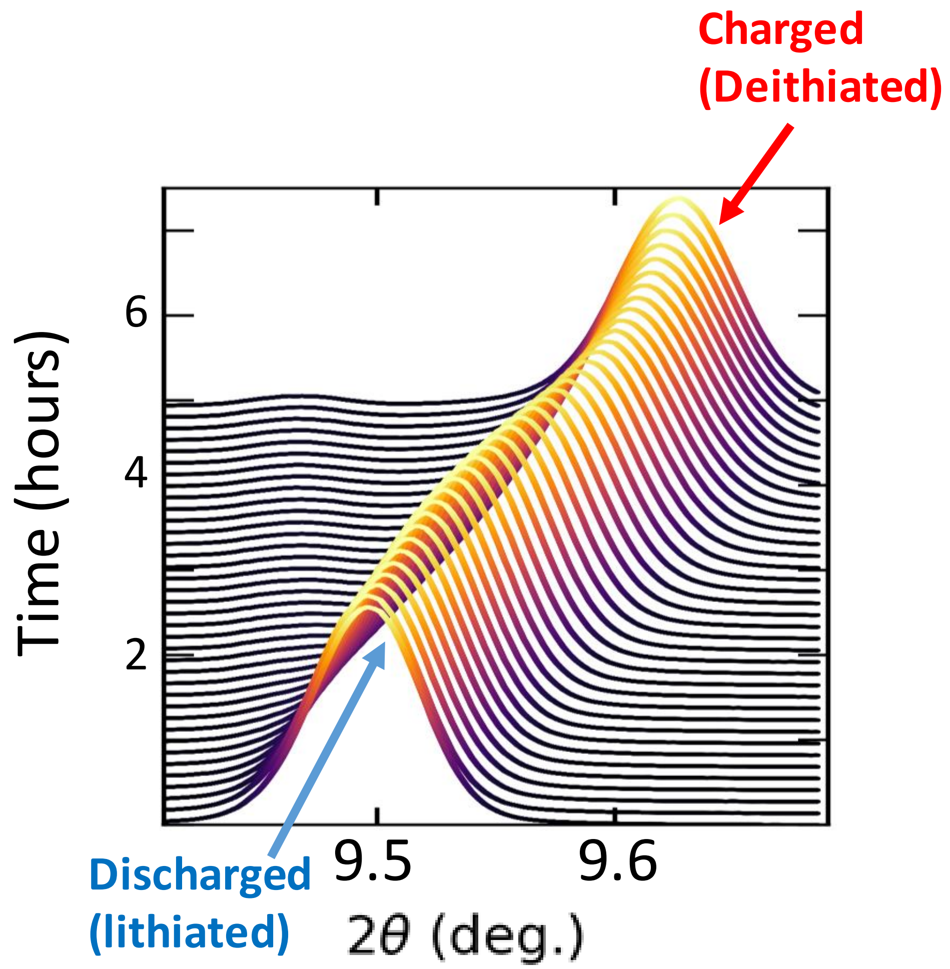
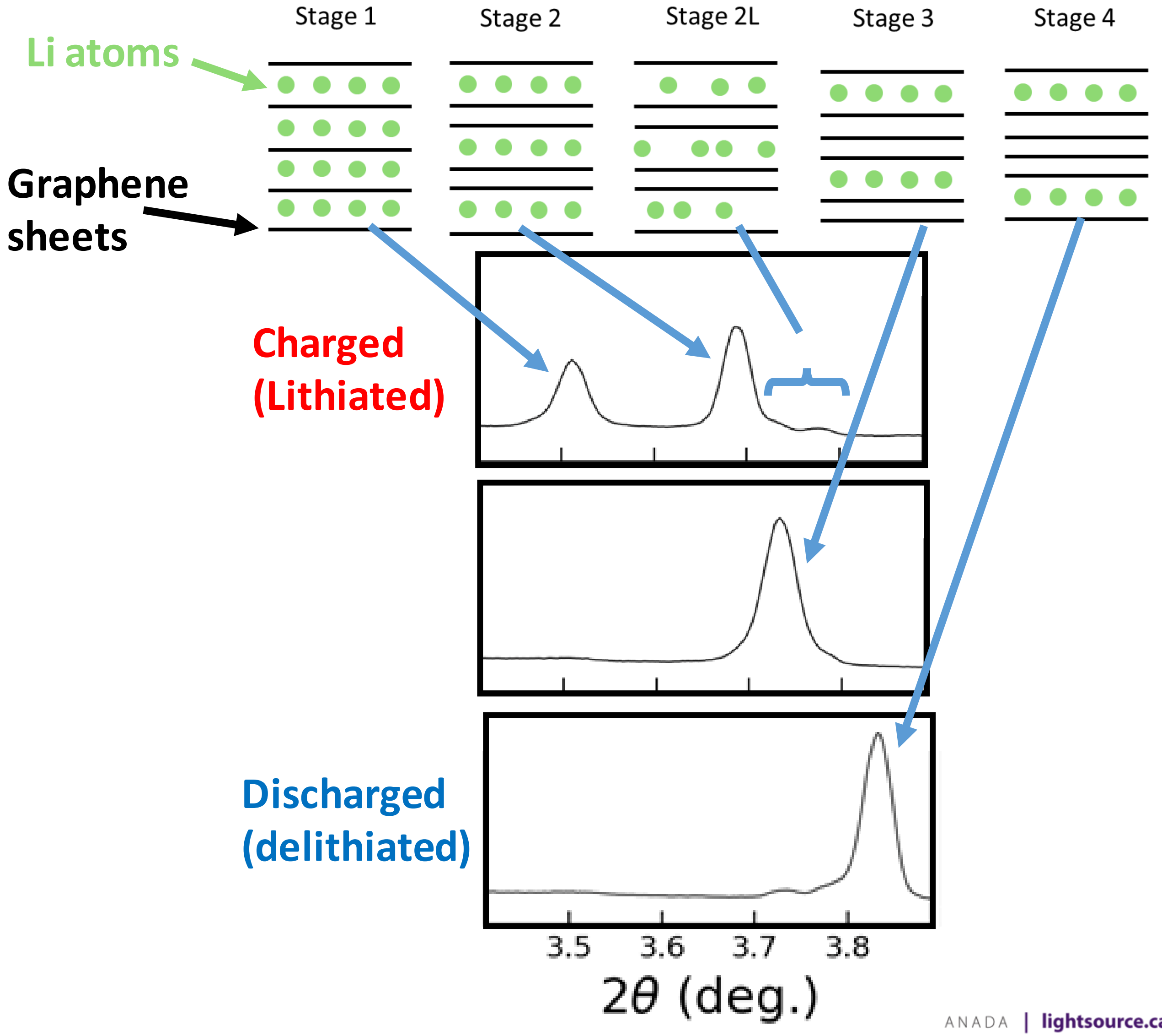
NMC (113) and graphite (00*l*) peaks

