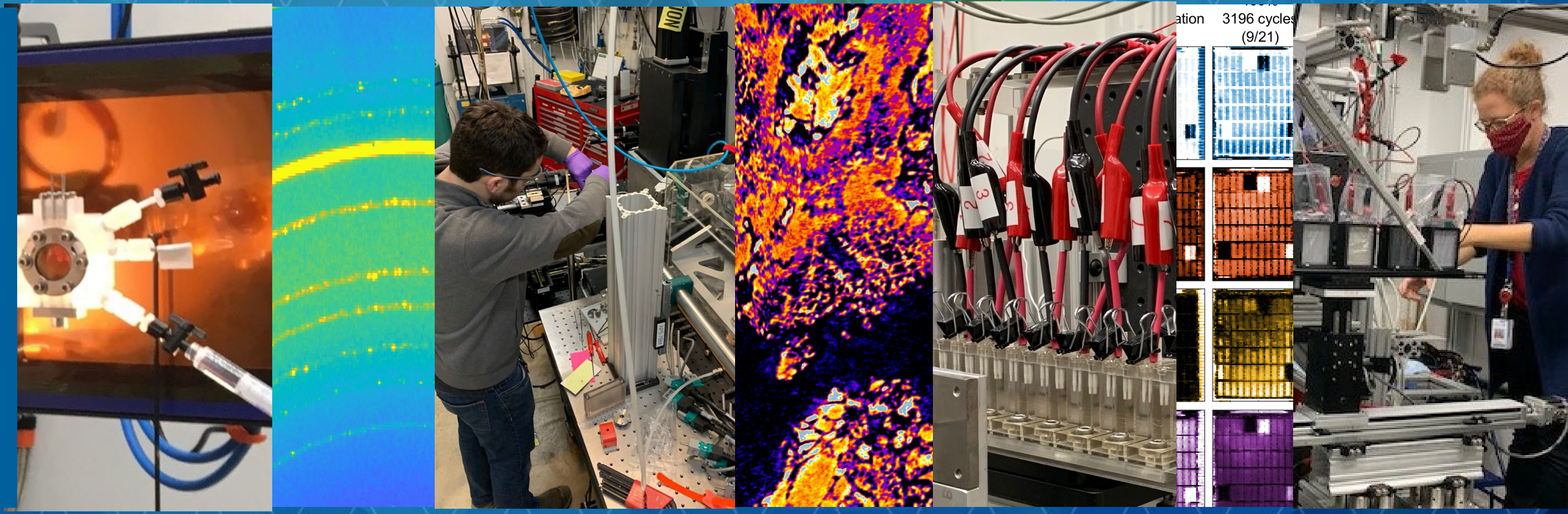
BCI/MPSC Lead Battery Symposium
December 15, 2022

IMAGING CHARGE ACCEPTANCE IN LEAD BATTERIES: A MULTISCALE CHALLENGE

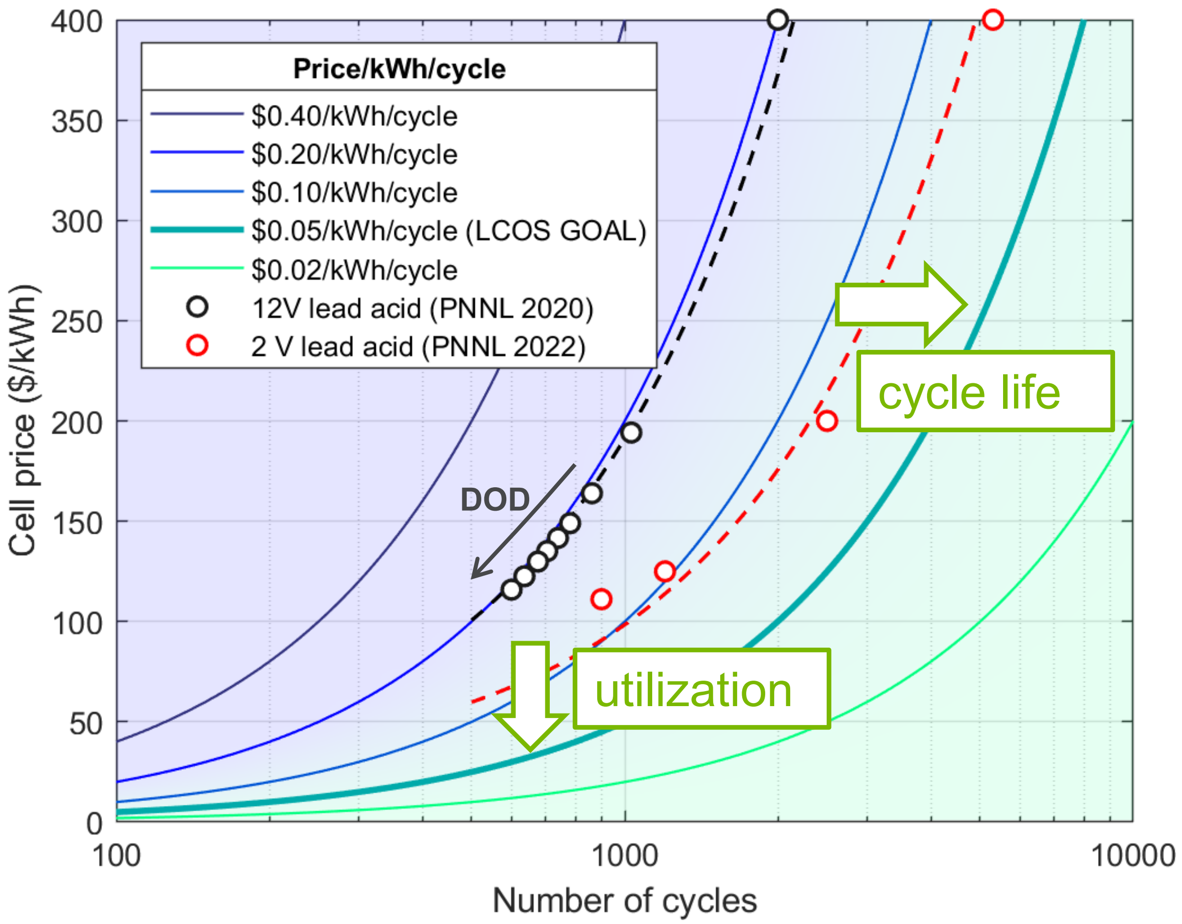


TIM FISTER, TIFFANY KINNIBRUGH, MARK WOLFMAN, JUAN GARCIA, HAKIM IDDIR, KEVIN KNEHR, MOHAMMED EFFAT, ANA SUZANA, PIETRO PAPA-LOPES
Argonne National Laboratory

MOTIVATION

Improving lead acid for pulse power *and* deep cycle applications

- Lead batteries are domestically manufactured, >99% recycled, and use inexpensive materials.
- At the ***cell level***, current lead acid cells already approach LCOS goals highlighted in the Energy Storage Grand Challenge.
- And despite being a mature technology, there is still significant ***room for growth*** in utilization and cycle life in lead acid.



MOTIVATION

Is there anything left to study?

- 150 years of heuristic knowledge, largely around:
  - Cell and grid design, modeling
  - Control of dopants, additives
  - Influence of morphology, porosity
- Lead batteries have largely relied on cycling data or *ex situ* data for evaluation.
- Tools unique to national labs can provide new *operando* information…

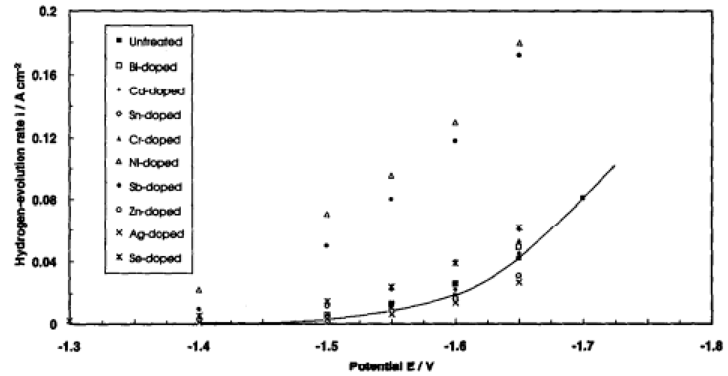
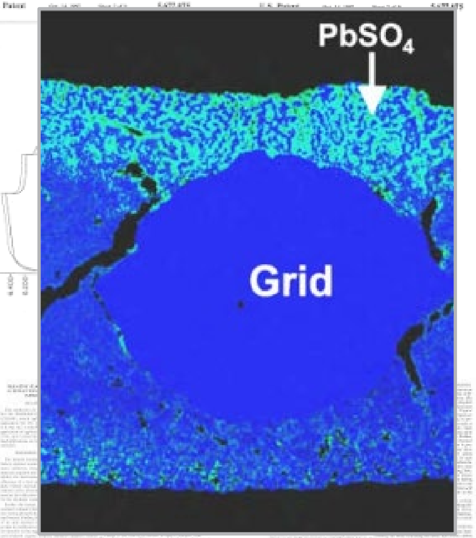
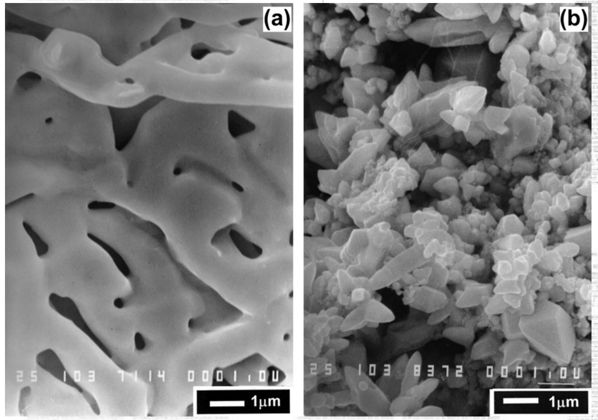


Fig. 6. Hydrogen evolution on untreated and doped/pasted electrodes.

Lam et al JPS 1994



Lam et al JPS 2004



Iliev and Pavlov, J. App. Electrochem. 1985

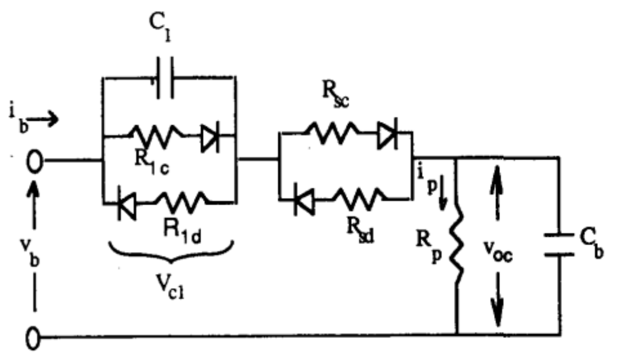


Figure 4: Battery Equivalent Circuit

Salameh IEEE 1992

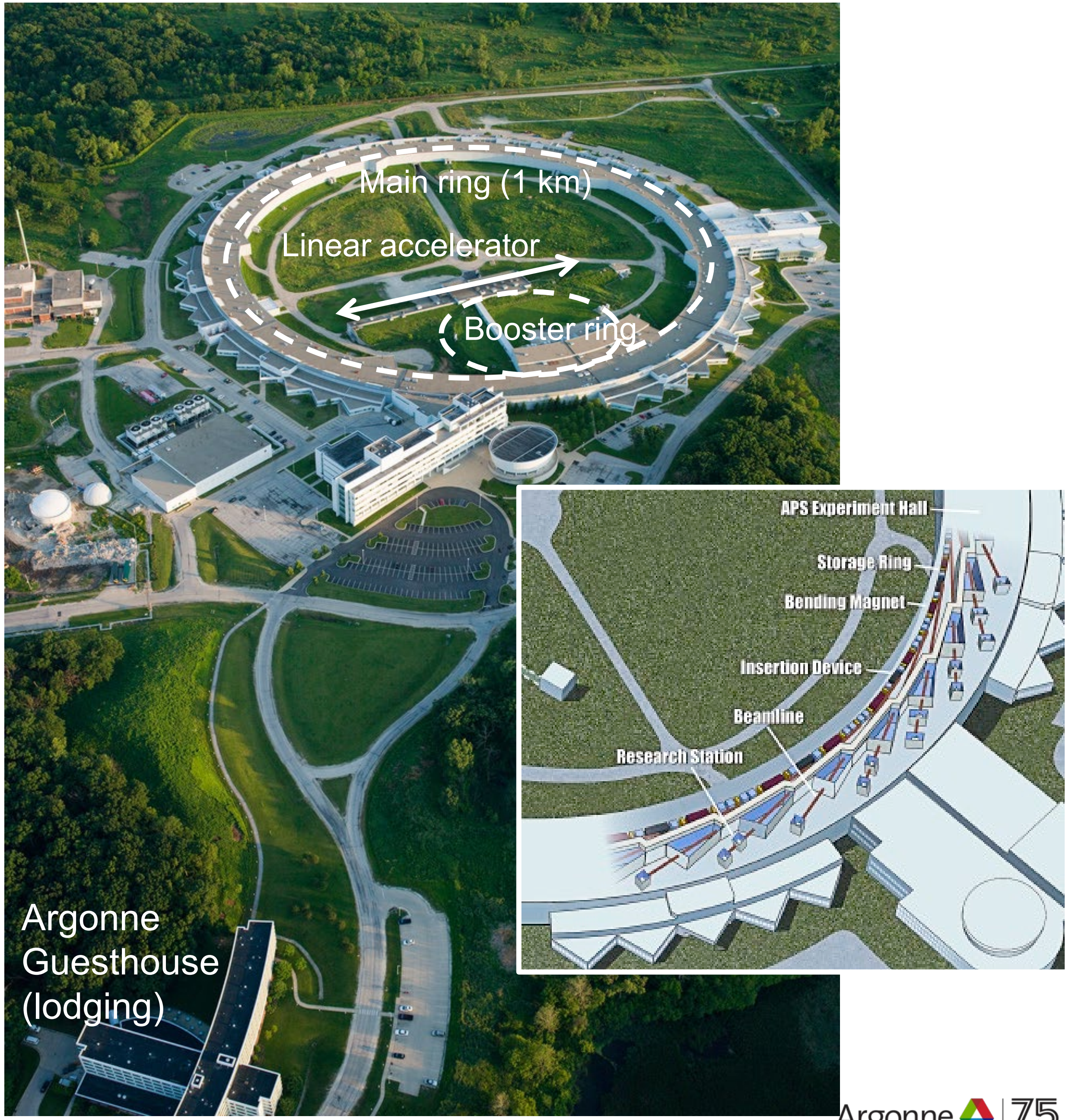
EXAMPLE

Advanced Photon Source (APS)

Synchrotrons: cutting edge x-ray sources capable of resolving complexity over many length scales.

- Higher energy = *in situ*
- Higher flux = *real time*
- Higher resolution = *resolve heterogeneity* (such as chemical gradients, particles)

APS is a *billion-dollar* instrument, the type of user facility made possible by the DOE national labs.



IMPROVING UTILIZATION AND CYCLE LIFE

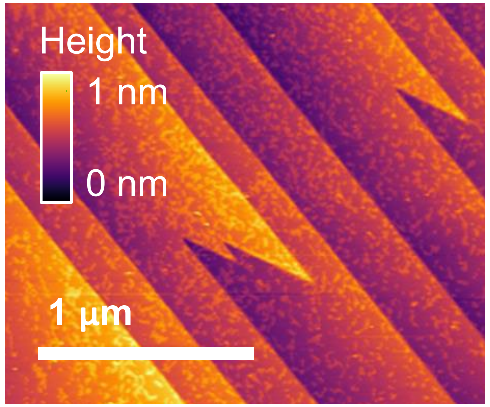
A challenge over many length scales

Improving utilization and lifetime is a multiscale problem involving **solid** and **liquid** species.

