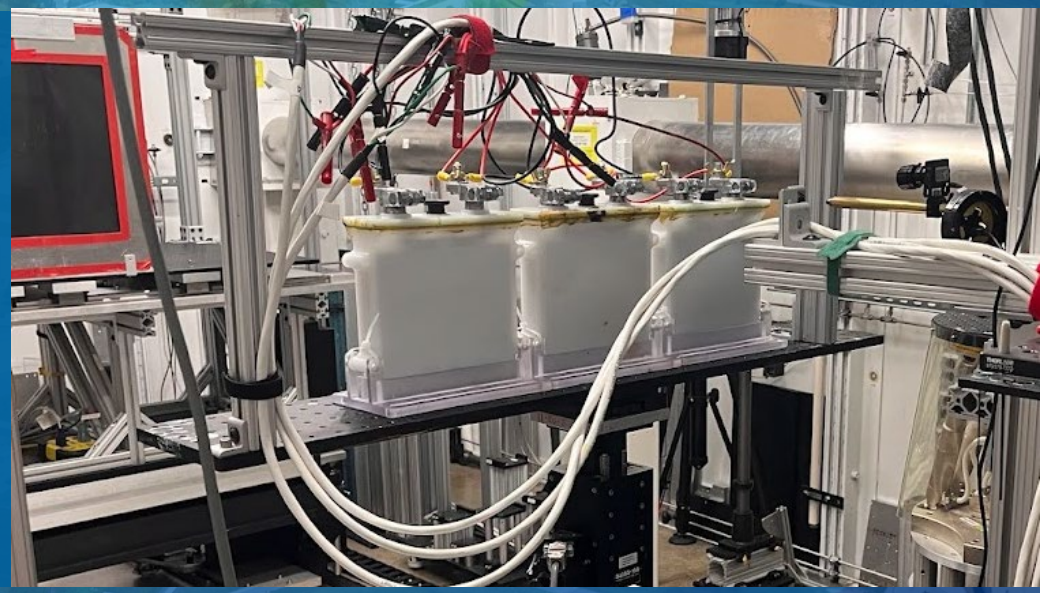
2026 OE Peer Review
Presentation #1001

MULTISCALE CHARACTERIZATION OF LEAD ACID BATTERIES

EFFECT OF POSITIVE ELECTRODE ADDITIVES ON FORMATION AND CYCLING



ANL: TIM FISTER, JUAN GARCIA, HAKIM IDDIR, MATTHEW NISBET, TIFFANY KINNIBRUGH, MOHAMMED EFFAT, KEVIN KNEHR, TIM OFFICER

PNNL: AJAY KARAKOTI, DAVID BAZAK, DAN THIEN NGUYEN, CARINNA LAPSON, BENJAMIN LEGG

INDUSTRY: MATTHEW SPENCE, JULIAN KOSACKI, MICHAEL BRADY, PHIL SHOLTES, MICHAEL VERDE, JACK SCOTT, SUBHAS CHALASANI

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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 growing and stabilizing the grid.

FY2026

Summary

Manuscripts

- Garcia, Fister, Iddir, “Role of defects on PbO_2 structure, conductivity and phase stability: insights from DFT calculations,” in review, Journal of Physical Chemistry
- Two additional manuscripts in preparation for FY26.

Patents

- US12567599, “Pumping charge & discharge electrolytes” (2026)
- US20240186592A1: “Electrode Manufacturing” (2026)
- IN-26-014 (provisional): “Acoustics signatures…” (2026)

Peer review posters

- Effat et al: “Consortium for Lead Battery Leadership: Red Team 2, Failure Analysis and Modeling”
- Fister et al: “Multiscale characterization of lead acid batteries: effect of positive electrode additives on formation and cycling”

