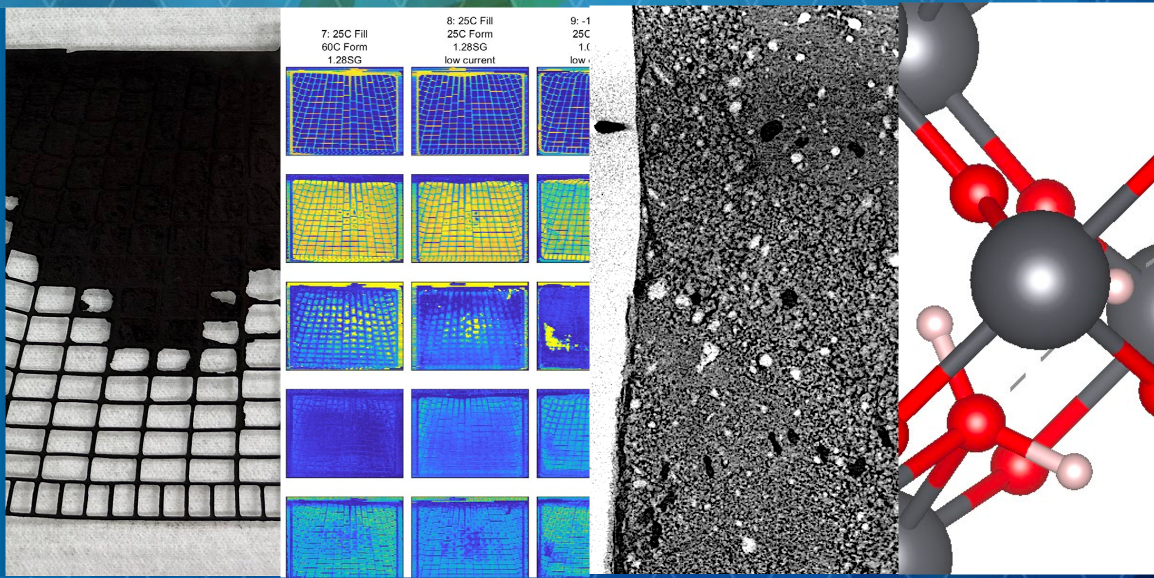
2025 OE Peer Review
Presentation #1001

ORIGINS OF POSITIVE ELECTRODE FAILURE MODES IN LEAD ACID BATTERIES



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PROJECT OVERVIEW

- **Project goal**: Our goal is to understand mechanisms leading to failure modes in lead acid batteries and identify routes for improving utilization and cycle life.
- **Current practice**: Lead acid batteries are widely used for automotive applications, telecom backup, and industrial motive power and have historically emphasized power density over cycle life. Based on characterization and modeling, we are exploring alternative conditions and cell architectures for stationary applications.
- **Why ANL**: Our characterization uses the Advanced Photon Source at ANL to follow reactions in batteries during cycling. Using high energy scattering and imaging, we correlate changing speciation with electrochemistry and resolve heterogeneity that builds up over repeated cycles.
- **Innovation**: We have developed unique tools to map charge acceptance and electrode/acid speciation during cycling. This multiscale approach connects macroscopic cell characteristics with atomic/microstructural features that lead to eventual failure. We are using these parameters to build and validate continuum models describing the battery's electrochemical response.
- **Impact**: Our research has identified $PbSO_4$ and PbO_2 crystal ripening mechanisms at the heart of most failure modes. This work has informed cycling protocols and acid conditions that have shown substantial improvements in cycle life.
- **Alignment**: Lead acid batteries are manufactured at scale in the US using a domestic, circular supply chain. Adapting lead acid batteries to stationary applications will help meet the Administration's goals for affordable, secure, and reliable energy.

FY25

Summary

Manuscripts

- Knehr, Kinnibrugh, Scot, Chalasani, Fister "Role of $Pb/PbSO_4$ Morphologies in Dynamic Charge Acceptance of Lead Acid Batteries," Journal of Electrochemical Society, 2025
- Kim, Kastengren, Scott, Chalasani, Kinnibrugh, Wolfman, Fister, "Operando observation of internal structural changes of a lead-acid cell by synchrotron X-ray micro computed tomography" J. Power Sources (accepted)
- Garcia, Fister, Iddir, "Role of defects on PbO_2 structure, conductivity and phase stability: insights from DFT calculations," submitted Journal of Physical Chemistry C (after OE review)

Peer review posters

- Garcia, Fister, Iddir: "Role of defects on the structure of lead oxides, conductivity, and phase stability: insights from density functional theory"
- Officer, Babinec, Fister: "Acoustic Characterization of Lead Acid Batteries"

- FY25 DOE SCGSR fellow (Leo Jiang, University of Houston): organic electrodes for lead acid.

INTRODUCTION & MOTIVATION

IMPROVING LEAD ACID CYCLE LIFE

Failure mechanisms

- High rate (~1C), PSOC operation: negative sulfation ($PbSO_4$ ripening)
- Low rate (~$C_{/10}$): acid and PbSO4 stratification (gravity)

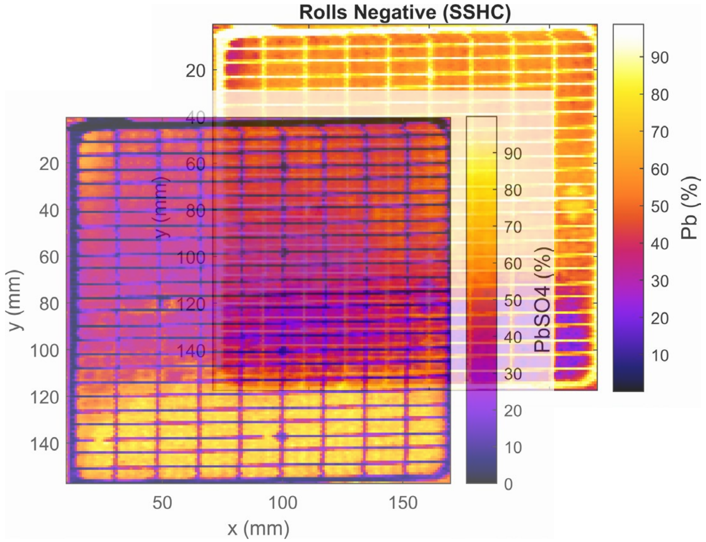
Not charging enough: mostly a problem on the negative electrode. **See next talk by PNNL!**

- Dry-out (OER/HER)
- Negative “overexpansion” (NAM compression)
- **Positive active material “softening” and “shedding:” PbO_2 ripening, loss of αPbO_2.**
- Positive grid corrosion

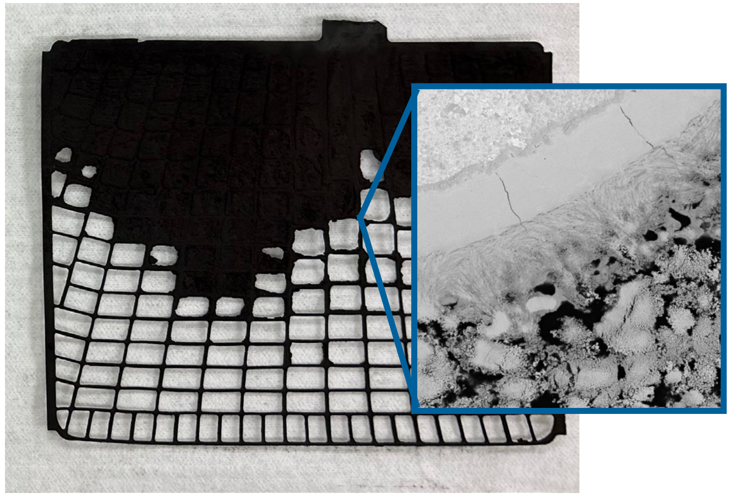
Charging too much: mostly a problem on the positive electrode and PAM/grid interface

FY25 focus

FY22 and FY23 talks



FY21 and FY24 talks



POSITIVE FAILURE MECHANISMS

Effect of growth defects: from atoms to electrodes

Problem: positive active material ‘softening’ and ‘shedding’

Illustration of “Kugelhaufen” model (Winsel JPS 1990)

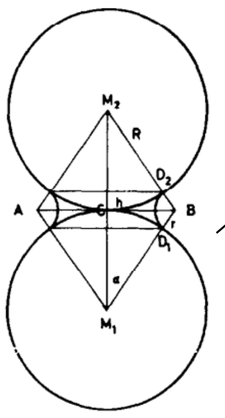
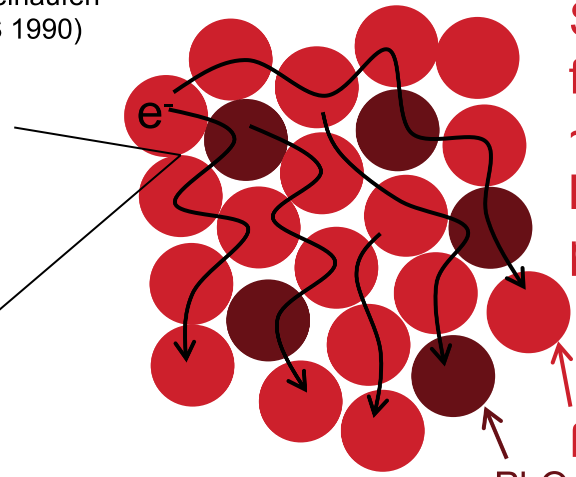
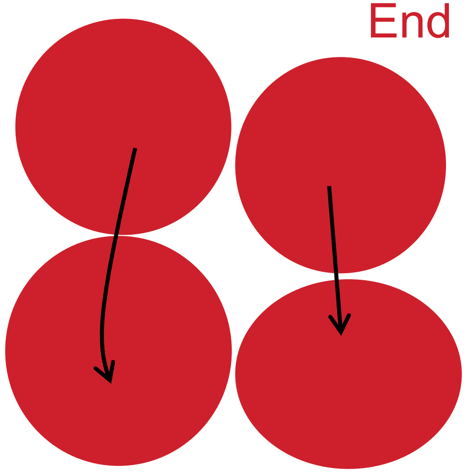


Fig. 6. Simplified model of two spheres and the neck between.



Start: newly formed PbO$_2$ ~20 nm particles: lots of conductivity pathways.



End of life: ripened PbO$_2$ (~100-1000 nm): limited connection points = higher resistance, increased fragility.

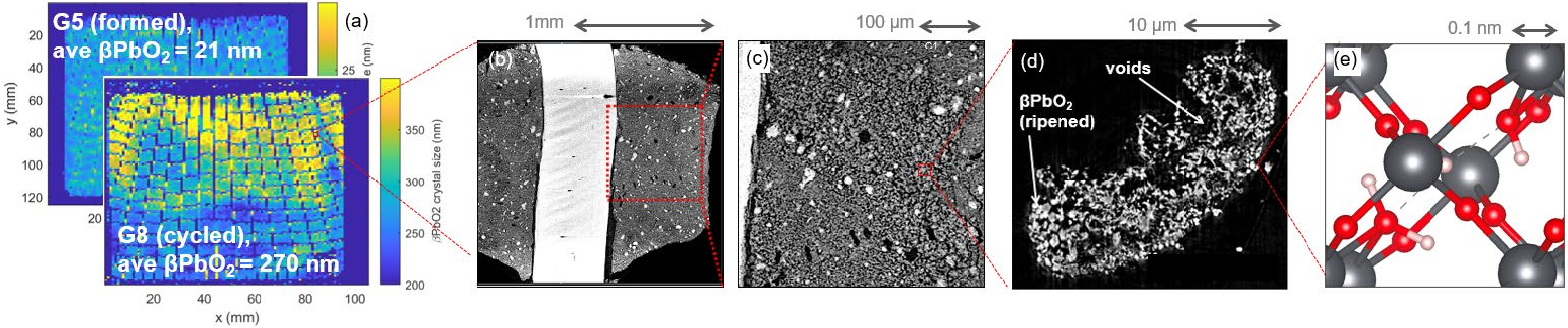
Cause: PbO$_2$ crystal ripening and α → βPbO$_2$ conversion.

- Large particles reduces interparticle connectivity (“aggregation of spheres” or “Kugelhaufen” model): increased resistance and reduced adhesion. DFT: Defective PbO$_2$ is intrinsically more conductive.
- αPbO$_2$: provides enhanced conductivity to positive active material, especially at deep discharge.