- Atomic level issues: $PbSO_4$ nucleation, Pb^{2+} solvation, acid dissociation, additives/dopants
- Particle level issues: sulfation/pore clogging, diffusion/tortuosity limitations for e^- and SO_4^{2-}
- Cell level issues: electrolyte stratification, grid corrosion, paste shedding/softening
- Battery level issues: charge/discharge procedures, impedance, electrolyte management, grid design

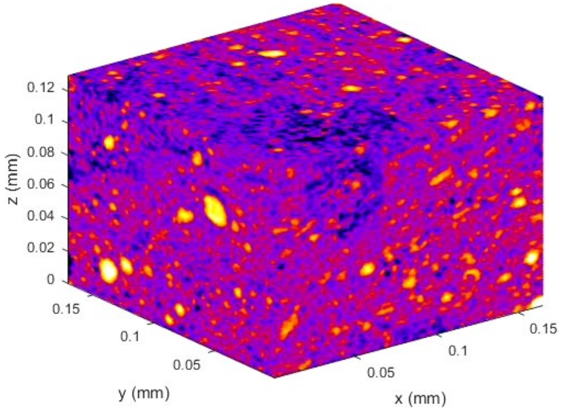
Atomic level (~nm, nAh)

Example: monolayer growth of $PbSO_4$ on barite 001.



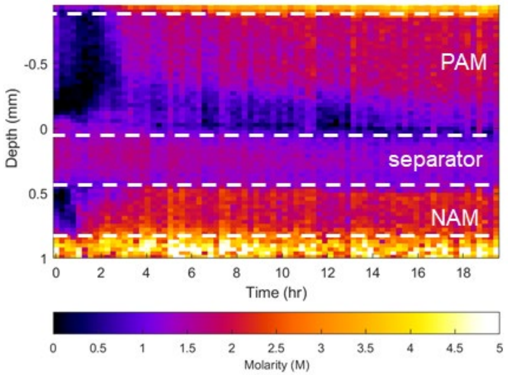
Particle level (~µm, µAh)

Example: Reconstructed volume from CT scan of a paste electrode (color = density)



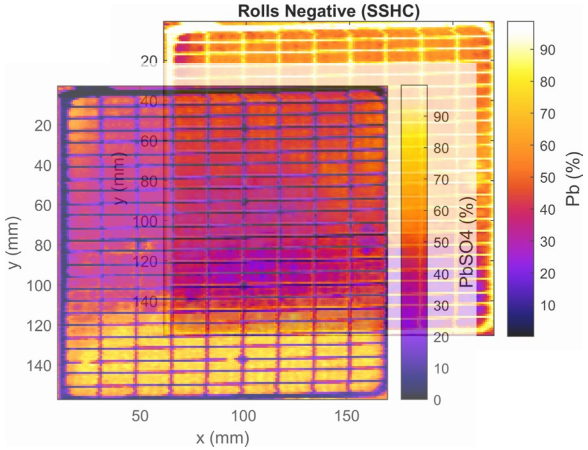
Cell level (~mm, mAh-Ah)

Example: Electrolyte mapping during formation using high energy x-ray scattering



Battery level (~100 Ah)

Example: cycling at PNNL and XRD from EOF battery plates



CURRENT PROGRAMS

Analysis from fundamental to applied

Model expanders

PIs: Papa Lopes, Lind-Kovacs

DOE/OE:

fundamental science
(PIs: Murugesan, Fister)

LBSRP

(Fister, Papa Lopes)

DOE/OE:

Testing and evaluation
(PI: Thomsen)

Atomic level (~nm, nAh)

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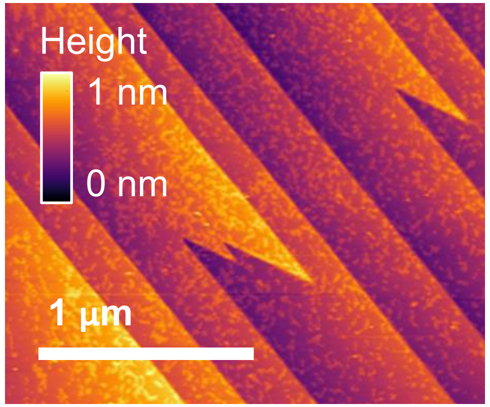

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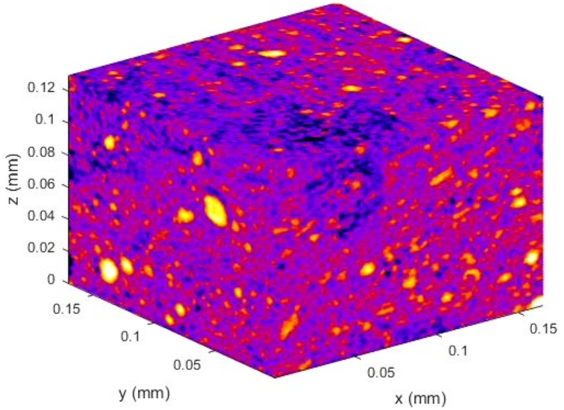
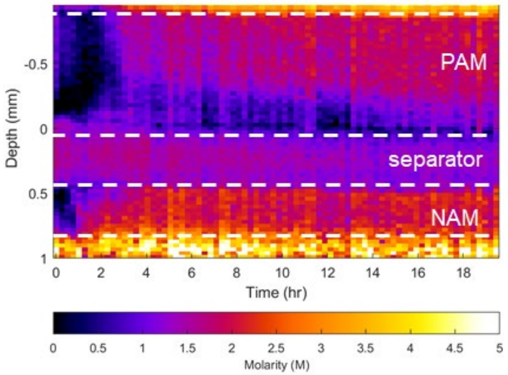


Cell level (~mm, mAh-Ah)

Example: Electrolyte mapping during formation



Battery level (~100 Ah)

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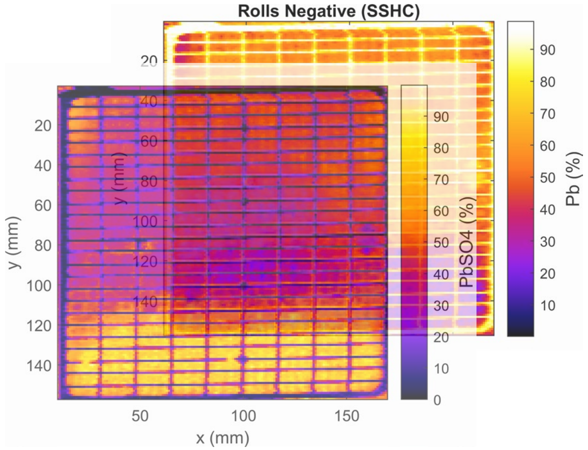


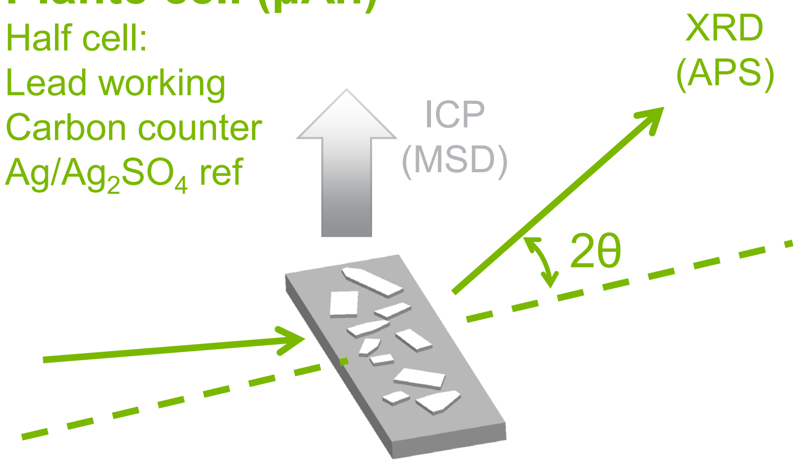
EXPERIMENTAL SETUPS

Increasing complexity

- Initial emphasis was on [simpler] processes taking place on negative electrode.
- Transitioned to pasted cells, but maintained emphasis on negative additives.
- Final phase (on-going): developing robust two-electrode cell to study failure mechanisms.

Plante cell (µAh)

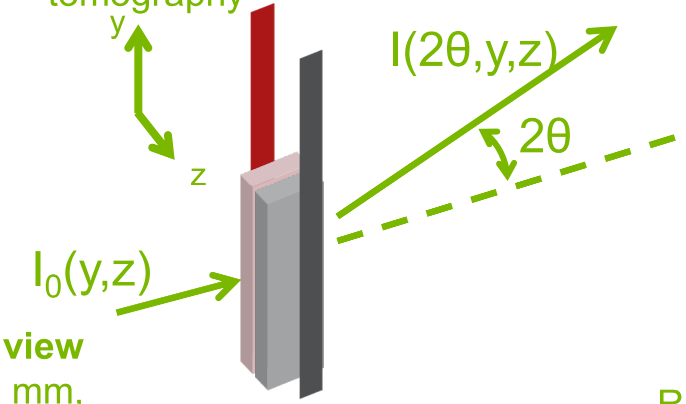
Half cell:
Lead working
Carbon counter
Ag/Ag_2SO_4 ref



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

Mini cells (mAh):

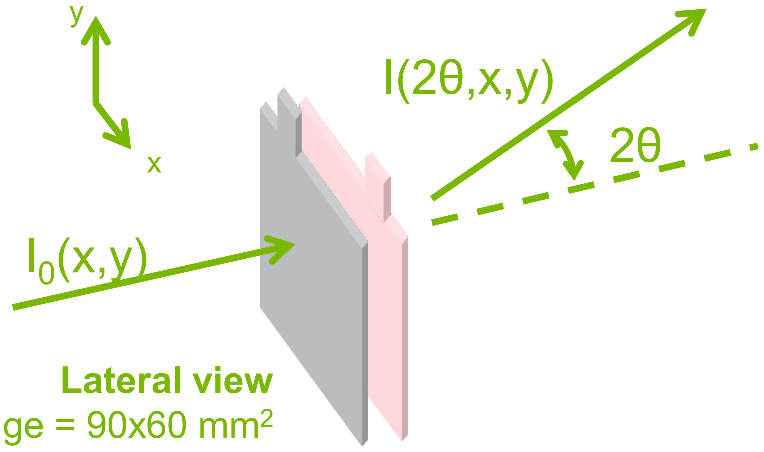
Depth profiling and computed tomography



Edge view
Range: 3 mm,
Δz = 0.03 mm

2V pasted cells (Ah)

2 electrode cells

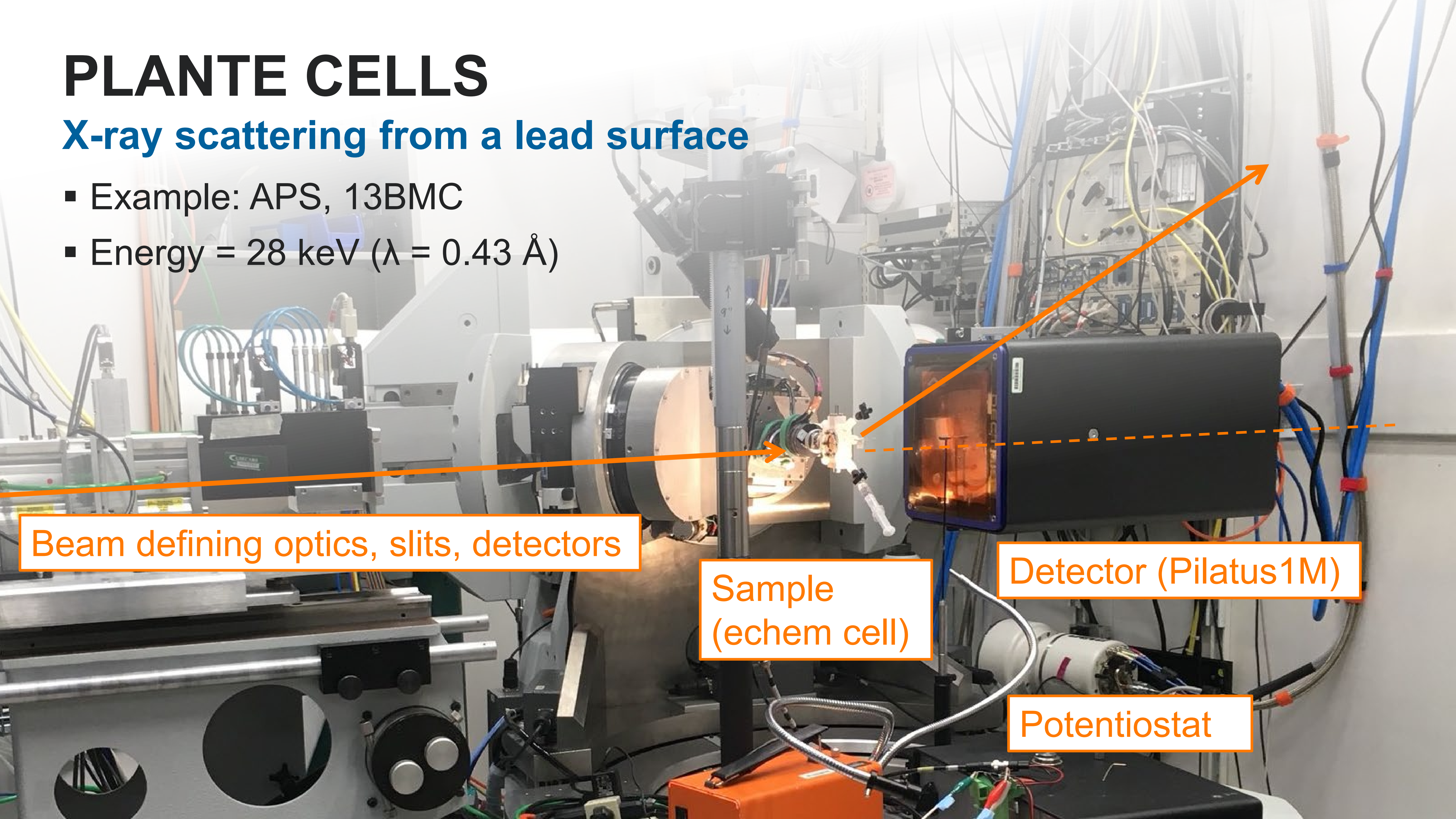


Lateral view
Range = 90x60 mm^2
Δxy = 1 mm^2

PLANTE CELLS

X-ray scattering from a lead surface

- Example: APS, 13BMC
- Energy = 28 keV (λ = 0.43 Å)



Beam defining optics, slits, detectors

Sample (echem cell)

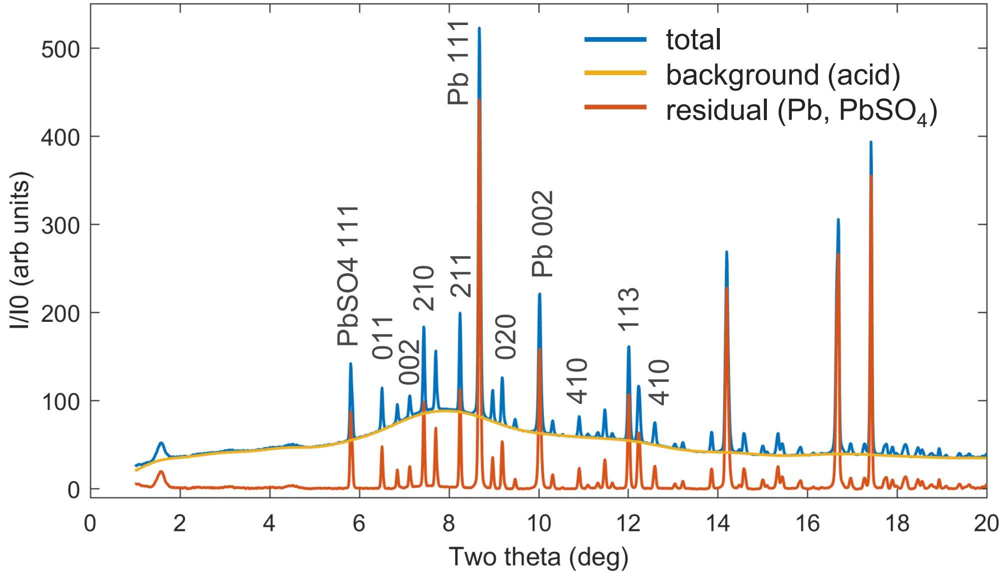
Detector (Pilatus1M)