NMC (113) peak



Graphite (00*l*) peak



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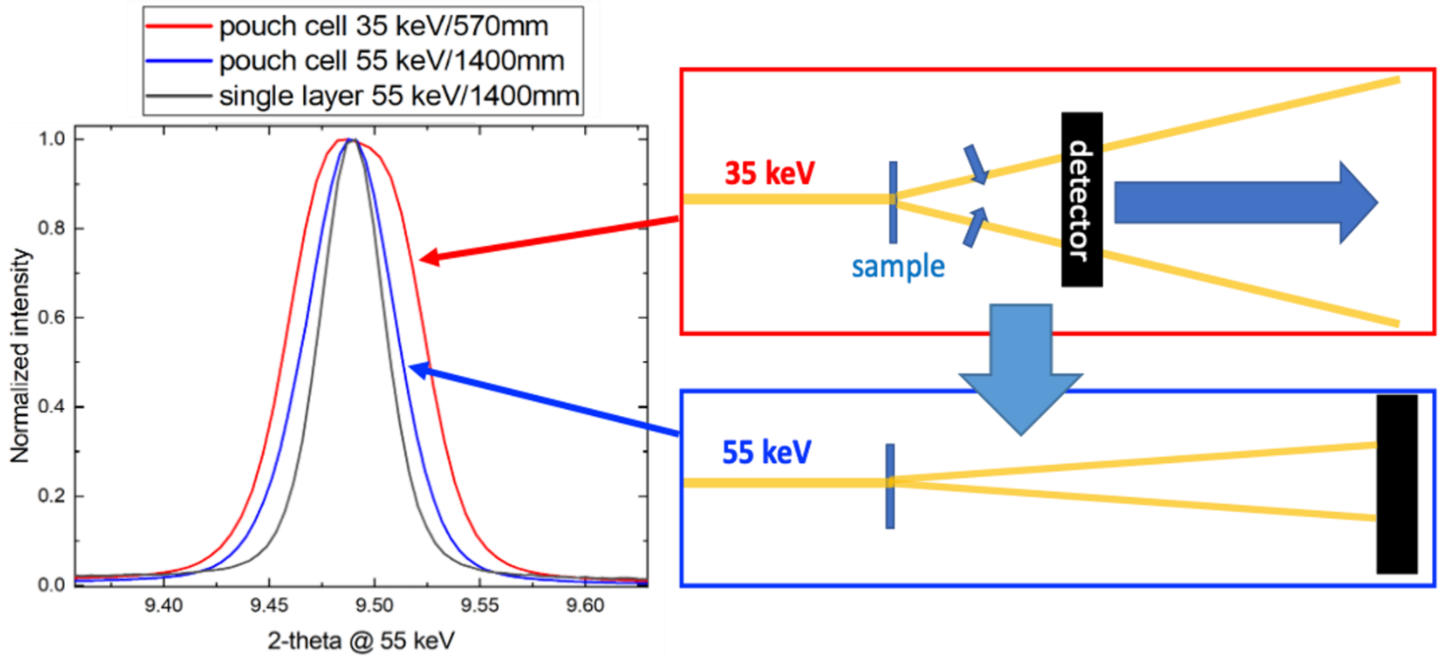
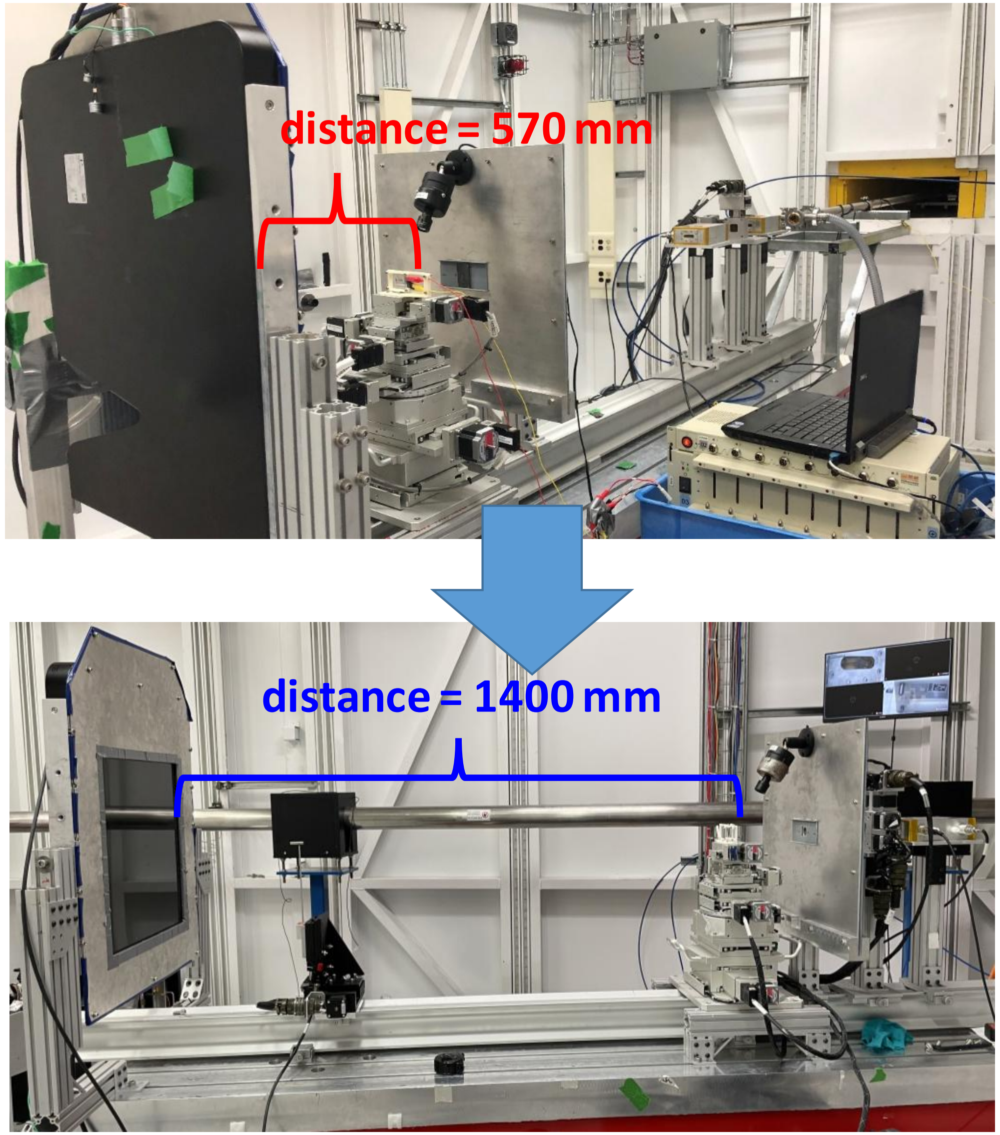
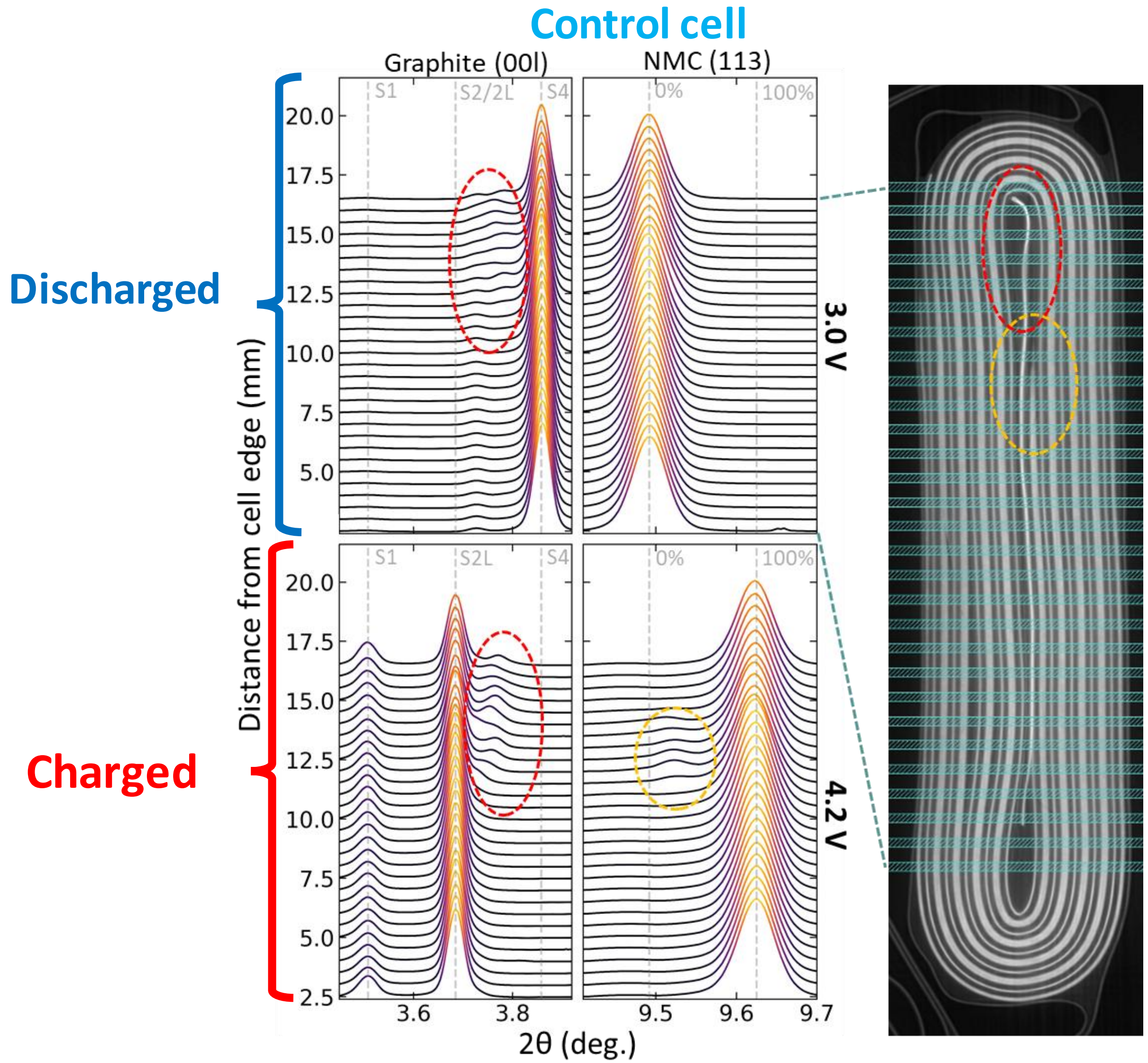
Thick samples require large sample-detector distance