ACTIVE MATERIAL SOFTENING/SHEDDING

A multiscale problem

Macroscopic problems in lead acid batteries have microscopic origins. We study these problems over many length scales using operando synchrotron techniques:



Section 1
Macroscale changes:
variables controlling speciation
during formation and cycling

Section 2
Changes in microstructure:
operando Tomography during
formation and cycling

Section 3
Atomic scale origins of ripening:
lattice defects in PbO_2

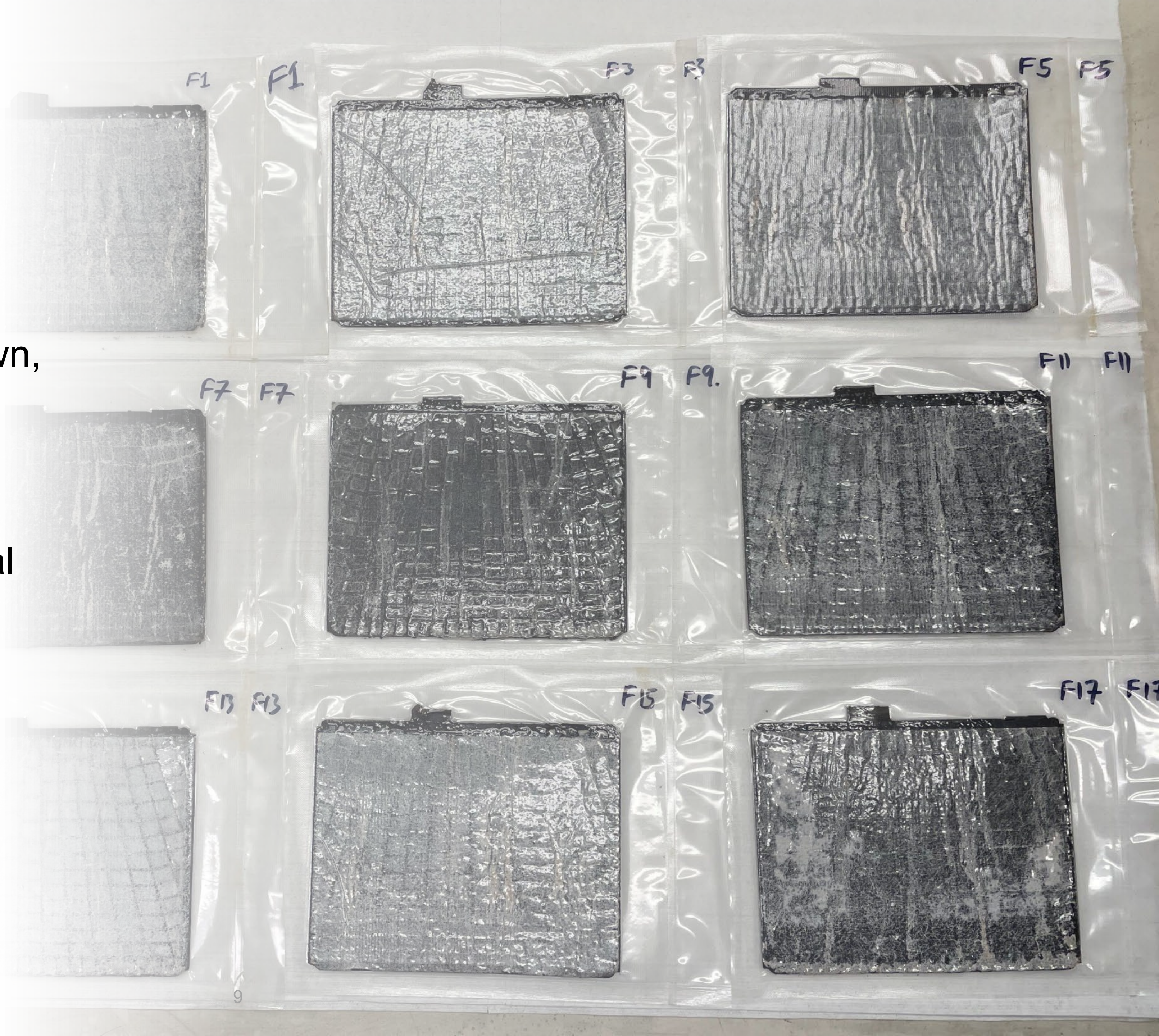
1. MACROSCALE CHANGES: VARIABLES CONTROLLING SPECIATION DURING FORMATION AND CYCLING

COMMERCIAL ELECTRODES

Flooded cells: formation

Formation: the first charge for the battery, where PbO_2 is initially grown, plays a key role in its cycle life.

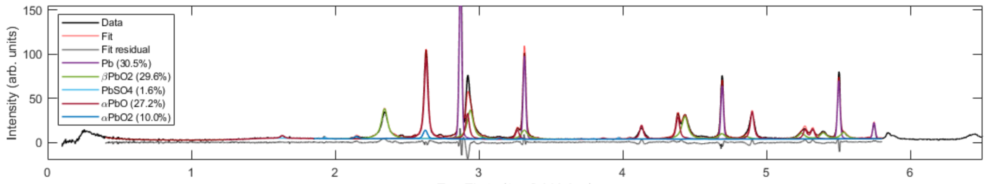
- In collaboration with Clarios, we have studied the effect of many formation variables in commercial flooded cells:
  - Acid concentration
  - Fill, formation temperature
  - Soak time
  - Current density



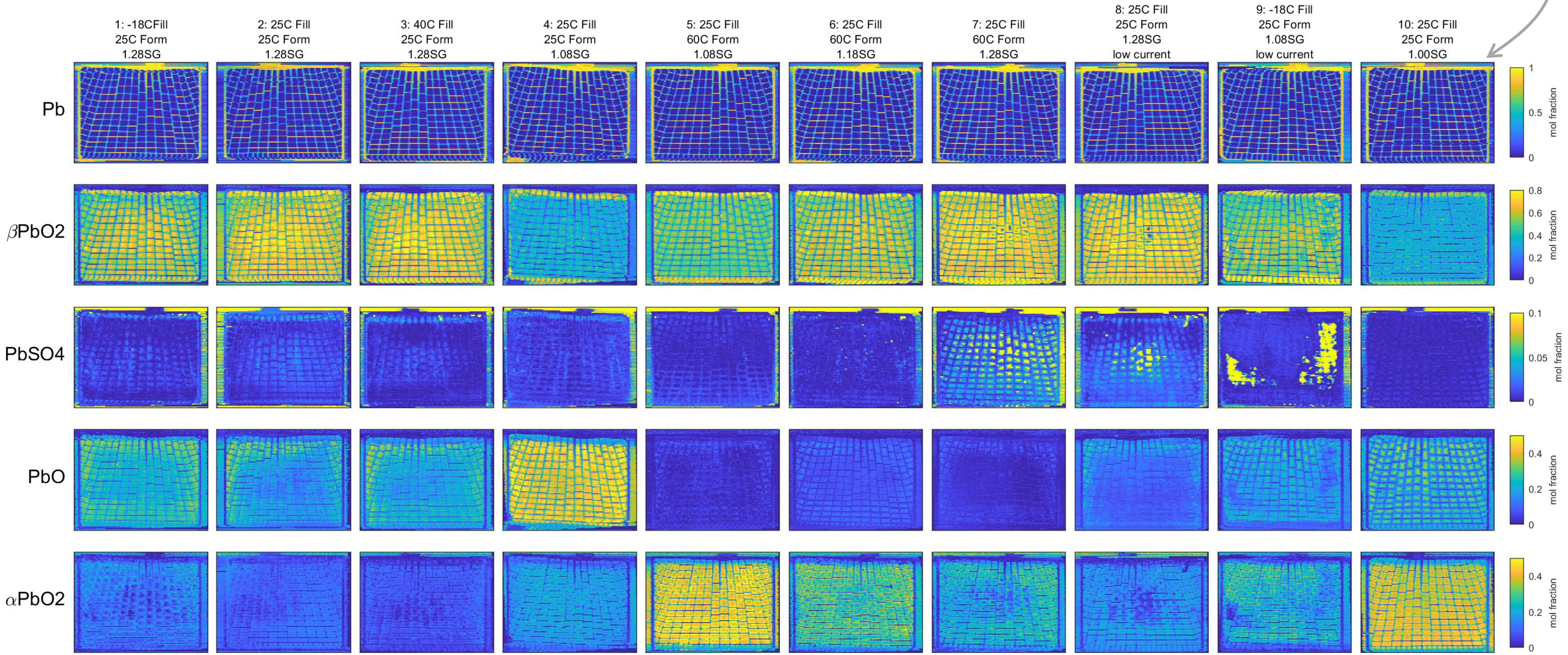
DESIGN OF EXPERIMENT

Formation variables, cycling

- After formation, XRD maps collected on positive plates.
  - Most important variables: acid concentration and formation temperature
  - High temperature leads to **neutral/alkaline conditions at start of formation → αPbO_2**



Each pixel corresponds to a XRD pattern (20,000 in each map)



DESIGN OF EXPERIMENT

Formation variables, cycling for accelerated failure

- Initial formation variables: soak time, soak/formation temperature, acid SG, current density
  - Focused on cells formed in 25C and 60C in 1080 and 1280 formation (and cell formed in neutral SG).
- Cycling: switched to 1.28SG (5M) sulfuric acid and cycled to ~80%DOD.

Cell #	Fill acid Temp C	Fill Cell Temp	Fill Acid SG	Pickle time, hr	Formation Temp	Current Density
F1	-18	-18	1.28	1	25	std
F3	25	25	1.28	1	25	std
F5	40	25	1.28	1	25	std
F7	25	25	1.08	1	25	std
F9	25	25	1.08	1	60	std
F11	25	25	1.18	1	60	std
F13	25	25	1.28	1	60	std
F15	25	25	1.28	1	25	low
F17	-18	-18	1.08	1	25	low
F19	25	25	60g/l Na2SO4	1	25	std

Cell #	Fill Temp	Fill Acid SG	Pickle time, hr	Form Temp	Current Density	Stop Point	Beamtime	Measurement
G1	25	1.28	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G2	25	1.28	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G3	25	1.28	1	25	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G4	25	1.28	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P1	25	1.28	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle
G5	25	1.08	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G6	25	1.08	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G7	25	1.08	1	25	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G8	25	1.08	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P2	25	1.08	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle
G9	25	1.08	1	60	std	After Formation (repeat)	Feb 10-12	After formation
G10	25	1.08	1	60	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G11	25	1.08	1	60	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G12	25	1.08	1	60	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P3	25	1.08	0.25	60	std	After Formation (short pickle)	Feb 10-12	Short pickle
G13	25	1.28	1	60	std	After Formation (repeat)	Feb 10-12	After formation
G14	25	1.28	1	60	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G15	25	1.28	1	60	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G16	25	1.28	1	60	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P4	25	1.28	0.25	60	std	After Formation (short pickle)	Feb 10-12	Short pickle
G17	25	1.00*	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G18	25	1.00*	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G19	25	1.00*	1	25	std	Spare (in situ cell)	Feb, April	Spare (at ANL)
G20	25	1.00*	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P5	25	1.00*	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle

