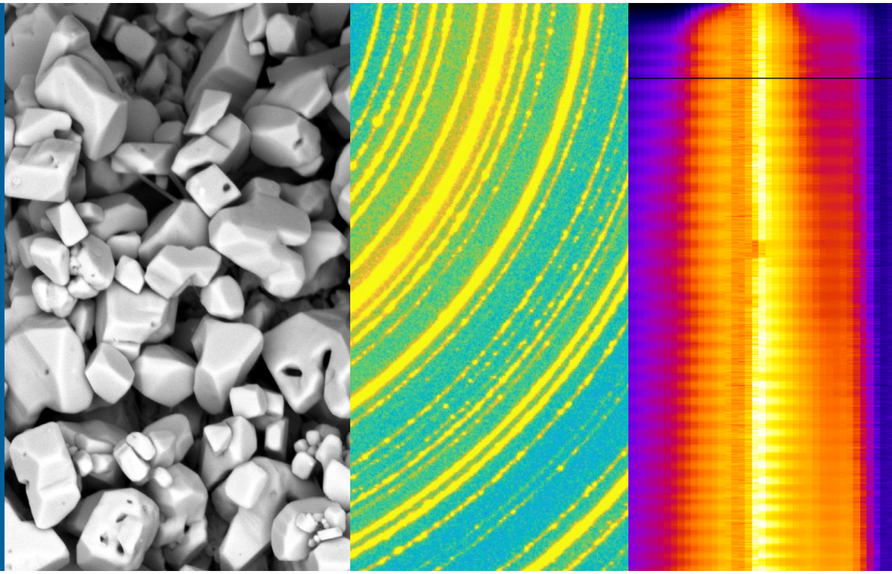
OE Energy Storage Peer Review
October 25, 2023
Presentation #705

Argonne NATIONAL LABORATORY

X-RAY CHARACTERIZATION OF SULFATION DURING CYCLING



TIM FISTER, TIFFANY KINNIBRUGH, SANG SOO LEE, JUAN GARCIA, HAKIM IDDIR
Argonne National Laboratory

VIJAY MURUGESAN, EDWIN THOMSEN, DAVID BAZAK, AJAY KARAKOTI
Pacific Northwest National Laboratory

SUBHAS CHALASANI, JACK SCOTT, KEVIN SMITH
East Penn Manufacturing

U.S. DEPARTMENT OF ENERGY
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OVERVIEW OF FY23 WORK

AQUEOUS BATTERIES LABORATORY (ABL)

Opened summer 2023

Funded by OE and partners from lead acid, iron air, and zinc battery industries.

- 3D printer: rapid prototyping of cell parts
- Acoustic mixer, curing oven, four hoods for cell pasting
- 112 total Maccor channels for small scale cell testing (-2 to 8 V, 5-40 A).

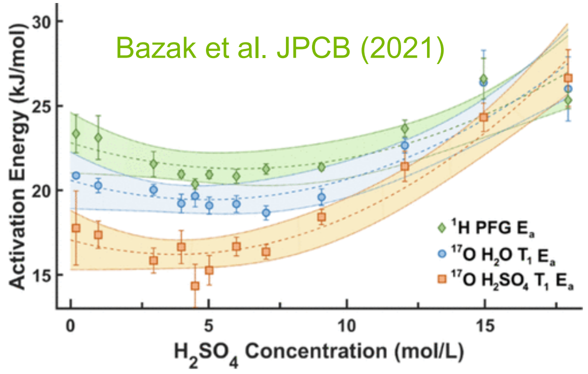
FY23 deliverables

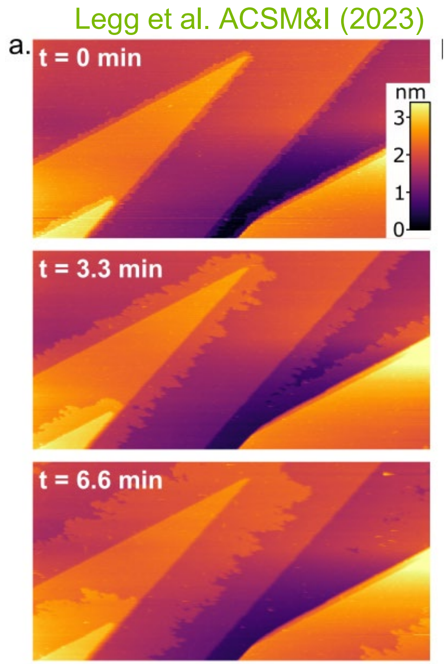
- 4 invited talks on lead acid
- 2 manuscripts published or submitted

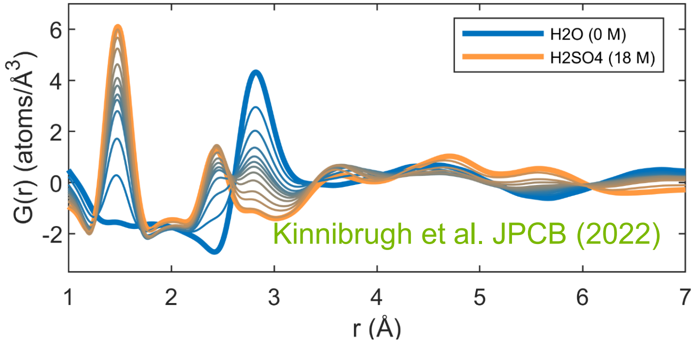
PREVIOUS TOPICS

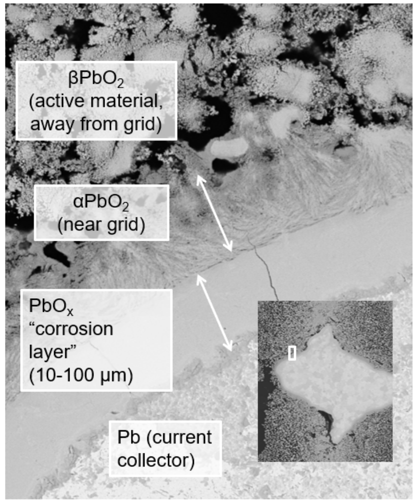
Yearly research themes

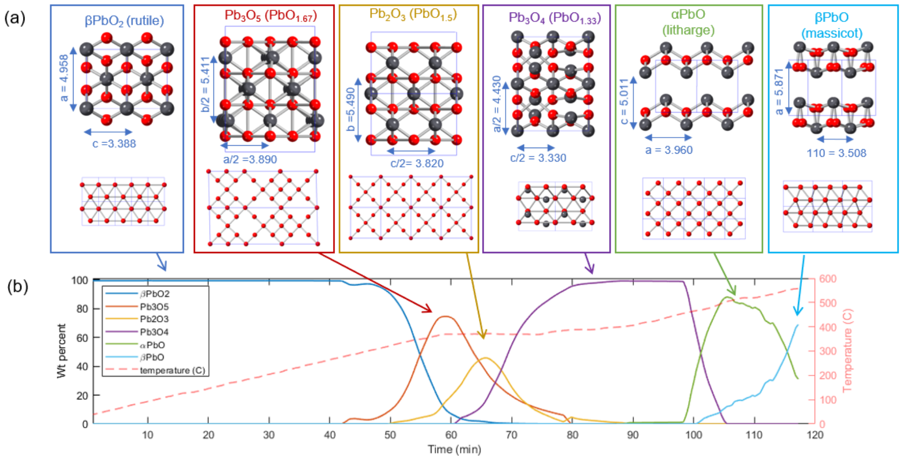
- FY20: solution structure
  - NMR, WAXS/PDF
- FY21: $PbSO_4$ nucleation
  - AFM, surface diffraction
- FY22: PbO_x species (corrosion layer; positive failure modes)
  - XRD, XAS, XPS, NMR
- FY23: sulfation (negative electrode failure modes)
  - XRD: pastes and Plante cells
- See posters and next talk!











Kinnibrugh et al. submitted Chem Mater (2023).

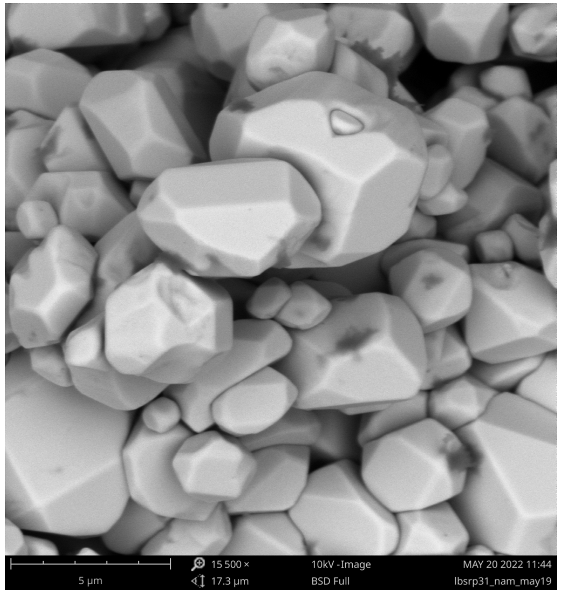
NAM FAILURE MODES

Origins of sulfation

- FY23 science goals: understand multiscale processes driving irreversible $PbSO_4$ growth on negative electrode during cycling.

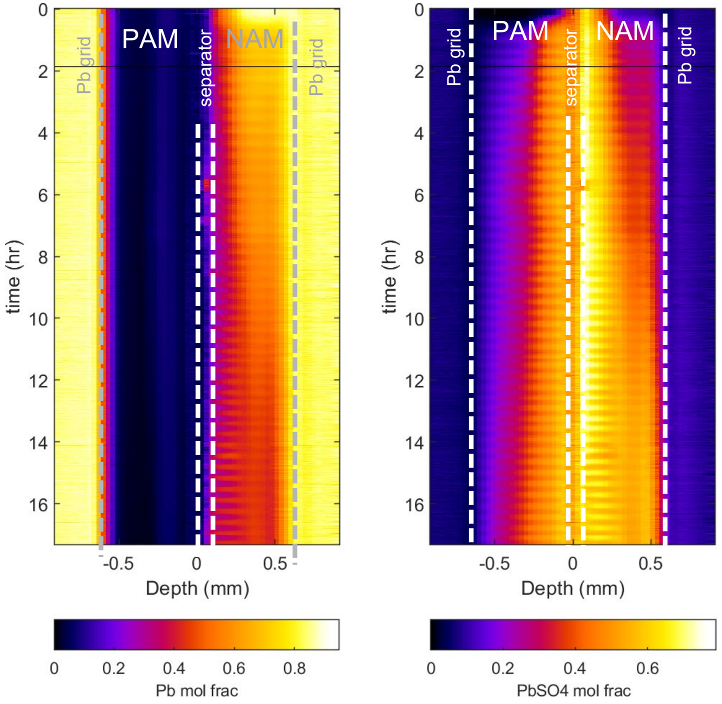
Microscale (~1 µm): increased size and faceting of $PbSO_4$

Example: active material from negative micro-cycled over 7000 times at Argonne



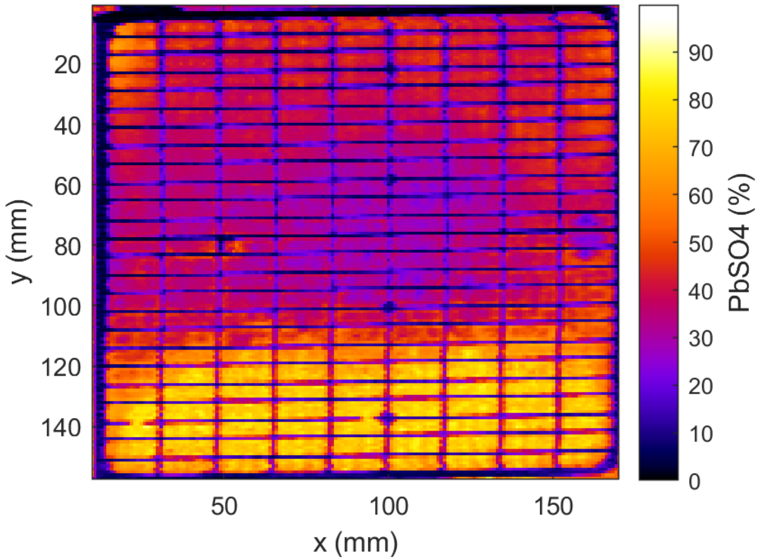
Electrode scale (10-1000 µm): Depth dependent changes