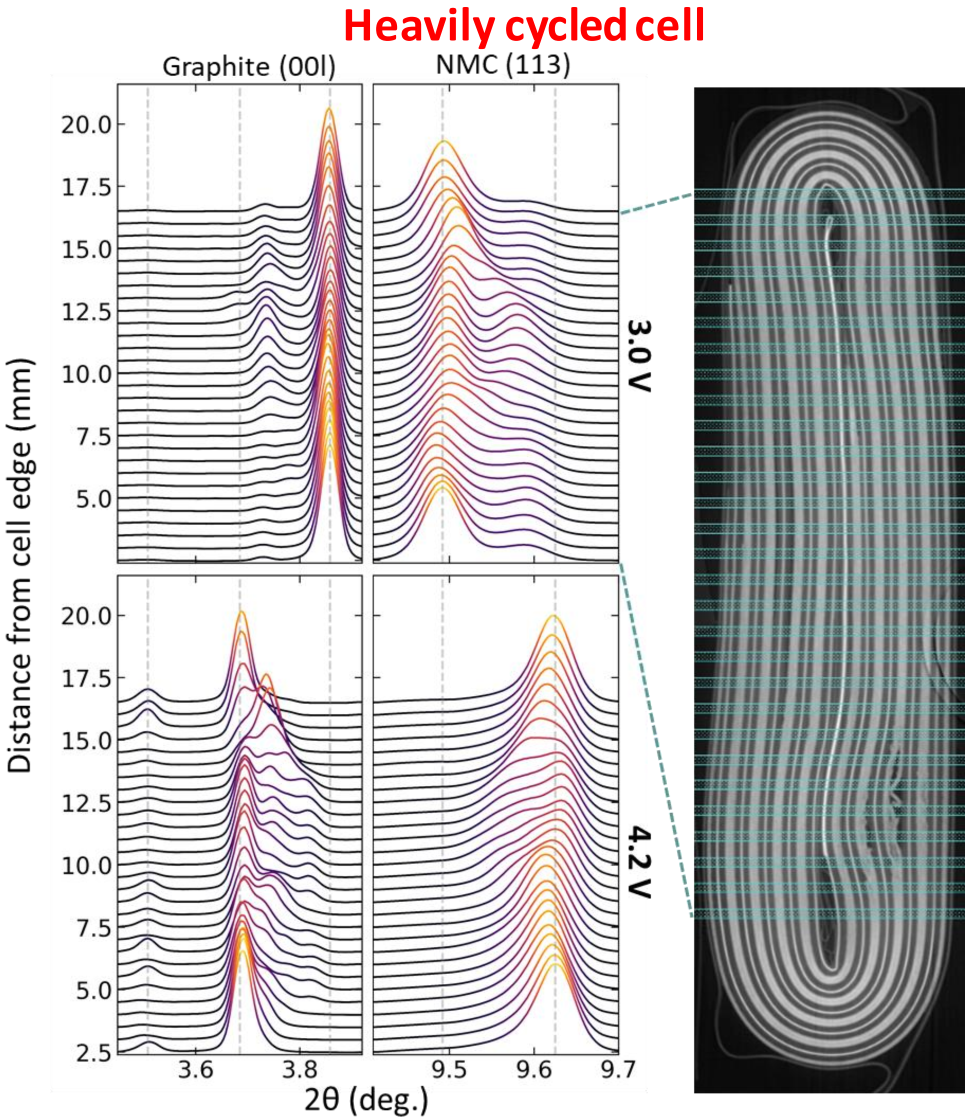
- We want to reduce peak broadening due to sample thickness
- You can do this by increasing sample-detector distance, but you also need to increase beam energy (reduce wavelength)
- We looked at two configurations:
  - Detector distance = 570 mm, Beam Energy = 35 keV
  - Detector distance = 1400 mm, Beam Energy = 55 keV



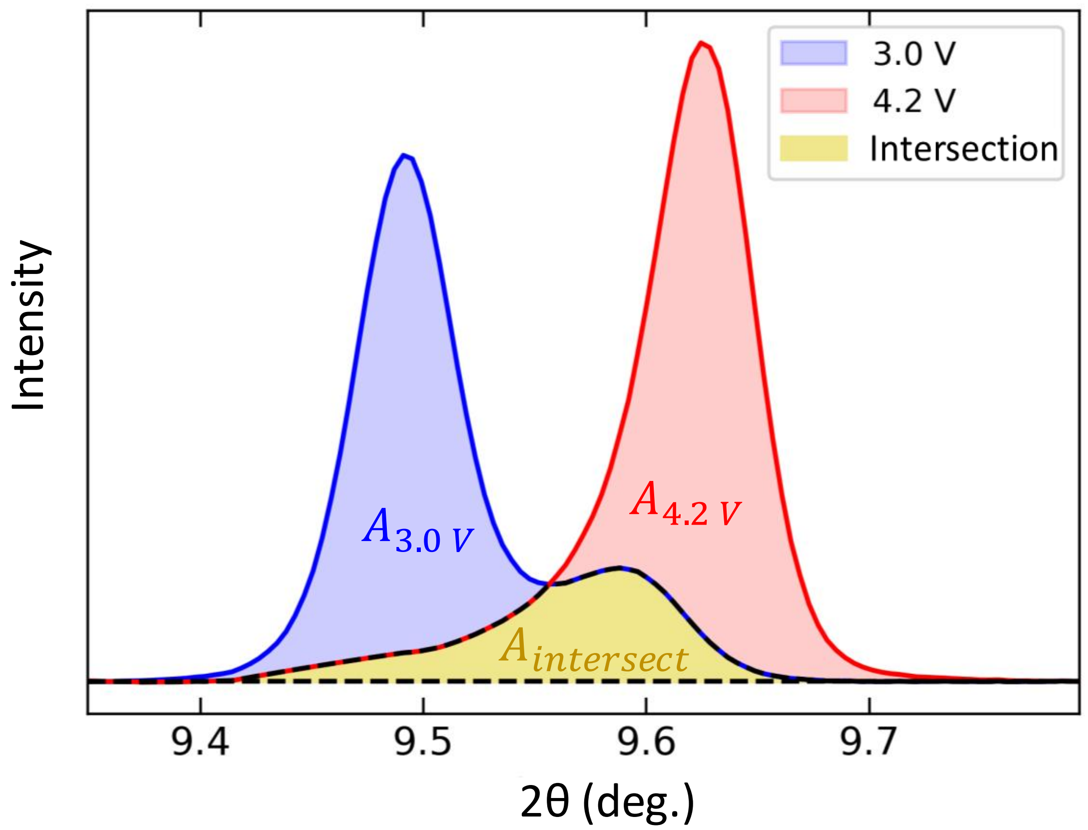


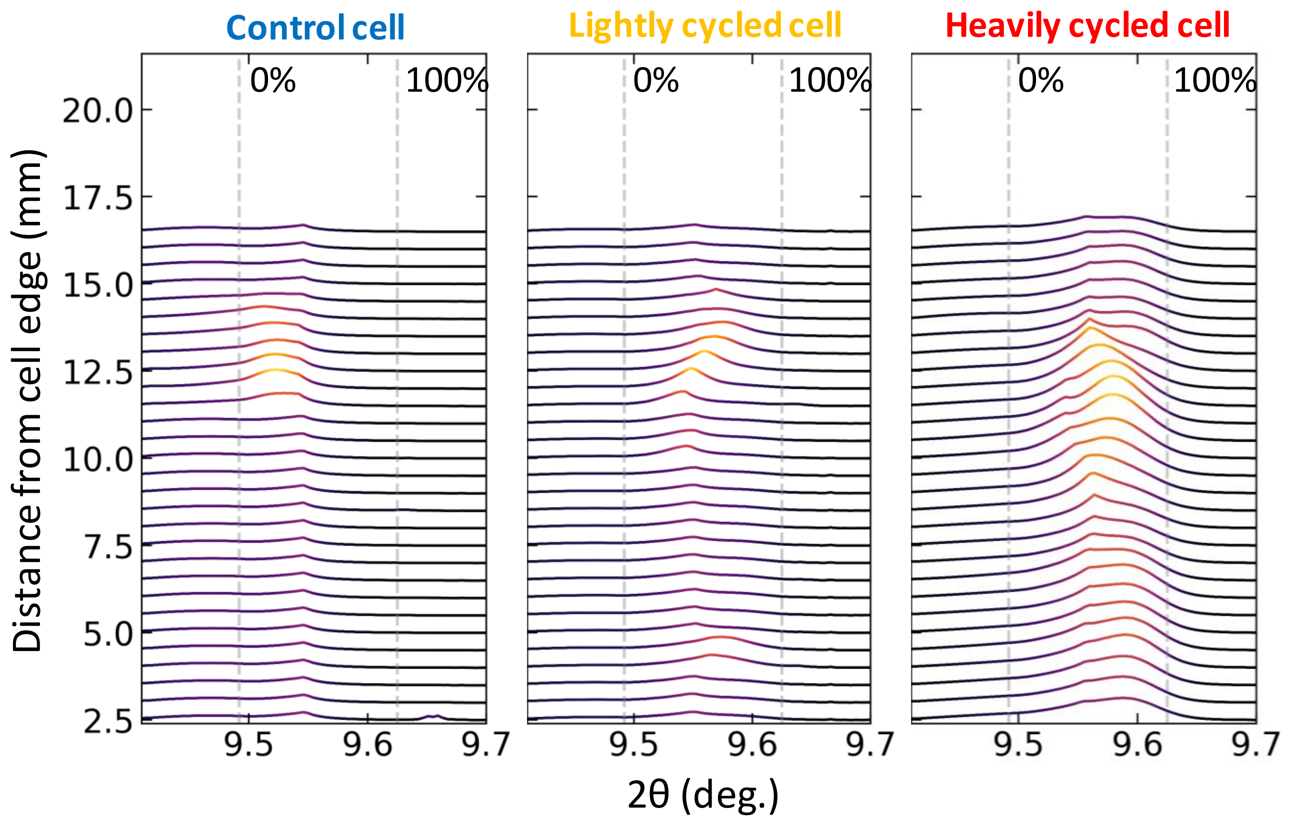
Near-equilibrium: XRD mapping after full charge/discharge