High βPbO_2 + PbO

High PbO

High αPbO_2

High βPbO_2

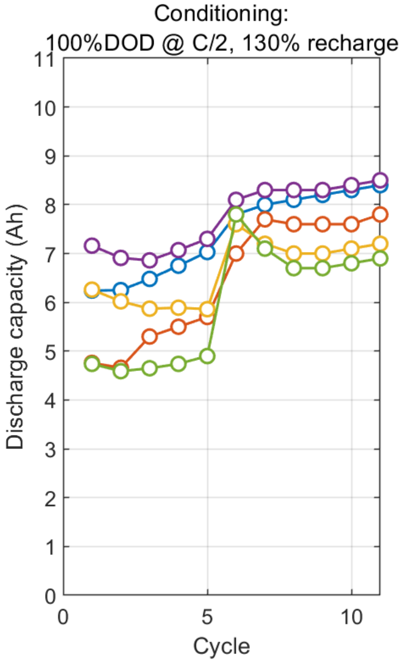
High αPbO_2 + PbO

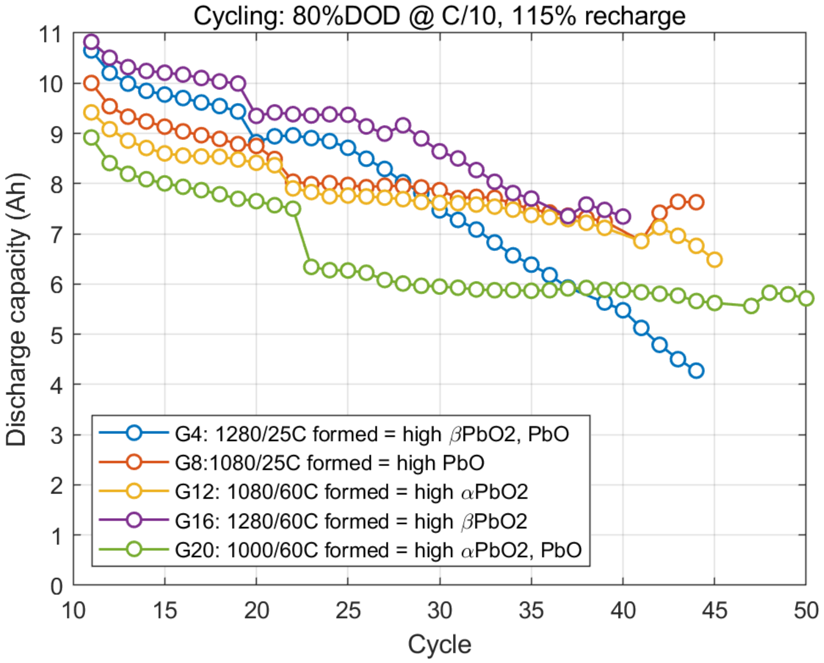
HIGH DOD CYCLING

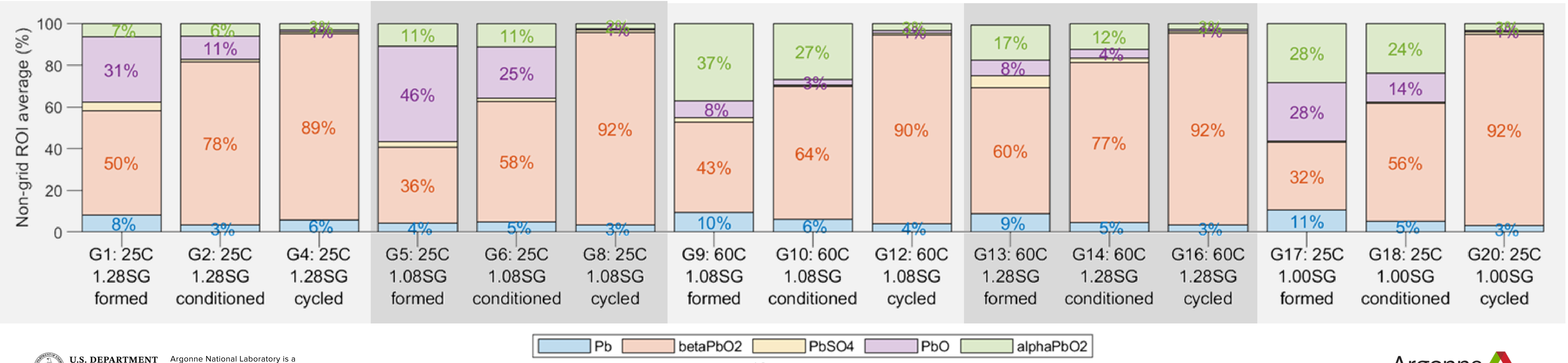
Change in composition

Cycling of flooded cells:

- Despite having very different compositions after formation, all batteries approach similar composition after 45-50 cycles: >90% βPbO_2.
- Cells formed in lower SG acid cycle better.







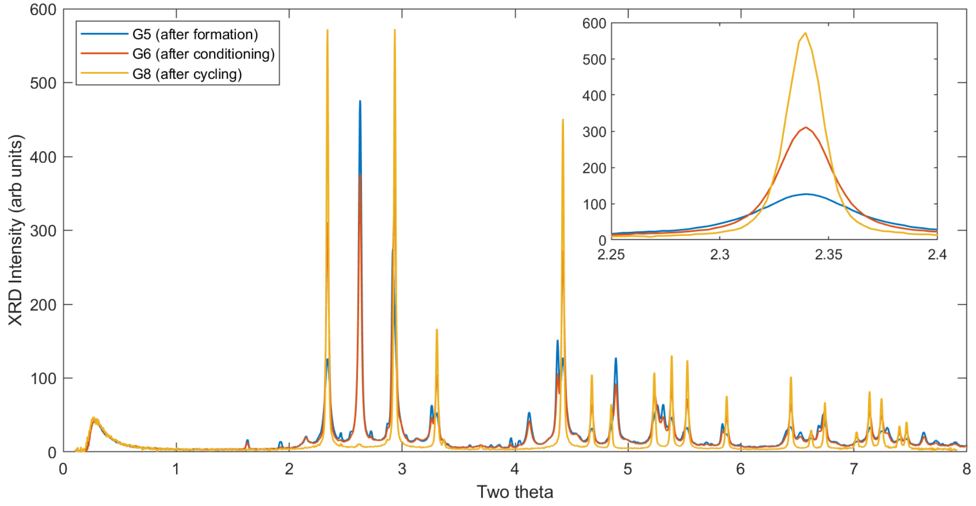
EFFECT ON PARTICLE SIZE

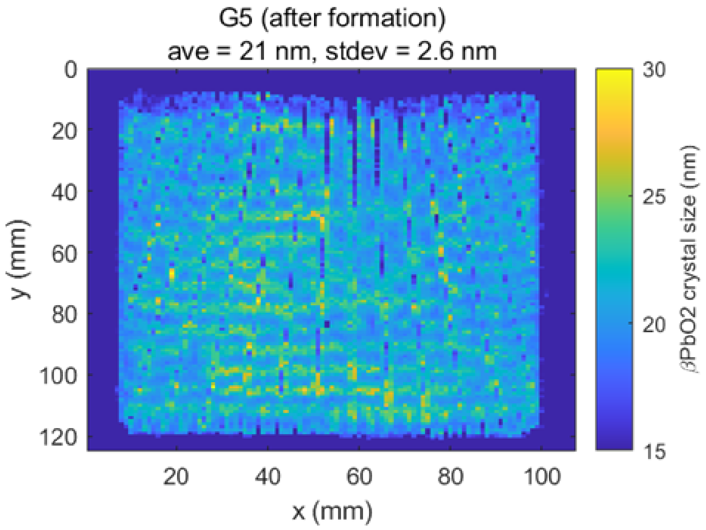
Cycling → PbO_2 ripening

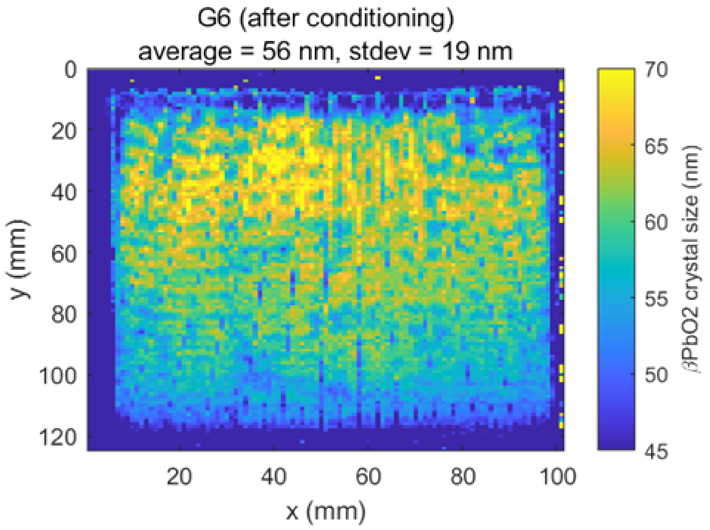
We can track and map the size of PbO_2 crystallites by diffraction line-shape.

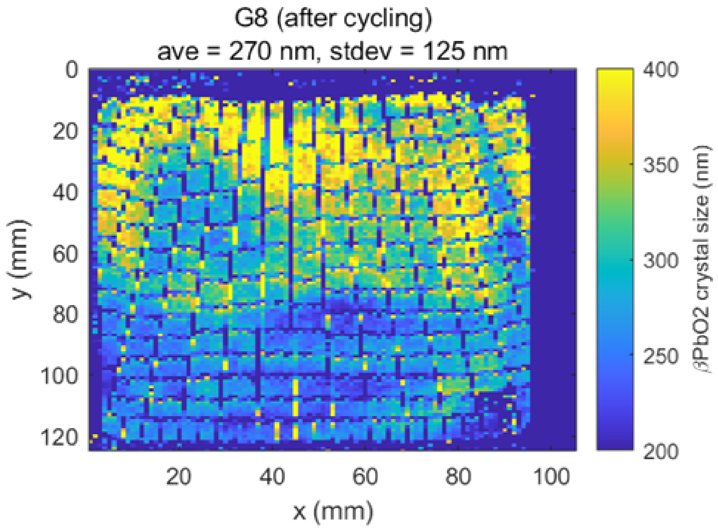
- After formation, βPbO_2 is extremely nanoscale and uniform over plate.
- Cycling leads to rapid βPbO_2 ripening and heterogeneity.

Example of data from one pixel in the map




G5 (after formation)
ave = 21 nm, stdev = 2.6 nm

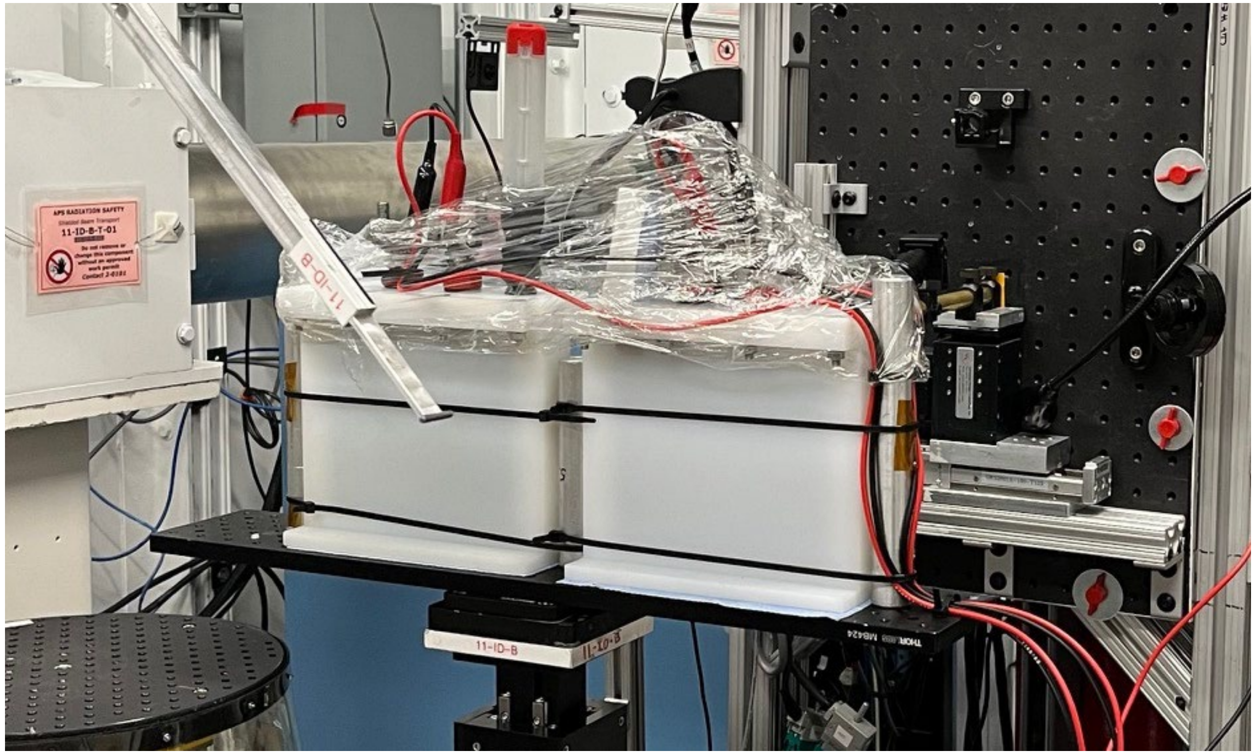

G6 (after conditioning)
average = 56 nm, stdev = 19 nm

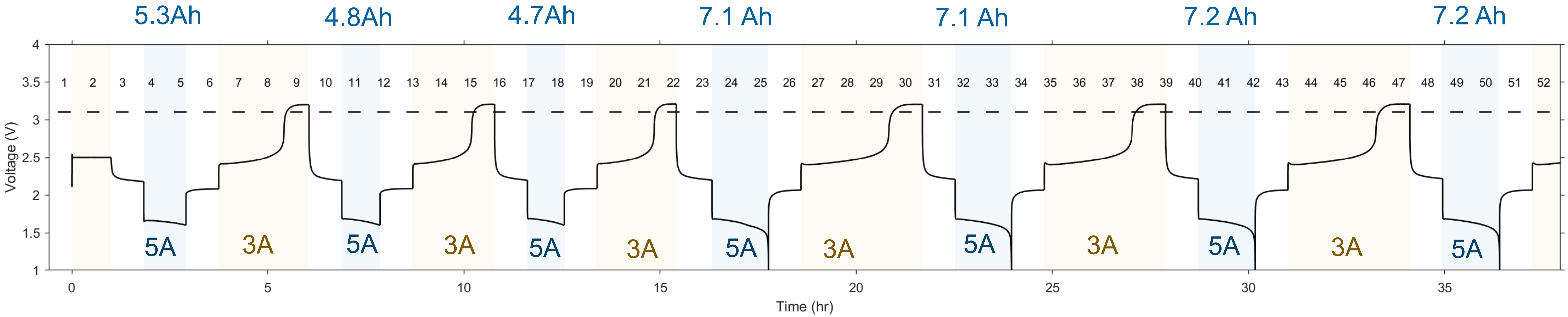

G8 (after cycling)
ave = 270 nm, stdev = 125 nm

OPERANDO CYCLING

Cells, cycling

- Accelerated 100% DOD testing:
  - 5A (1-2 hr) discharge at 65% and 100%DOD
  - 3A recharge (130%, no cutoff)
  - Rests to measure maps of fully charged/discharged cell