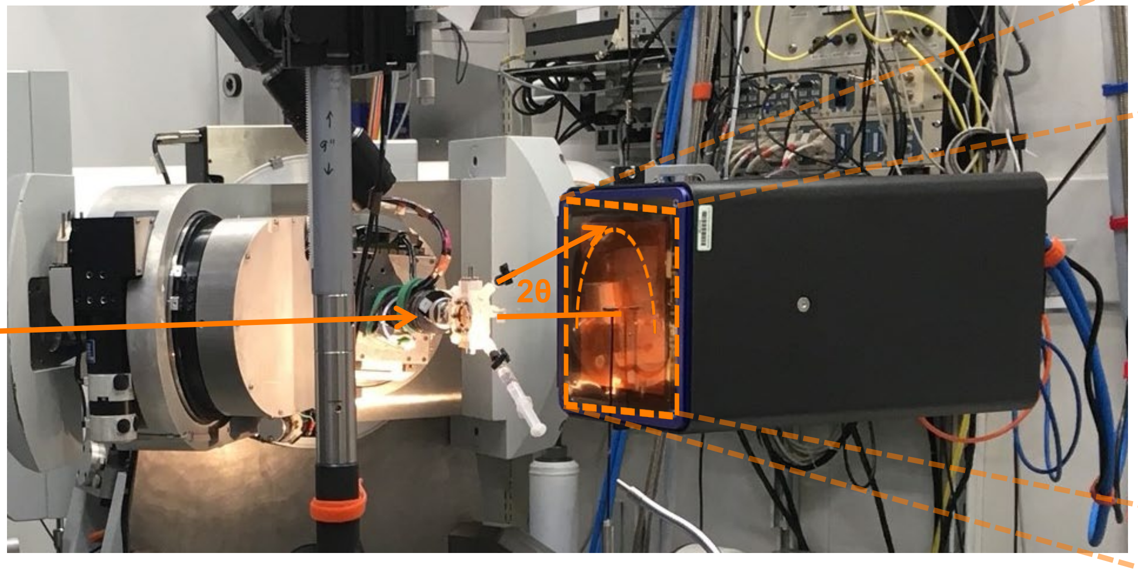
Potentiostat

EXPERIMENT

Scattering from a lead surface

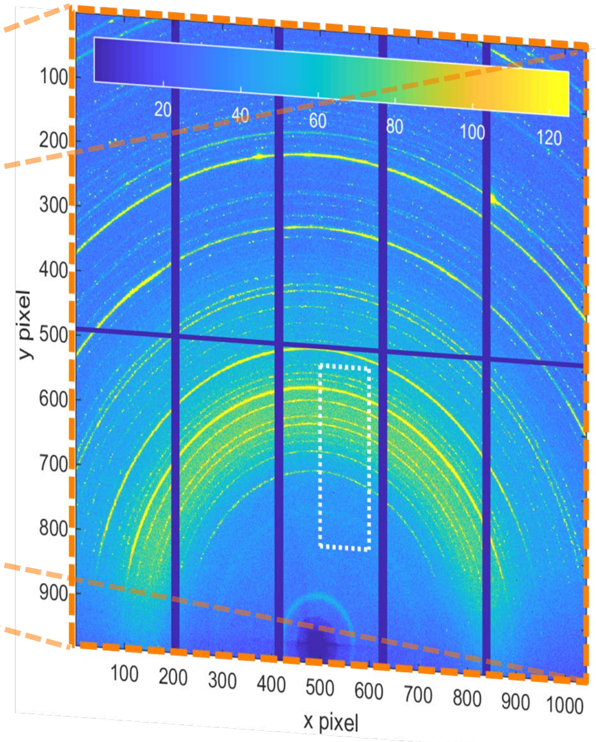
- A single detector image contains a wealth of information.
- Bragg peaks from active material phases (Pb, $PbSO_4$)
- Background from scattering from acid





X-rays

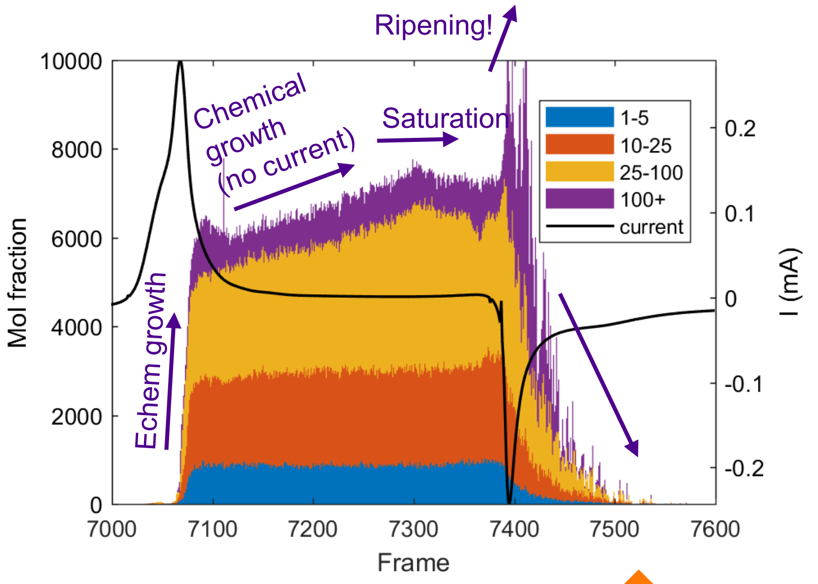
APS 13BM-C

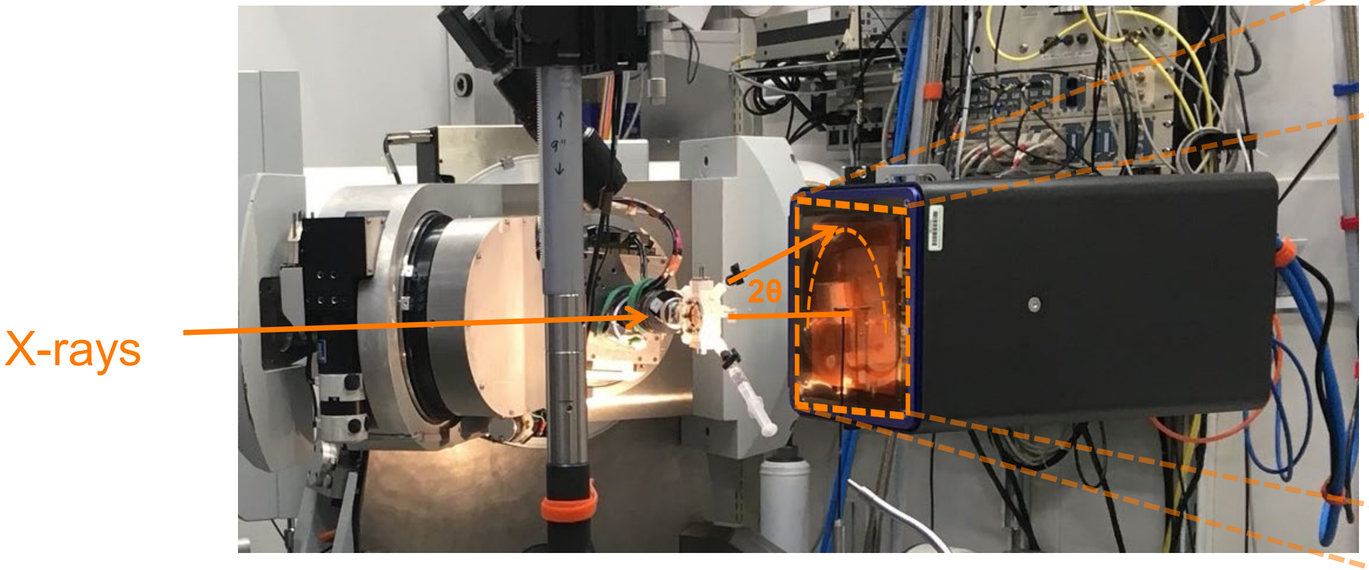


EXPERIMENT

Scattering from a lead surface

- A single detector image contains a wealth of information.
- Bragg peaks from active material phases (Pb, $PbSO_4$)
- Background from scattering from acid
- Powder lines = scattering from many crystals = statistics!





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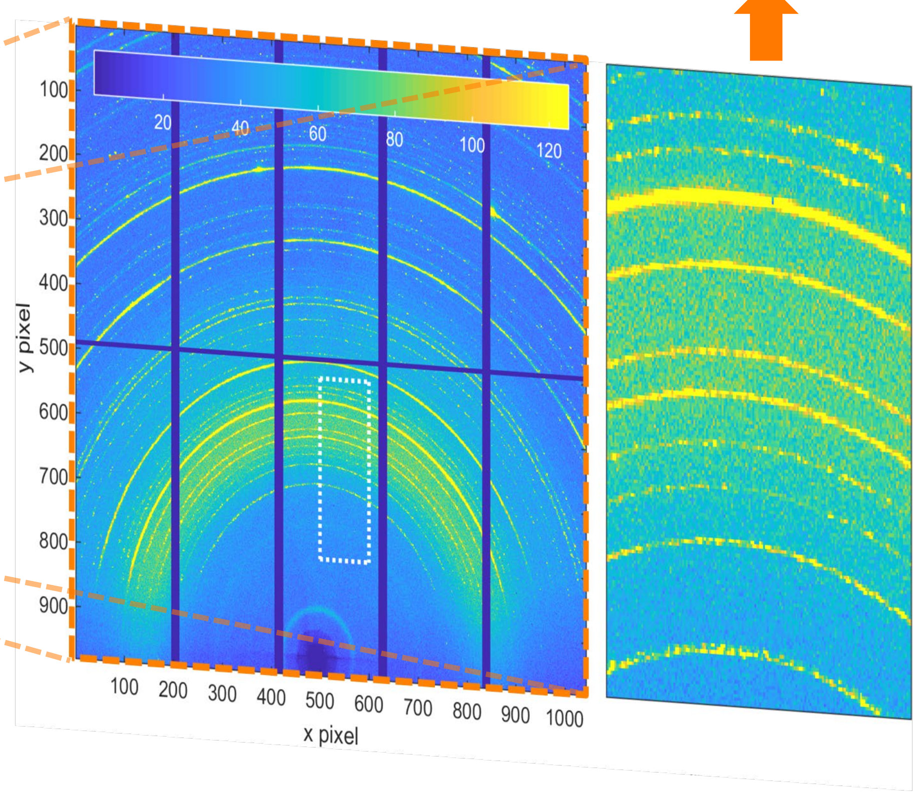
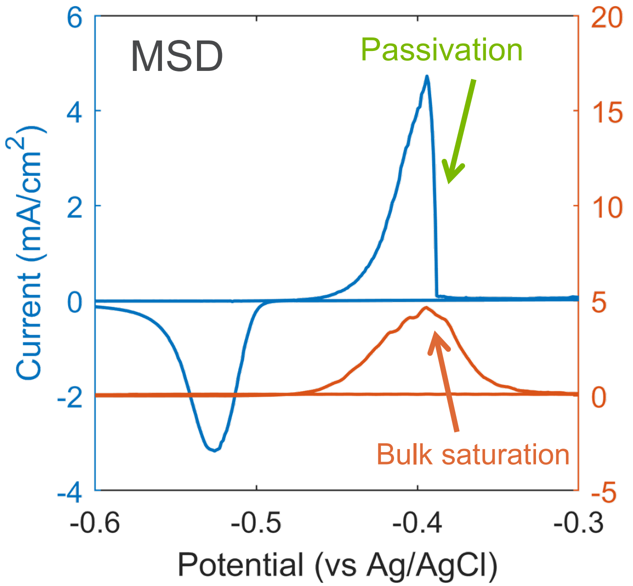


CV & XRD

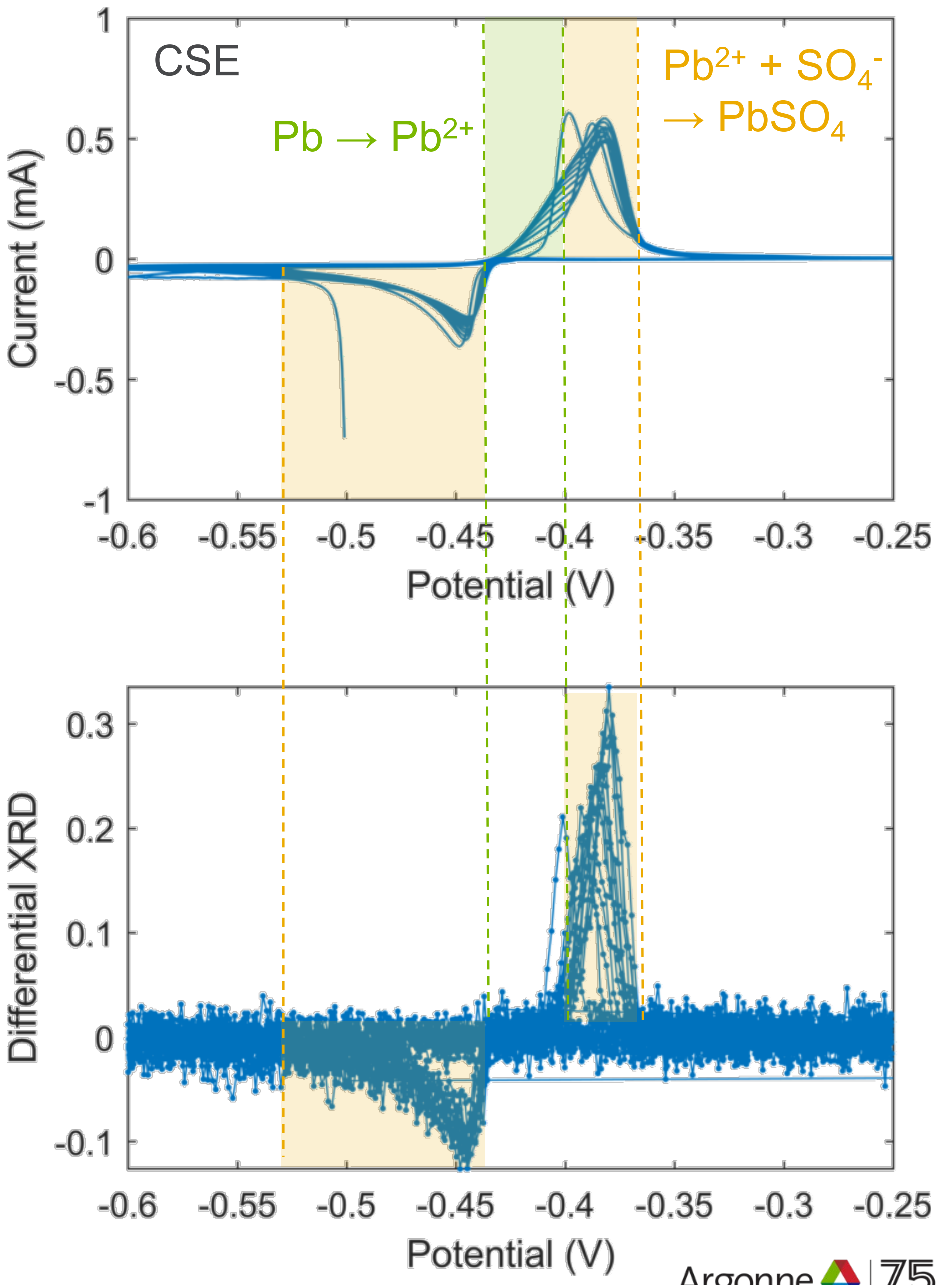
Onset, kinetics

Comparison of current response versus ***change*** in $PbSO_4$ signal.

- Discharge: $PbSO_4$ growth delayed from onset of current and is more abrupt, suggesting a two step process.
  - Fits into analysis by MSD using in situ ICP.
- Charge: $PbSO_4$ dissolution rate similar to cathodic current → crystal dissolution is the rate limiting step.