Mapping the distribution of inactive cathode material

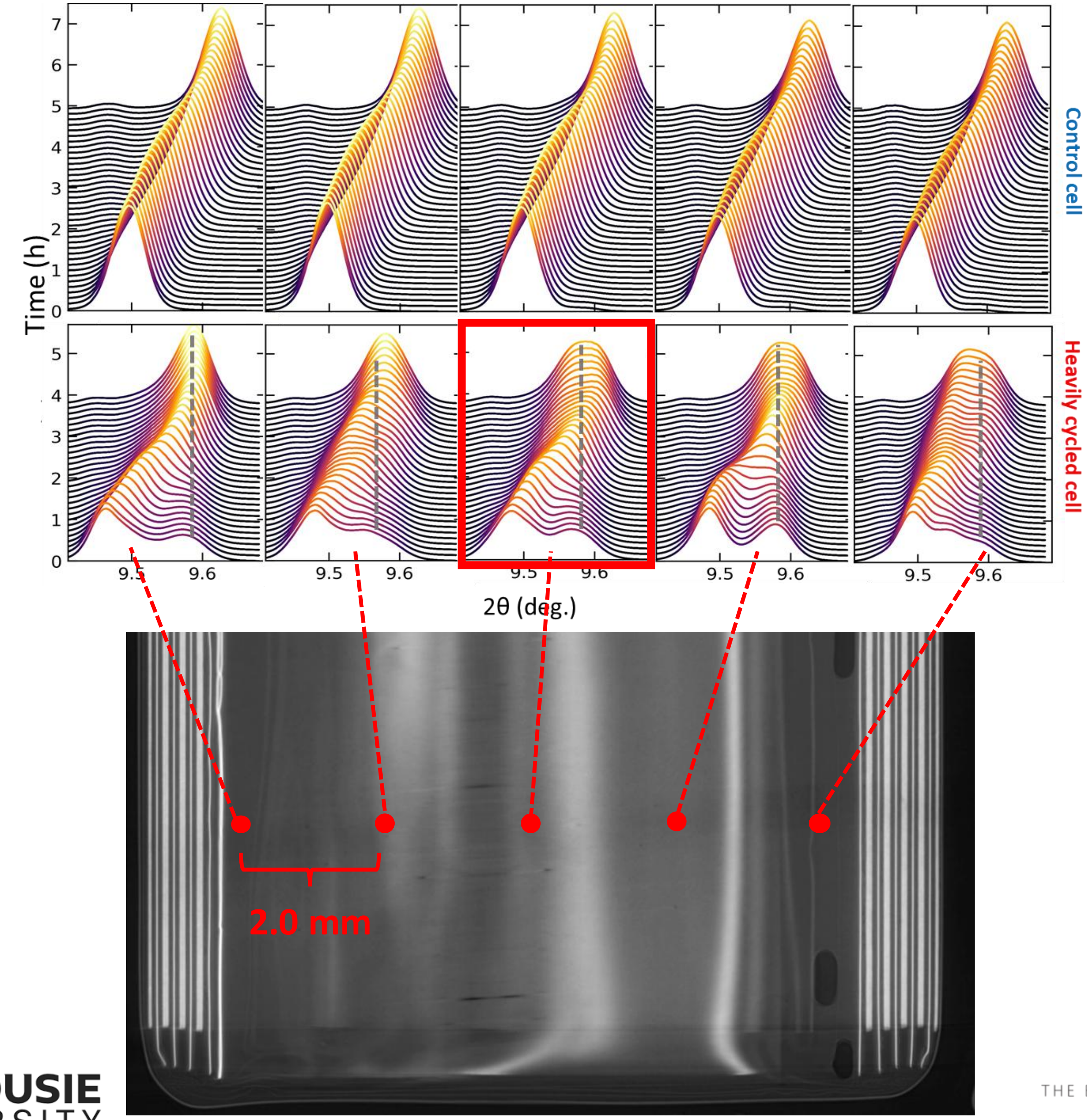




T. Bond et al., J. Electrochem. Soc. 171, 110514 (2024)

Non-equilibrium: operando XRD mapping

- If we repeat this raster scanning, we get both spatially and temporally resolved data
- Gray lines denote peaks that appear to be static



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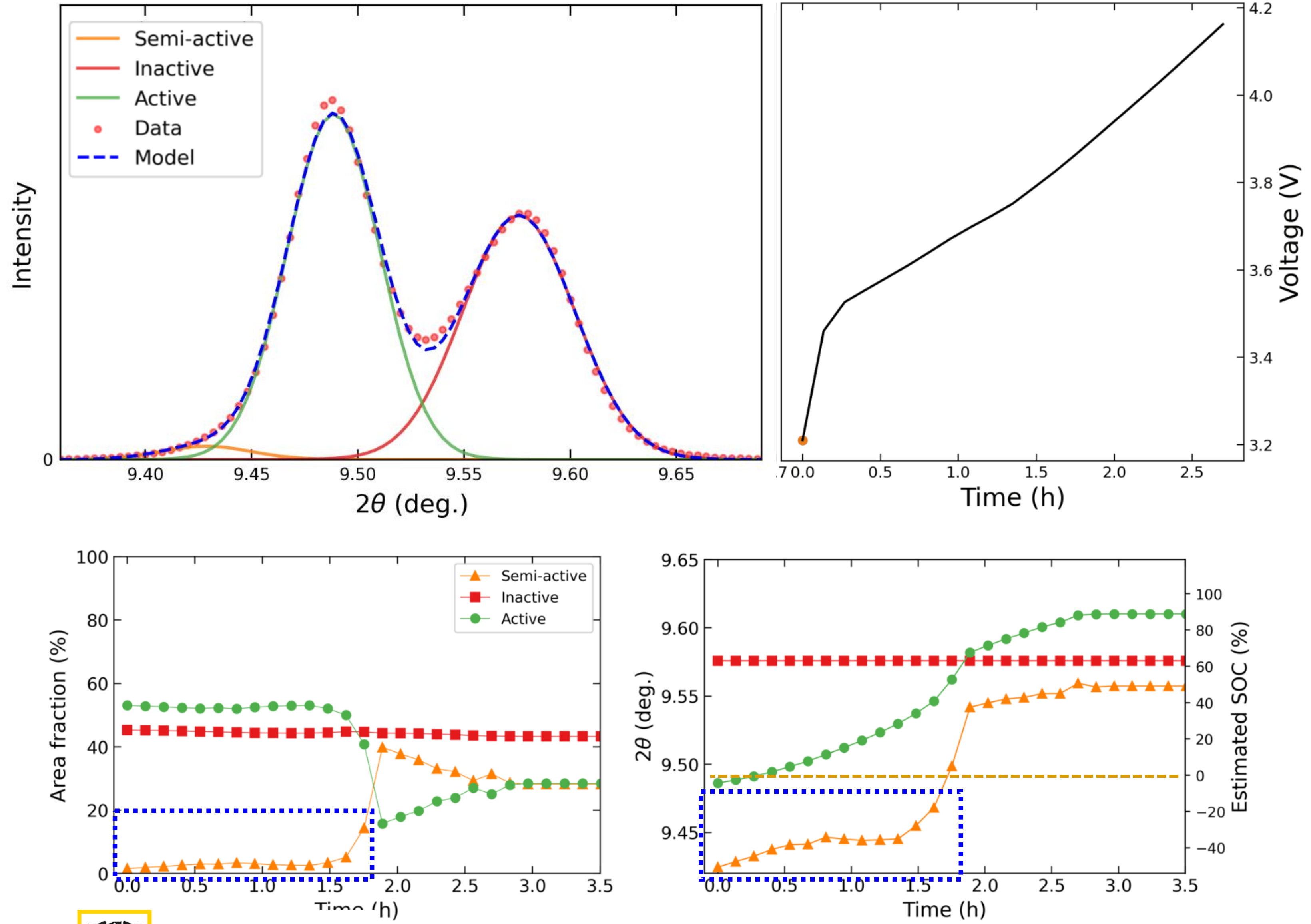
Peak fitting of time-resolved XRD data