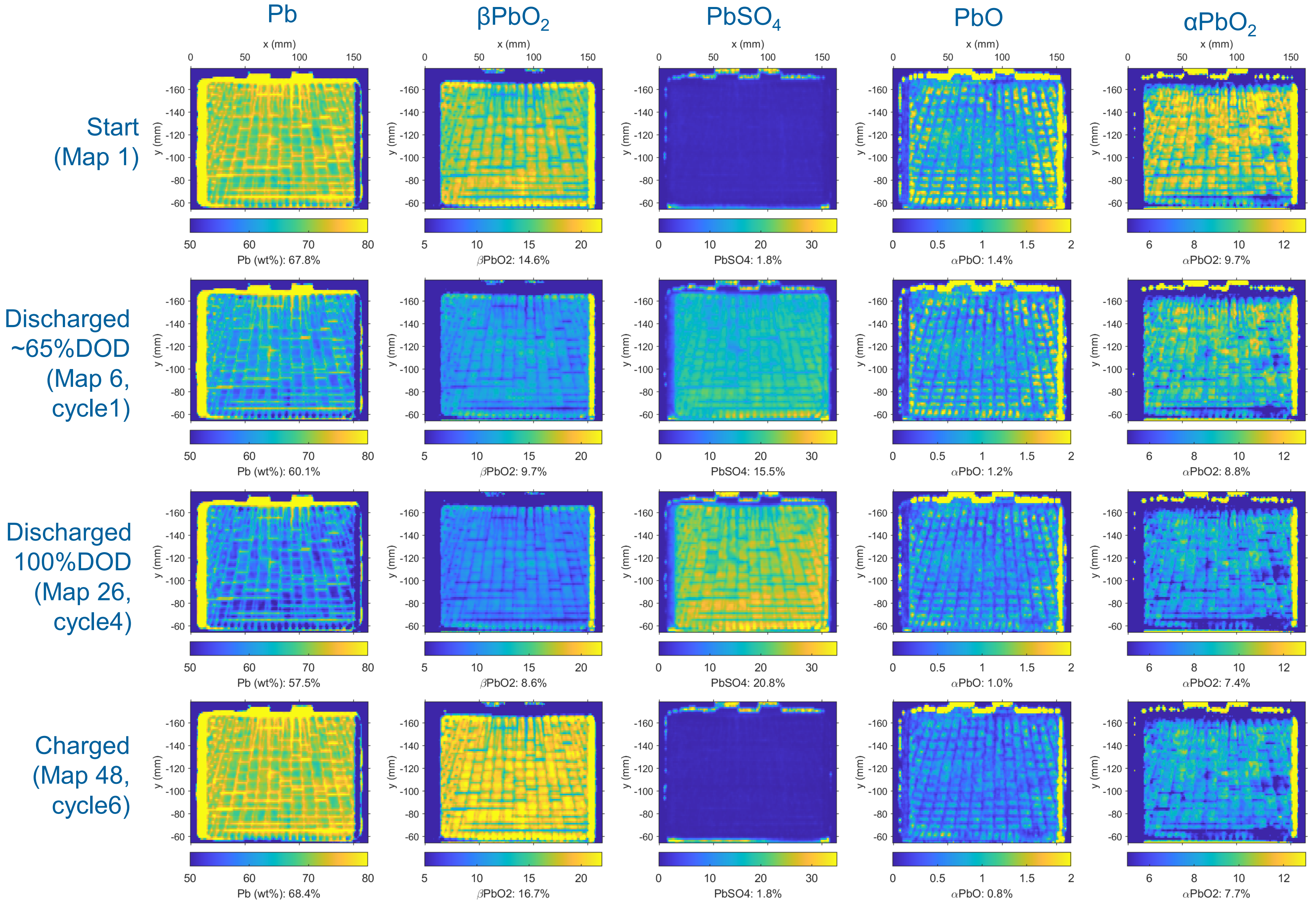


EARLY CYCLES

Overall phase fractions

Average composition of all three electrodes:

- $PbSO_4$ content consistent with cell utilization.
- See $\alpha \rightarrow \beta PbO_2$ conversion over 6 cycles and consumption of PbO.

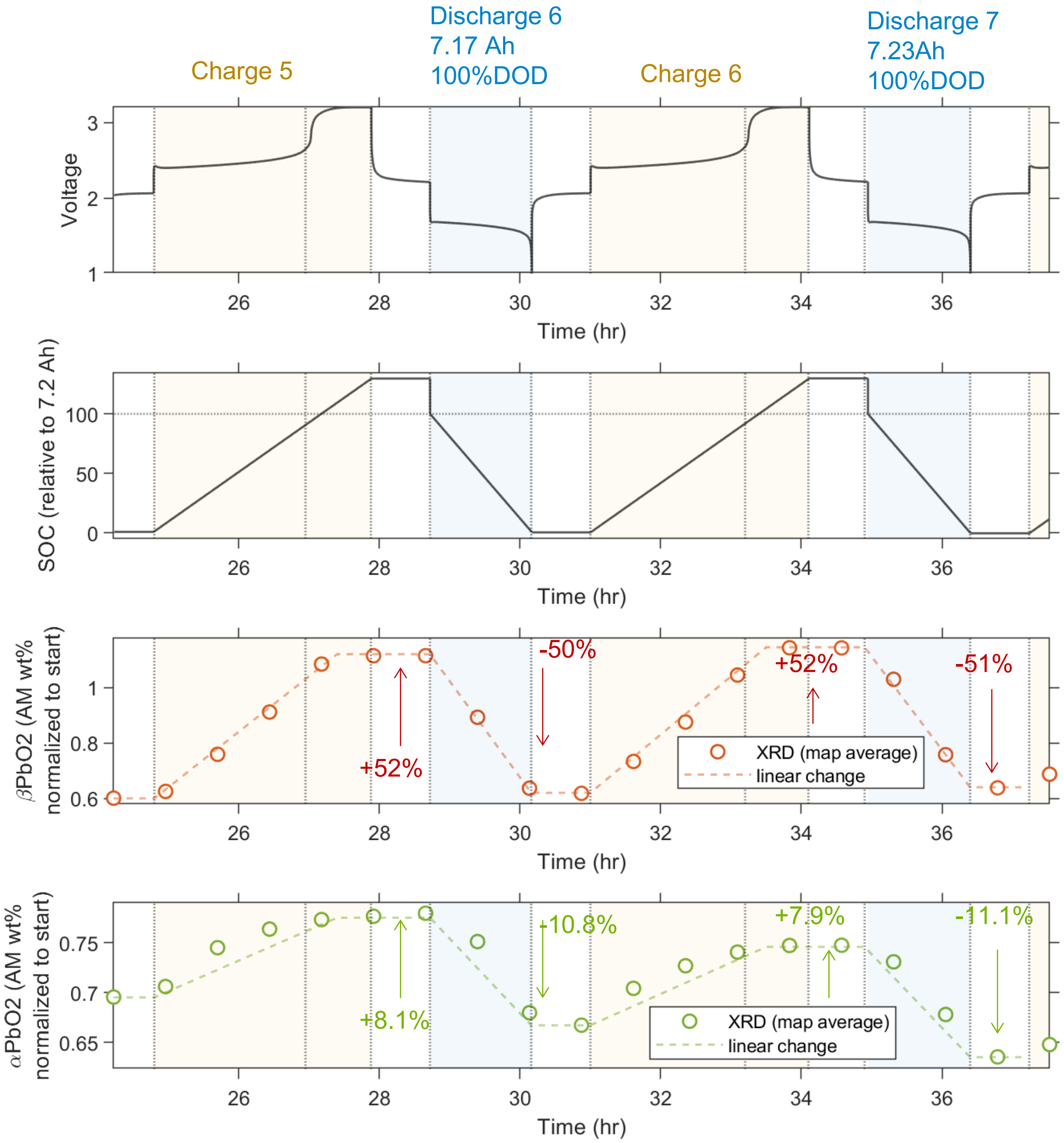


β- vs α-PbO_2

100% DOD: a closer look

For this plot: normalize to initial wt% to understand utilization of each species.

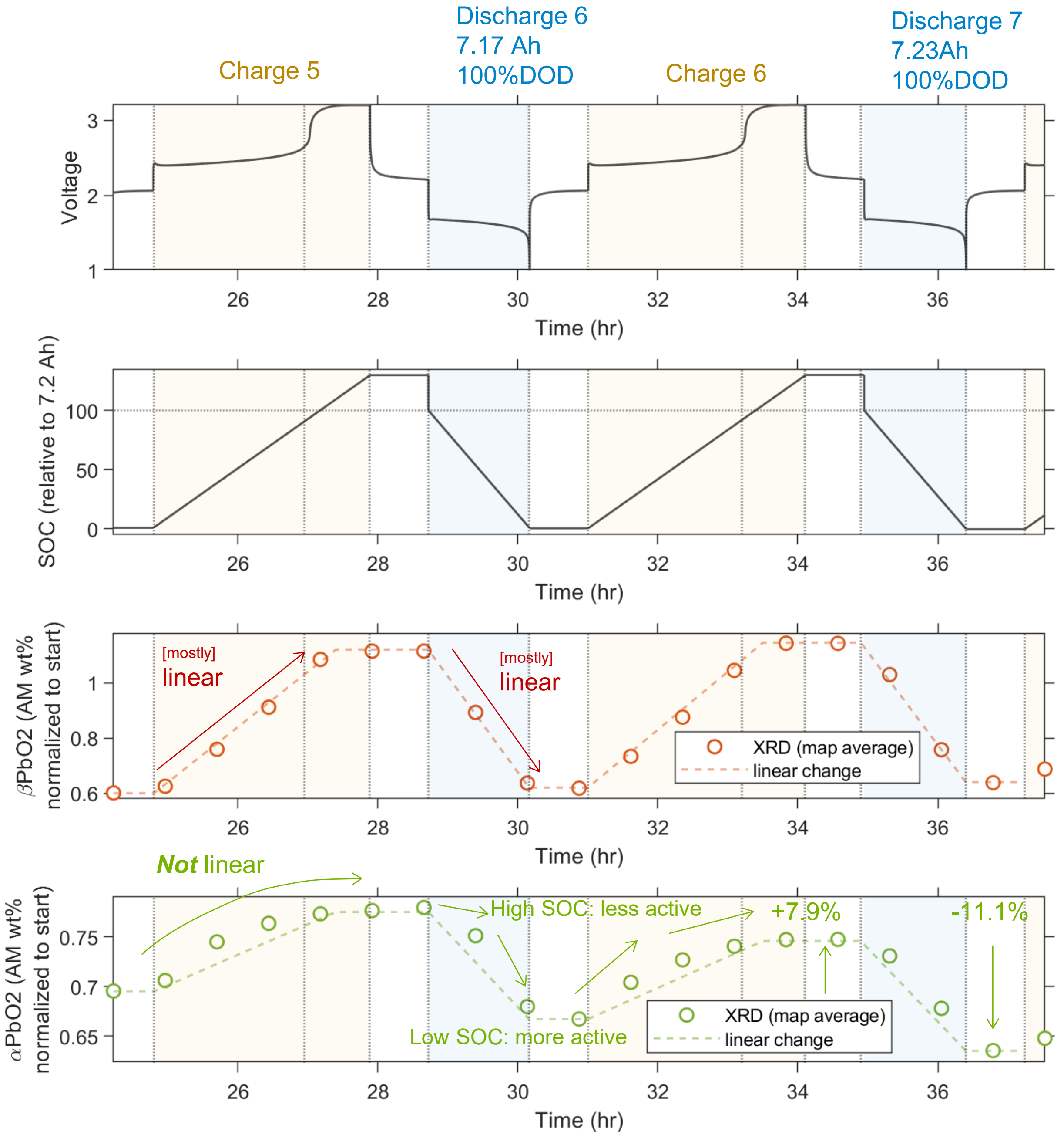
- Both PbO_2 phases are active, but much higher utilization for βPbO_2: ~50% vs. 11% for αPbO_2.
  - In other words: 22% charge carried by αPbO_2 at 100% DOD: consistent with earlier Plante measurements.