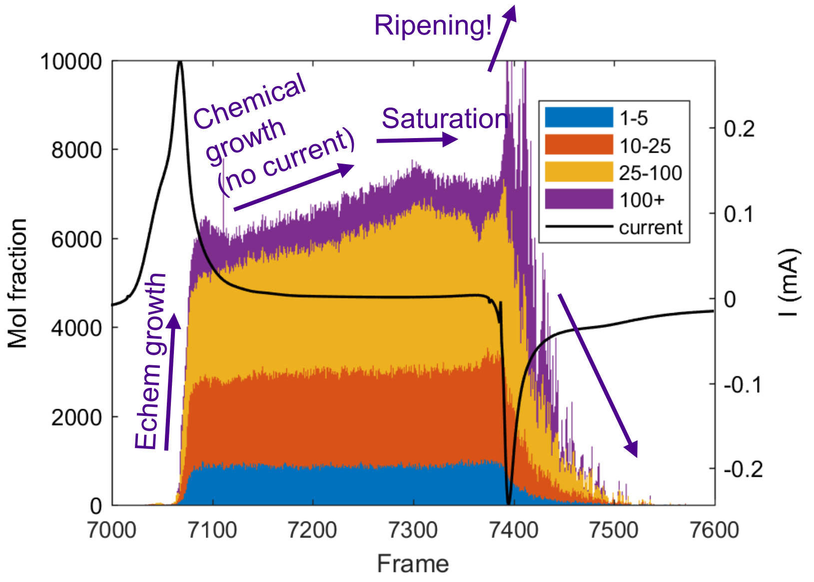
1.300 g/cm^3, 0.2 mV/s

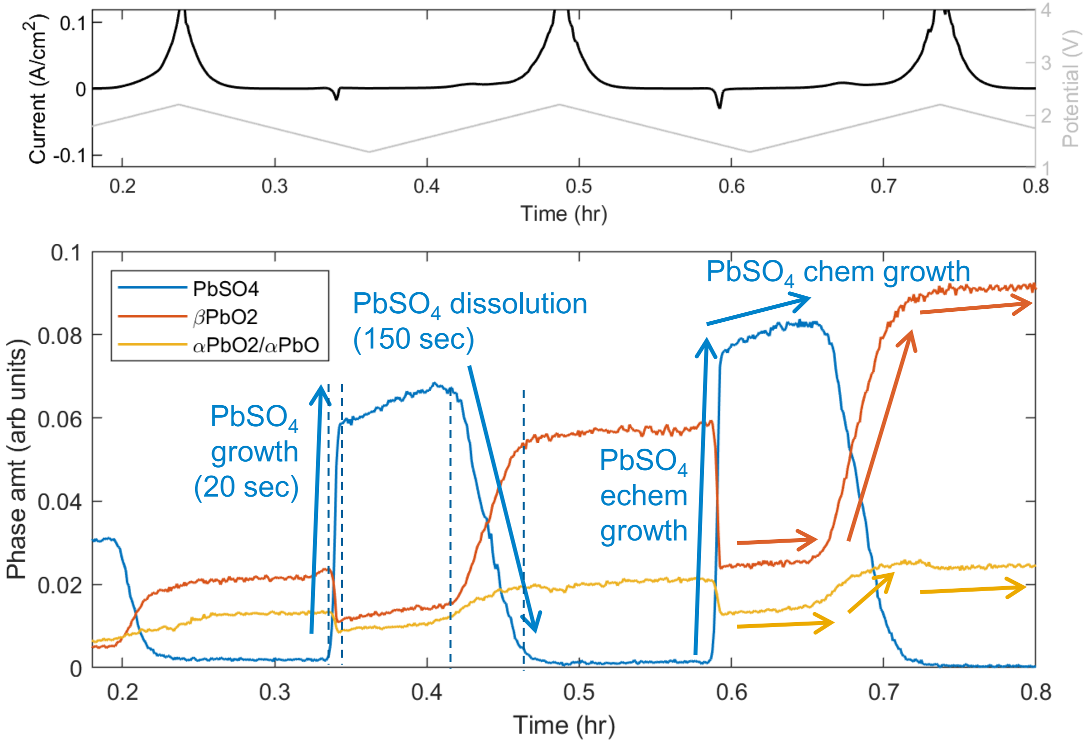


PLANTE POSITIVE

PbO, PbO_2, $PbSO_4$

- Cycles 1-3: discharge faster than charge, but charge process is fairly linear.
  – Note that PbO_2 dissolution is not reversible





$PbSO_4$ growth/dissolution is similar to negative electrode (figure from review presentation and 12/2018 and 2/2019 talks):

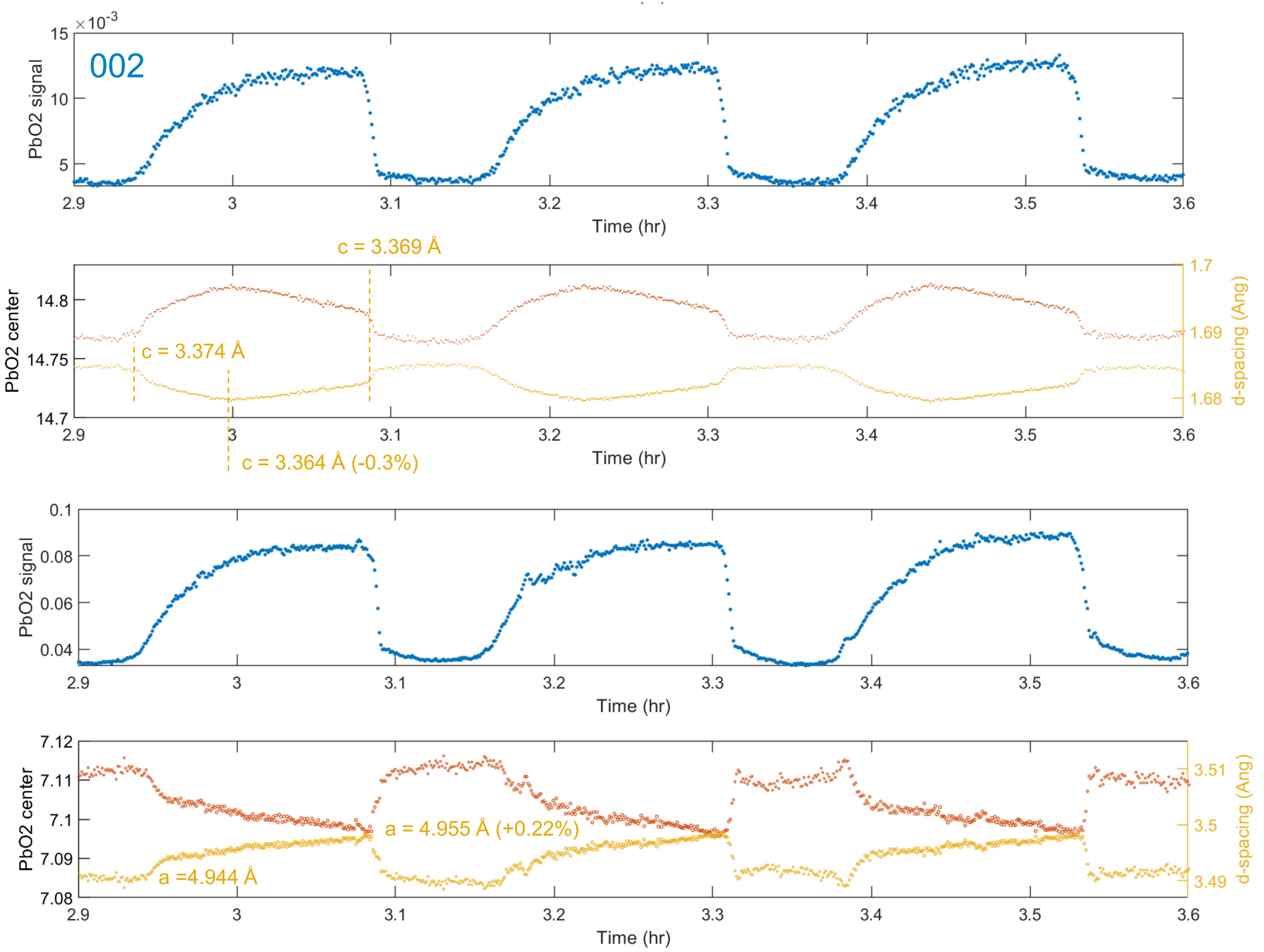
1) Rapid growth during cathodic wave
2) Slow growth after (chemical growth of $PbSO_4$ as Pb^{2+} concentration reaches equilibrium).

Note that PbO/PbO_2 also grows at this condition!

PLANTE POSITIVE

Peak shifts

- The crystal structure of each phase changes significantly during cycling.
- This is related to oxygen non-stoichiometry in PbO_2.
- Overall volume change of 0.3% (that’s a lot!)

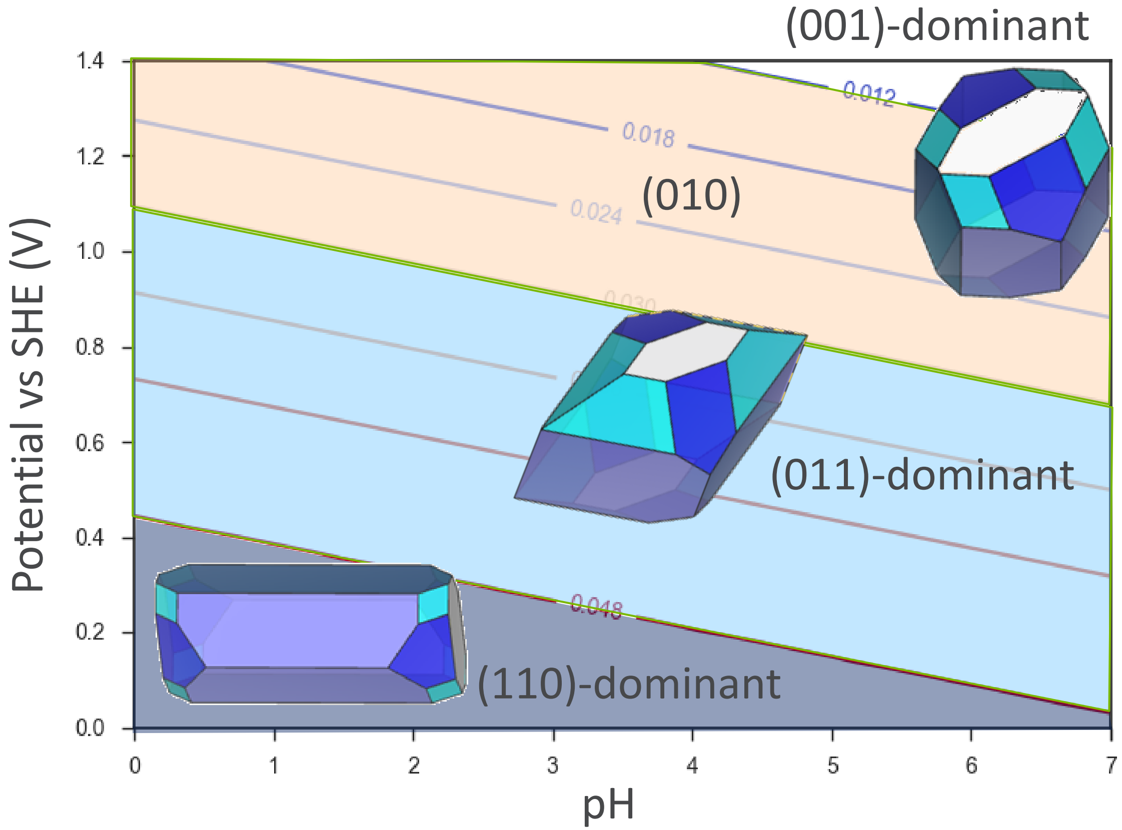


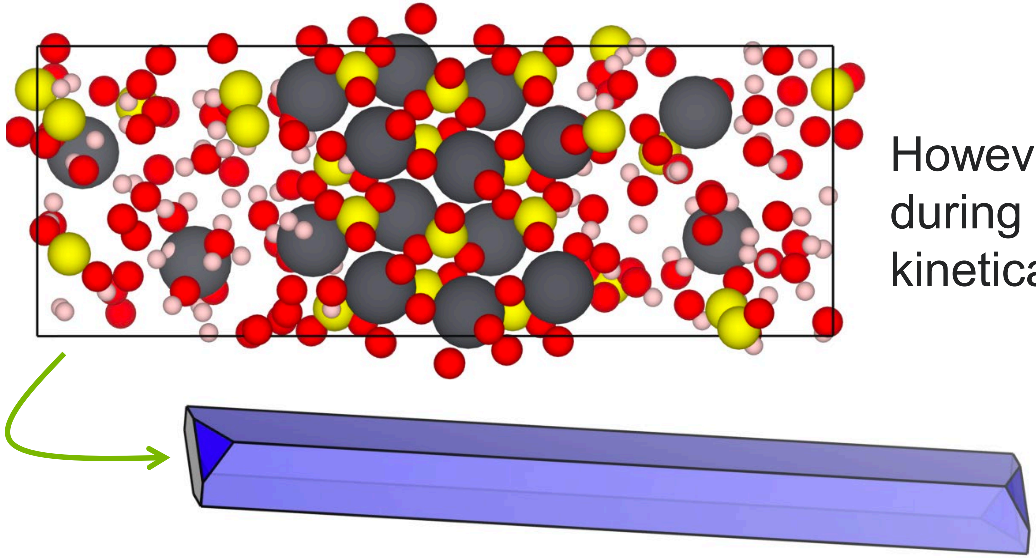
CRYSTAL HABIT

DFT/MD Approach

Big question: what is the most stable (or most reactive) $PbSO_4$ surface?

- DFT calculations of low-index $PbSO_4$ surfaces: equilibrium crystal shape
- Right: additional calculations were used to extend this approach to full range in pH.





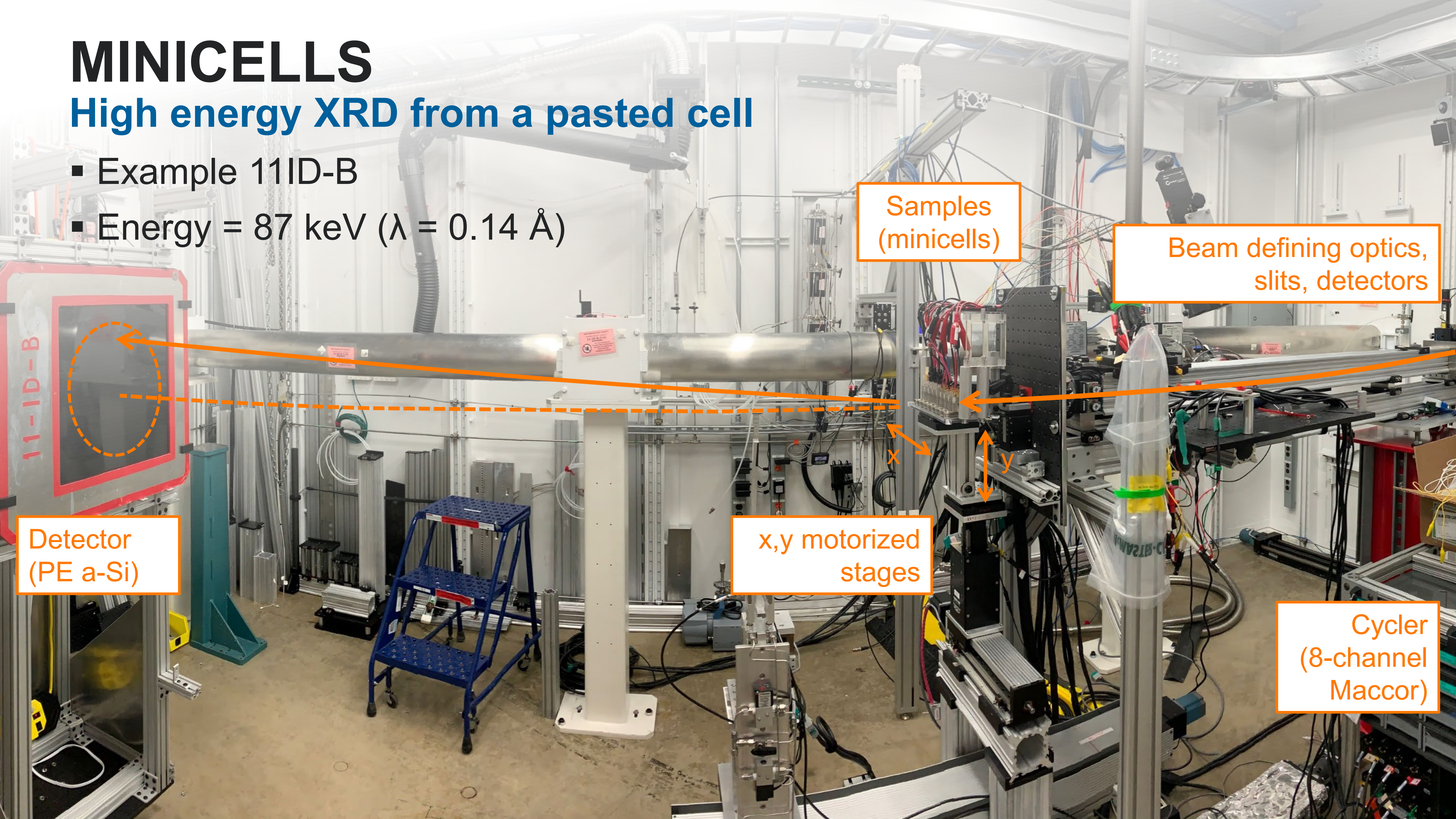
However, crystal growth/dissolution may not have time to equilibrate during charge and discharge. Ab initio MD (left) was used to study kinetically-limited processes, which have different looking crystal habits.