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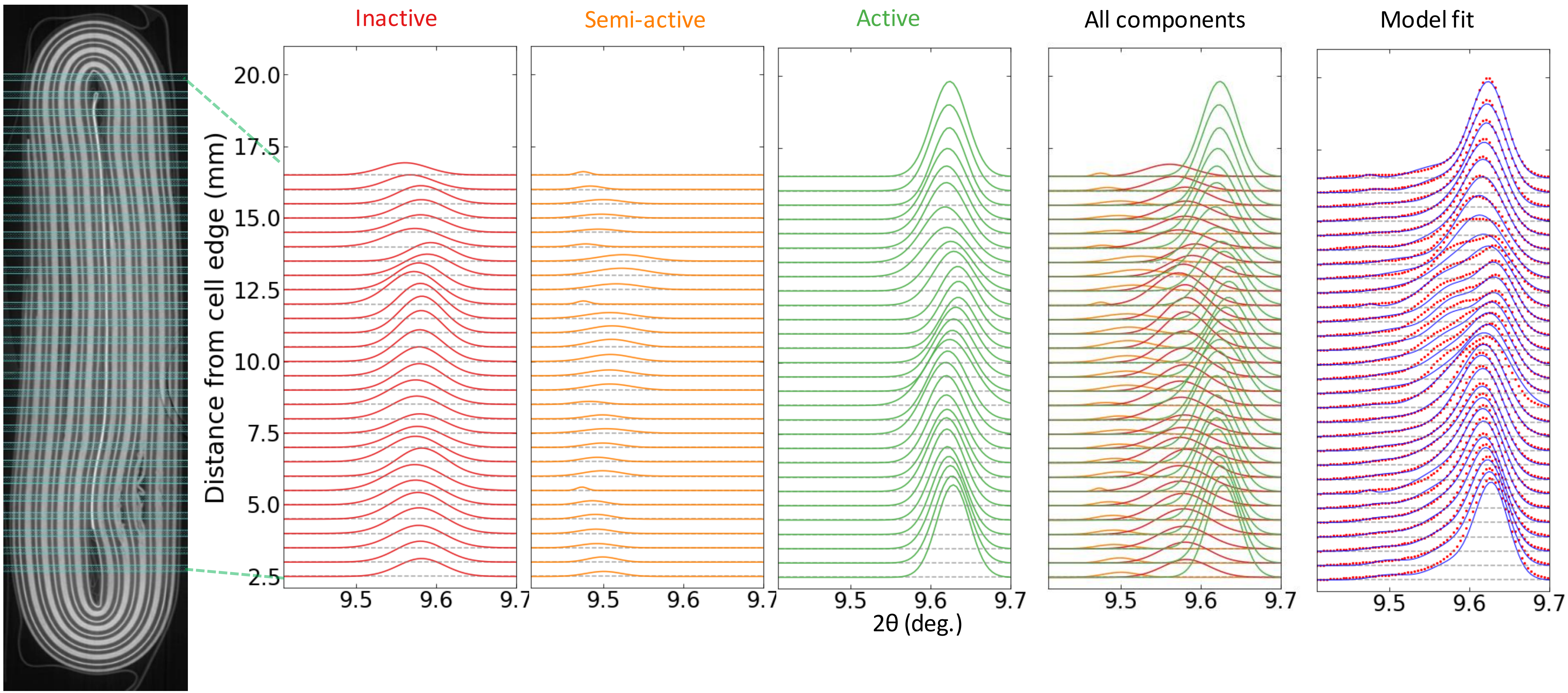
Spatial distribution of model components at equilibrium



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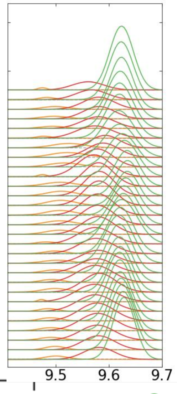
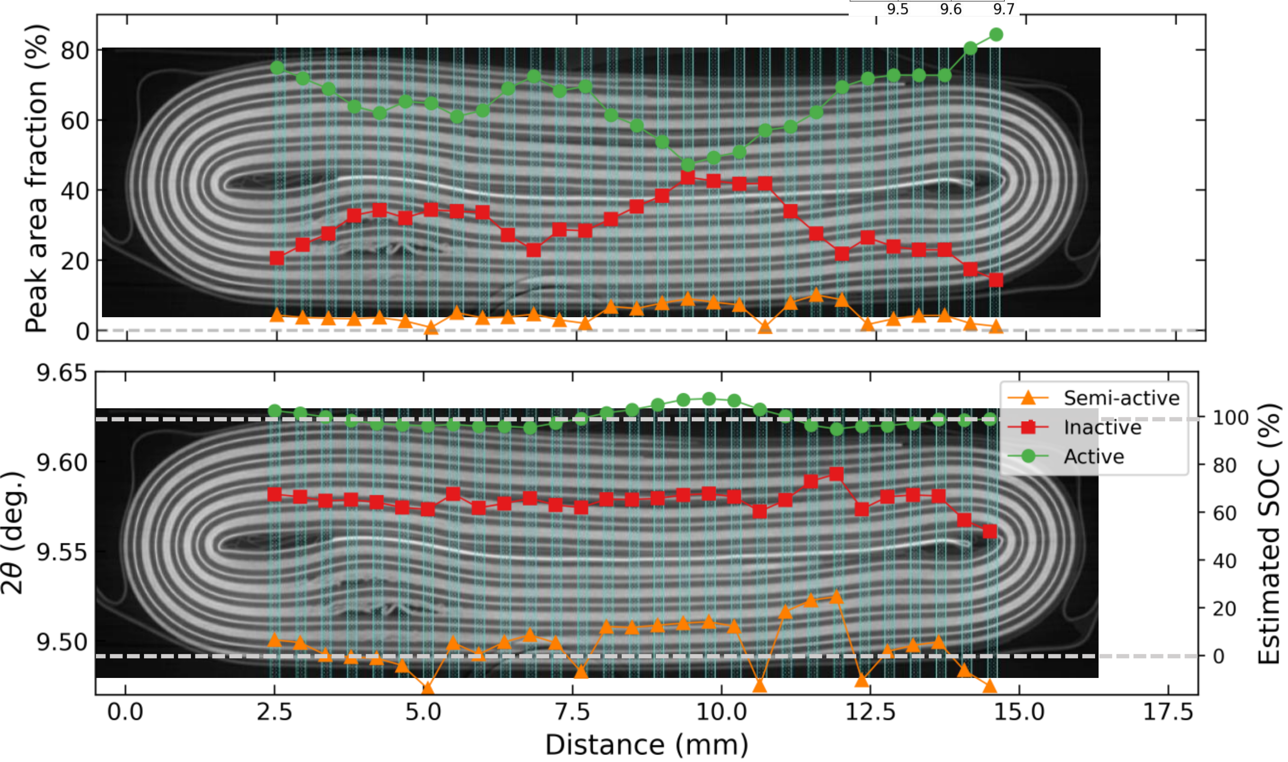
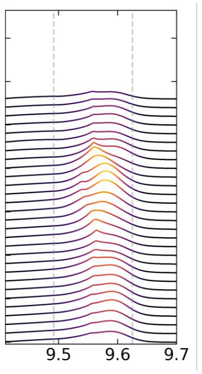
Spatial distribution of model components at equilibrium