β- vs α-PbO_2

100% DOD: a closer look

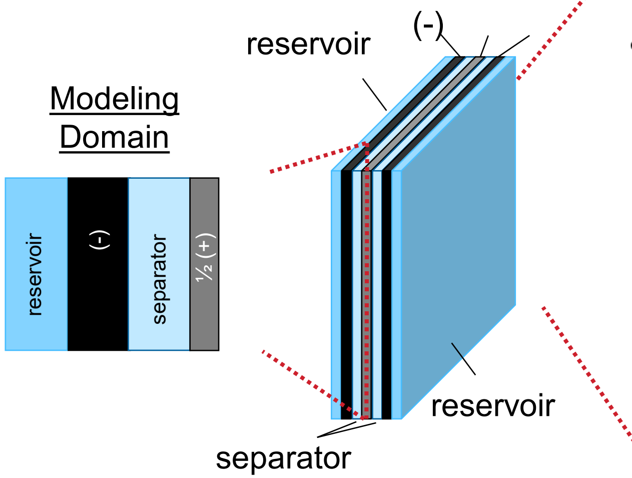
- Growth/dissolution rate of βPbO_2 is largely linear with SOC.
  This is NOT the case with αPbO_2.
  - **Dissolution (discharge) and growth (charge) of αPbO_2 is faster at low SOC**
- **Rate of $\alpha \rightarrow \beta PbO_2$ conversion faster at higher DOD**:
  - 0.77%/cycle at 65% DOD
  - -1.7%/cycle at 100%DOD: complete consumption of αPbO_2 after only 20 cycles!
- Not shown: **ripening is also accelerated at high DOD**.

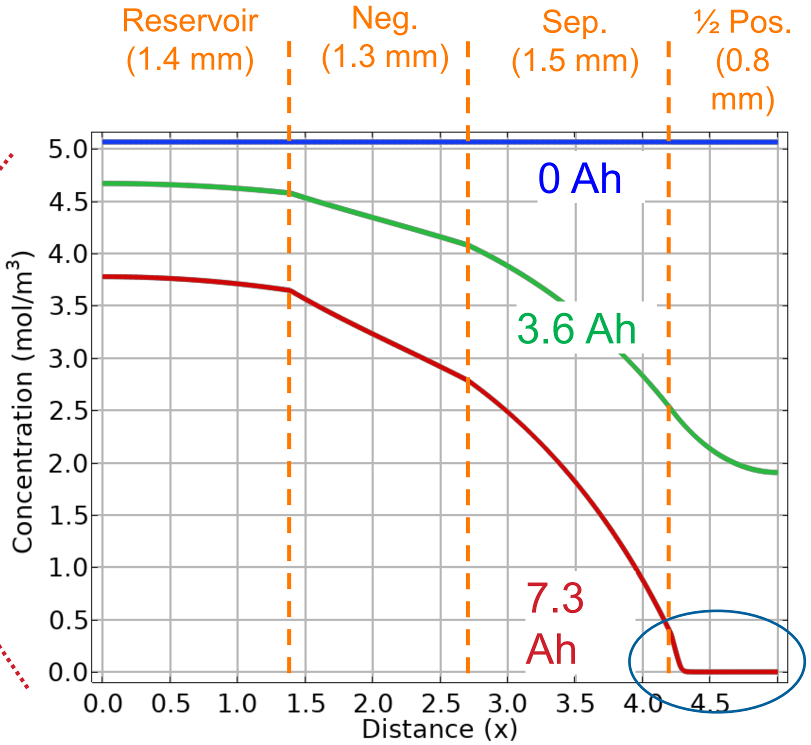


CAUSE: DILUTION AT DEEP DISCHARGE

Simulating 5A discharge at 1.280 SG

- Continuum model developed by Knehr (details: JES 2025):
  - **Cell capacity is acid limited** at 7.3 Ah (100%DOD) at 5 A.
  - Near end of discharge PAM is at neutral (or even alkaline!) pH:
  - **Lower concentration acid = more α-PbO_2 redox** (consumed at discharge)



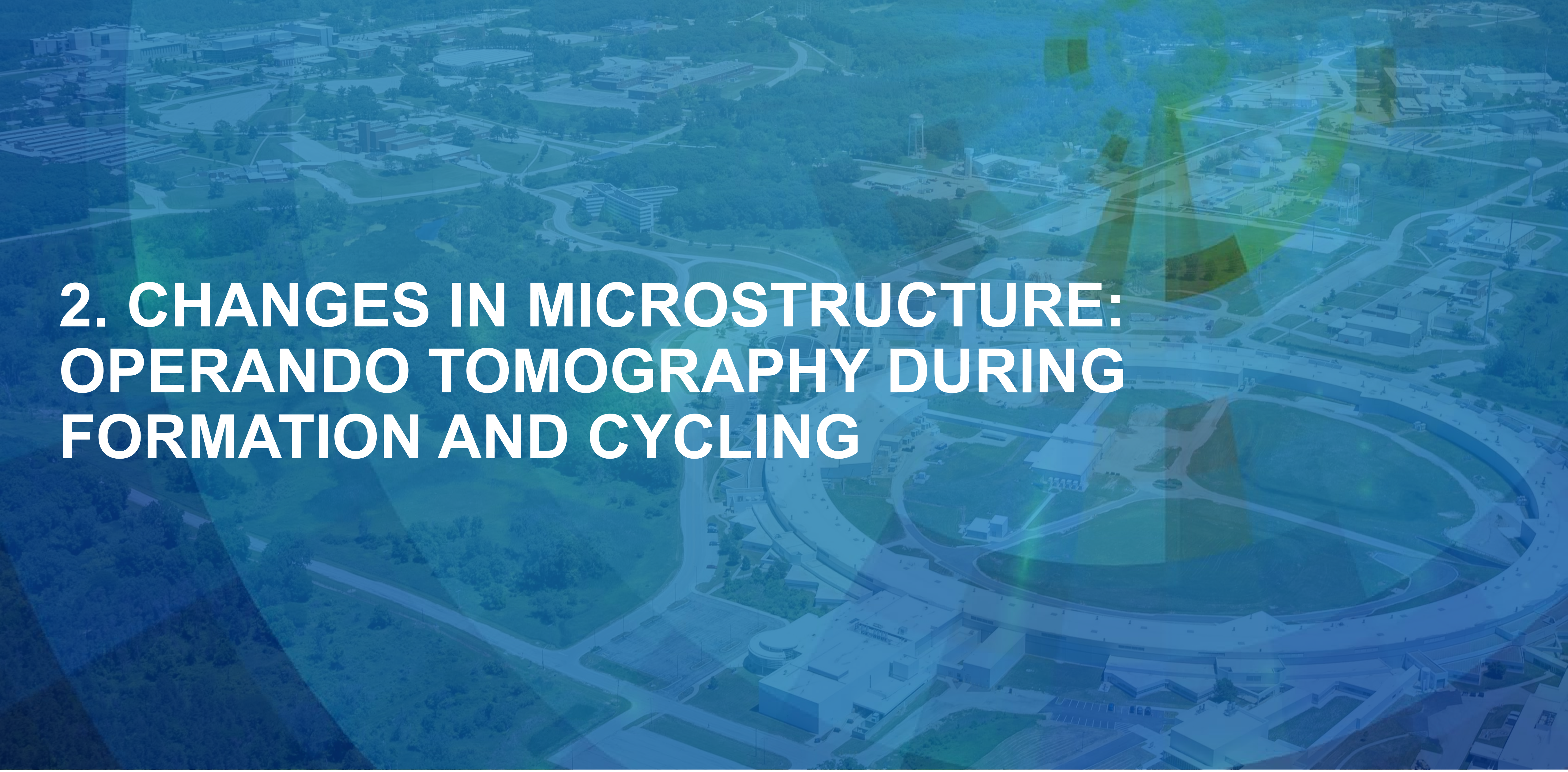


Near zero acid conc.

Why is αPbO_2 slowly replaced by βPbO_2?

By charging slower and resting for 45 min at end of discharge, we are allowing acid to reach higher SG at start of charge: this preferentially converts α → βPbO_2.

Future: modified cycling protocols and more modeling on SG/SOC during charge.

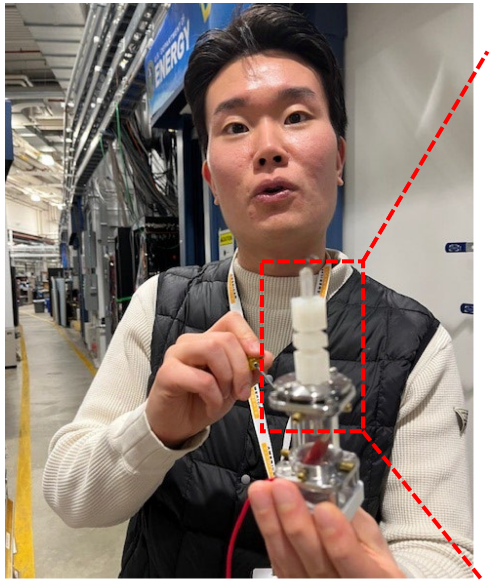


2. CHANGES IN MICROSTRUCTURE: OPERANDO TOMOGRAPHY DURING FORMATION AND CYCLING

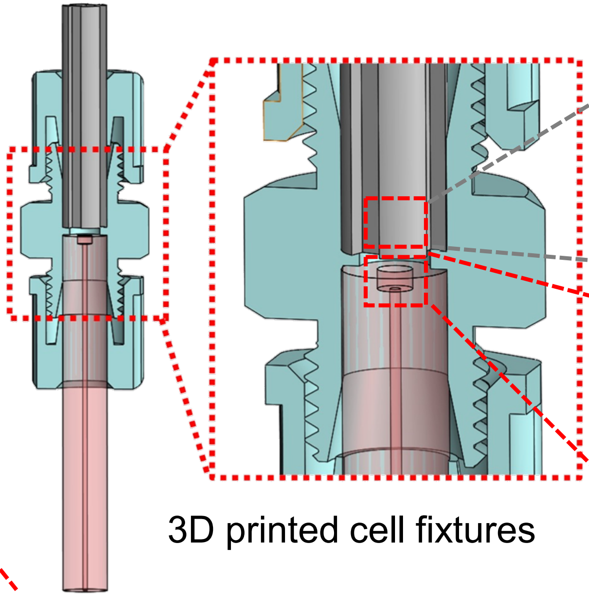
OPERANDO CT SCANS

Computed tomography: 3D microscopy

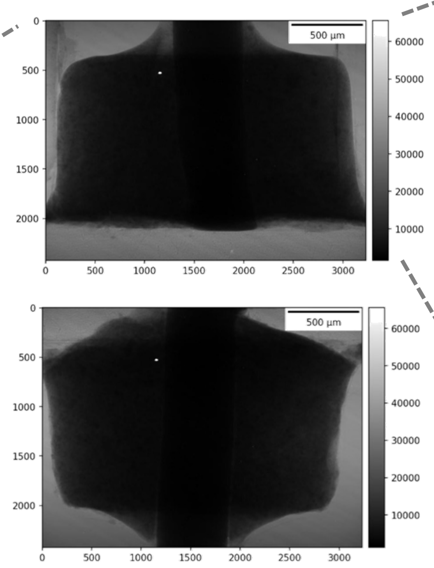
- Cell has coaxial geometry: active material is pasted in a “cup” fixture with a 0.5 mm Pb wire in the middle. Similar to a tubular lead acid battery, pasted at East Penn Manufacturing.
- Electrodes are fixed in 3D printed fixtures and held in place using a plastic compression fitting.
- APS 7BM: collected 80Tb of CT data and commissioned energy dispersive diffraction setup.



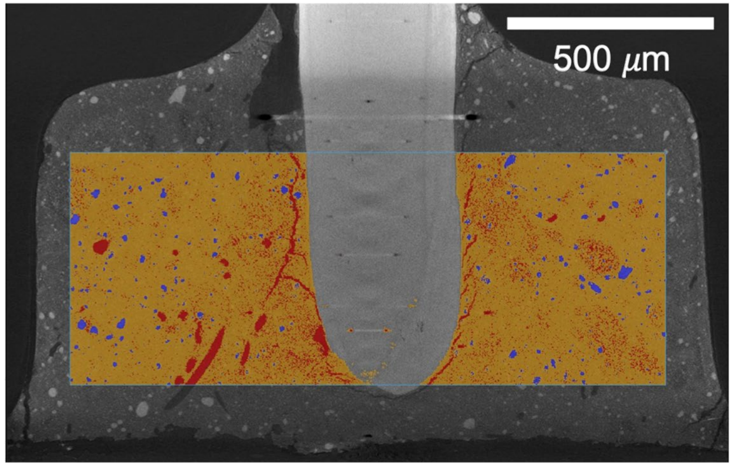
Seong-Jun!



3D printed cell fixtures



Radiographs (collected 2561 angles)

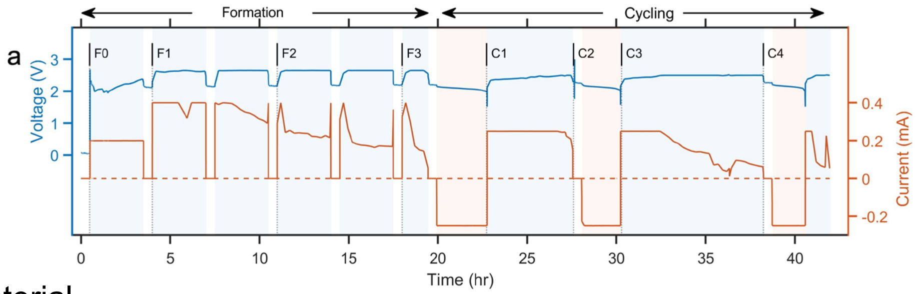


One slice from reconstruction: 700 nm voxels, 3200x3200x2500 total voxels.