Can we use this information to **design** $PbSO_4$ crystals (or $BaSO_4$) with faster dissolution kinetics?

MINICELLS

High energy XRD from a pasted cell

- Example 11ID-B
- Energy = 87 keV (λ = 0.14 Å)



Samples (minicells)

Beam defining optics, slits, detectors

Detector (PE a-Si)

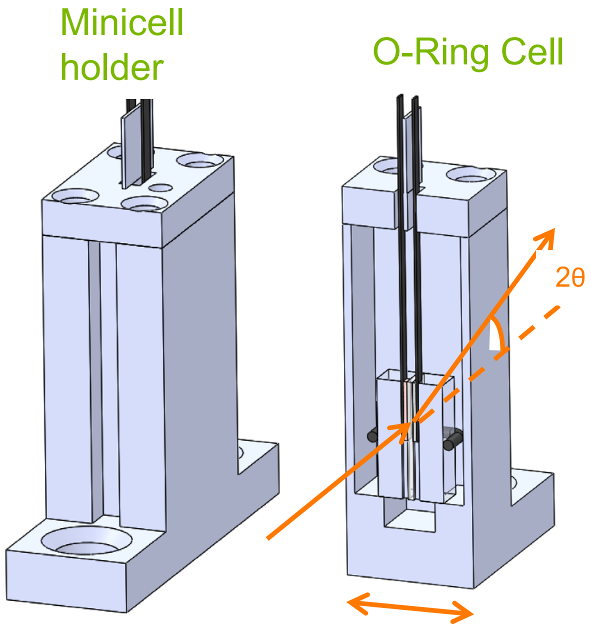
x,y motorized stages

Cycler (8-channel Maccor)

MINICELLS

Construction

- Minicells developed at East Penn for x-ray depth profiling.
- Initial cells used O-ring(s) to define compression, but later designs used an external shell.
- Parts were printed or machined from acrylic.

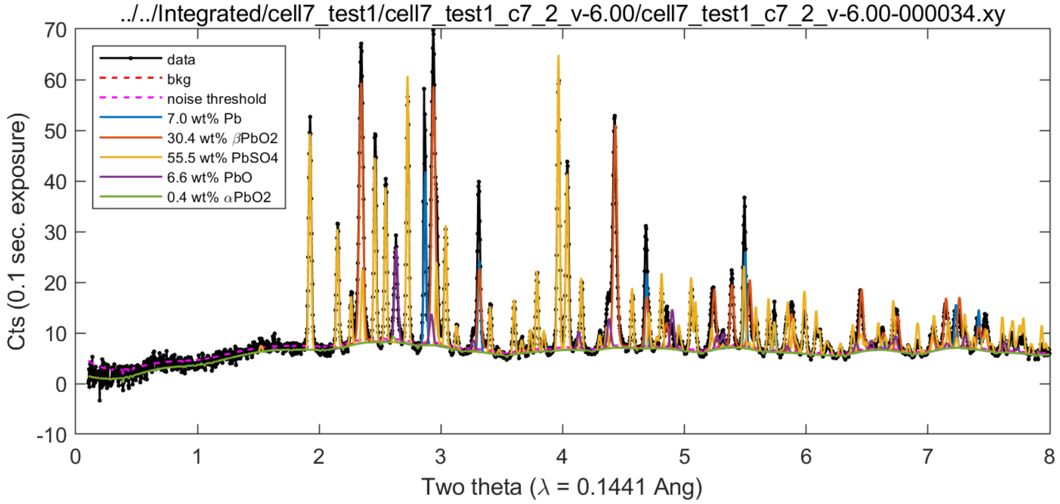


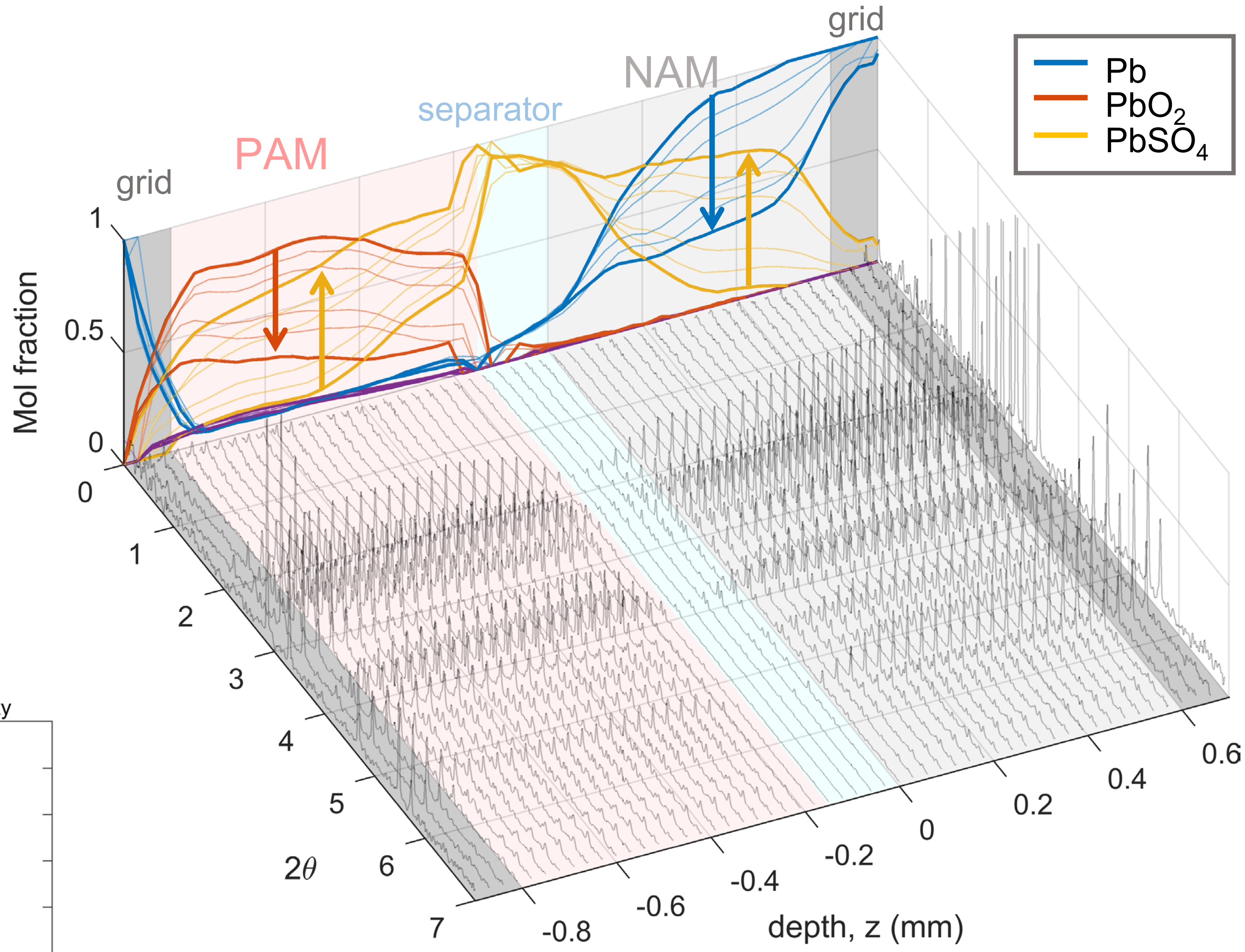
Depth, z = ±1.5 mm
(100 steps: 30 µm/step)

DEPTH PROFILING

Example

- Typical step size of 0.03 mm through the cell with 0.1 sec integration time.
- Example of data from PAM, below.



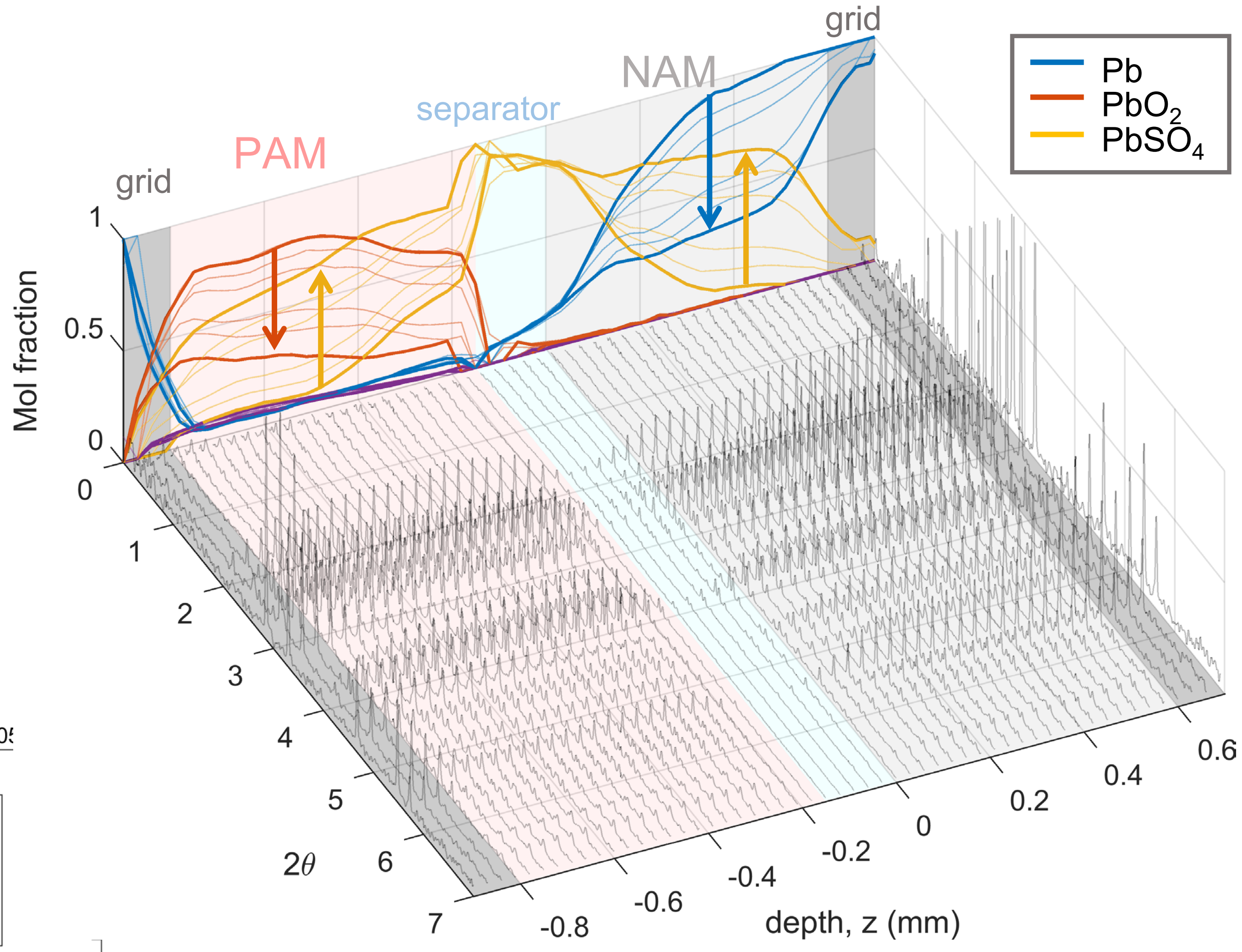


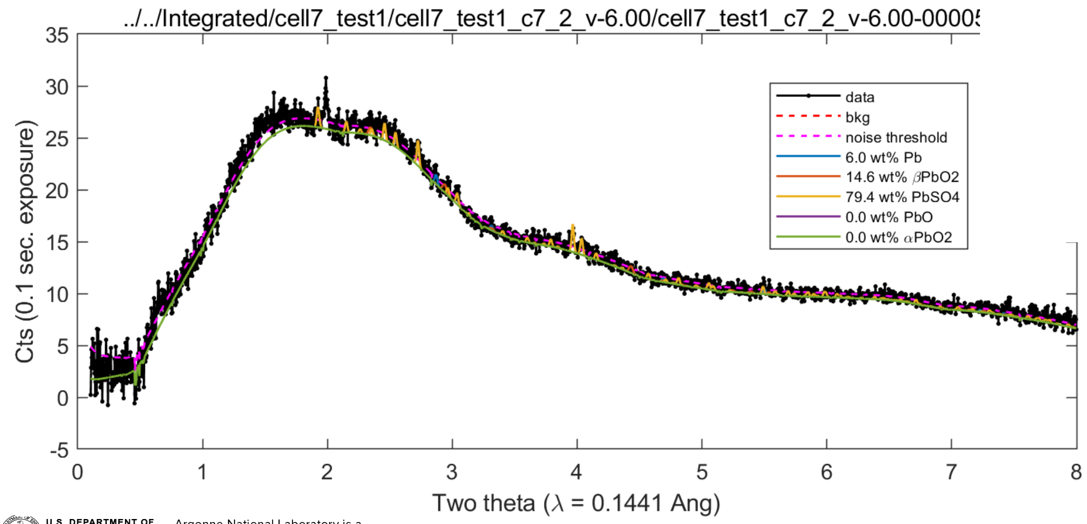
Important: minicells get **60-80%** utilization at 1C rates, yet macrocells/batteries get 20-30% utilization at 1C.