Example: changes in Pb and $PbSO_4$ speciation during high rate PSOC cycling



Battery scale (1-100mm): lateral changes

Example: changes in $PbSO_4$ distribution in deep-cycle batteries from PNNL driven by sulfation and stratification



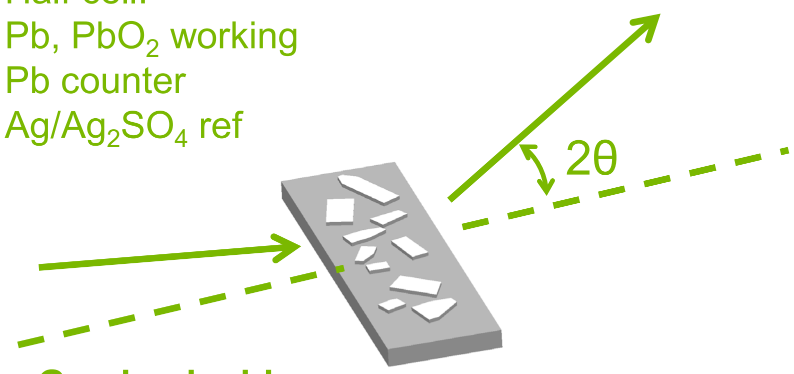
NAM FAILURE MODES

Origins of sulfation

- FY23 science goals: understand multiscale processes driving irreversible $PbSO_4$ growth on negative electrode during cycling.
- We have developed test cells for each regime:

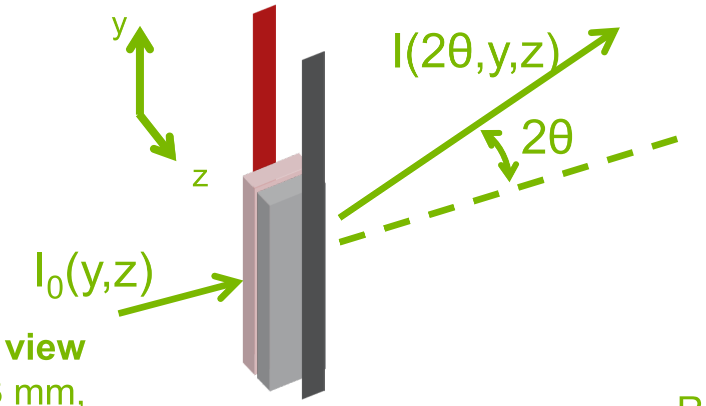
Microscale (~1 µm): Particle changes	Macroscale (10-1000 µm): depth dependent changes	Grid-scale (1-100mm): lateral changes

Plante cell (µAh)
Half cell:
Pb, PbO_2 working
Pb counter
Ag/Ag_2SO_4 ref



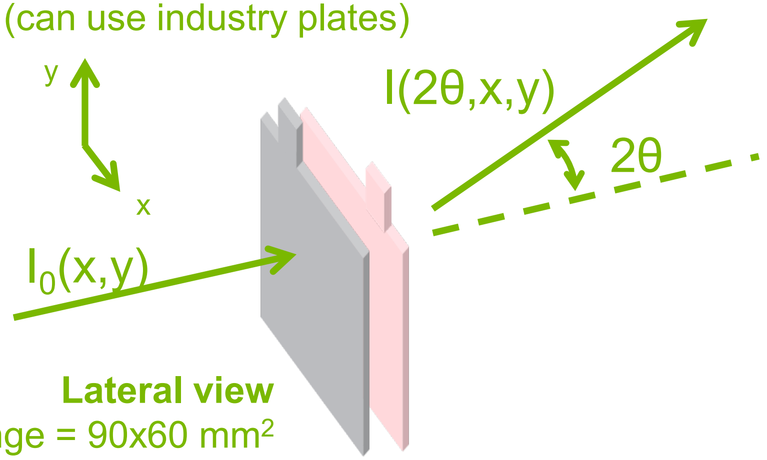
Grazing incidence
Beam = 1x3 mm^2
Sample = 8x3 mm^2

Mini cells (mAh):
Suitable for depth profiling



Edge view
Range: 3 mm,
Δz = 0.03 mm

2V pasted cells (Ah):
2 or 3 electrode cells: 2D maps
(can use industry plates)



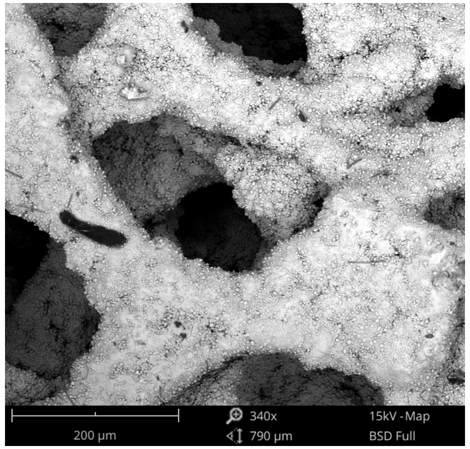
Lateral view
Range = 90x60 mm^2
Δxy = 1 mm^2

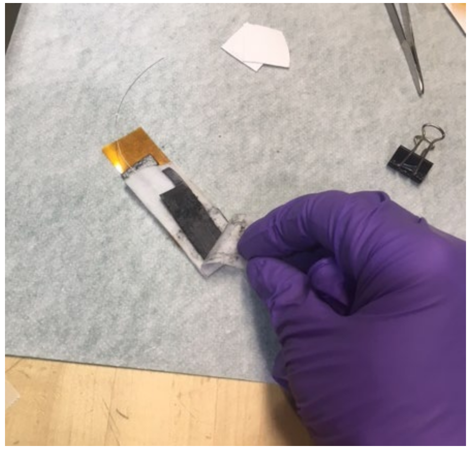
MICROSTRUCTURAL ORIGINS OF SULFATION

EXPERIMENT

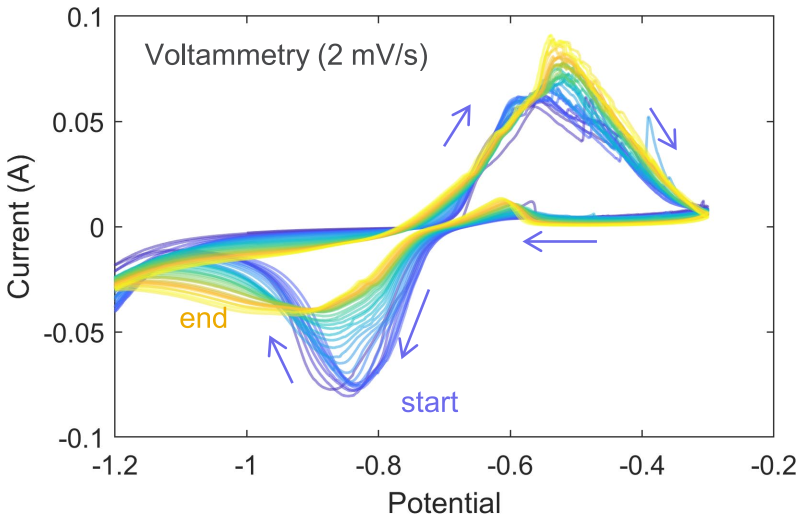
"3D Plante cell"

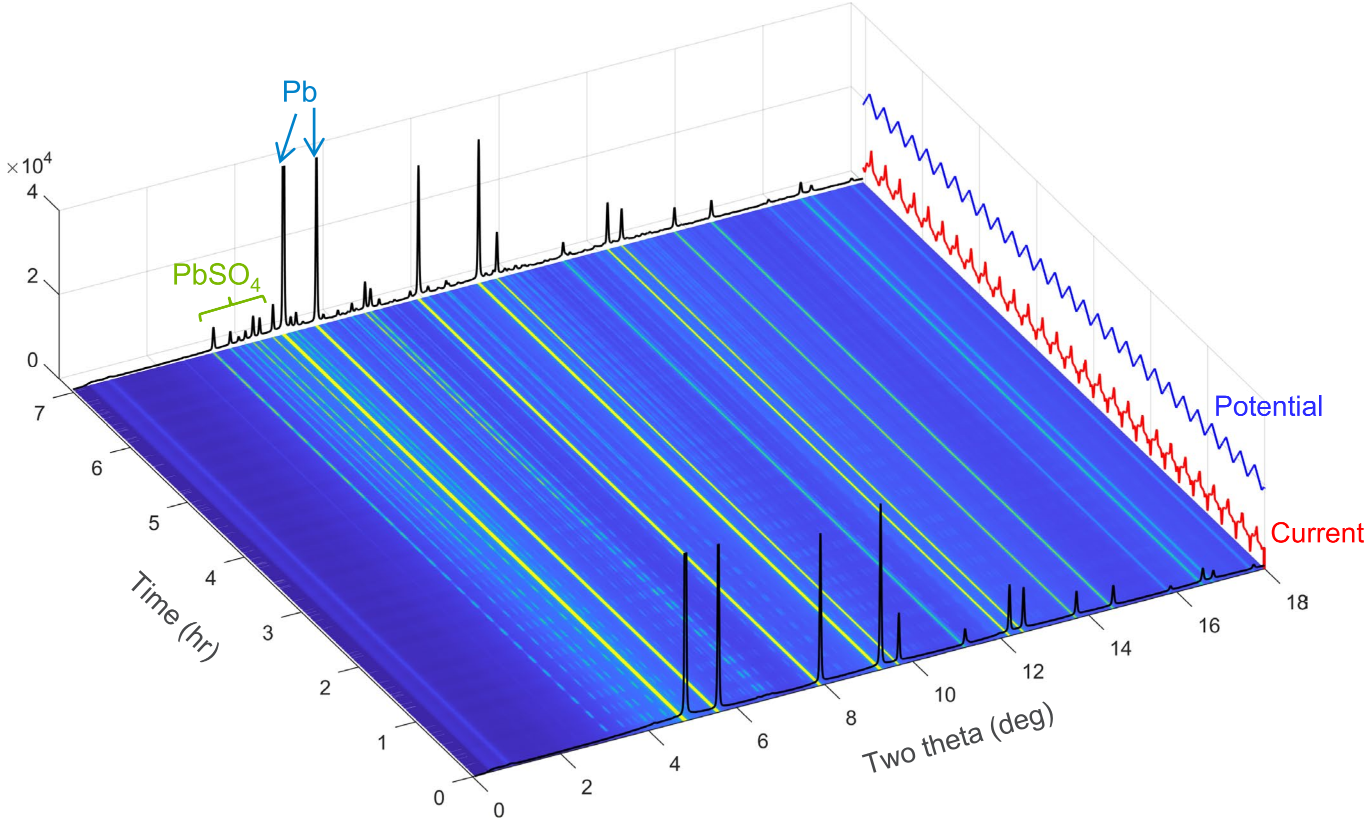
- To increase the surface area, we use a Pb-coated carbon foam (East Penn Manufacturing).
- Analyze changes in $PbSO_4$ diffraction during cyclic voltammetry.
- Can clearly see $PbSO_4$ growth/dissolution during charge discharge conditions.