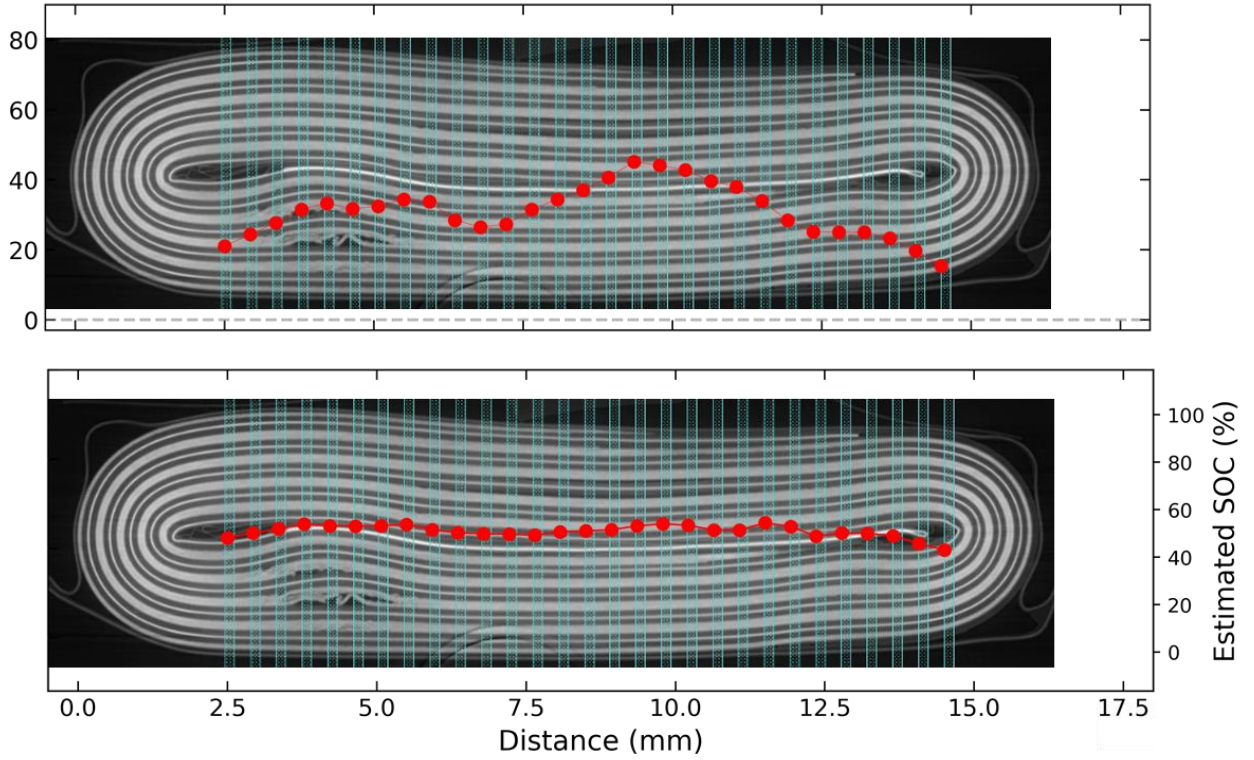
Peak fitting method





Peak overlap method





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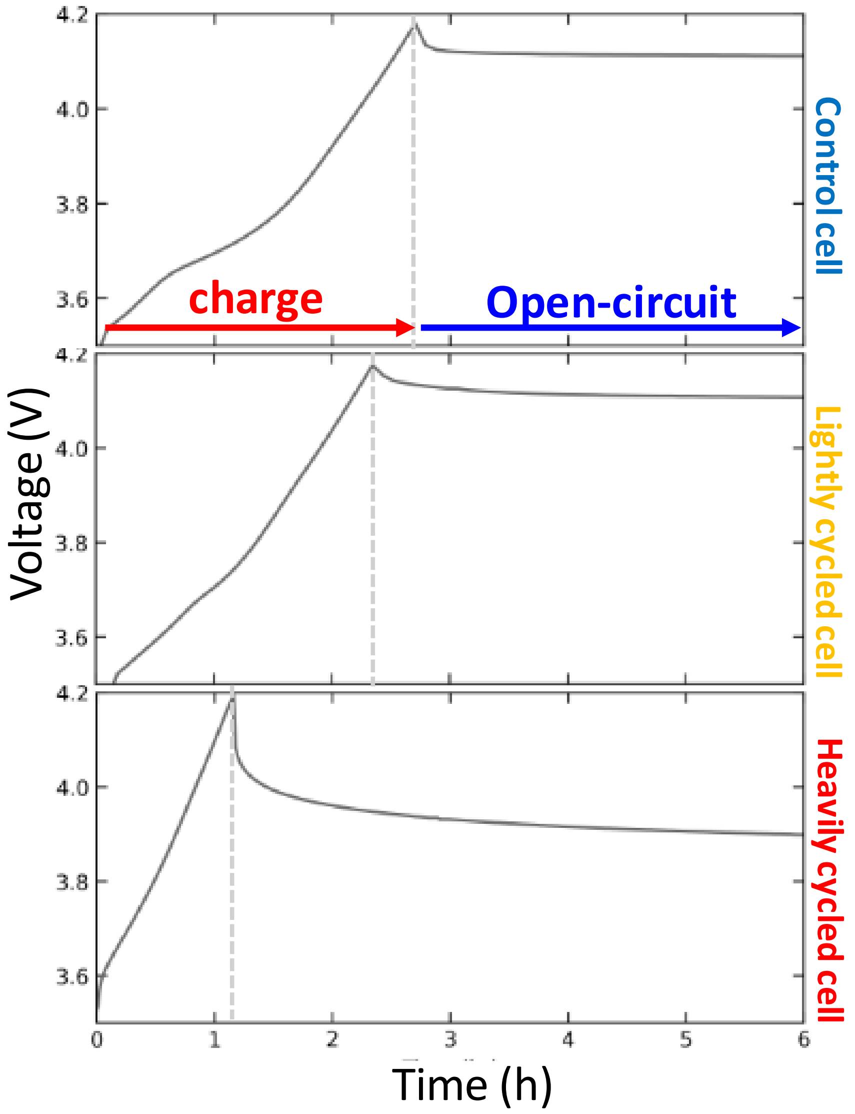
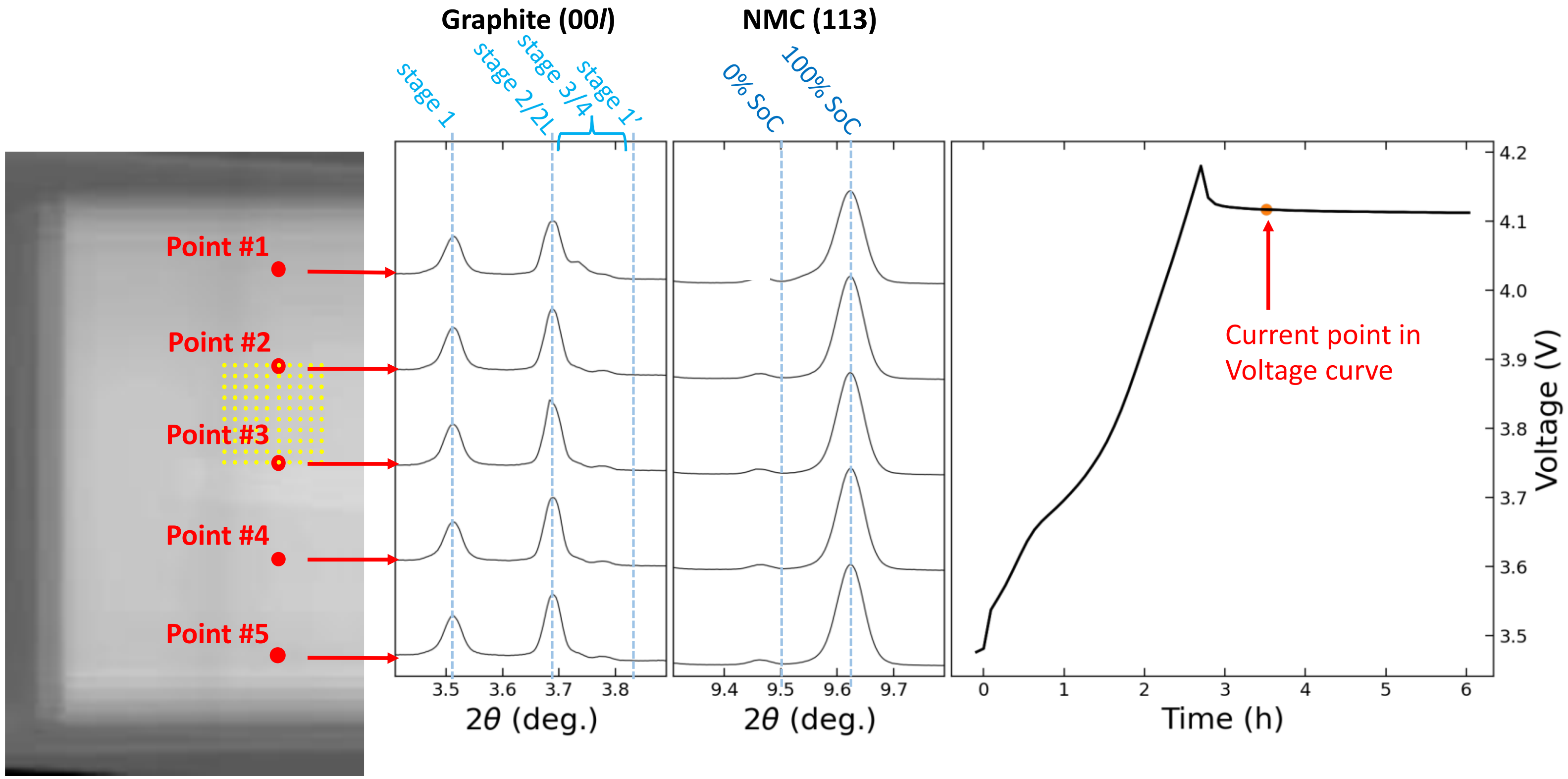
Time-resolved XRD mapping during Open-circuit relaxation





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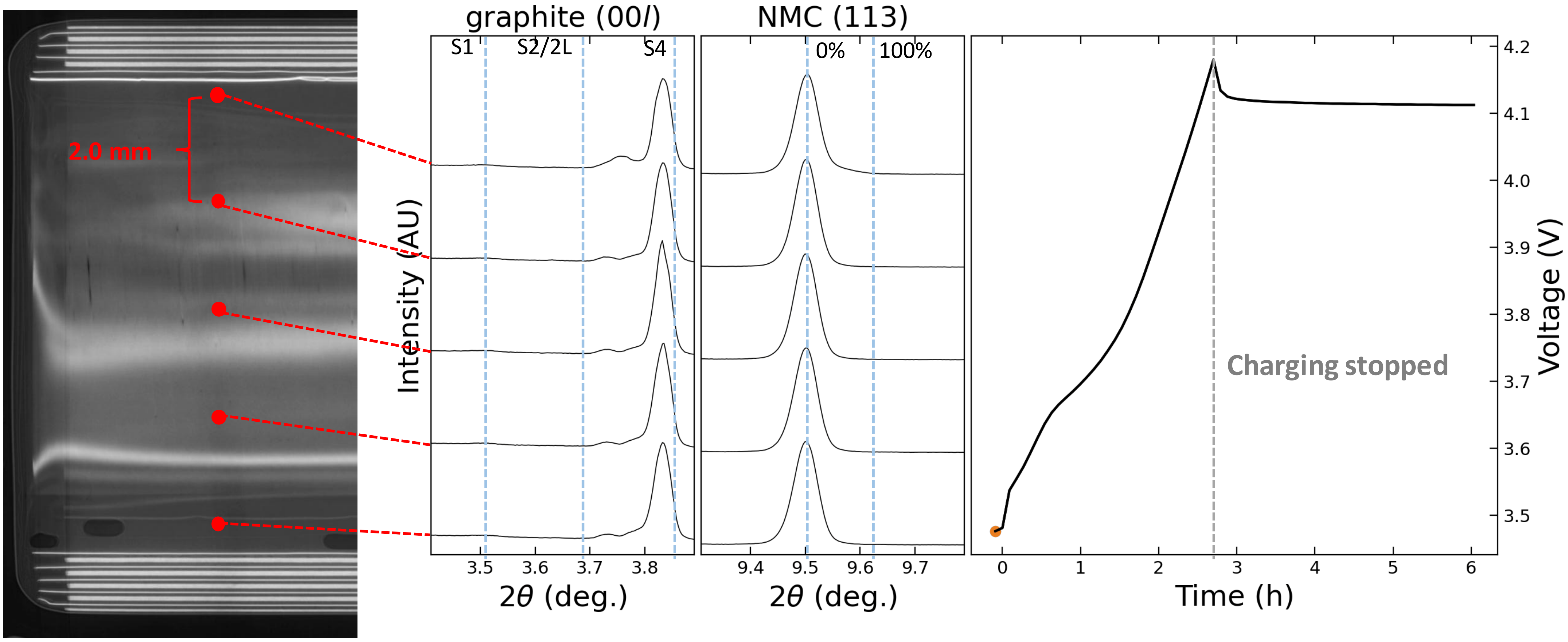
Open-circuit relaxation: control cell