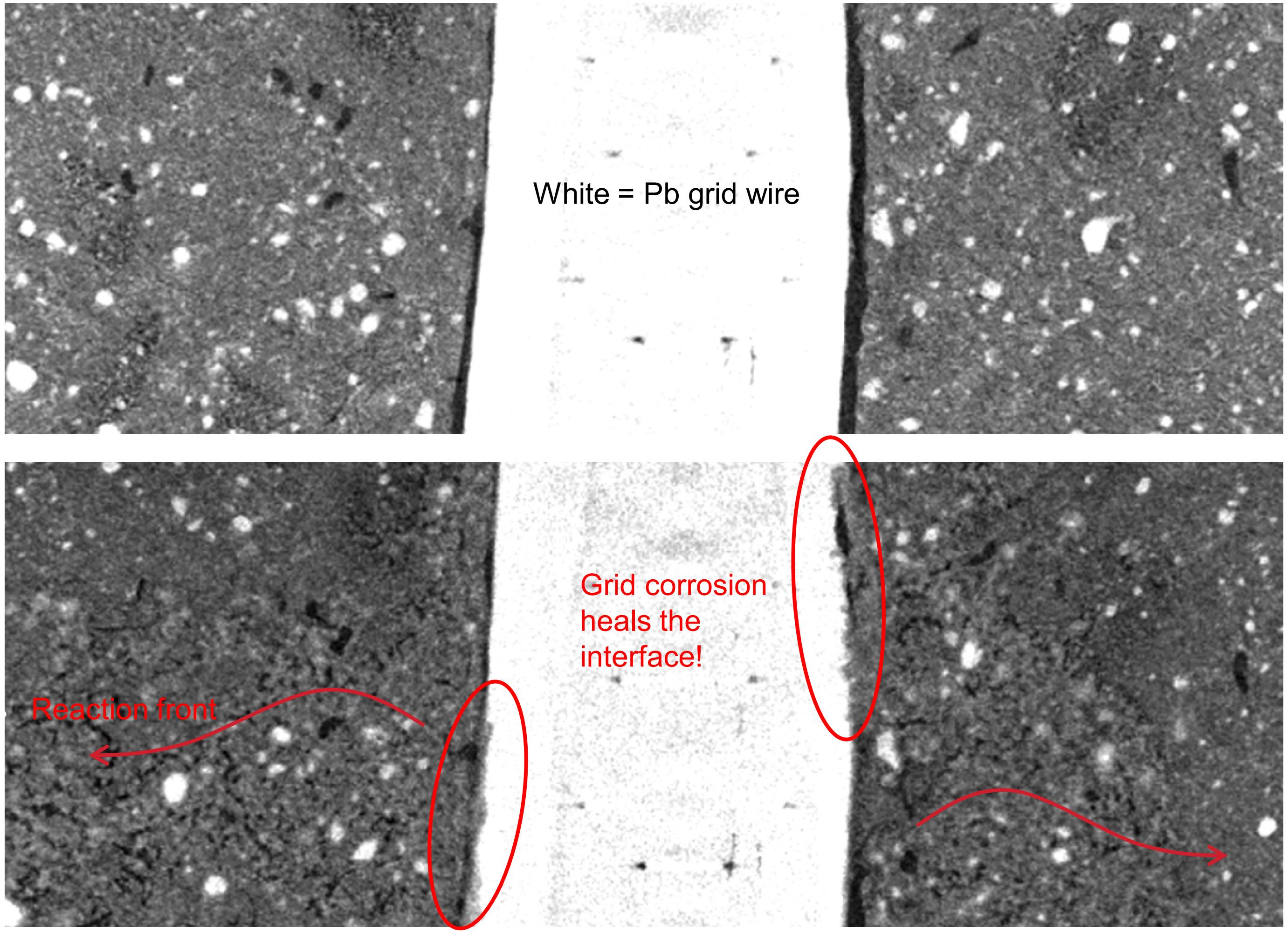
POSITIVE ELECTRODE

Start and end of formation

- Slice from CT reconstruction.
  - Grayscale proportional to density
- Reaction proceeds from grid outward.
  - Agrees with previous XRD mapping.
- Active materials becomes “sponge-ier”.
  - Some void coarsening during cycling.
- Free lead largely preserved, even at oxidizing conditions (although less than start).
- Positive ‘grid’ corrosion observed, especially in regions with poor paste adhesion.
  - Largely occurs at start of charging step.



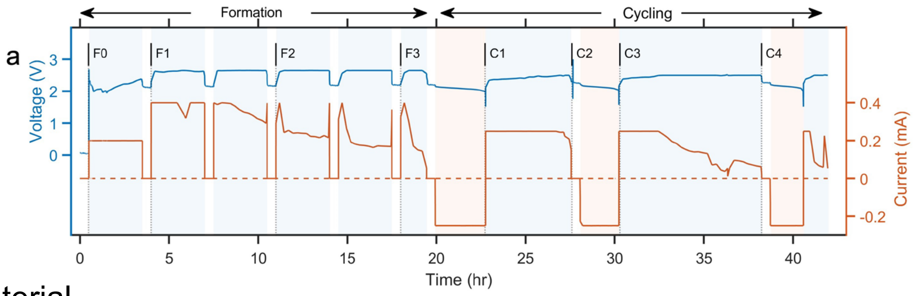
Gray region = Positive active material



NEGATIVE ELECTRODE

Start and end of formation

- Slice from CT reconstruction.
  - Grayscale proportional to density
- Reaction more patchy – less radial than positive.
  - Possibly more dependent on access to acid.
- Voids are coarser.
- Pre-existing voids/cracks are nucleation points for larger voids that form during end of formation (i.e. with hydrogen evolution).
- Contraction may be related to fragility of sponge lead and larger scale voids: precursor for "over-expansion?"



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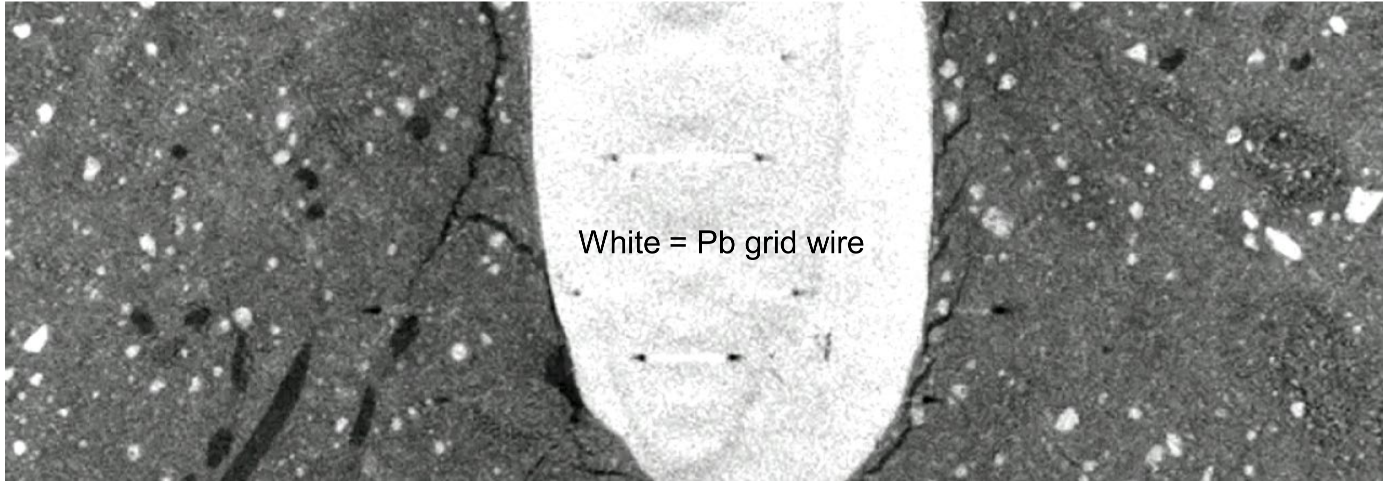
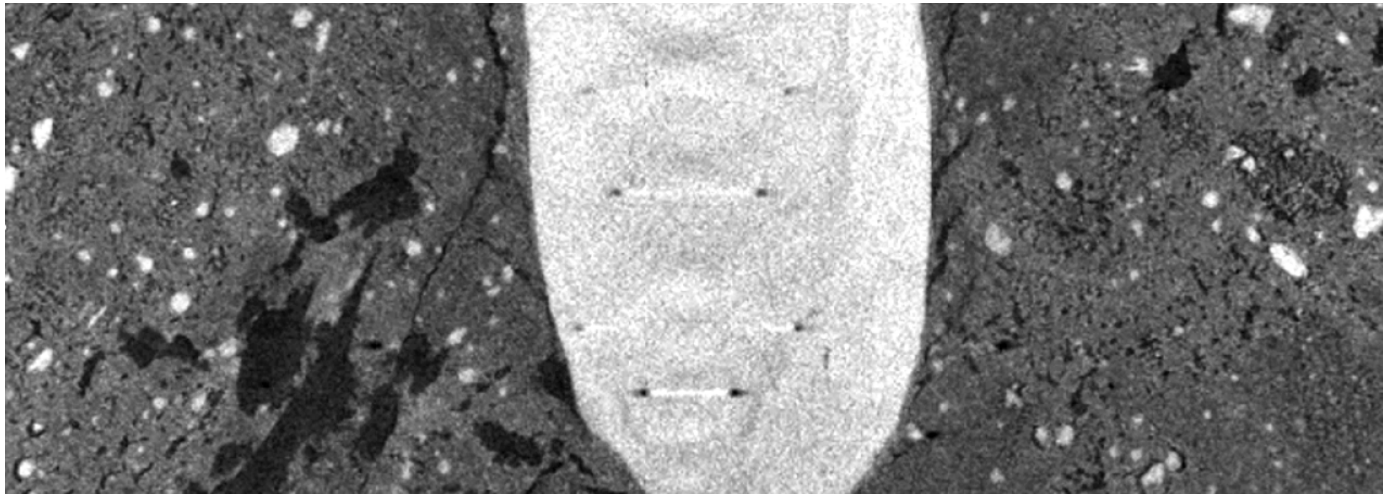


White = Pb grid wire



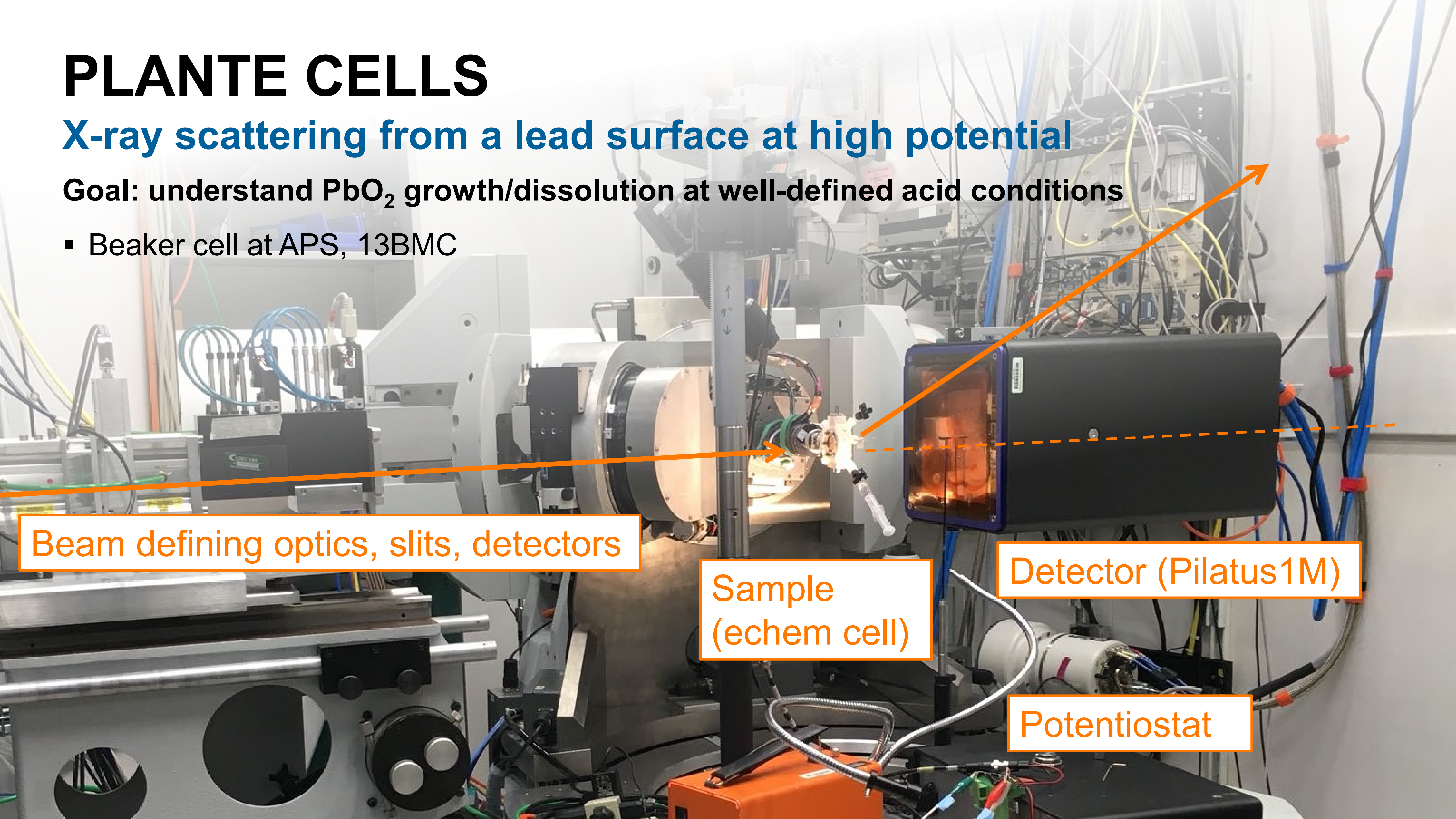
3. ATOMIC SCALE ORIGINS OF RIPENING: LATTICE DEFECTS IN PbO_2