3D Plante cell: Lead foam (ex situ SEM after discharge), combined with an electrochemical half cell (Pb foam, C counter, Ag wire pseudo-reference)



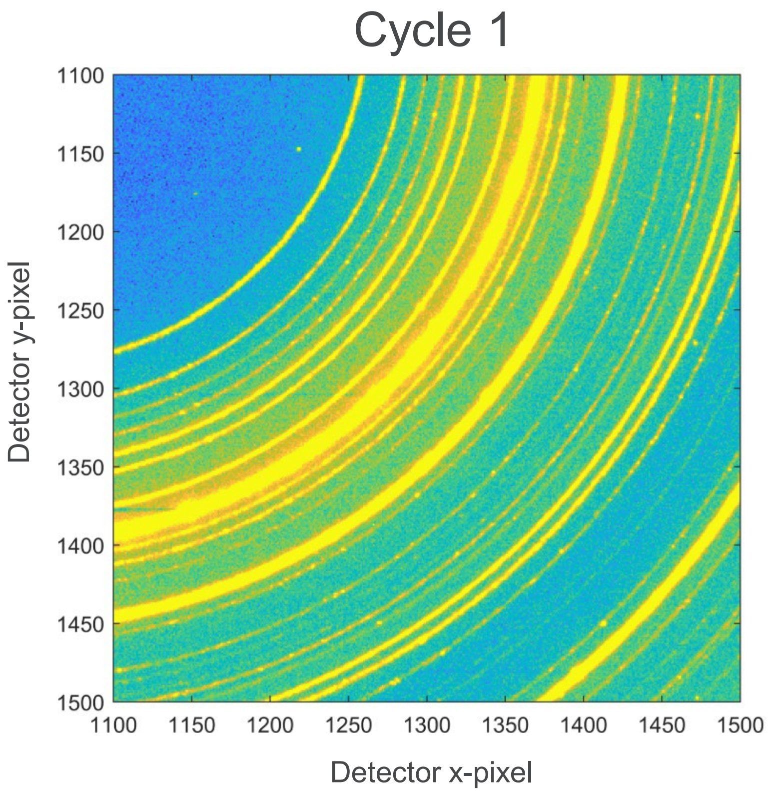


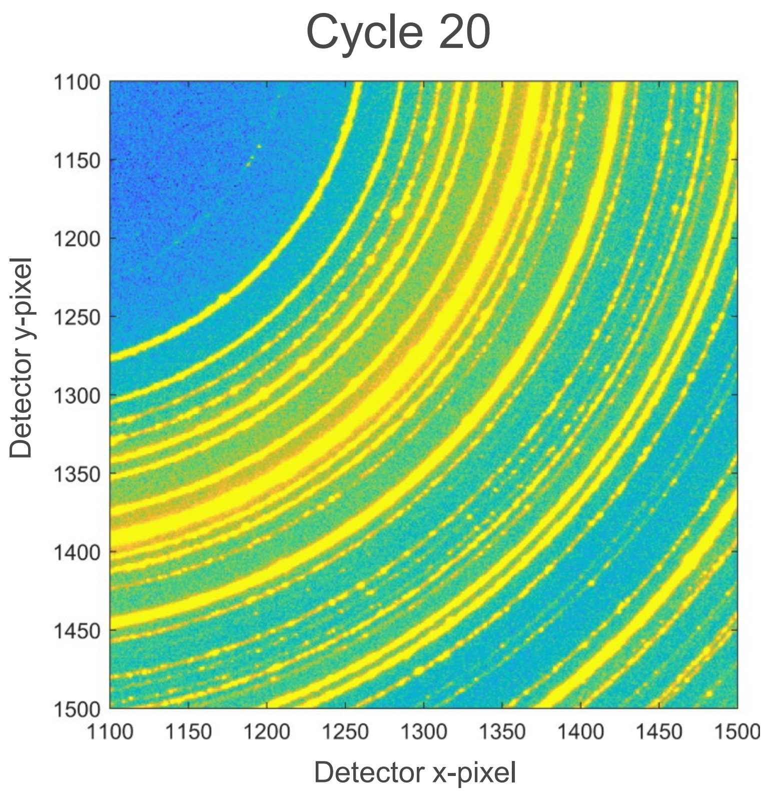
PARTICLE SIZE *DISTRIBUTION* FROM XRD

Hidden statistics in powder diffraction

- Particle ripening (i.e. sulfation) leads to increasingly coarse rings. These spots are related to discrete crystals.

- Nonuniform rings are not ideal for lineshape analysis, but represent scattering from distinct crystallites.
- Can we extract ***statistics*** on particle size by applying line shape analysis at each point around the ring?

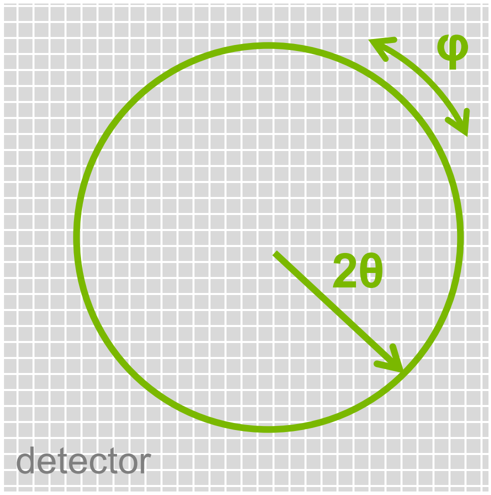




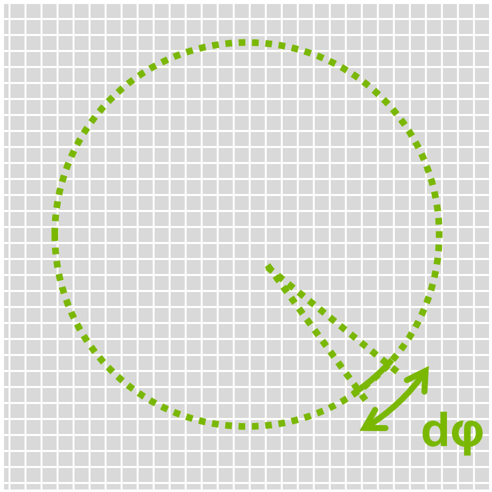
METHOD
Azimuthal Scherrer Analysis

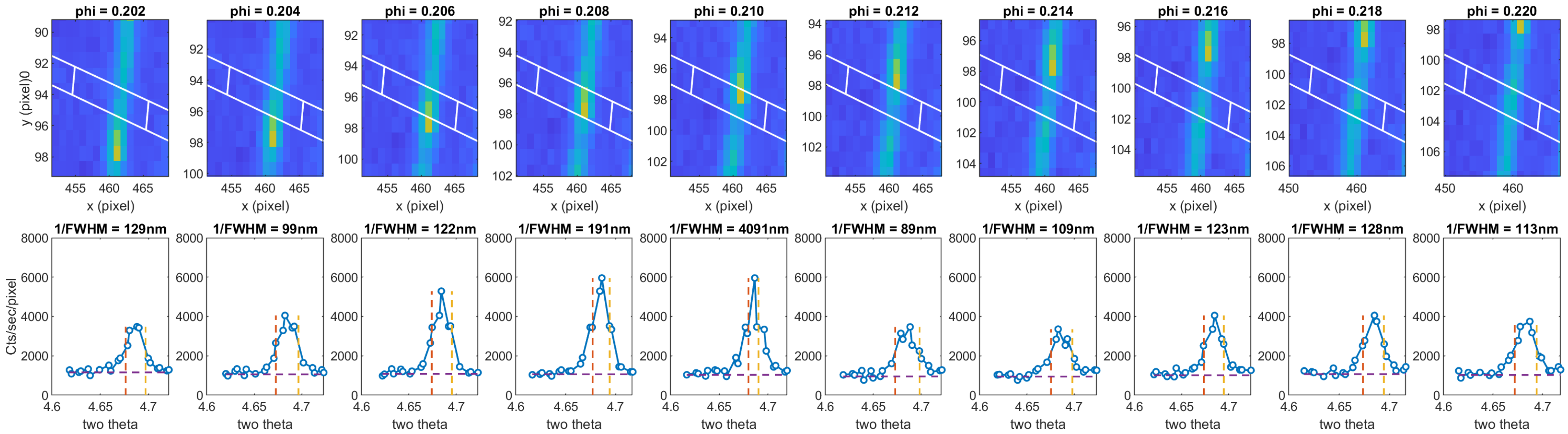
- Instead of integrating over azimuth, let's cut the powder ring into azimuthal pieces and study the variation in line shape.
  – Example: early cycling, $PbSO_4$ 113 ring (chosen for strength, relatively high 2θ)

Powder Ring (total)



Powder Ring (segment)





METHOD

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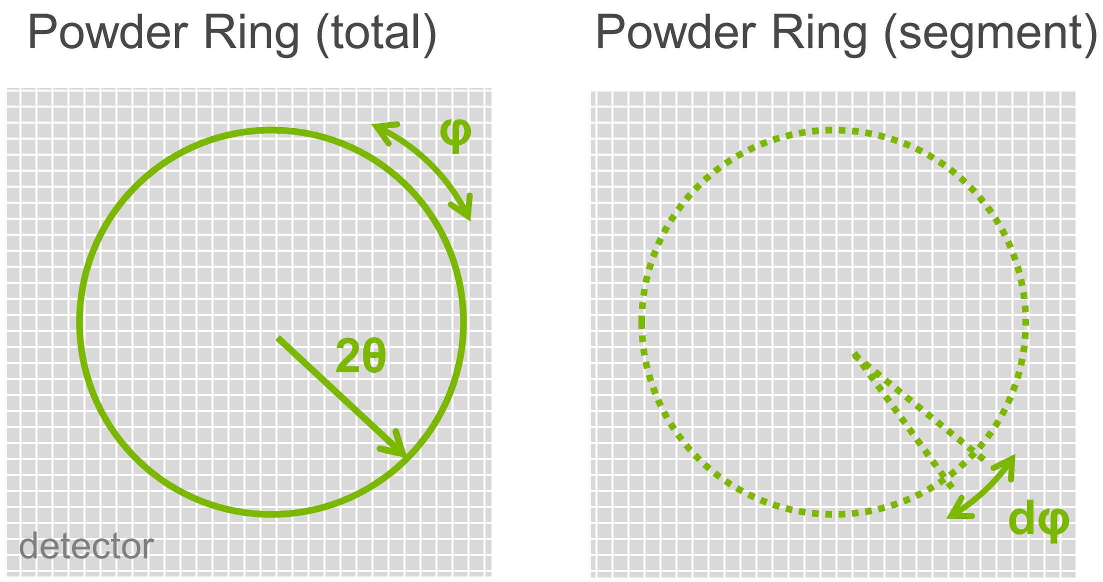
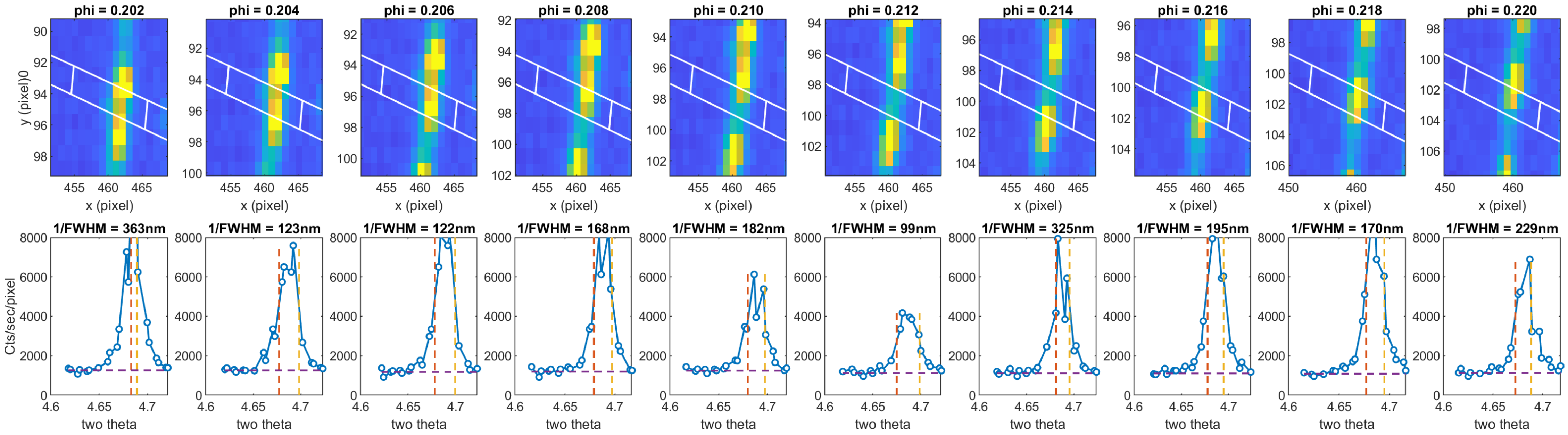
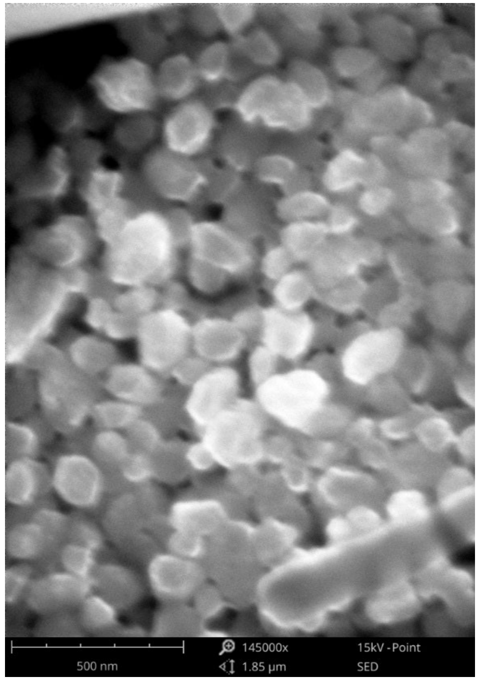