DEPTH PROFILING

Example

- Typical step size of 0.03 mm through the cell with 0.1 sec integration time.
- Example of data from separator region, below:





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DEPTH PROFILING

Example

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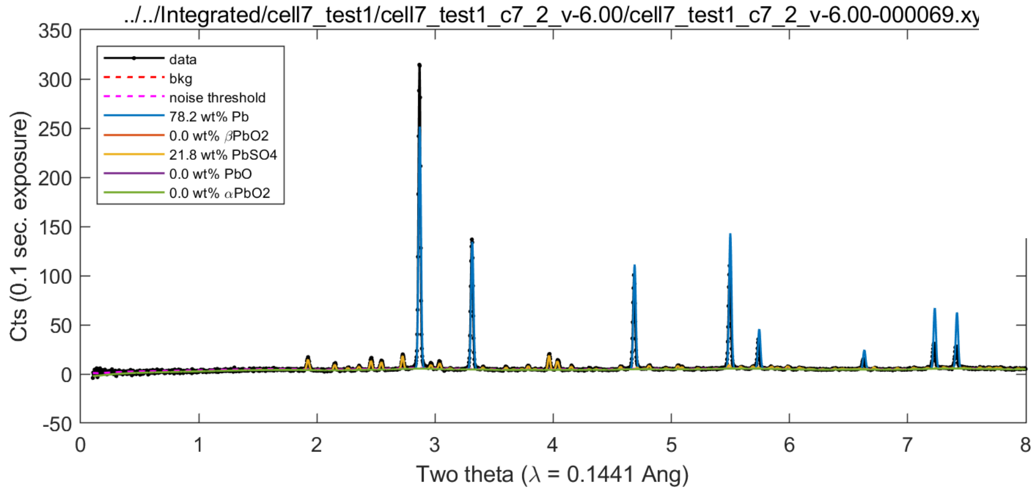
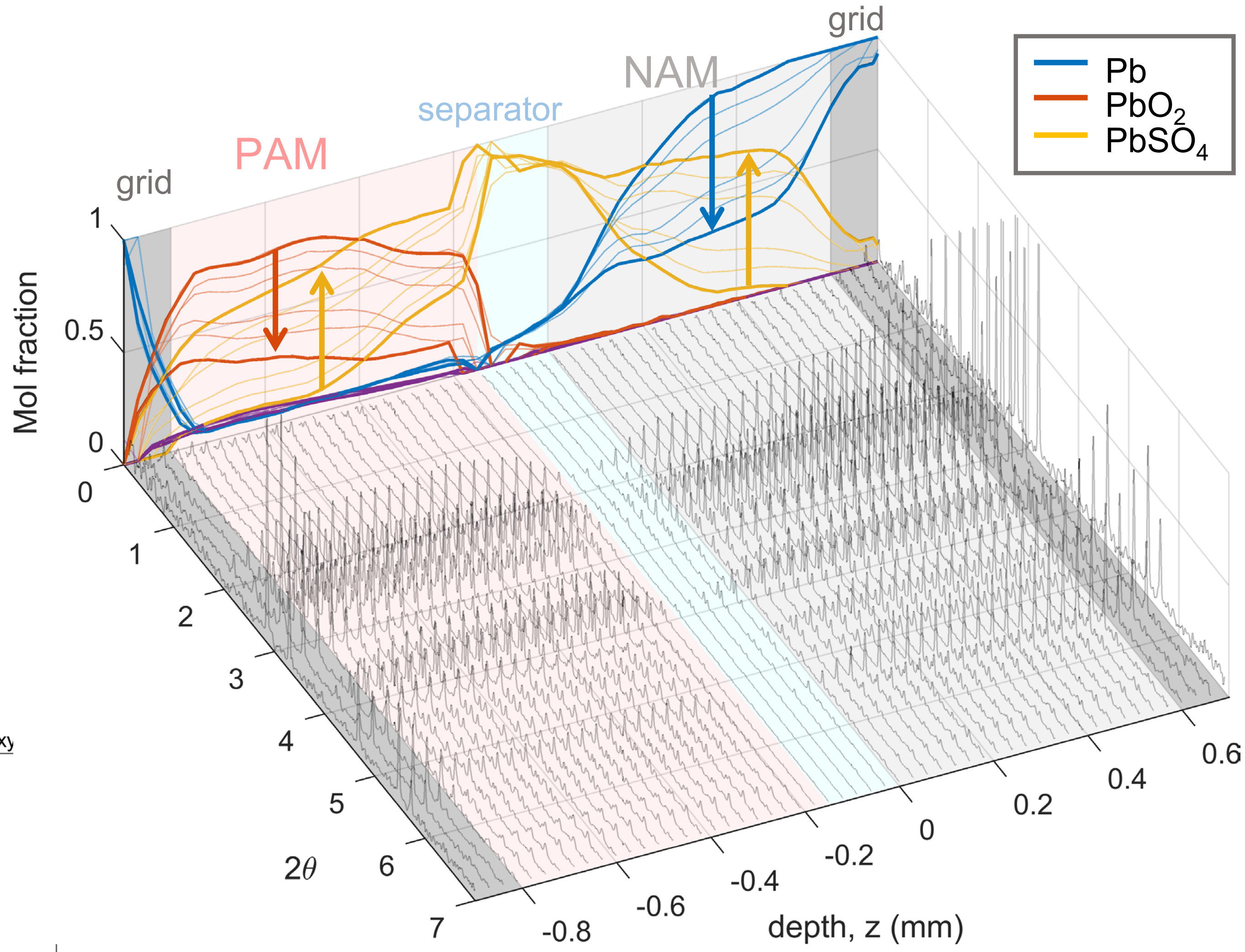
- Example of data from NAM, below.





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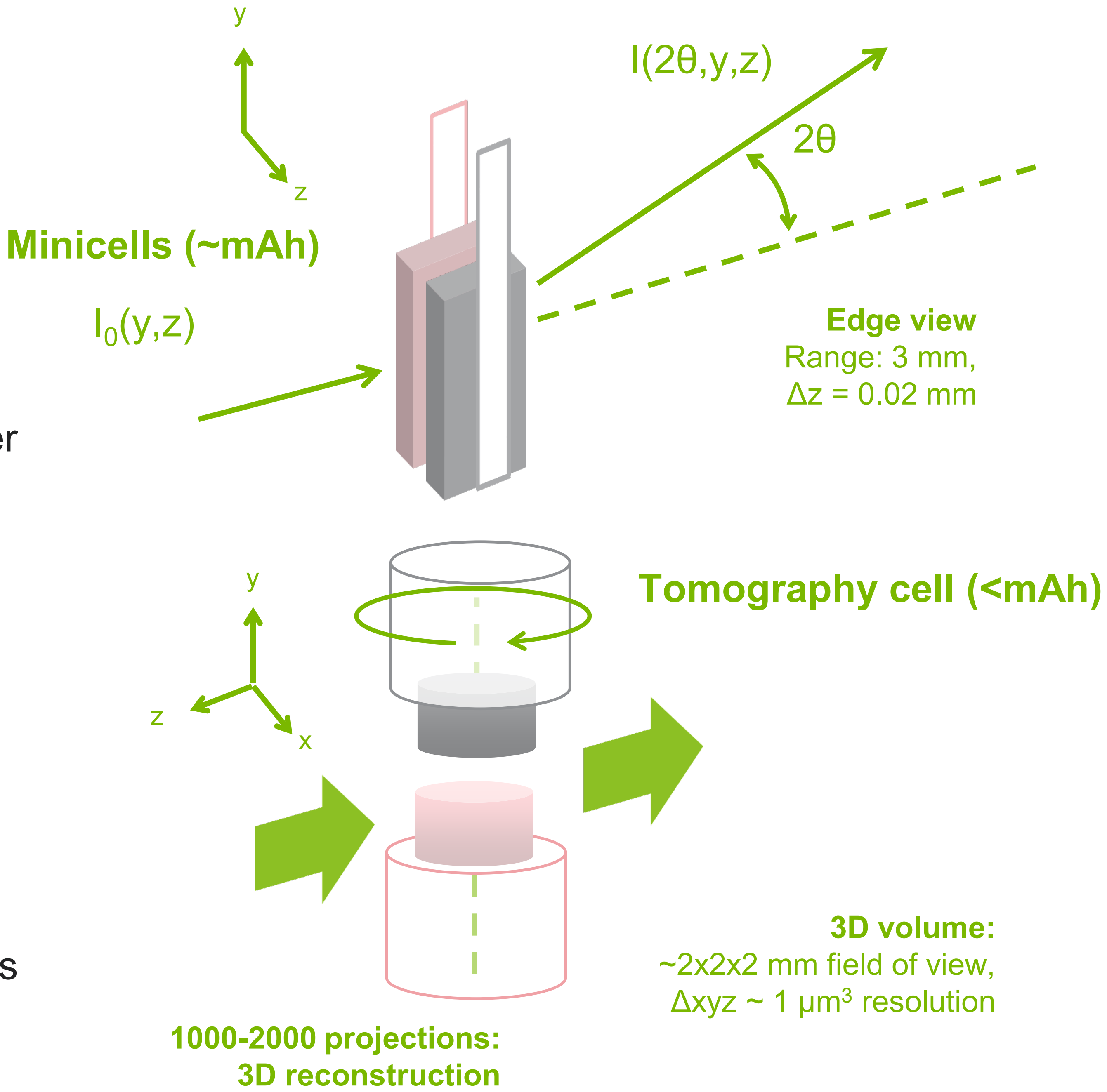
MINICELLS FOR TOMOGRAPHY

Cylindrical geometry

- Unlike 1D depth profiling, computed tomography requires ~1000 projections over 180° rotation.
- Minicells were explored for CT studies, but suffered from artifacts from the highly absorbing lead tabs on the sides.
- Wolfman developed a cylindrical cell, with top and bottom electrodes that provided much better reconstructions. Pasting/curing is still a challenge.
- Recent upgrades at sector 7BM have incorporated energy dispersive diffraction as a secondary probe.



Minicells (~mAh)

Edge view
Range: 3 mm,
Δz = 0.02 mm

Tomography cell (<mAh)

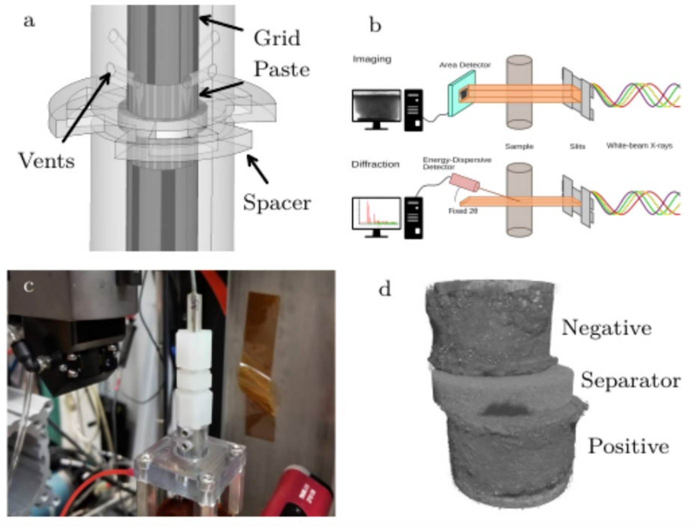
3D volume:
~2x2x2 mm field of view,
Δxyz ~ 1 μm^3 resolution

1000-2000 projections:
3D reconstruction

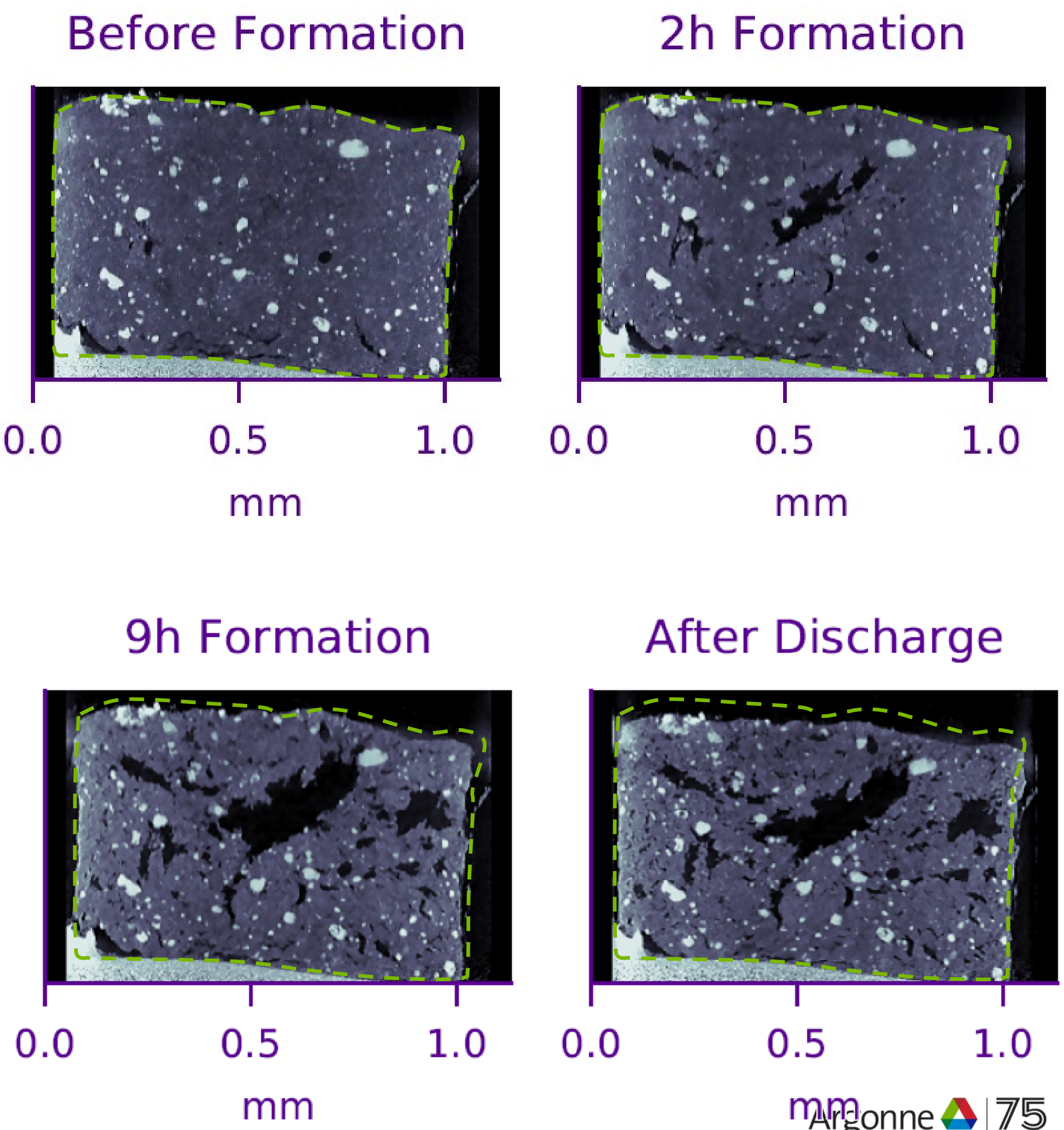
MICRO-CT

Imaging a whole electrode

- Biggest changes in porosity found during formation, especially on negative.
- These voids lead to densification of the active material.



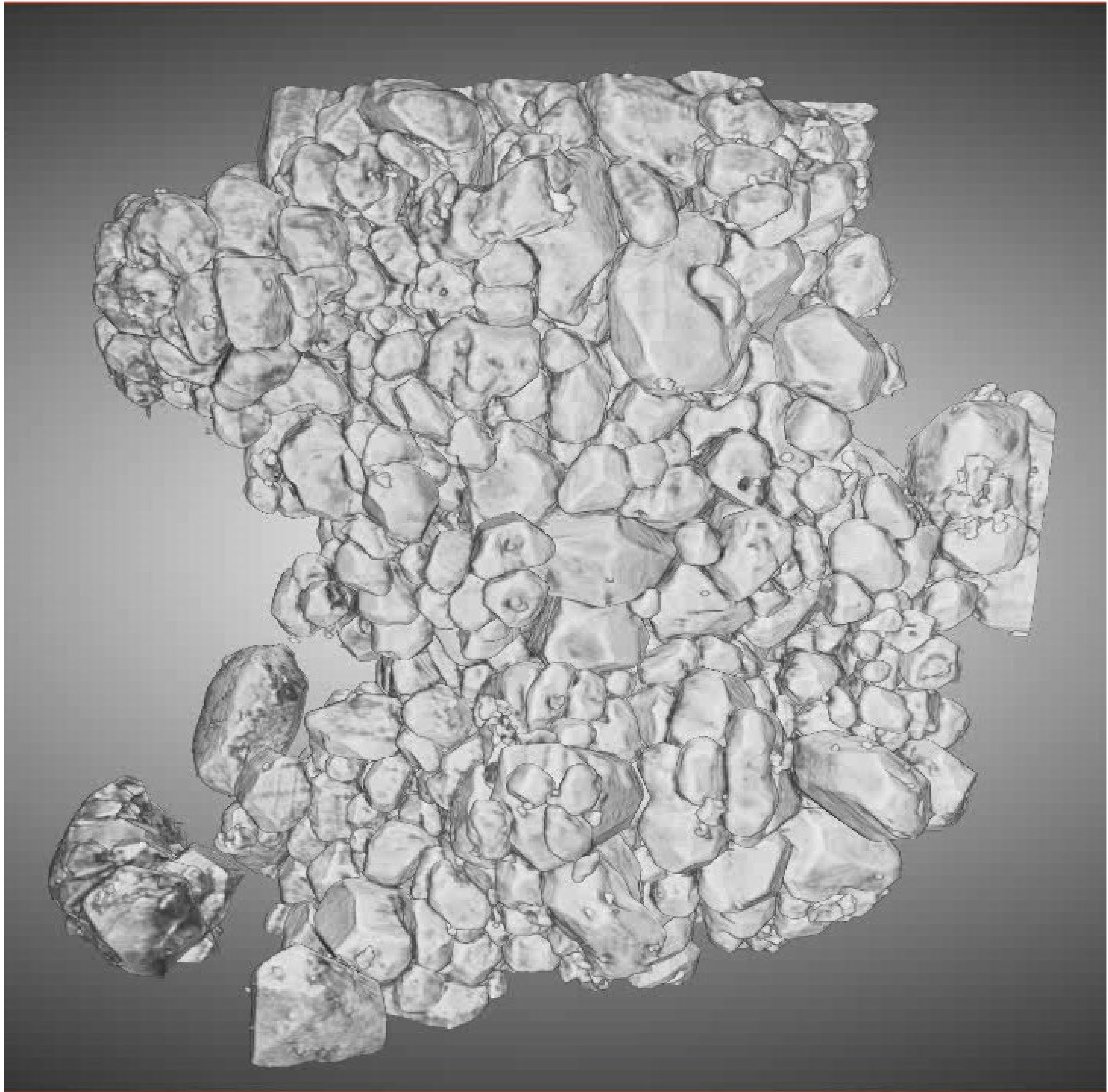
NAM cross-section during formation and cycling