INTRODUCTION & MOTIVATION

MOTIVATION

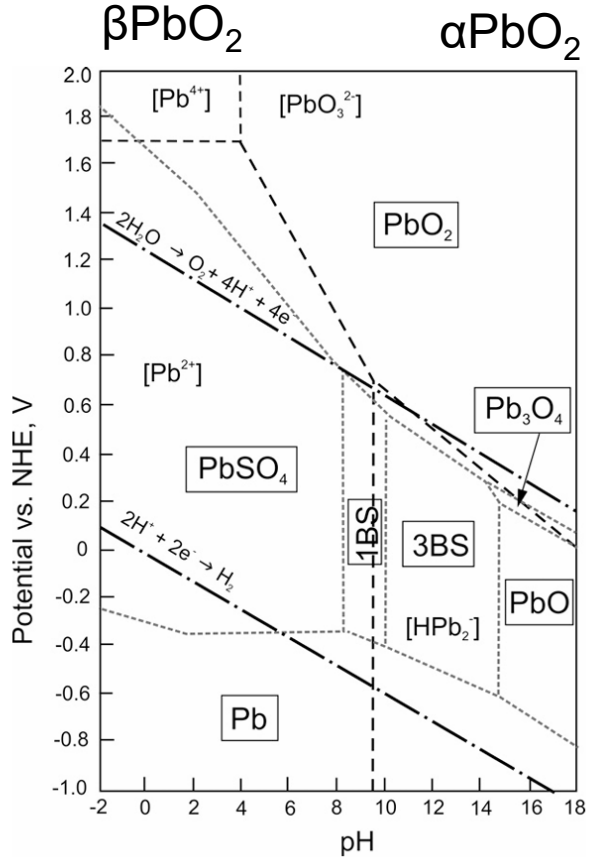
Overview

- Key indicators for cycle life
  - — Negative electrode failure
    - • Inhibiting negative sulfation
    - • Inhibiting stratification
  - — Maintaining αPbO_2 content
  - — Health corrosion layer
  - — Inhibiting PbO_2 ripening

Solved with conductive additives (carbon)

Electrolyte/cell management

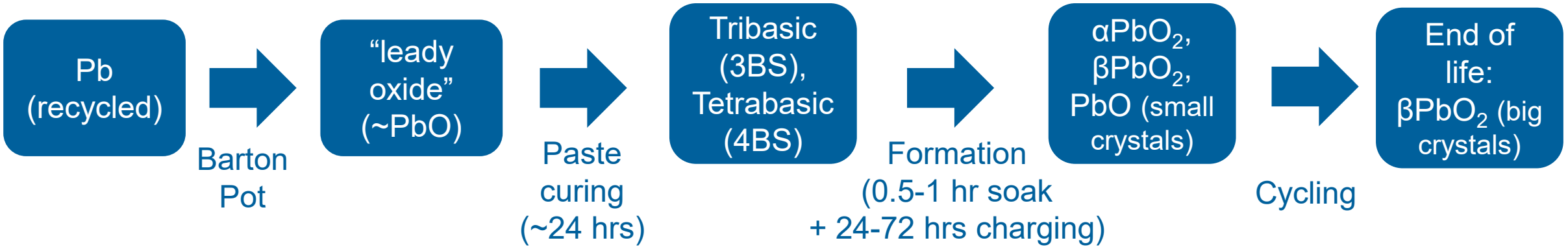
Composition/morphology dictated by formation: maintaining “alkaline” species is key.



IMPROVING POSITIVE ELECTRODES

Why study formation?

- Formation is a major cost driver for lead acid batteries.
  - Positive electrode formation is the bottleneck: batteries are charged 5-6x rated capacity. Curing/forming is a multiday process.
  - Formation also plays large role in cycle life by templating the composition and morphology of the positive active material (PAM).