PLANTE CELLS

X-ray scattering from a lead surface at high potential

Goal: understand PbO_2 growth/dissolution at well-defined acid conditions

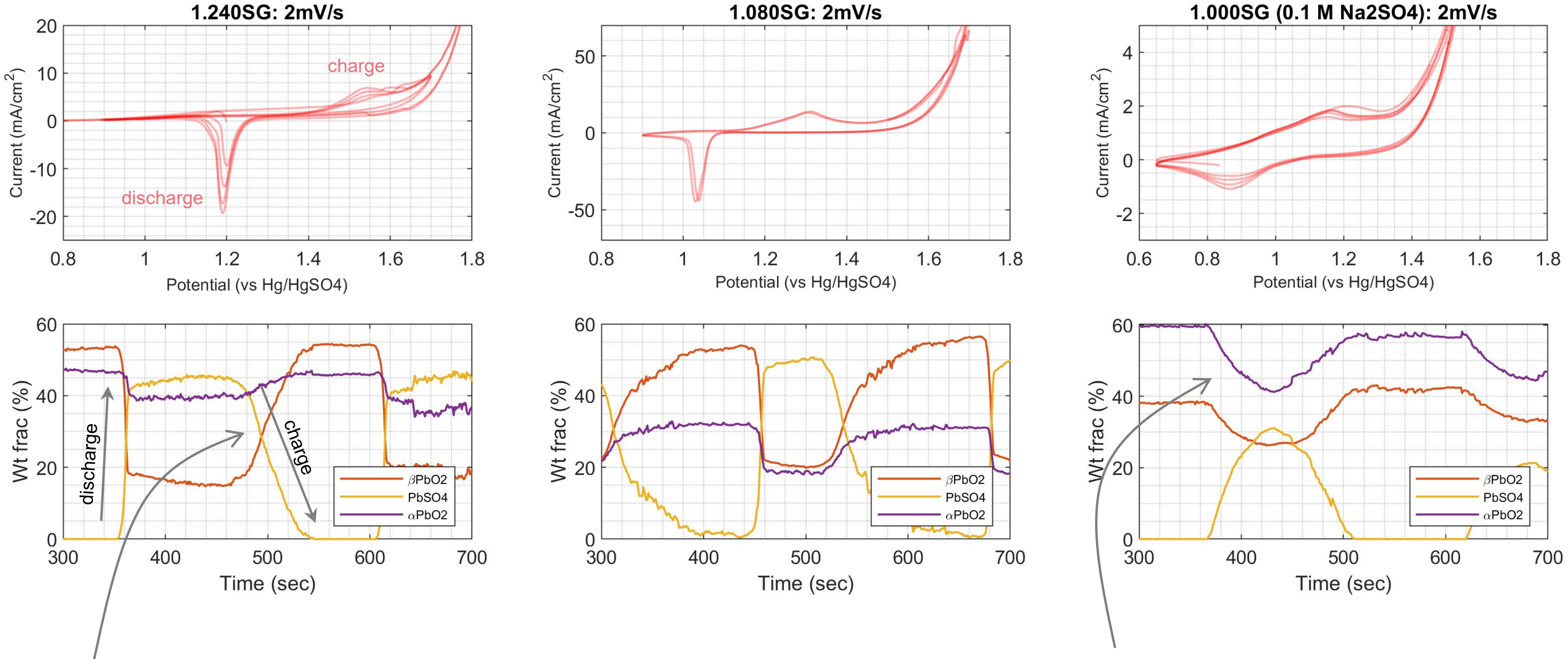
- Beaker cell at APS, 13BMC



OVERVIEW

Role of acid concentration/pH: voltammetry

- Higher acid SG (first cycles): changes mostly from βPbO_2, similar difference in α/β activity as pasted cells.
- Note that αPbO_2 is still active during discharge *and* charge.
- Neutral acid conditions: 50/50 α/β PbO_2.
- Alkaline conditions (not shown): only αPbO_2.



Acidic: ΔβPbO_2 > ΔαPbO_2

Neutral: ΔβPbO_2 = ΔαPbO_2

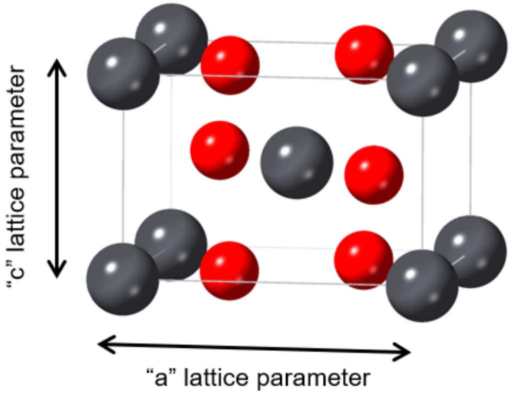
PbO_2 crystal structure

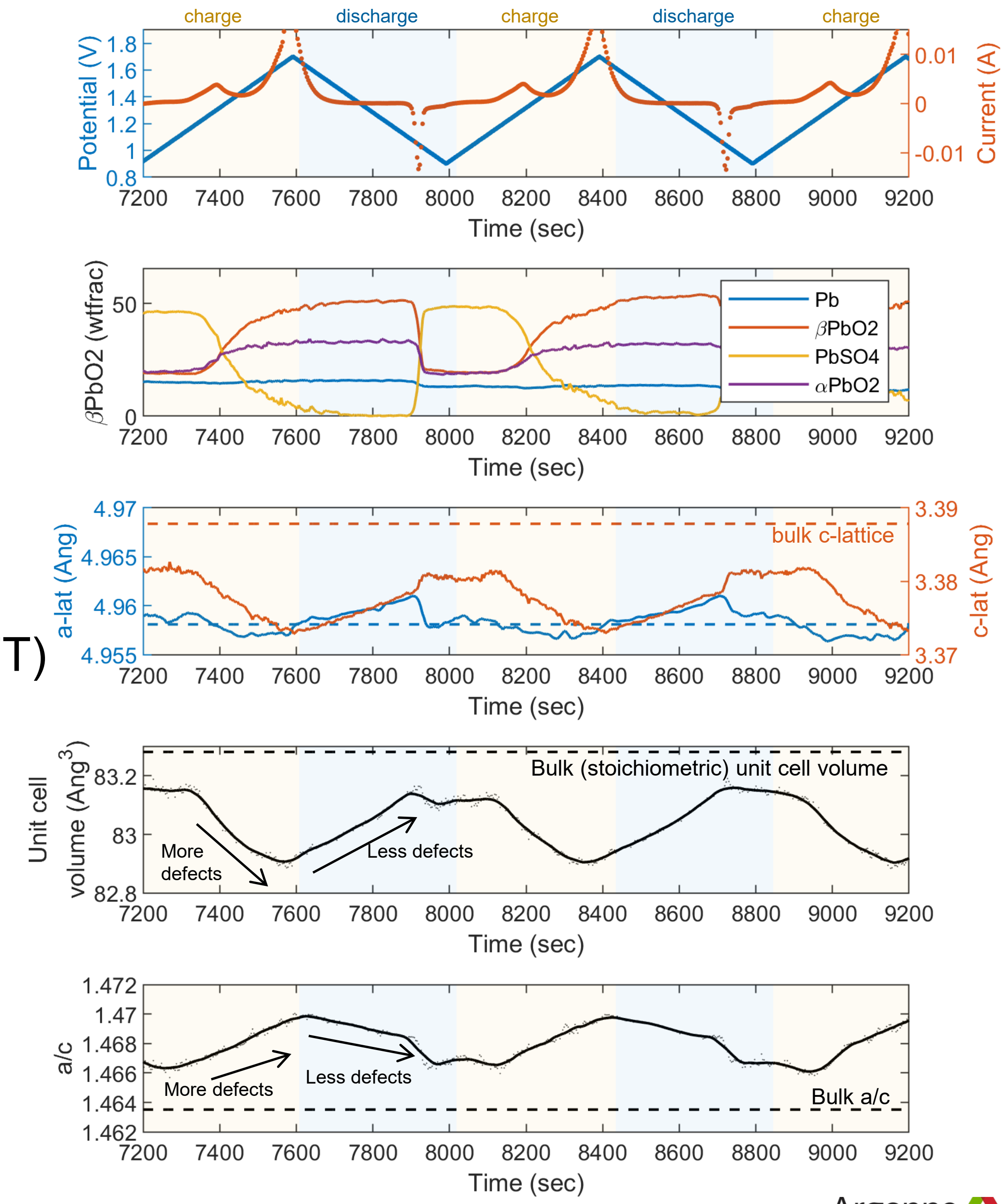
Lattice changes = lattice defects

In addition to composition, changes in *crystal structure* (lattice constants) was found **during** cycling. These changes are likely due to lattice defects.

- In general, βPbO_2 deviates ‘pure’ (stochiometric) values, especially at end of charge, at high potential.
  - Deviation is consistent with Pb vacancies (DFT)
  - Similar changes found in 1.240 and 1.00SG samples.
- DFT (Garcia poster) used to correlate defect energetics and effect on crystal structure.

Tetragonal (rutile) βPbO_2



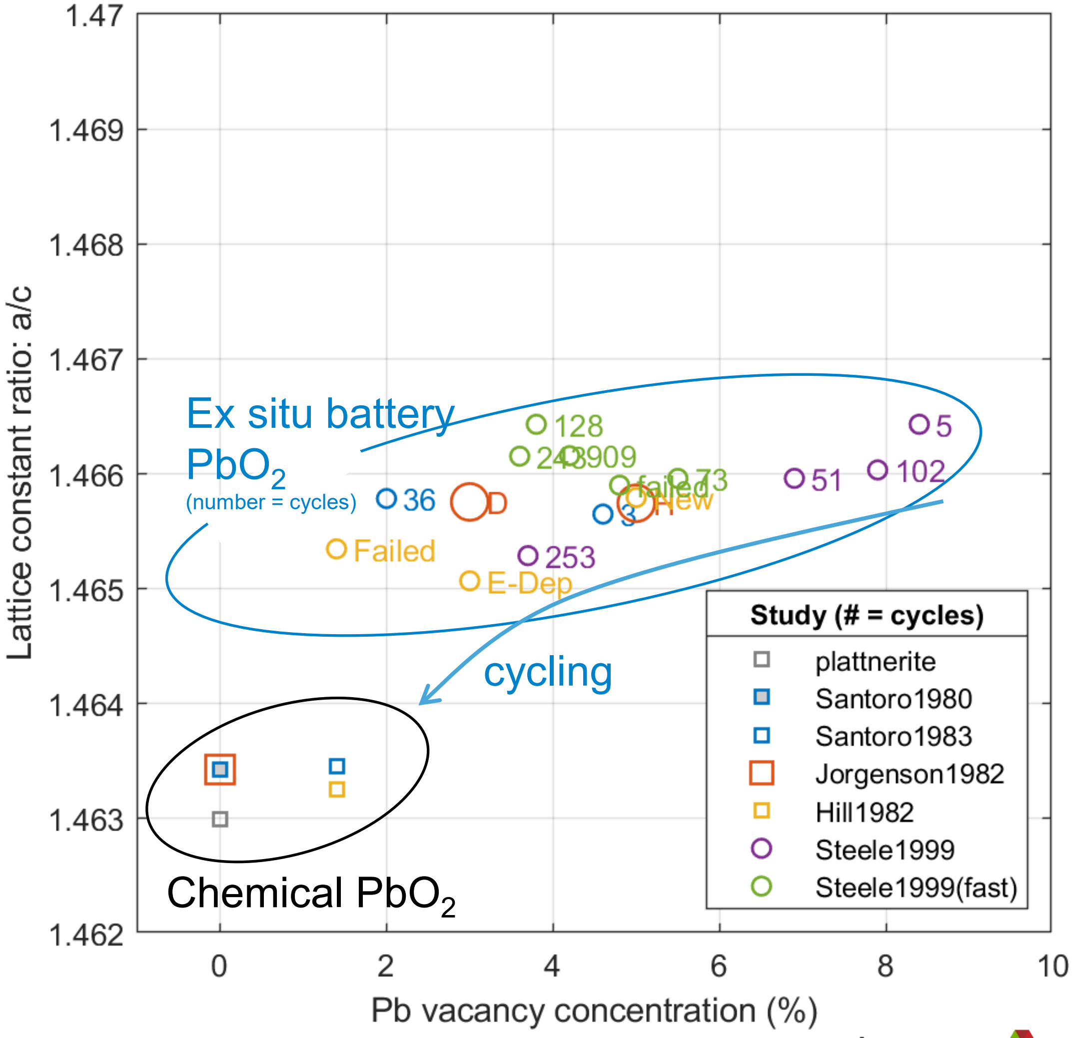


DYNAMIC DEFECTS

Need for operando measurements

Defects are good. previous ex situ neutron scattering showed reduction in Pb defects later in cycle life.