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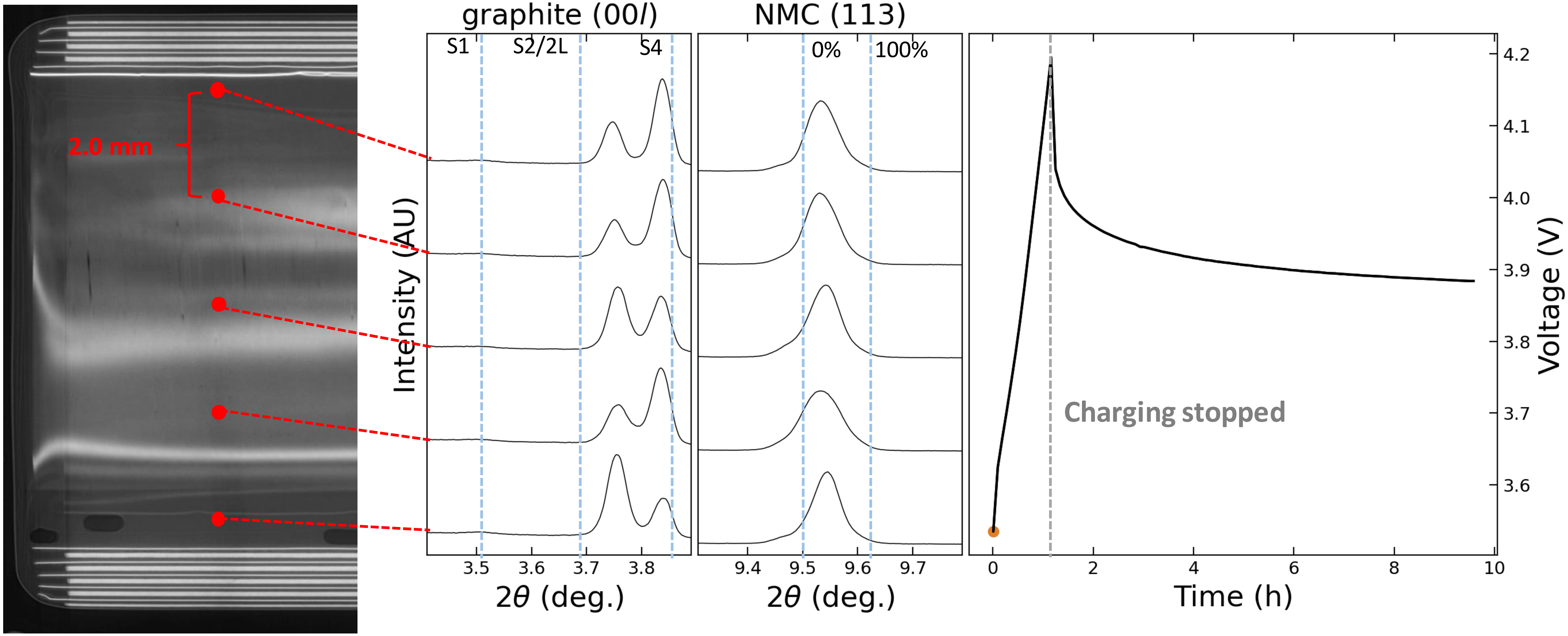
Open-circuit relaxation: heavily cycled cell



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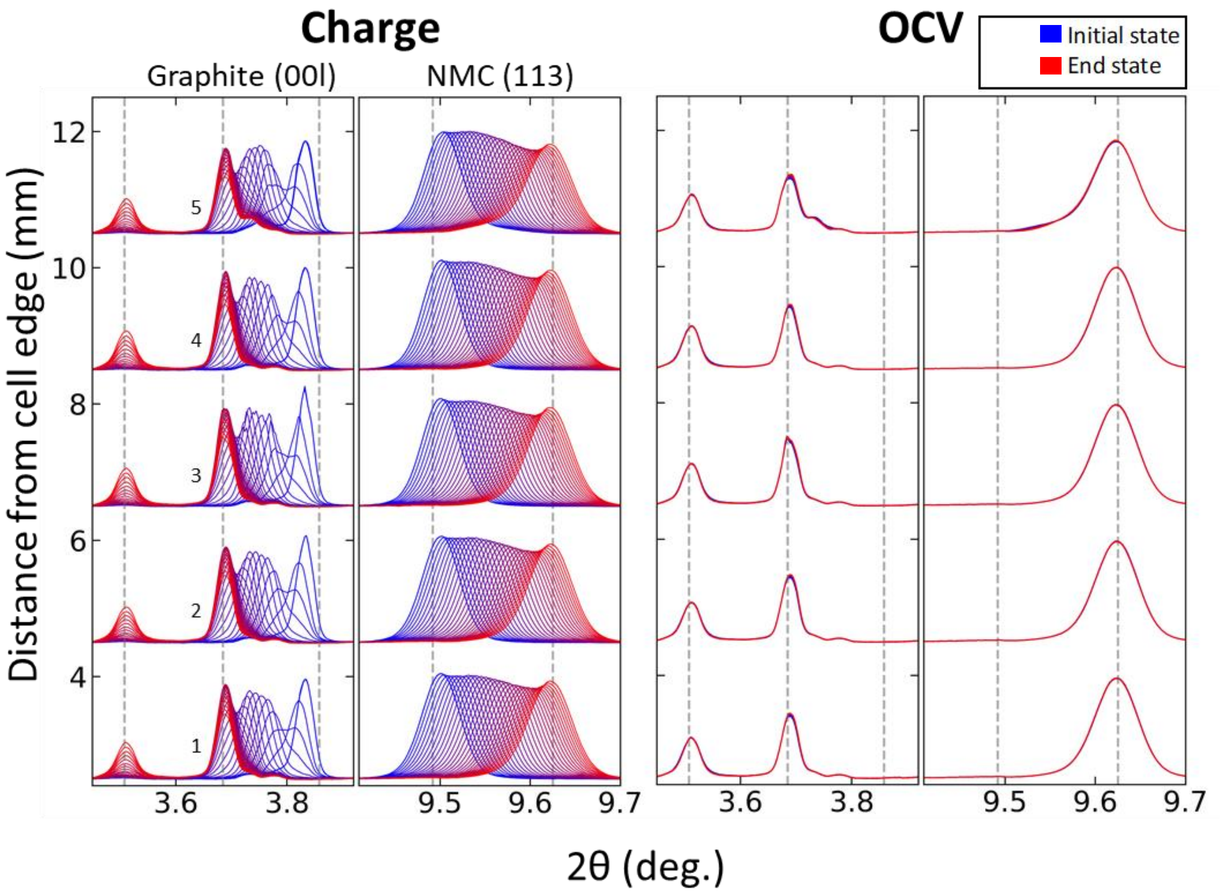
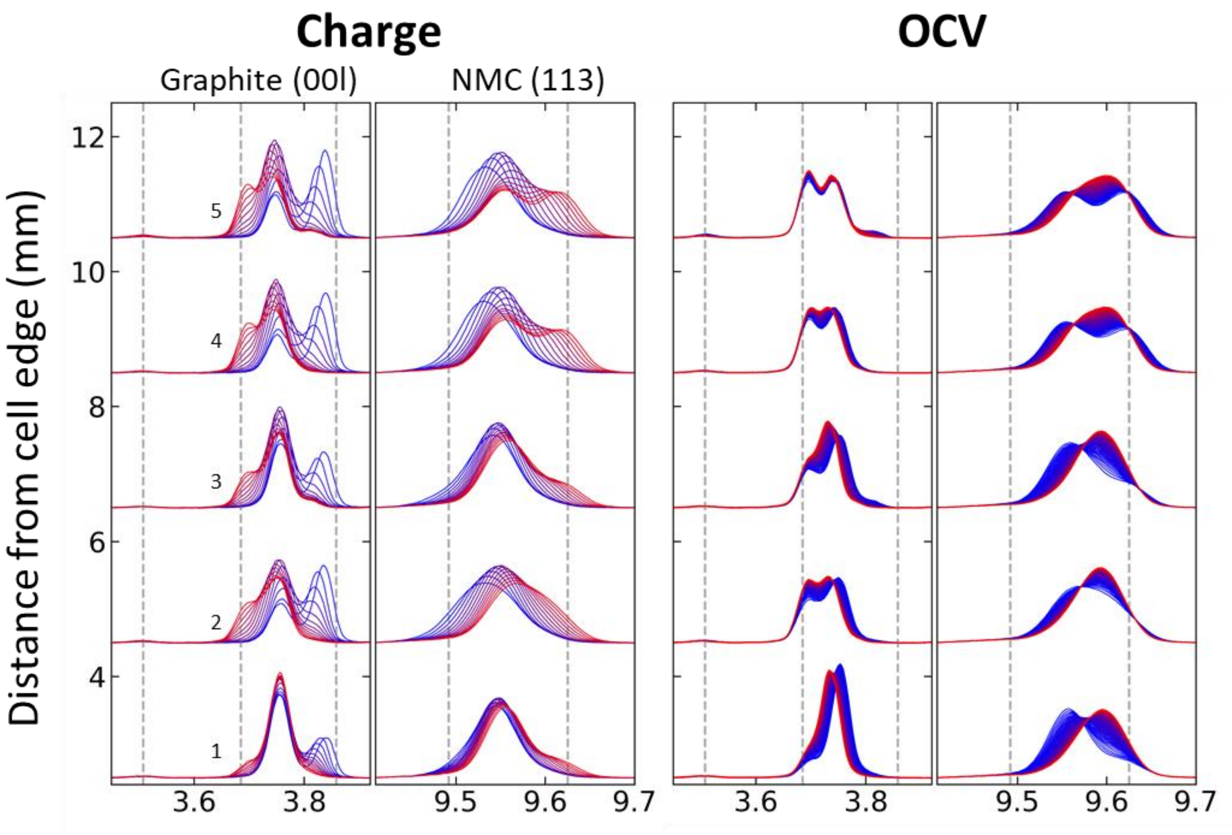
[T. Bond et al., J. Electrochem. Soc. 171, 110514 (2024)]