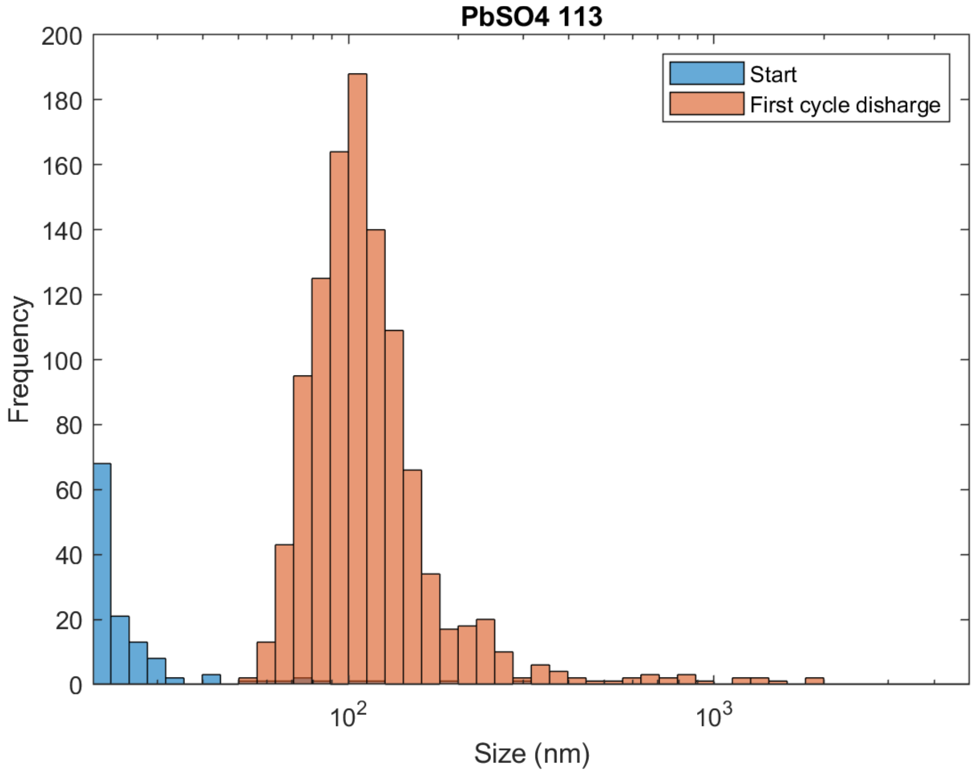


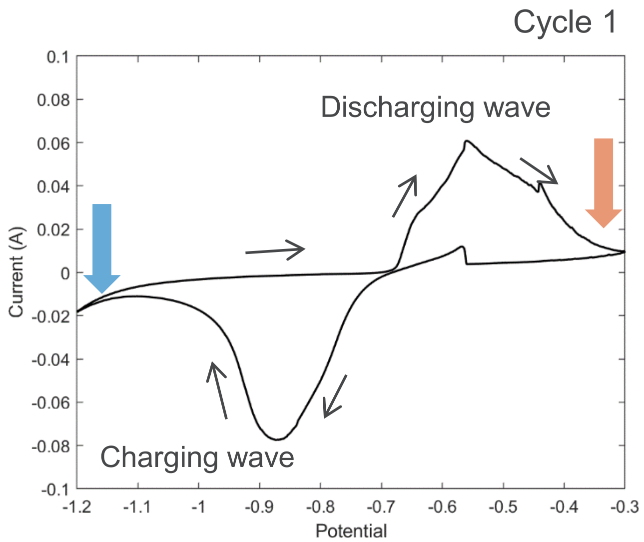
HISTOGRAMS

Average particle size → particle size *distribution*

- Repeat method over ~1000 pts on the ring and study distribution in size (using log-size distribution).
- Example #1: one second image after first discharge



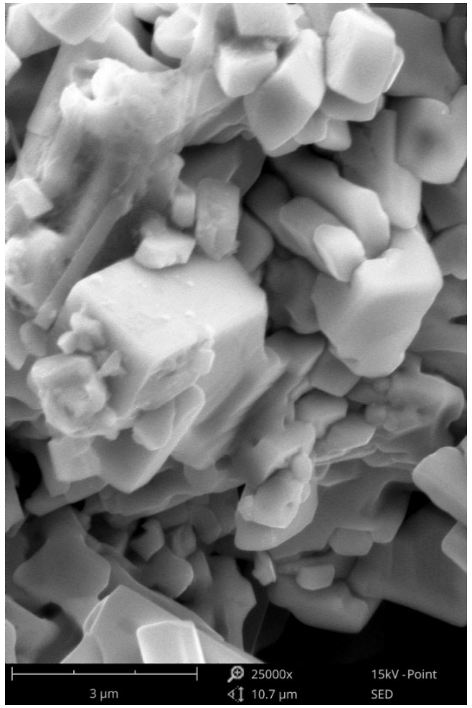


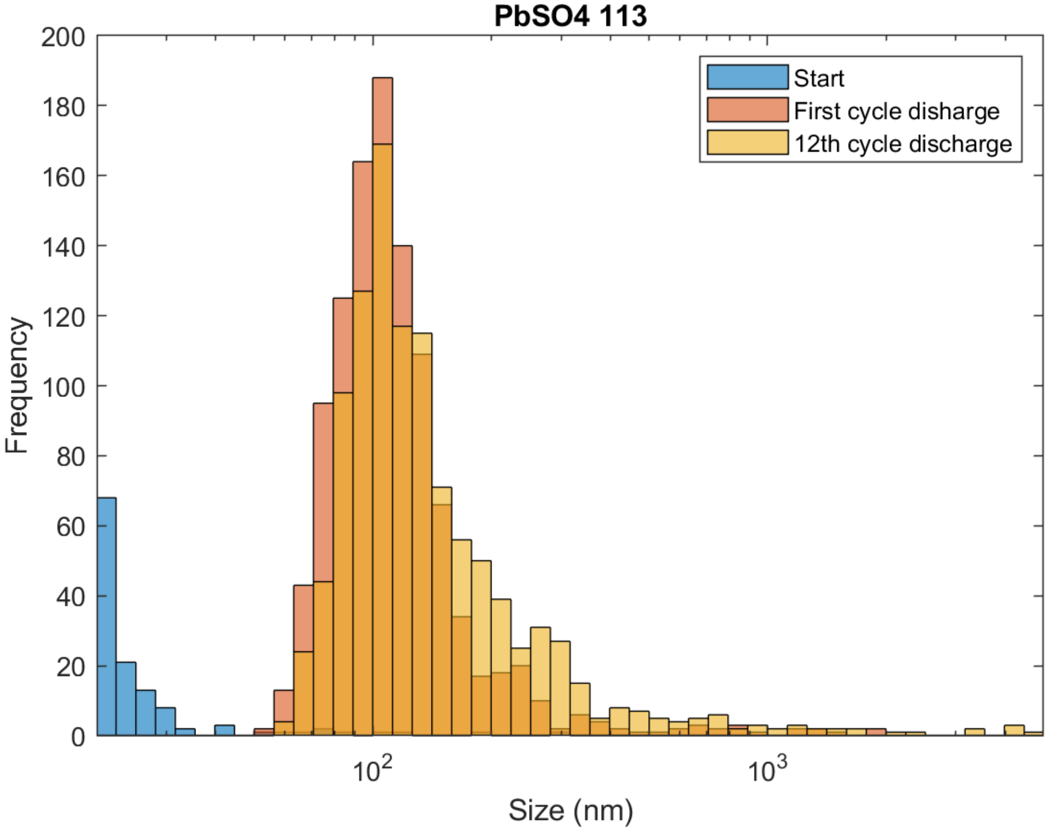


HISTOGRAMS

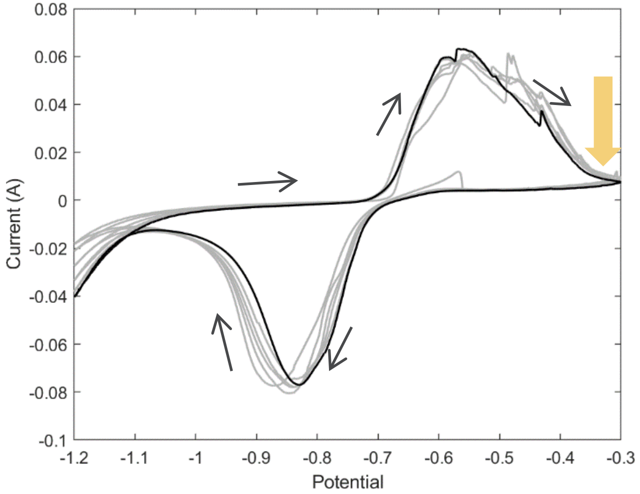
Average particle size → particle size *distribution*

- Repeat method over ~1000 pts on the ring and study distribution in size (using log-size distribution).
- Example #2: one second image after twelfth discharge