- Trends can be found by looking at the *ratio* of the a- and c-lattice constants (‘tetragonality’).
  - — Clear difference between electrochemical and chemical PbO_2.



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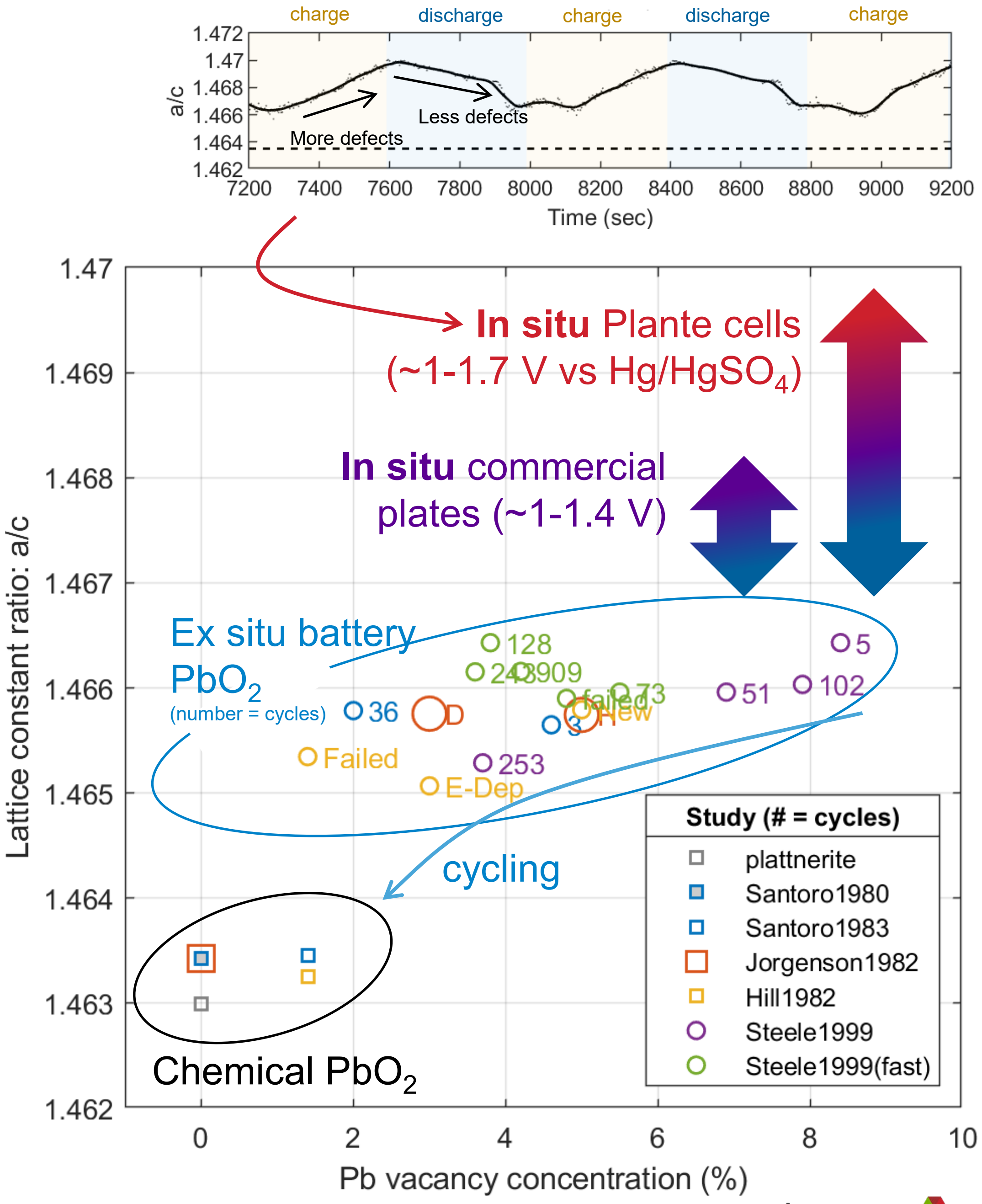
- Trends can be found by looking at the *ratio* of the a- and c-lattice constants (‘tetragonality’).
  - — Clear difference between electrochemical and chemical PbO_2.
  - — **New: even larger difference found in operando measurements.**
- DFT (Garcia/Iddir) suggests changes with potential are driven by varying proton content.
  - — Exact Pb, H occupancy: neutrons, NMR (PNNL)



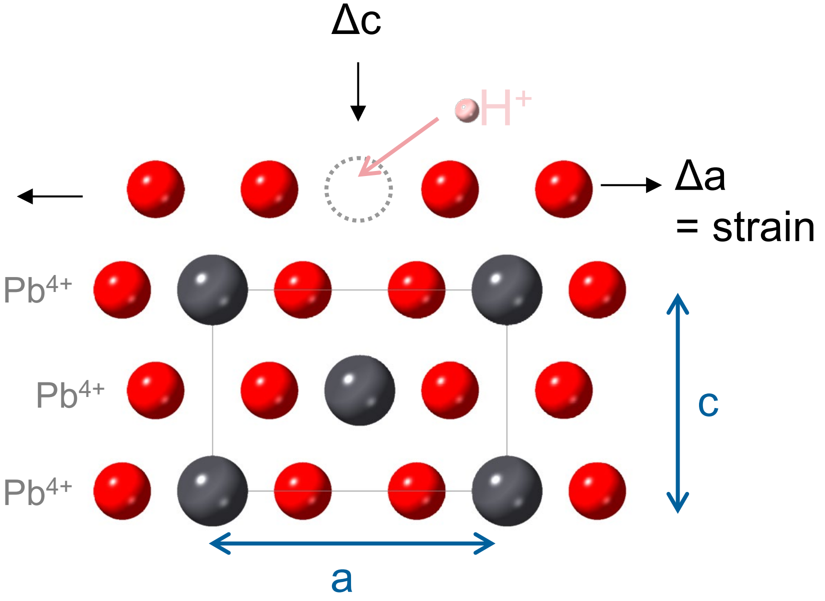
EFFECT ON CRYSTAL SIZE

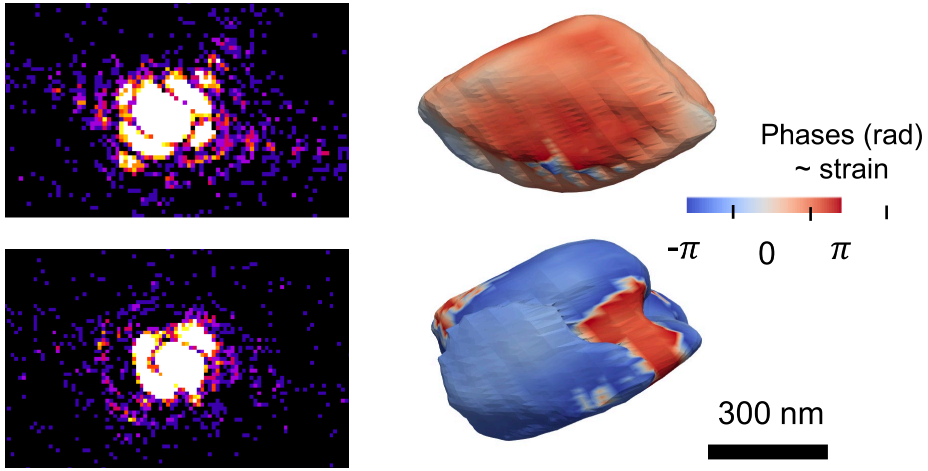
Lattice defects (strain) prevents ripening

Lattice defects and particle size are interconnected:

- **Correlation**: Pb vacancies (and H interstitials) likely form during growth; smaller particles = more defects.
- **Causation**: **defects lead to localized lattice strain within PbO_2. Strain and chemical mismatch inhibits further growth, leading to smaller particle size.**
  - Deep discharge helps release/remove defects, leading to ripening during recharge.
  - Higher current, temperature, and acid SG could be used to tune defect concentration/particle size.

Future: *Coherent* diffraction in the \$815M APS Upgrade is the perfect technique for measuring lattice defects and strain.





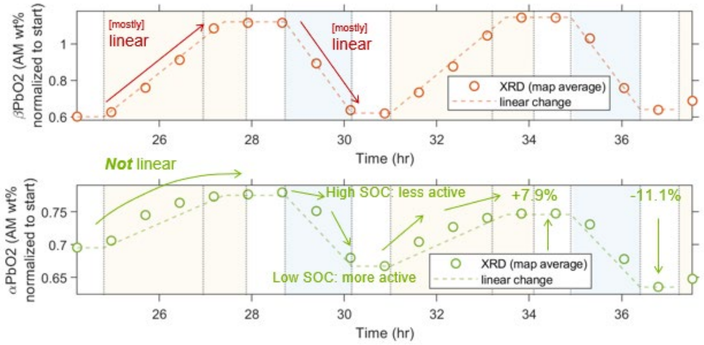
Coherent diffraction reconstructions of $PbSO_4$ nanoparticles (Suzana, Papa Lopes). Can we do similar things for PbO_2?

SUMMARY

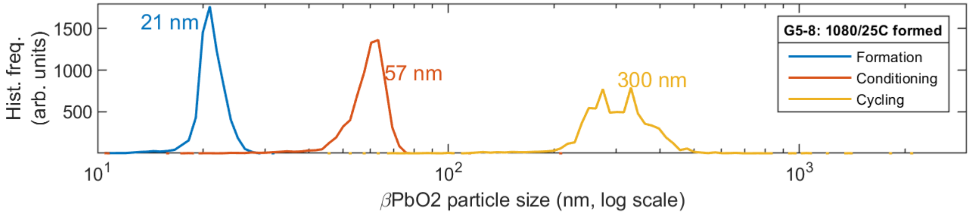
SUMMARY: OVERALL MECHANISM

DOD, defects and PbO_2 ripening

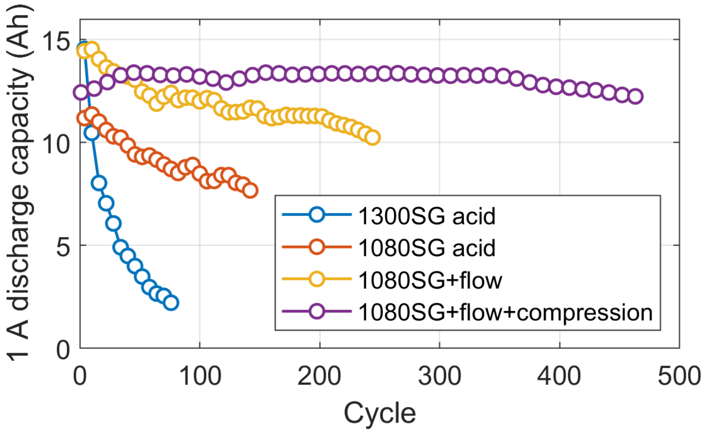
- **α → βPbO_2 conversion**
  - — αPbO_2 active at higher pH (early formation, deep discharge)
  - — Consumption of acid at high DOD activates αPbO_2 which can be partially converted to βPbO_2 during recharge.



- **Defects and particle size**: "Ruetschi defects" (Pb vacancies and H^+ interstitials) are intrinsic to electrochemical PbO_2.
  - — Lattice strain from these defects produces a nanoscale active material.
  - — Cycling, especially at deep discharge, removes these defects. Releasing strain → ripening.
  - — PNNL collaboration: measure H^+ species with NMR!



- **Future work**: Use mechanisms to help define optimal SOC windows and acid conditions for cycling.
  - — Conditions during formation can inform charging protocols: low SG acid, fast charging may help (see FY24 presentation).
  - — Image strain using coherent diffraction. Use dopants to engineer strain in PbO_2.



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