NANO-CT

3D microstructure

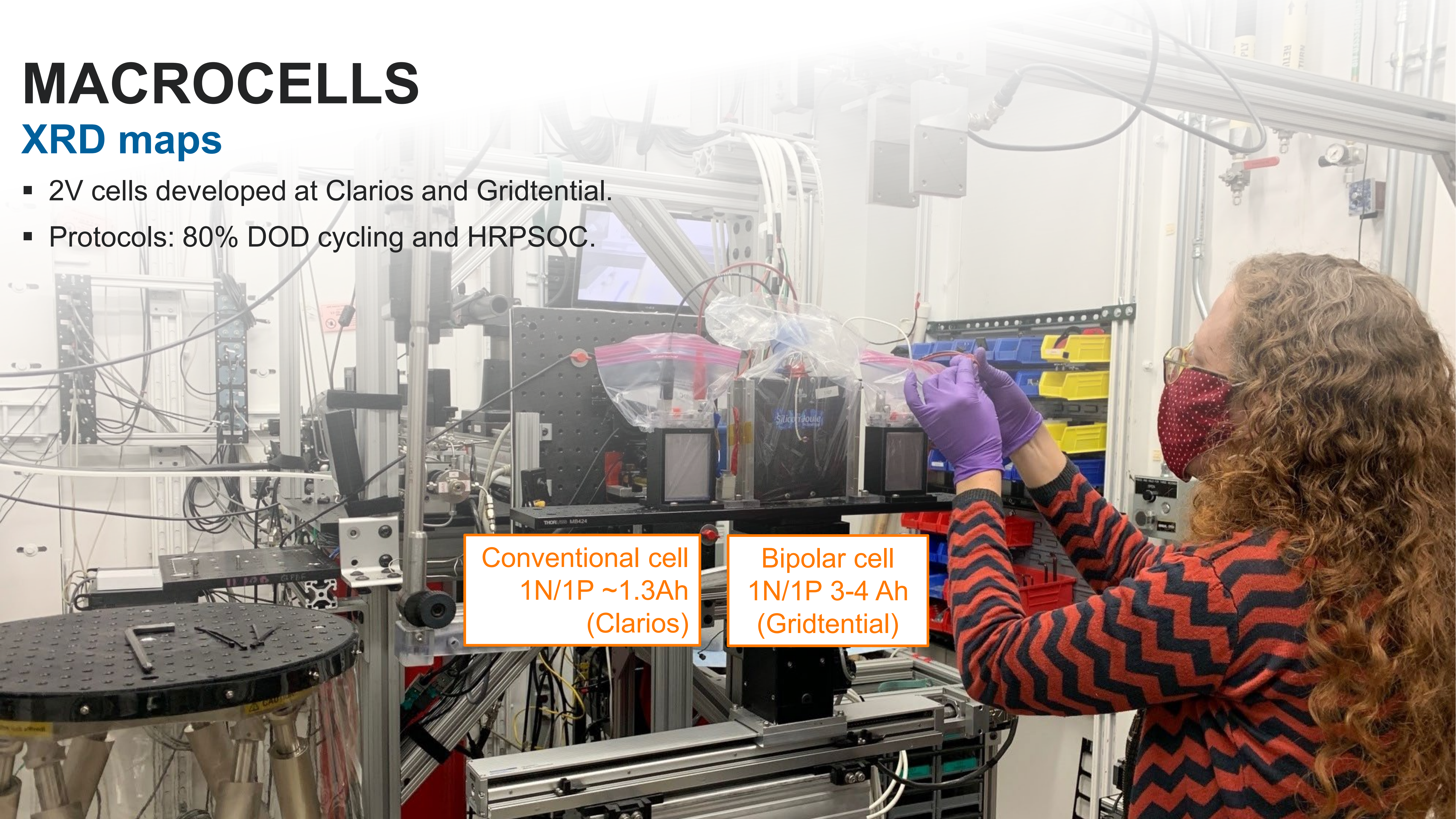
- Transmission x-ray microscopy (TXM) reconstruction on end-of-life negative active material (40 nm resolution).
- Reconstruction: can isolate species, including pores and sponge lead.
  - Lead network crucial for utilization, rechargeability.
- Understanding surface area, pore distribution, tortuosity, etc. important for modeling these processes.



MACROCELLS

XRD maps

- 2V cells developed at Clarios and Gridtential.
- Protocols: 80% DOD cycling and HRPSOC.



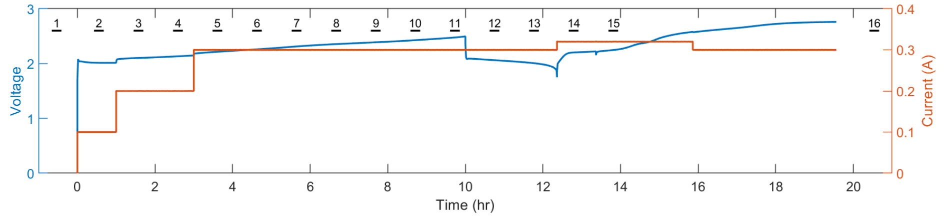
Conventional cell
1N/1P ~1.3Ah
(Clarios)

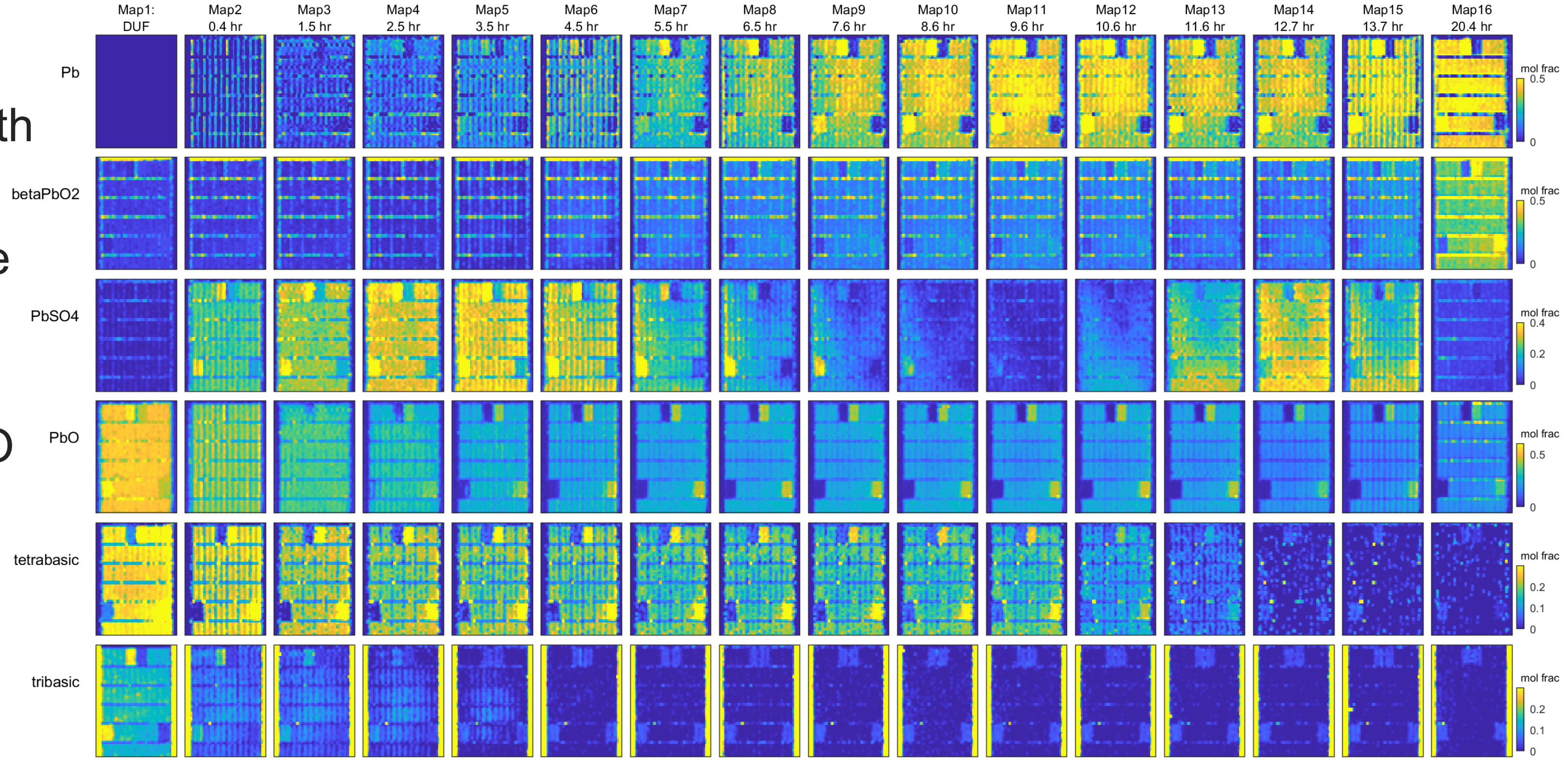
Bipolar cell
1N/1P 3-4 Ah
(Gridtential)

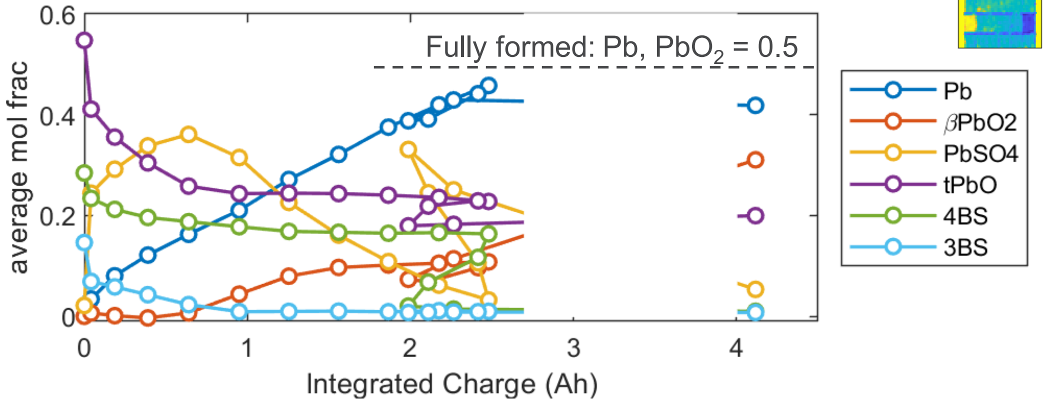
FORMATION

In situ diffraction maps

- Example: formation on gen4 cell with 4BS positive and 3BS negative.
- See variation in $PbSO_4$ and alkaline phases, driven by accessibility to acid.
- 4BS lasts longer than 3BS, but PbO is present at the end of formation.
- Windows show that PbO is present only on positive.

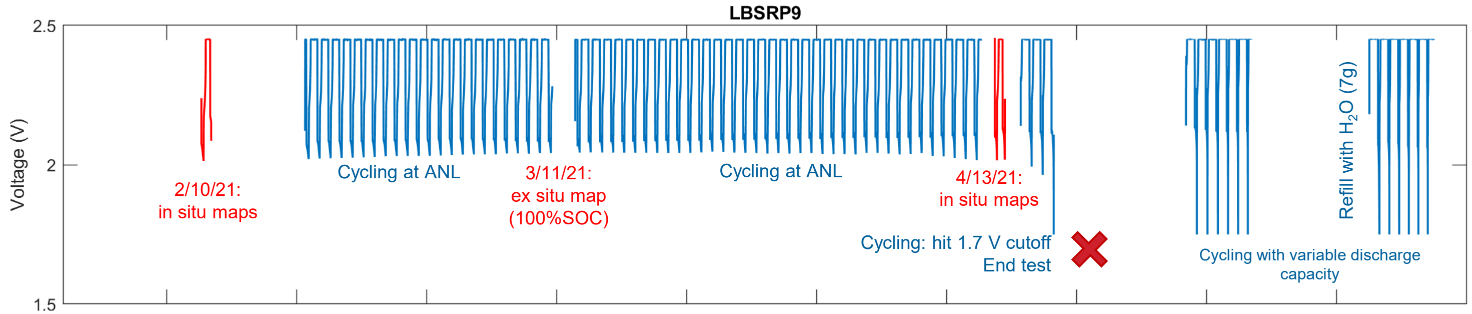






CYCLING

Conventional cell



2/10/21:
in situ maps

Cycling at ANL

3/11/21:
ex situ map
(100%SOC)

Cycling at ANL

4/13/21:
in situ maps

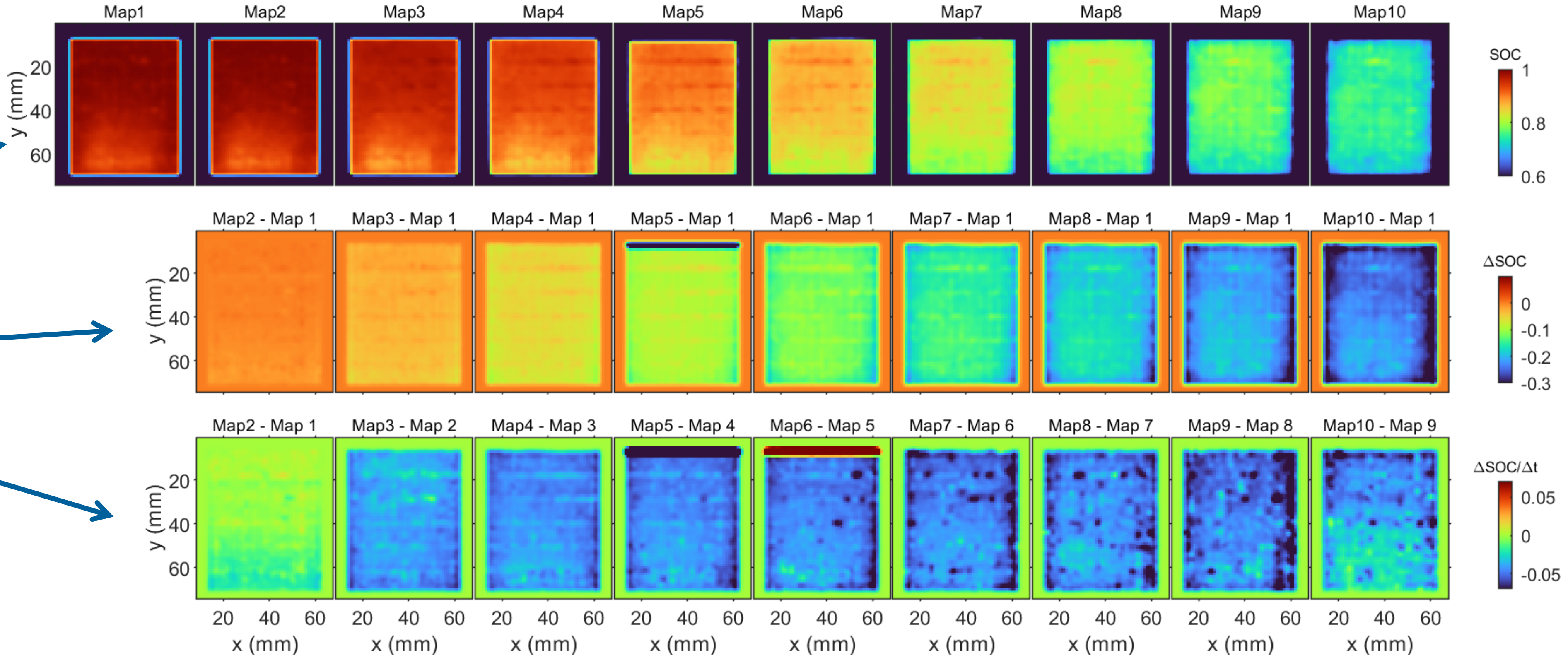
Cycling: hit 1.7 V cutoff
End test

Cycling with variable discharge
capacity

Example from baseline cell. Maps:

- **Overall SOC**
- Change in SOC from t = 0
  = utilization
- ΔSOC/Δt
  ~ current density

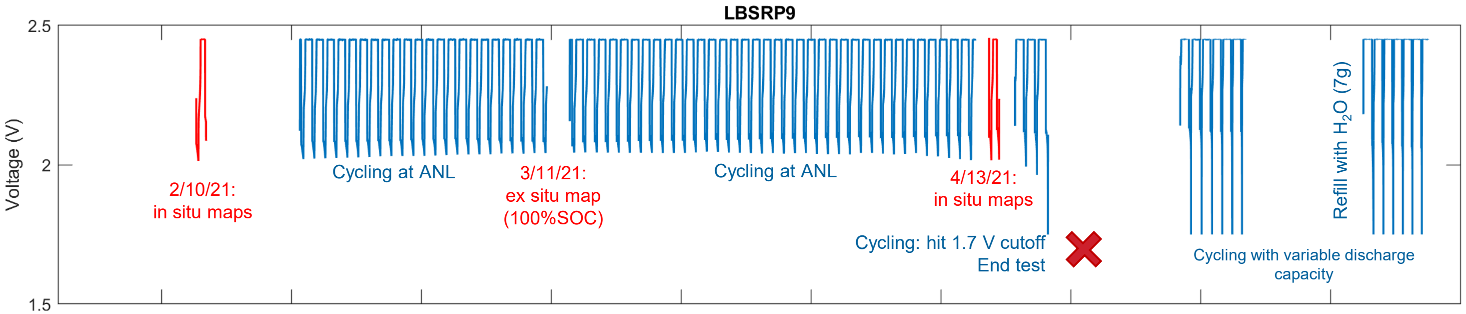
Initial cycling shows largely uniform charge acceptance.