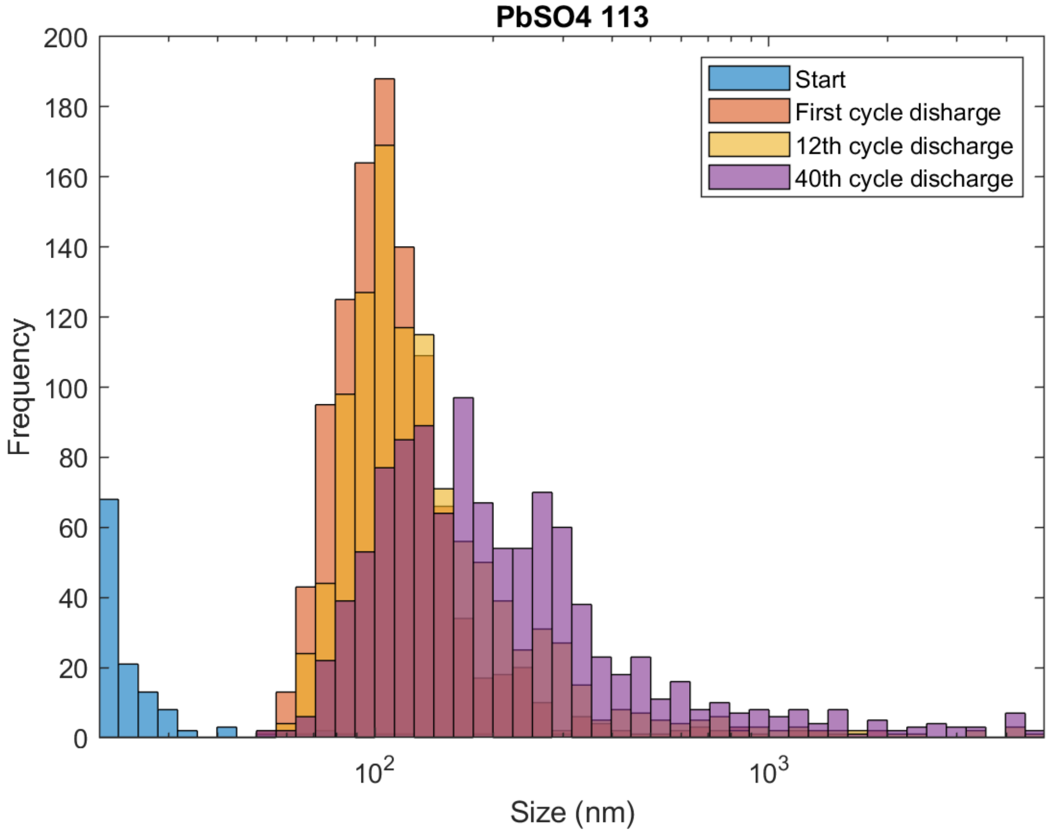
Cycles 1-12
(cycle 12 bolder)



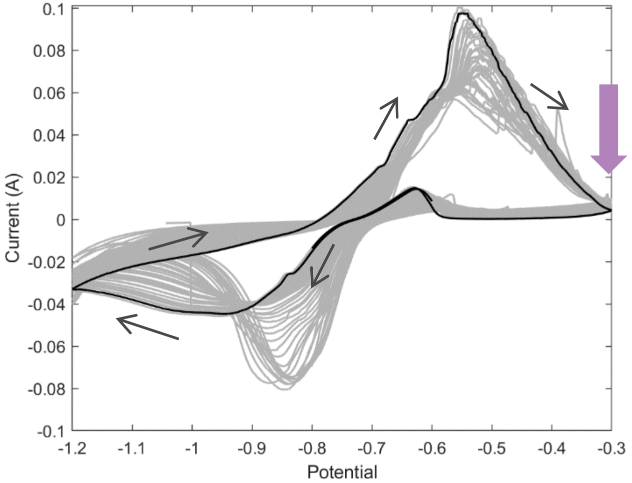
HISTOGRAMS

Average particle size → particle size *distribution*

- Repeat method over ~1000 pts on the ring and study distribution in size (using log-size distribution).
- Example #3: one second image after 40th discharge



Cycles 1-40
(cycle 40 bolder)

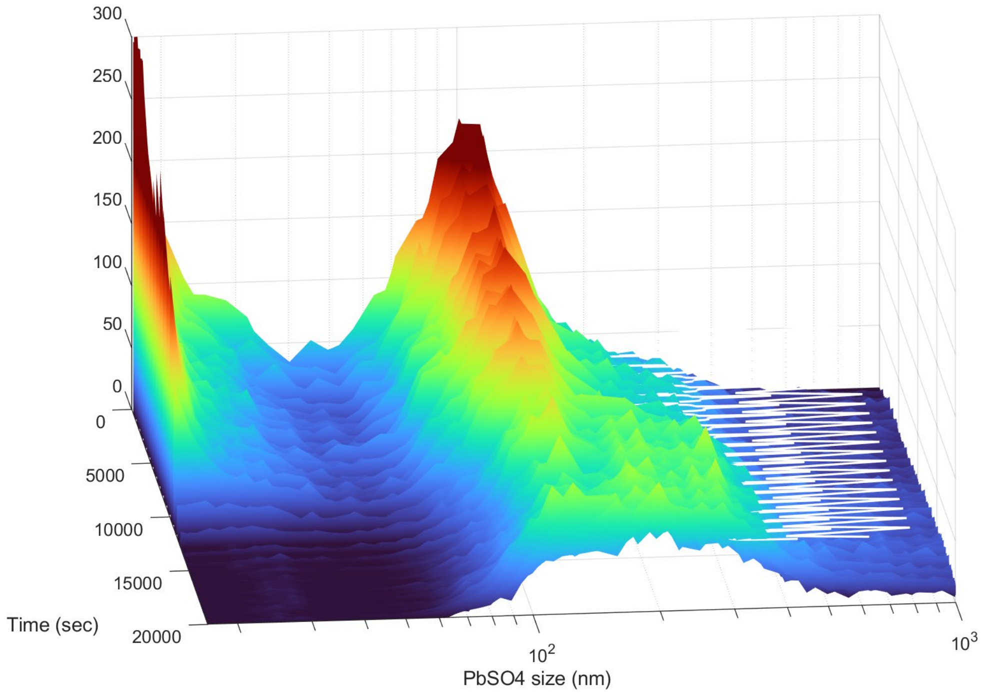


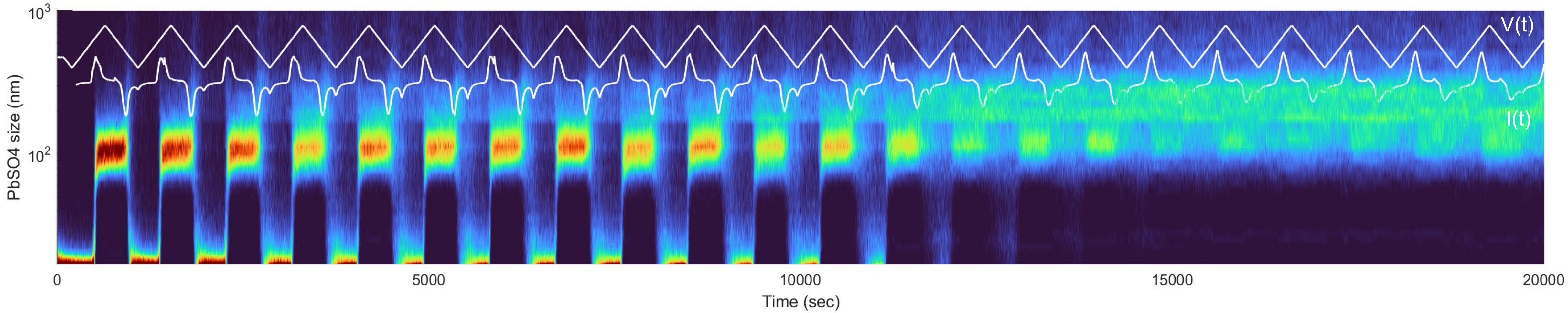
DYNAMICS

Origins of sulfation

Look at *time dependence* of the particle size distribution:

- Early cycles: tight distribution of $PbSO_4$ (~100 nm); nearly complete dissolution
- Later cycles: accumulation of larger particles.

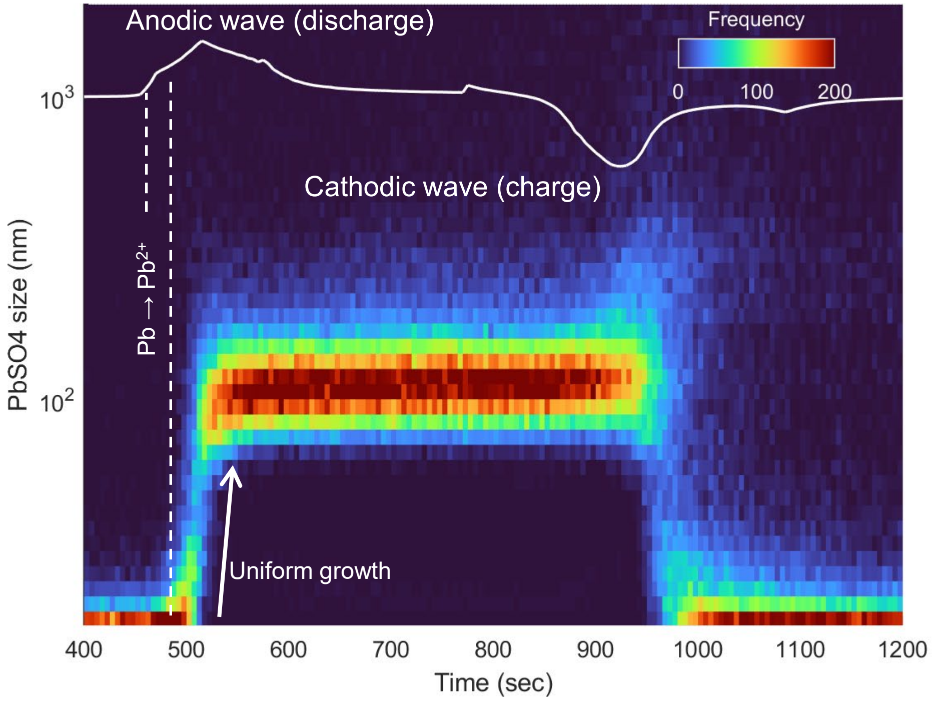


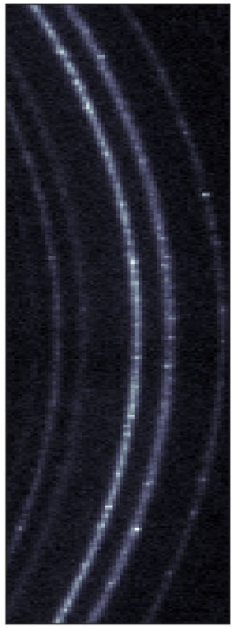


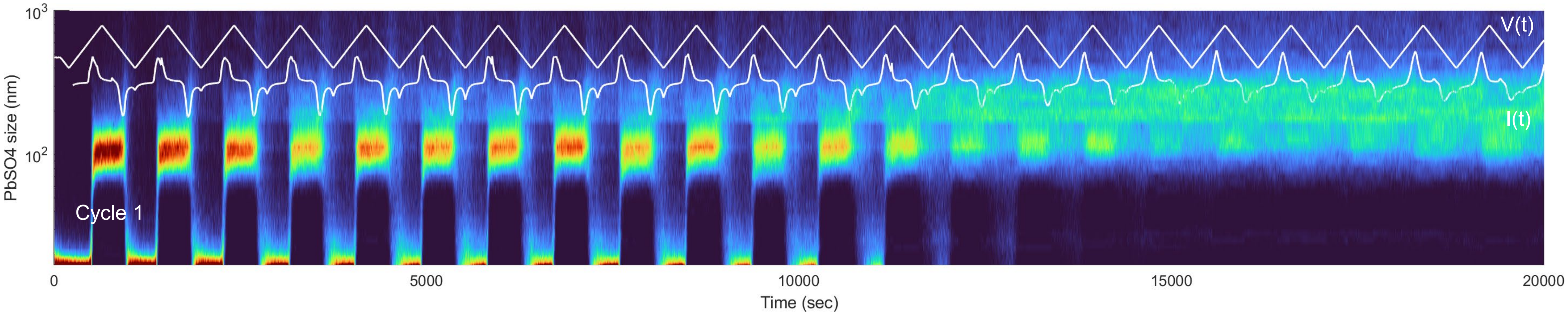
DISCHARGE: GROWTH

Comparison with voltammetry

- Cycle 1 discharge: onset of growth slightly delayed from initial anodic current (Pb dissolution precedes
  - Growth largely consists of small particles that uniformly grow to ~100 nm.