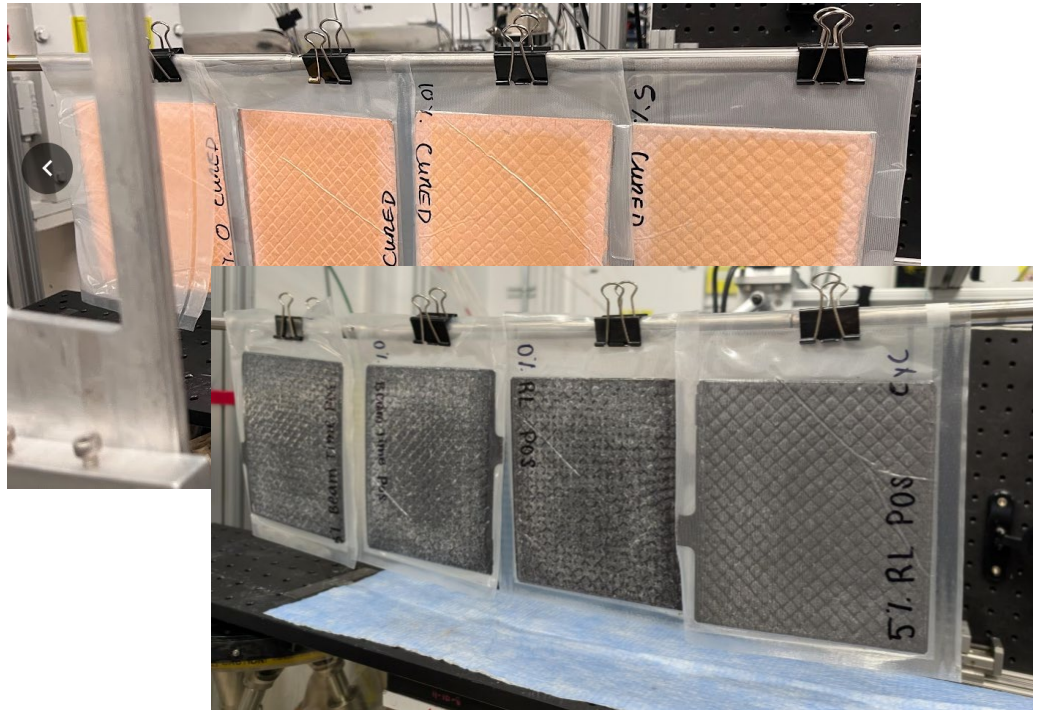


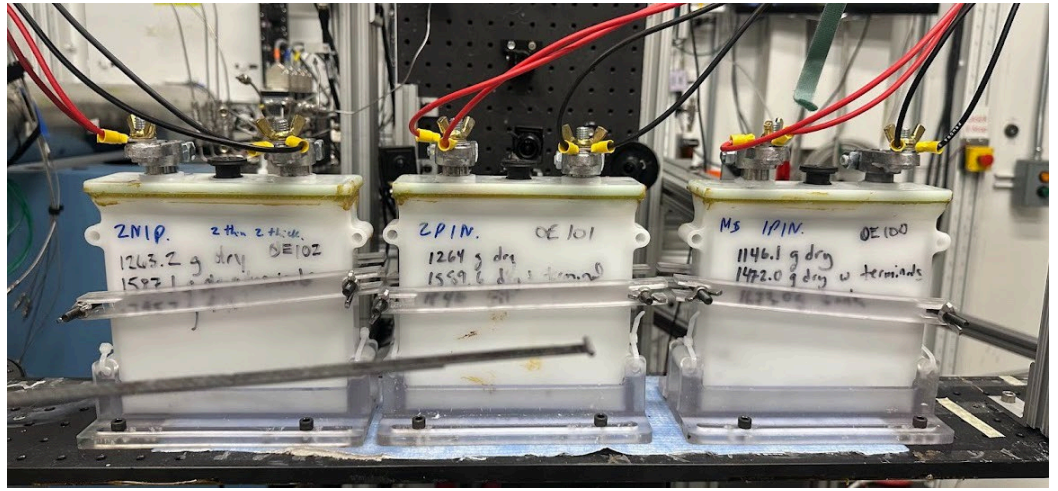
Formation and curing variables (time, temperature, current density, acid concentration) dictate the final composition of the positive electrode: **understanding formation is critical for capacity and cycle life and can inform recharge over life of battery.**

FY26 PROJECTS

Overview: core OE research

- Collaboration with Clarios: tribasic vs. tetrabasic formation and effect of “red lead” (Pb_3O_4) on positive electrode formation and cycling.
- Collaboration with Trojan: role of Sb in deep cycle batteries
- Collaboration with East Penn and PNNL: depth profiling electrodes during micro-cycling. Effect of carbon and $BaSO_4$
- Collaboration with PNNL: DFT calculations of lignin molecules on $PbSO_4$ and measurements on PNNL $(Ba,Sr)SO_4$ nucleation additives





FORMATION: TRIBASIC VS TETRABASIC

COLLABORATION WITH CLARIOS

BASIC SULFATES: 3BS VS 4BS

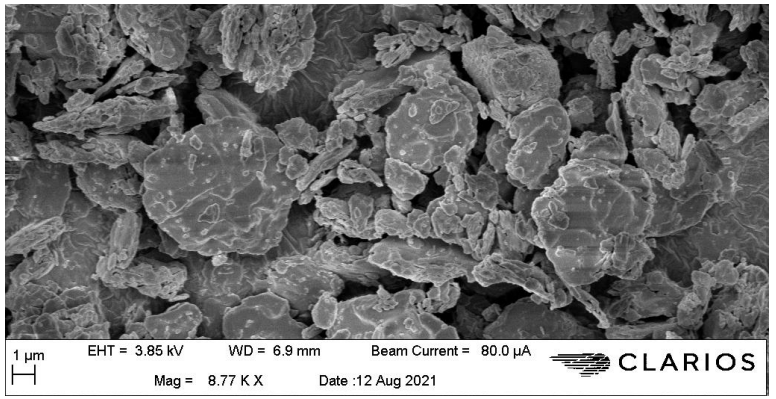
Curing variables

Curing: mixing PbO and sulfuric acid to form basic lead sulfate.