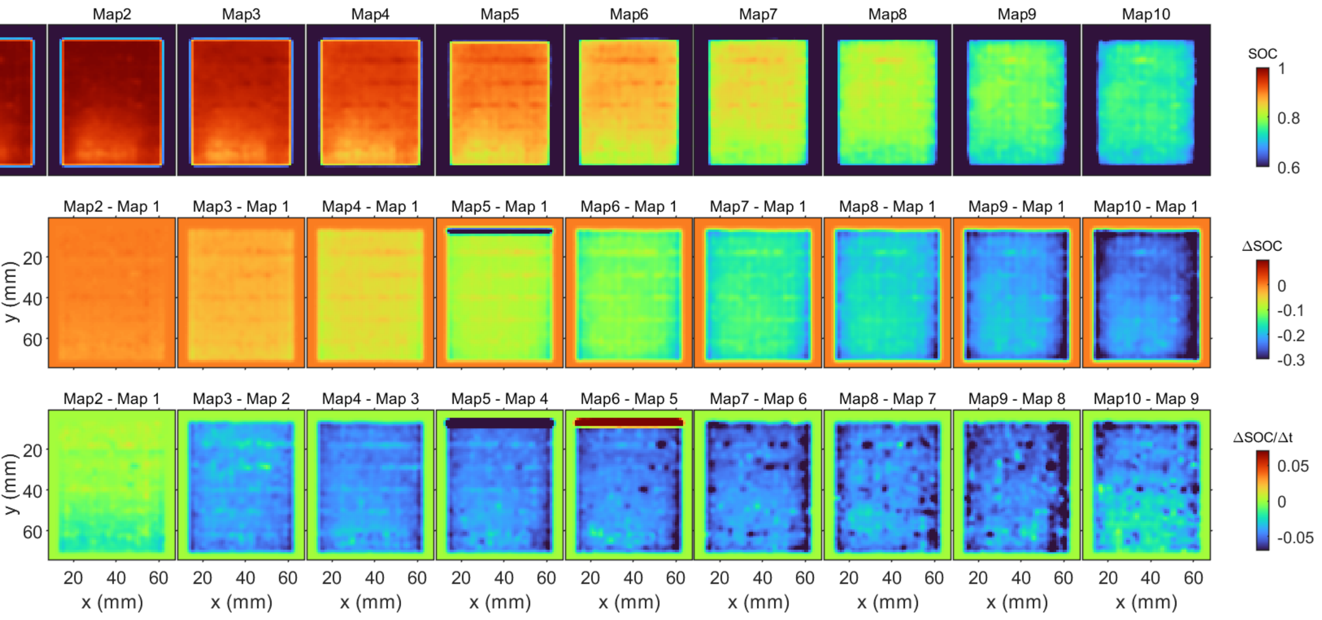
CYCLING

Conventional

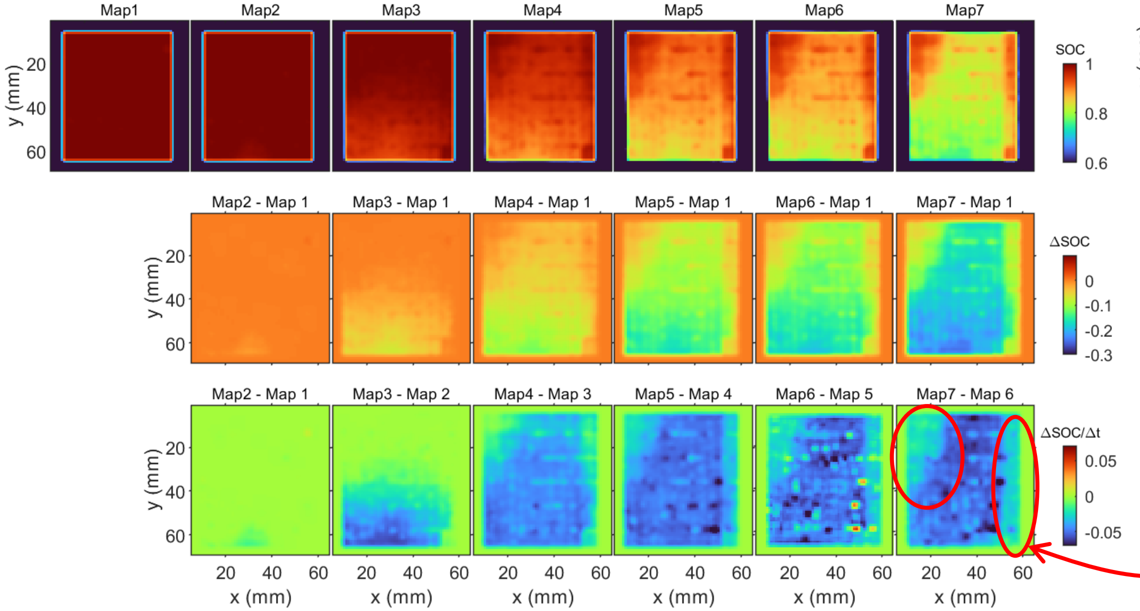
- Initial cycling (2/21 experiment) showed uniform charge acceptance during discharge, apart from $PbSO_4$ accumulation around periphery at high DOD.



2/21 experiment



4/21 experiment



- After 2 months of deep cycling, utilization is much more nonuniform. This driven by the PAM, which does not form $PbSO_4$ during discharge in these problem regions.

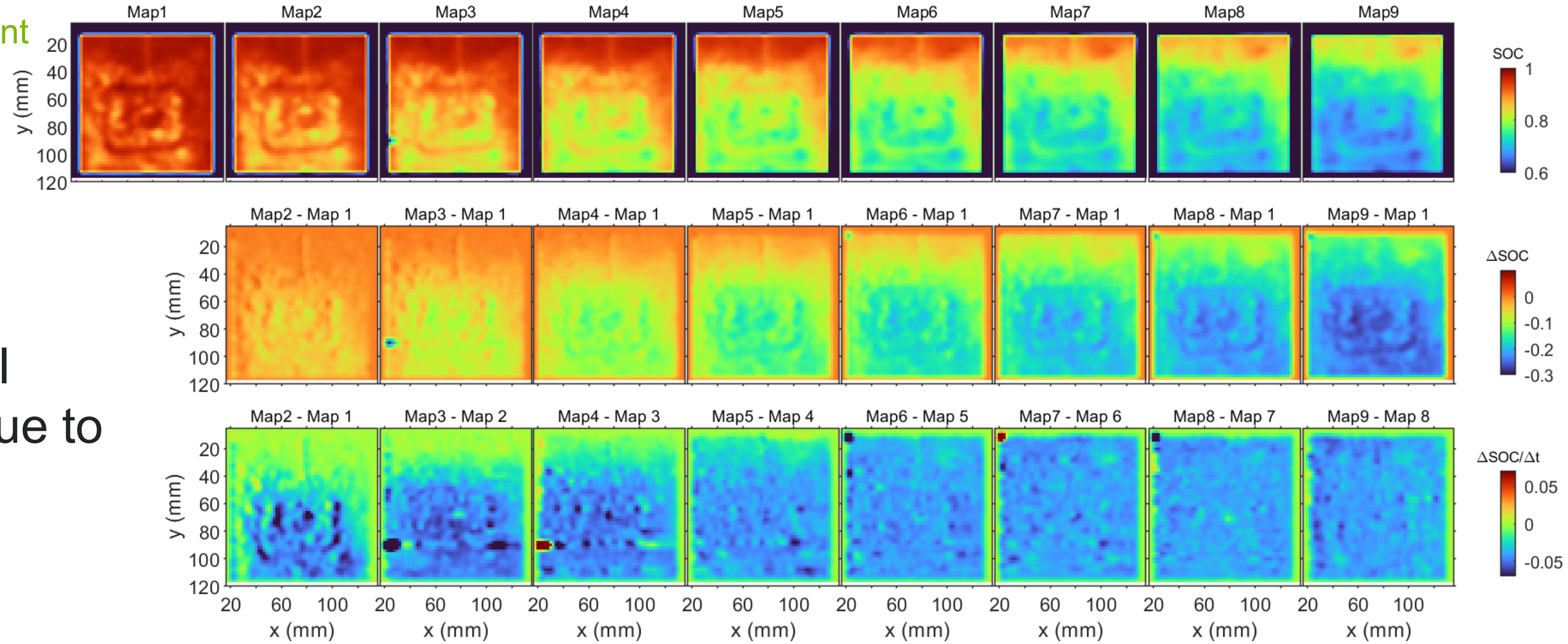
Inactive regions

CYCLING

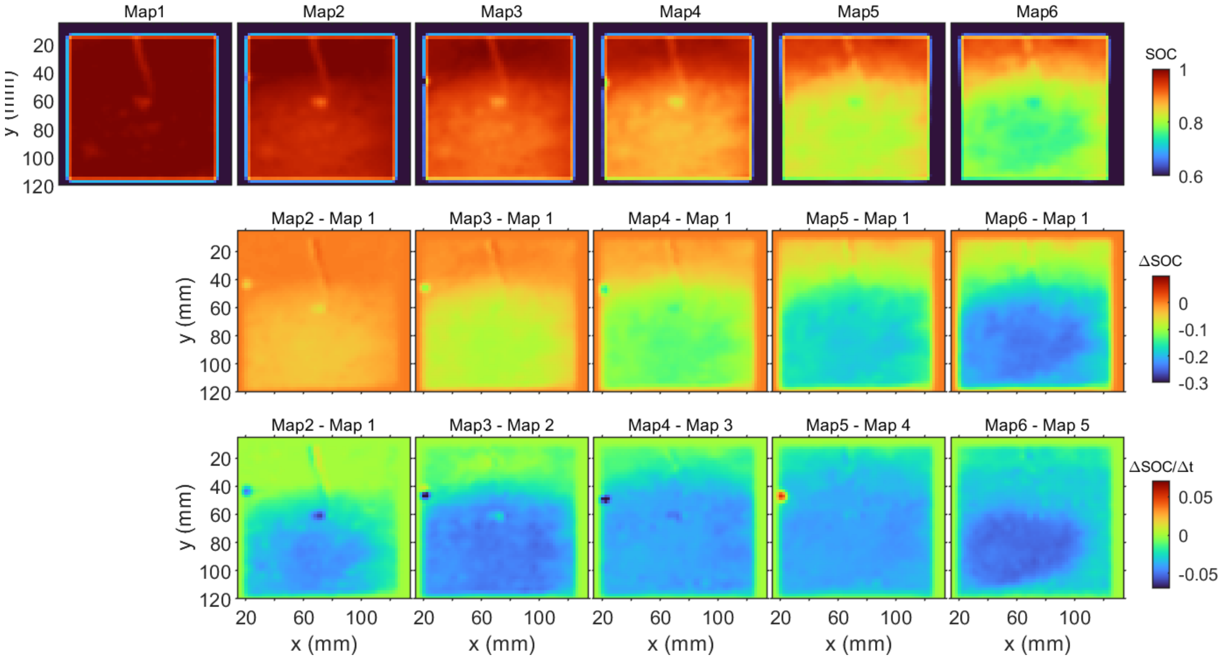
Bipolar

- Data from our first bipolar cell shows heterogeneity, likely due to vacuum filling at first.

2/21 experiment



4/21 experiment



- After two months cycling, the bipolar cell has improved uniformity (apart from inactive region near the top).
- Even the current density is highly uniform compared to earlier cycling and monopolar cells.
- Cycle life was ultimately limited by 0.1 mm lead layer, which has been increased to 0.4 mm.

SUMMARY AND FUTURE

LEAD ACID AT NATIONAL LABS

Current work

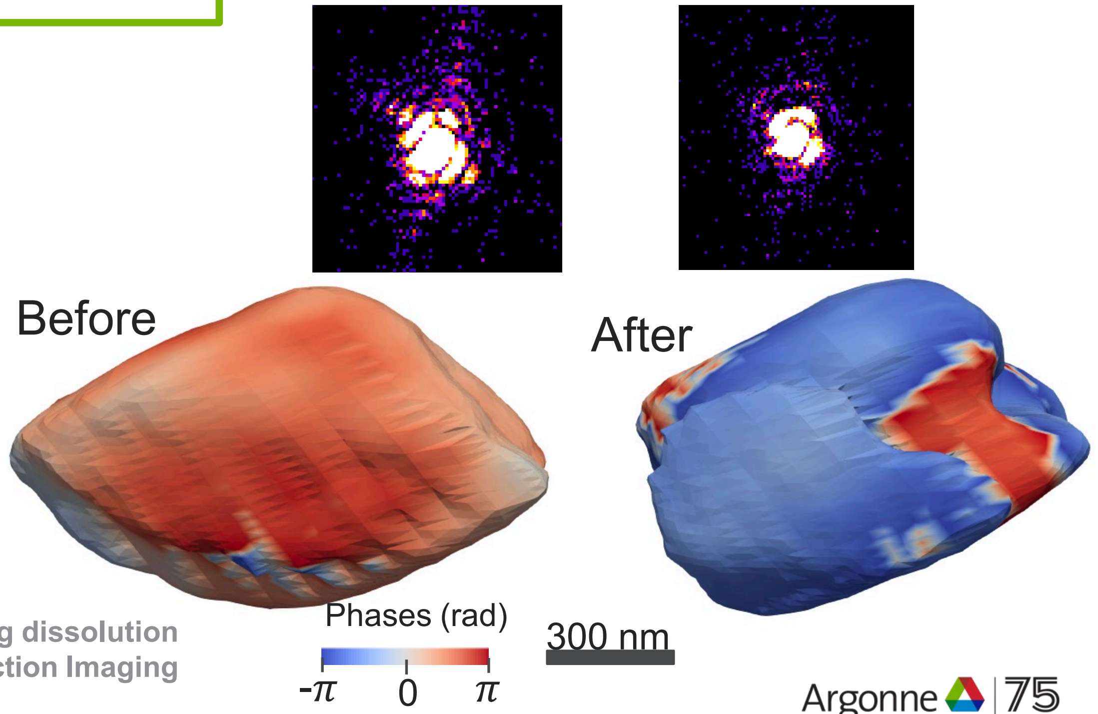
- There is still a tremendous amount to learn about the science of lead acid batteries.
- There is still room for lead acid to improve in utilization and cycle life.

Communication between national labs and industry is crucial to make advances!

Future work

- APS is undergoing a $815M upgrade that will revolutionize this approach.
- Smaller, coherent beams: isolate and watch change in size and shape of individual crystallites

2023: debut of APS-upgrade and Aurora supercomputer at Argonne



Data collected on synthetic $PbSO_4$ during dissolution using Bragg Coherent Diffraction Imaging

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