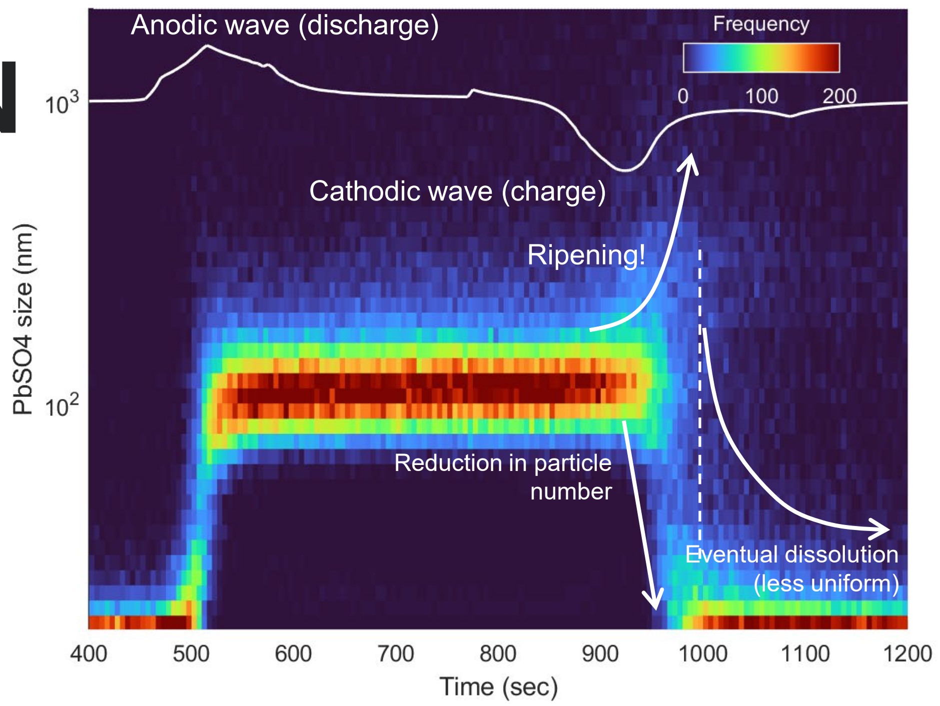


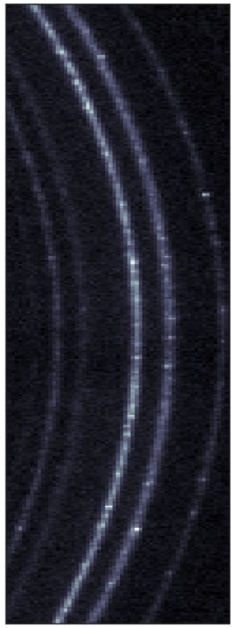


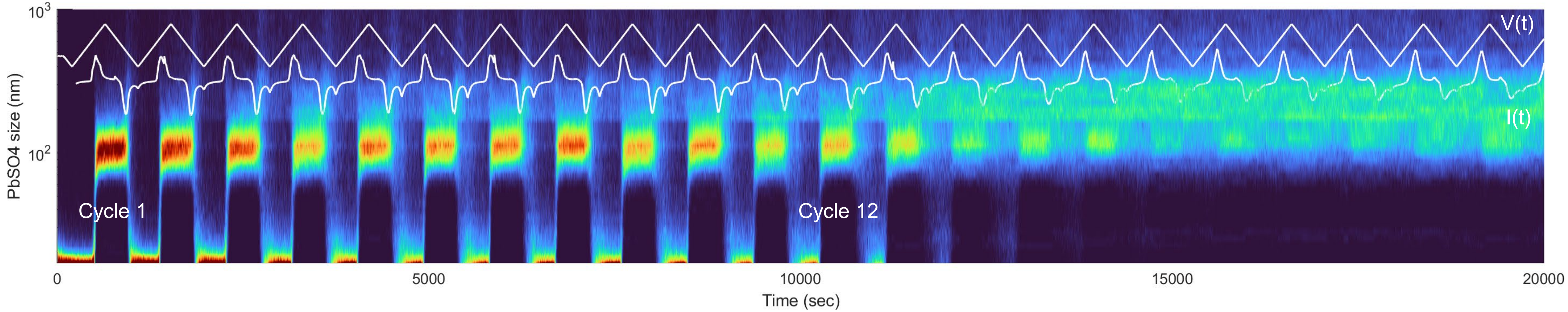
CHARGE: DISSOLUTION

Comparison with voltammetry

- At onset of dissolution: see evidence of *ripening* before and during dissolution.
  - Eventually particles dissolve, but less uniformly, probably owing to wider range in particle size.



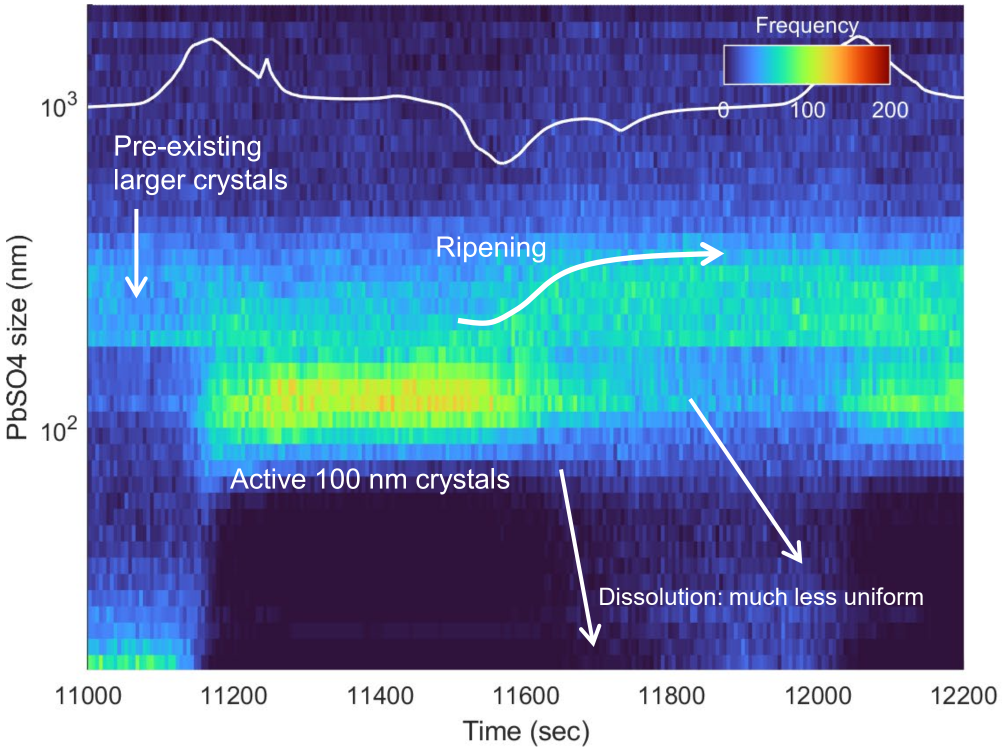


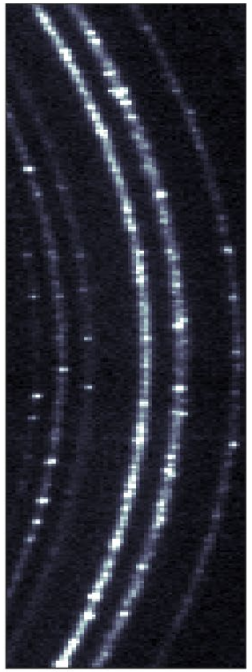


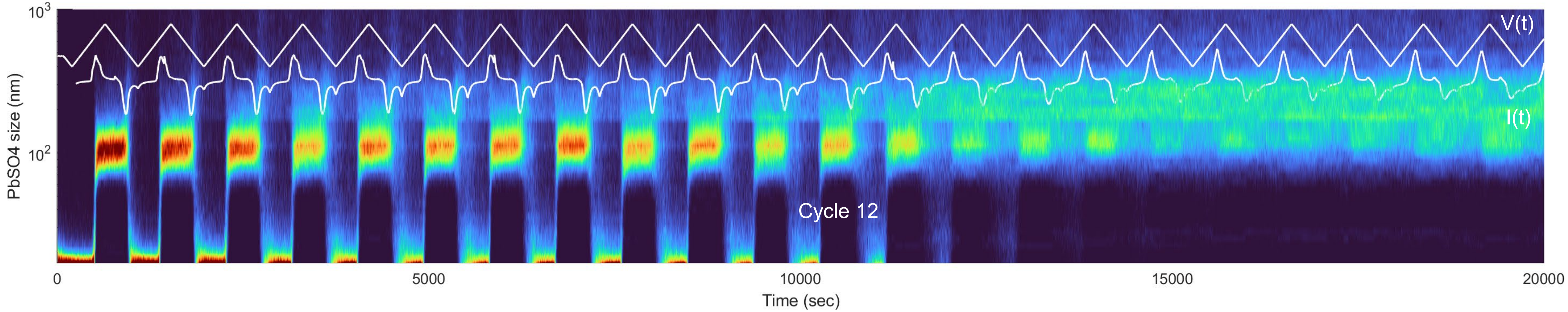
LATER CYCLES

Irreversible $PbSO_4$

- Before growth there is now an existing distribution of larger crystals (200-500 nm) before discharge.
- “Active” crystals are still ~100 nm.
- Simultaneous ripening/dissolution. Dissolution is less well-defined and over longer time.