OCV relaxation: comparison





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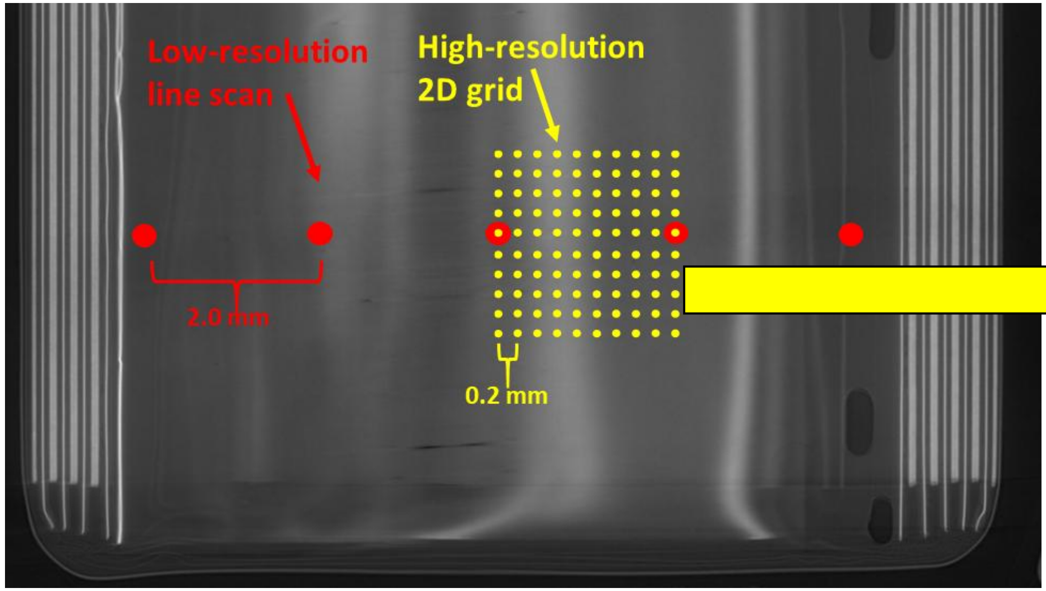
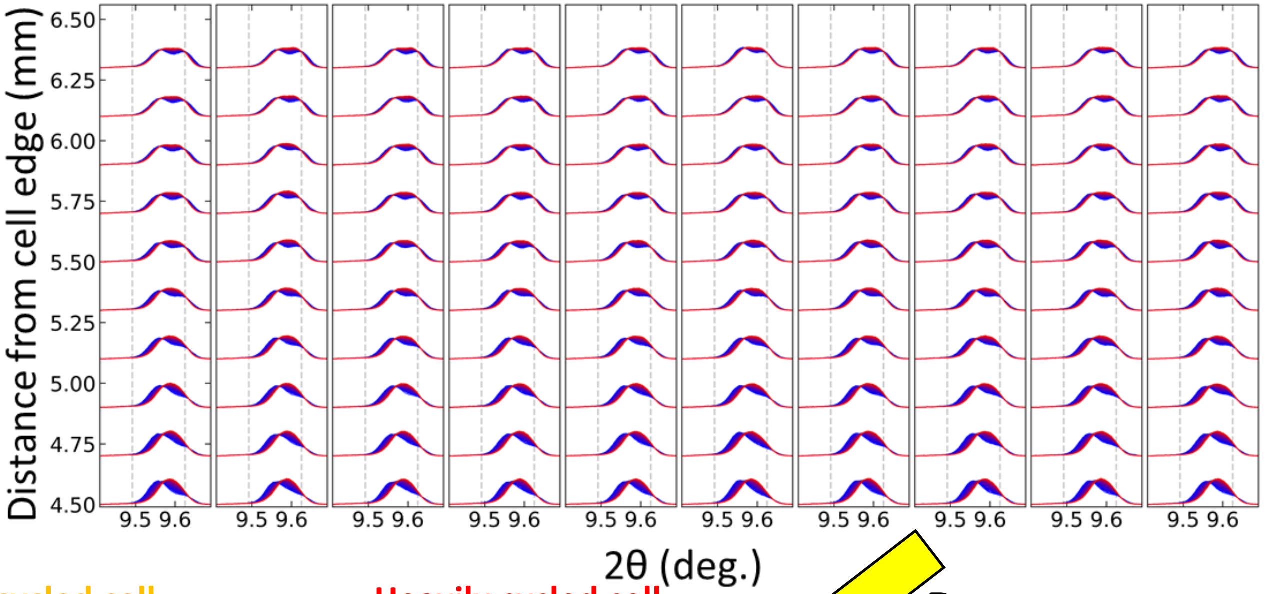
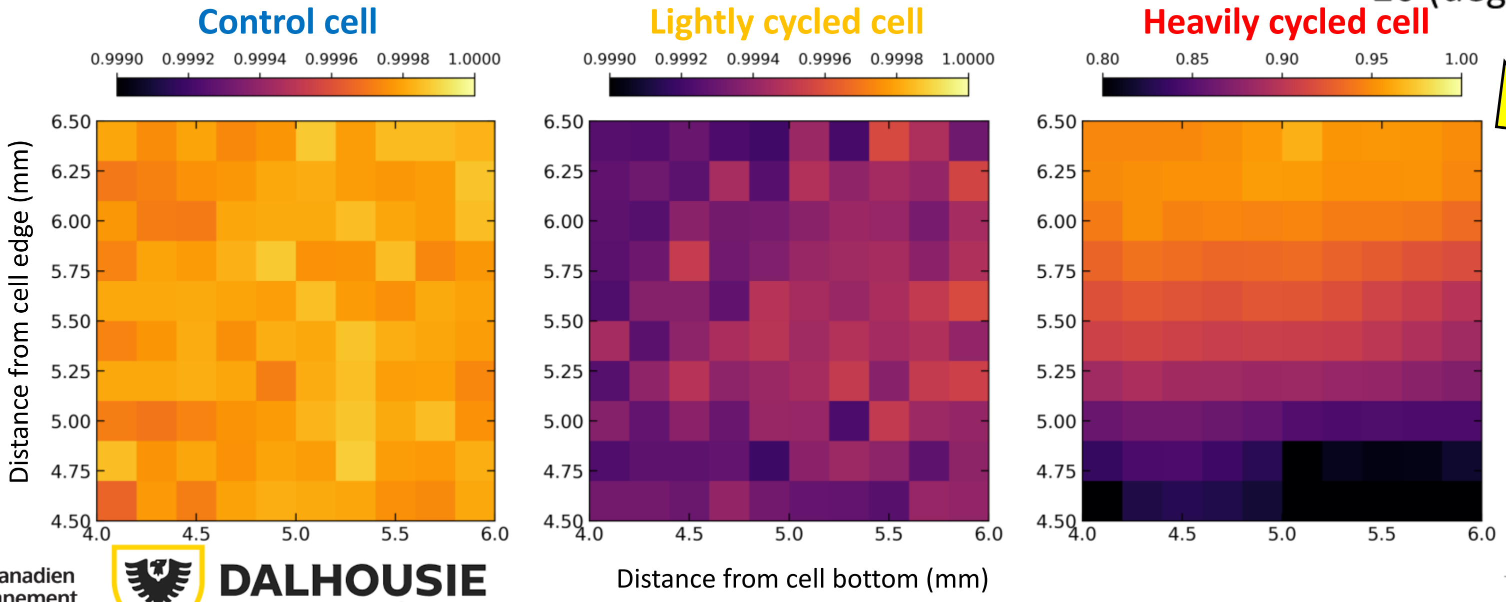
OCV relaxation: 2D mapping







Pearson Correlation Coefficient:

$$\rho_{X,Y} = \frac{\mathrm{cov}(X,Y)}{\sigma_X \sigma_Y}$$

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Summary

- Real-world materials and devices can be very complicated
- You're often working with incomplete or messy data that requires flexibility
- You need time to experiment with both data collection and analysis
- Synchrotron XRD is a great tool for this kind of work

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Thank you

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