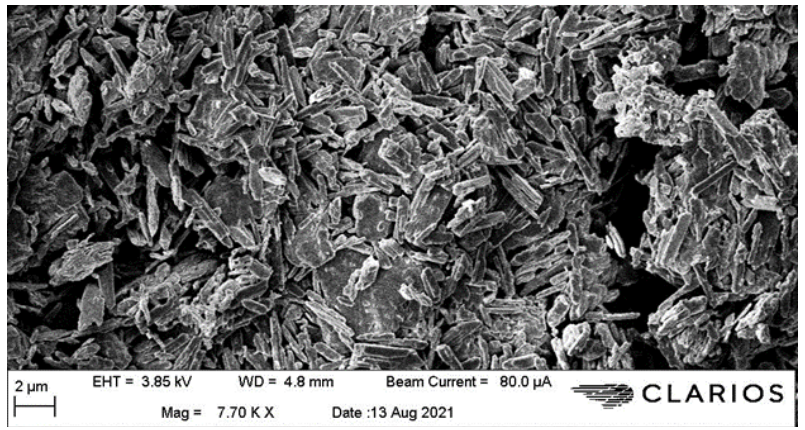
- **Tribasic lead sulfate** (3BS): most commonly used, promotes small crystals and small pores
- **Tetrabasic lead sulfate** (4BS): more common in thick plate, deep cycle batteries: large crystals and large pores
  - Commonly assumed that 4BS only partially reacts, forming a ‘reticular’ structure for the positive active material.

Popular wisdom: 4BS partially remains during formation and cycling, forming a “reticular backbone” that promotes longer cycling.

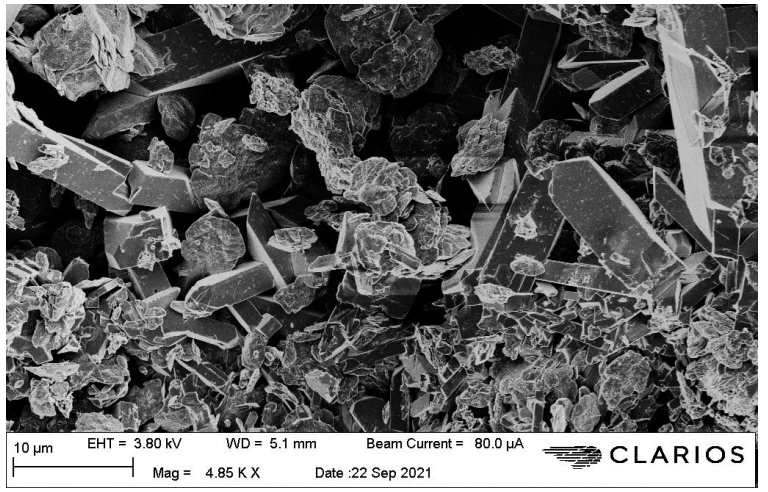
“Leady oxide” ~PbO



Tribasic lead sulfate (3BS)



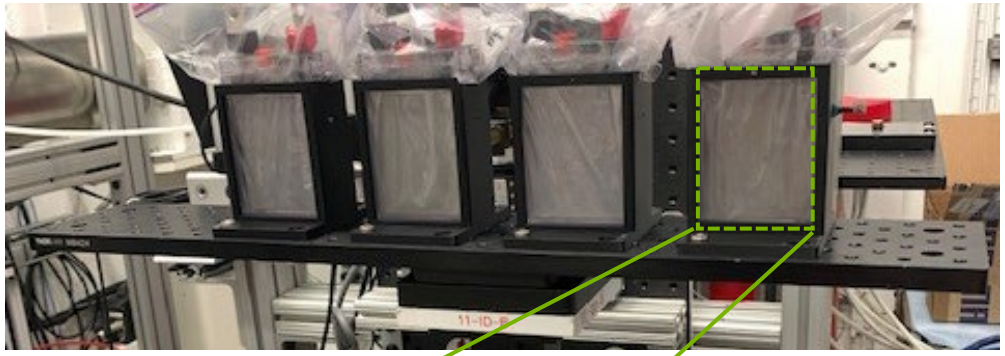
Tetrabasic lead sulfate (4BS)