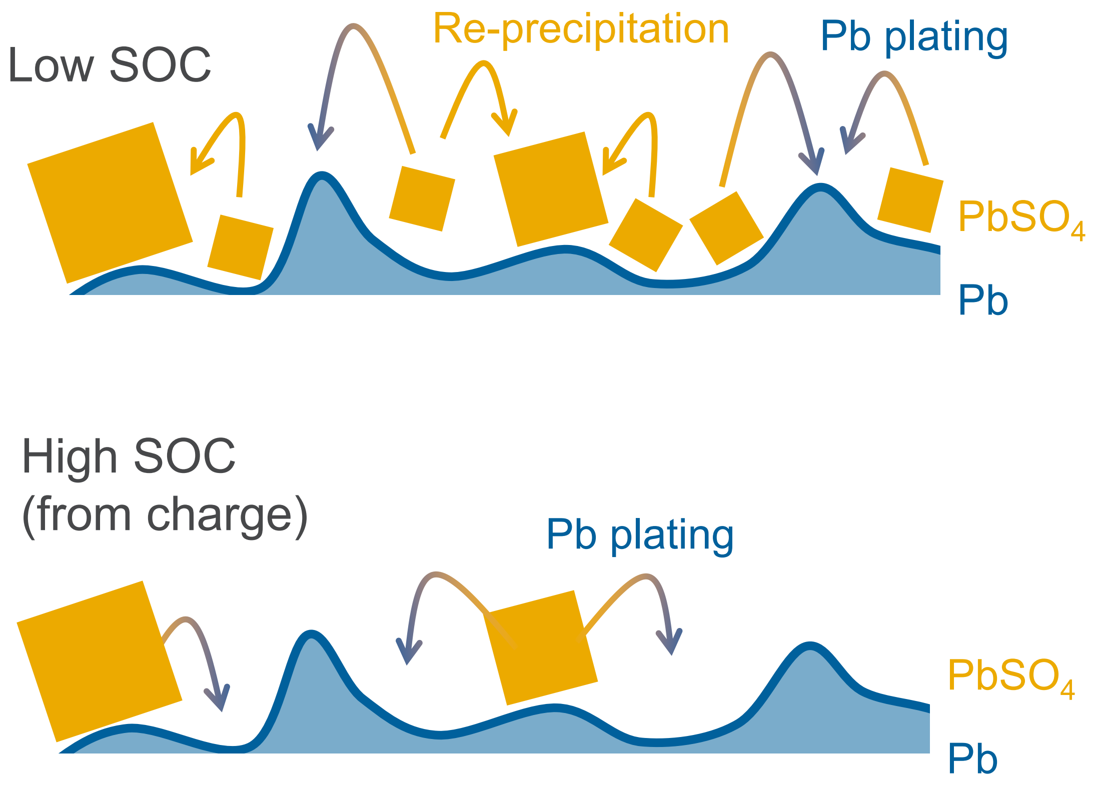




IMPLICATION

Changes in dynamic charge acceptance

- Onset of charge: small particles preferentially dissolve.
  - Some Pb^{2+} ions also re-precipitate on larger particles, much like Ostwald ripening.
- At high SOC, only larger particles (with low surface area) remain, leading to poor dynamic charge acceptance ("DCA memory effect").
- Also explains why partial state of charge (PSOC) cycling can lead to sulfation…
- Future: apply similar methods to pastes, compare different diffraction conditions.
- APS-U: combine this approach with coherent diffraction imaging on single Bragg spot.

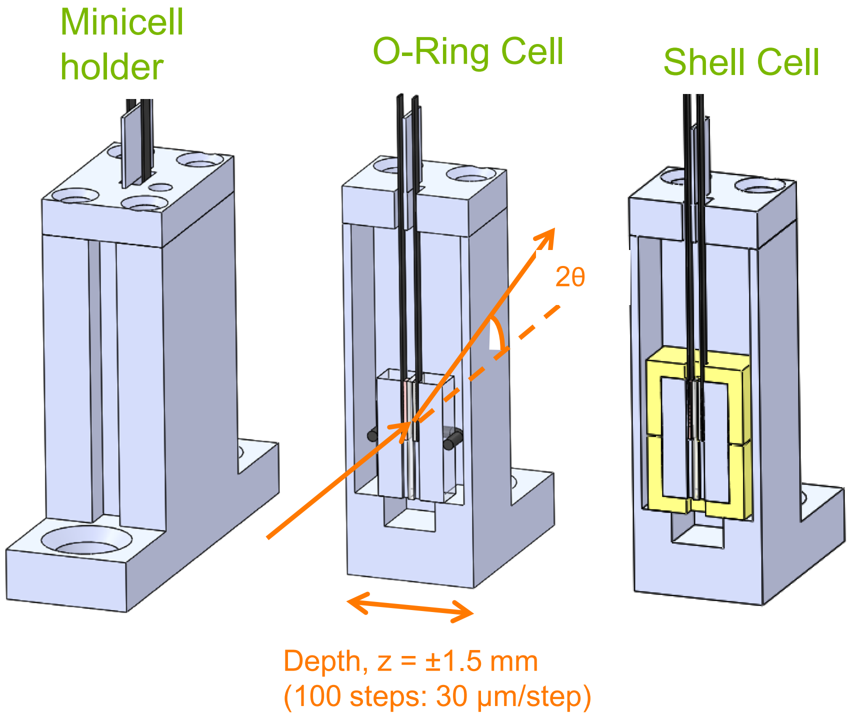


DEPTH PROFILING CHARGE ACCEPTANCE DURING PSOC CYCLING

MINICELLS

Depth profiling lead acid batteries

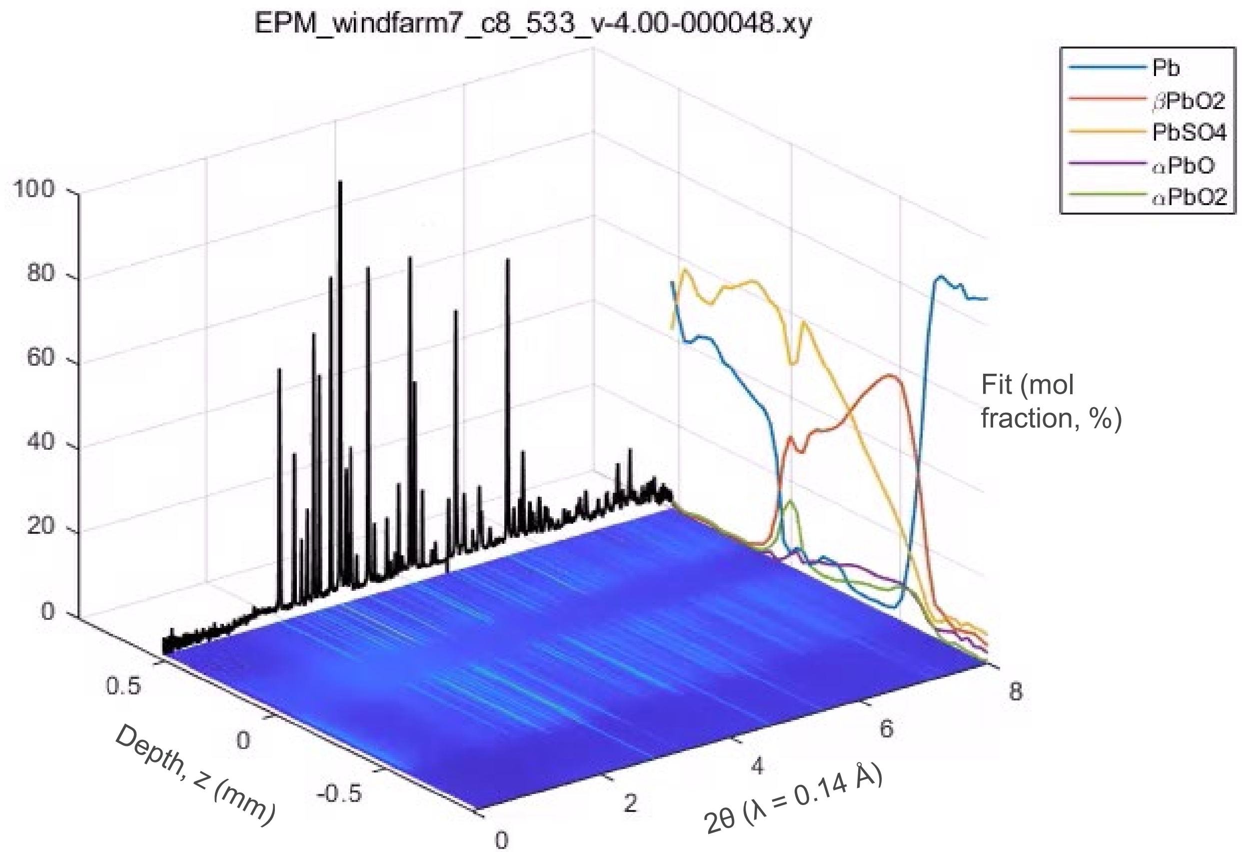
- Minicells developed at East Penn and Argonne for x-ray depth profiling.
  - Pasting defined within small acrylic fixtures.
- Compression using O-ring or external shell.
- Parts were 3D printed.

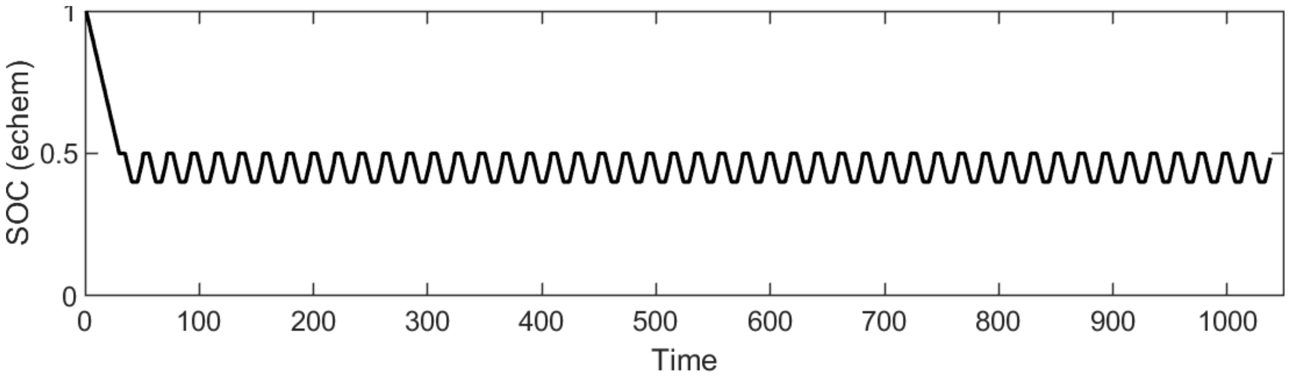


PROCEDURE

Depth profiling & high-rate partial state of charge (HRPSOC) cycling

- Modified version of East Penn's "windfarm" protocol.
- Rapid cycling (1C) between 50 and 60% SOC with 5 minutes rests in between.
- During HRPSOC: line scan in middle of cell to look at changes in negative active material (NAM) and positive active material (PAM).
- HRPSOC studied in 1.08, 1.20, 1.30 SG flooded/AGM conditions.
(“1300 starved” includes only acid in separator and active material).



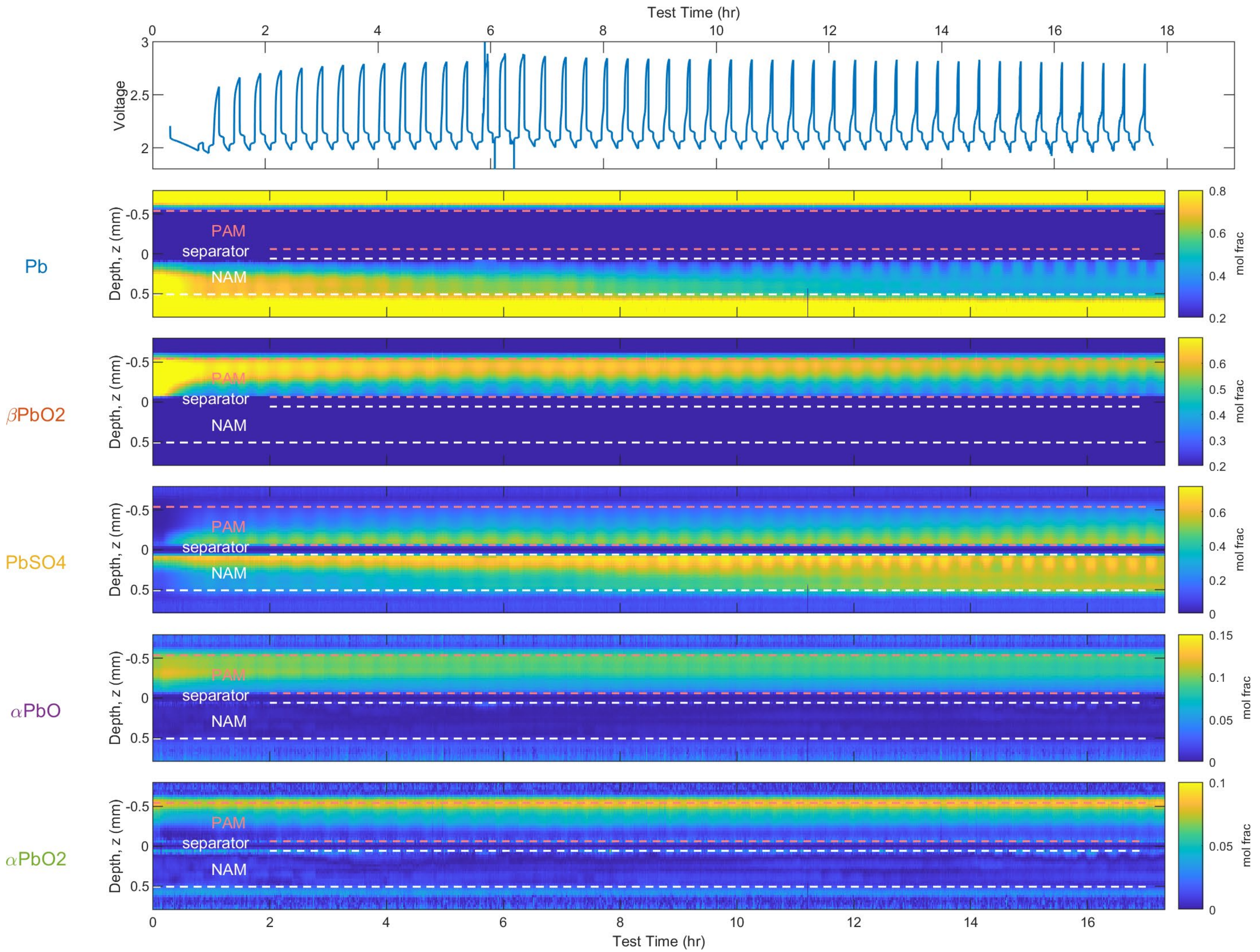


SPECIES

Depth profiling 1300 starved cell

Fit at each point (60,000 XRD patterns) and extract mol fractions, n ($\Delta n \propto \Delta Q$)

- Individual species show changes consistent with HRPSOC protocol.
- Largest changes in Pb, βPbO_2, and $PbSO_4$.
- We do see changes in "alkaline phases" αPbO_2 and PbO (PbO_x?), especially near grid.



CHARGE ACCEPTANCE

Coulomb Counting with x-rays

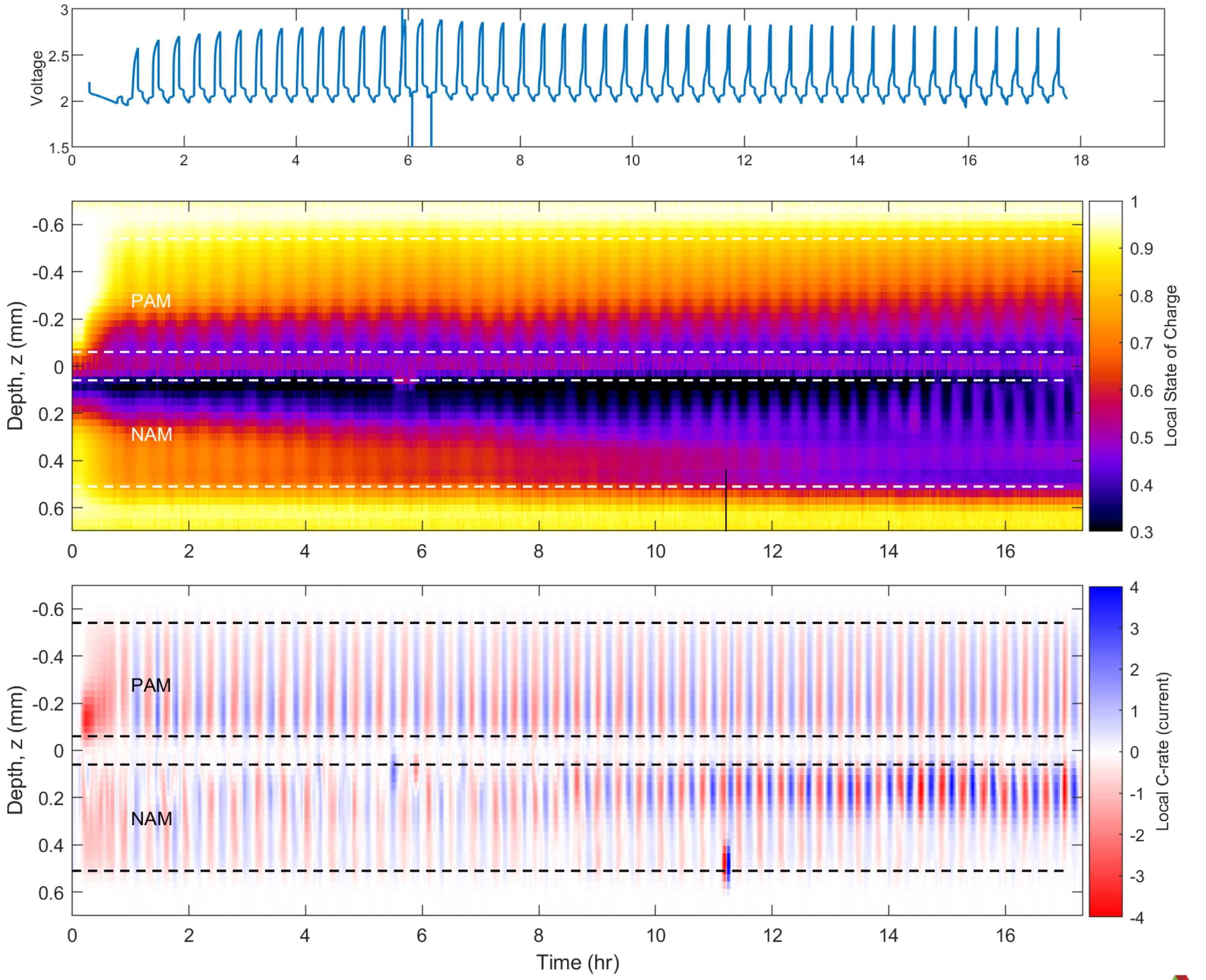
Can compute a local state of charge using mol fractions (n):

$$SOC = \frac{n_{Pb} + n_{PbO2}}{n_{Pb} + n_{PbO2} + n_{PbSO4}}$$

Using this SOC, we can also compute the local current density using:

$$I = \frac{Q}{\eta}\frac{\Delta SOC}{\Delta t}$$

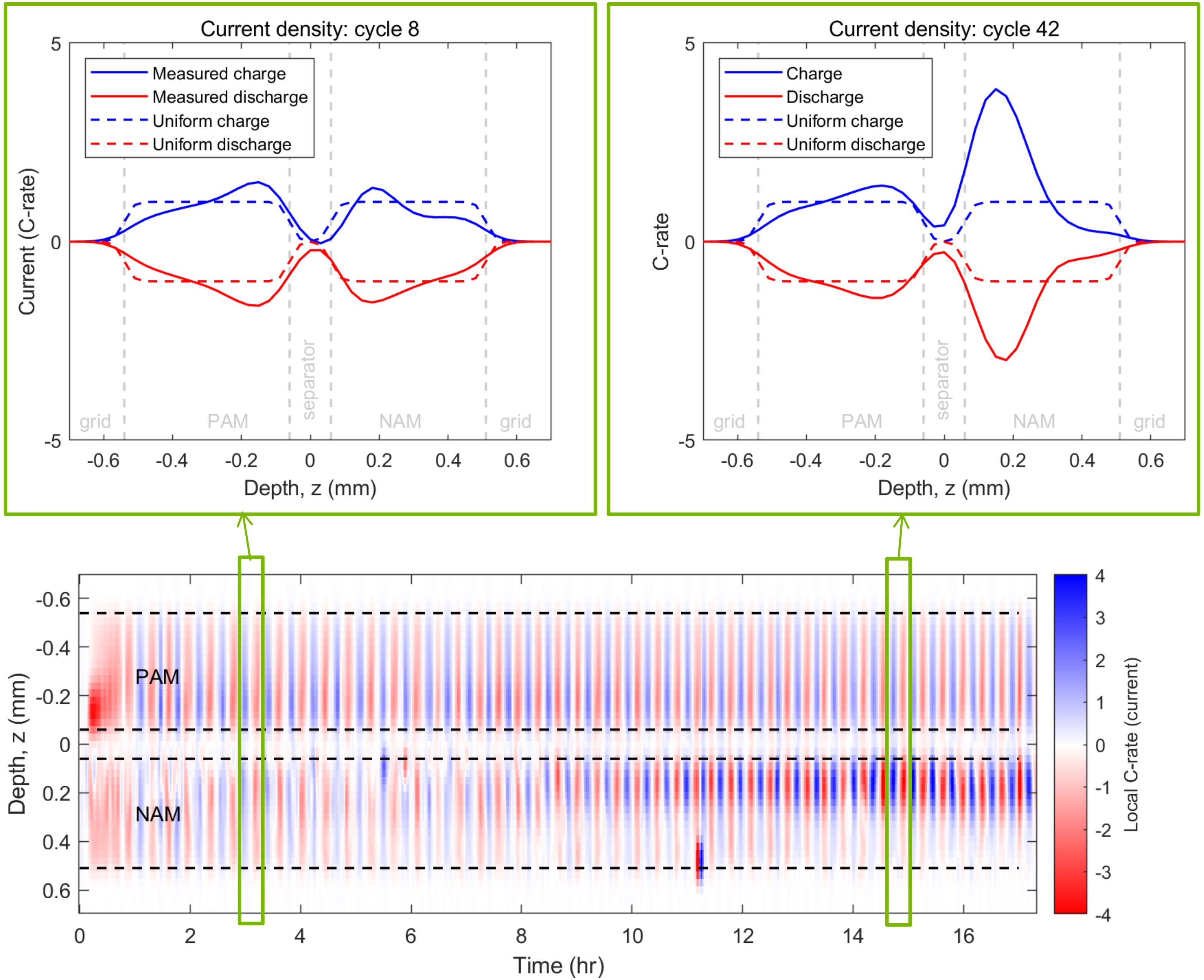
where Q is the measured capacity and η is the measured utilization



RESULTS

Trends

- High $PbSO_4$ content present near separator from start (incomplete formation, pre-charge).
- PAM: similar charge acceptance throughout, with slight enhancement near separator due to 1C rate.
- NAM at start (cycles 1- 20) also similar charge acceptance profile.
- NAM at end (cycles 30-50): Surface (near separator) becomes more active, carrying most of the charge (4C currents!).
- Surface sulfation: is the active surface the cause or effect of $PbSO_4$ pore-clogging?



SUMMARY, FUTURE DIRECTIONS

Real-time measurements of sulfation

<u>Particles:</u>

- Developed method for extracting particle size distribution from 2D XRD data.
- Result: sulfation is triggered at the onset of charge.

<u>Cells:</u>

- Developed method for depth profiling ‘mini’ lead acid electrodes during cycling.
- Can visualize local SOC and current density from XRD.
- HRPSOC cycling: NAM becomes highly active at separator. Precursor for sulfation?

<u>Future:</u>

- What is the effect of carbon on PSOC cycling?
- What is effect of C-rate and SOC window on cycling?
- APS-U: how do individual particles dissolve?

ACKNOWLEDGEMENTS

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APS: SECTORS 17BM, 11ID