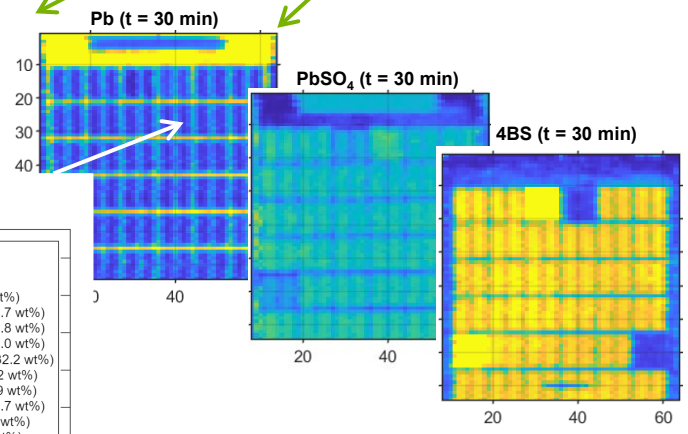
EXPERIMENT

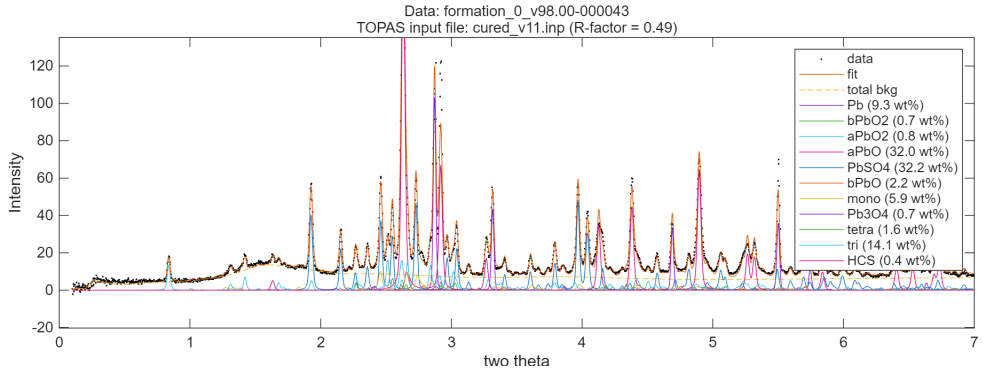
Formation on 3BS and 4BS electrodes: in situ XRD

- APS (11IDB): XRD maps
  - Cells from Clarios (~1Ah)
- Variables: 3BS vs 4BS and constant current vs stepped formation profiles
  - Ongoing: extended cycling in PSOC and deep cycle regimes for both variants



XRD is collected from model 2V cells, mapped across the entire cell.



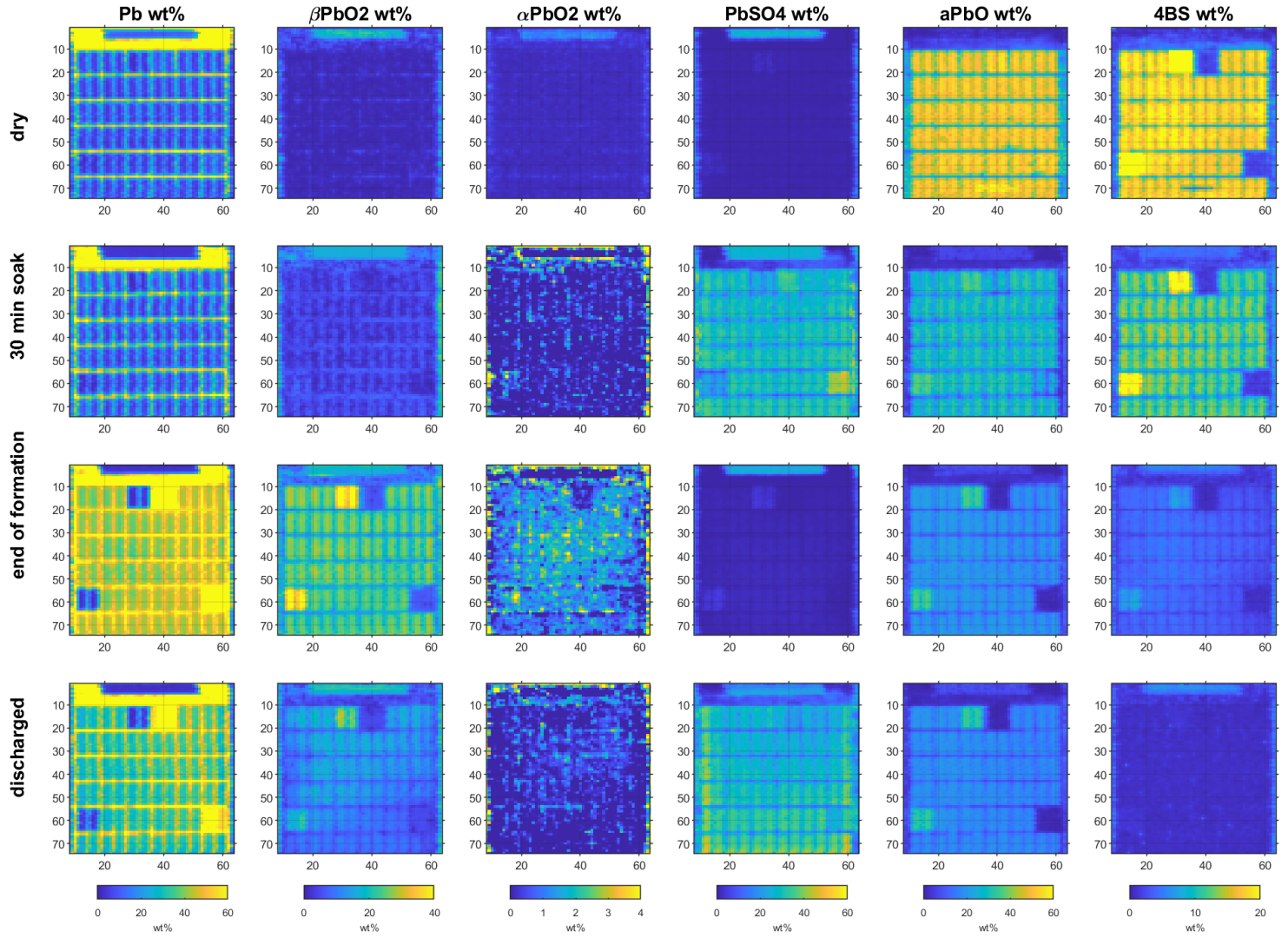


MAPS

Example: 4BS + stepped formation

Key findings:

- Cells are well-formed at 3 Ah (additional charge is unnecessary)
- 4BS in positive reacts during first *discharge* (not charge).
- More αPbO_2 in 3BS positives, forms at same rate as βPbO_2
- Positives are under-formed due to residual PbO



COMPARISON

3BS vs 4BS, stepped/constant current formation

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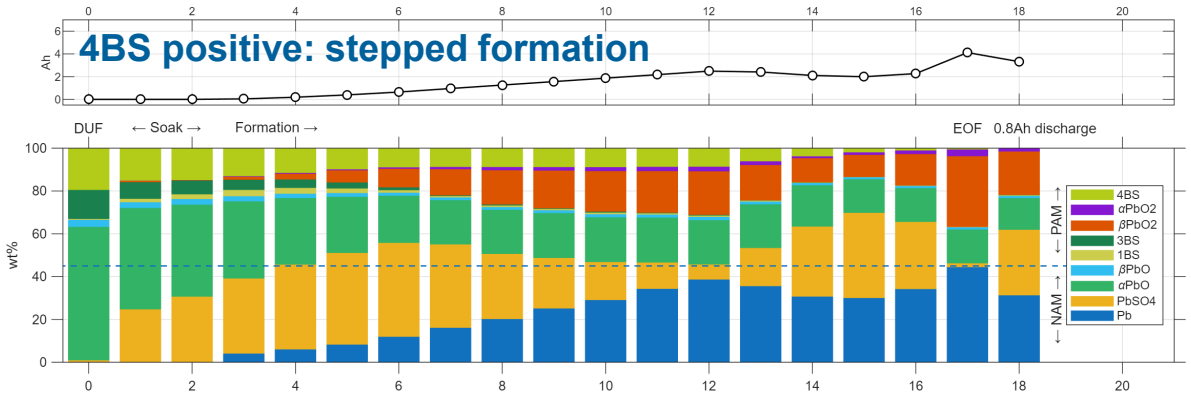
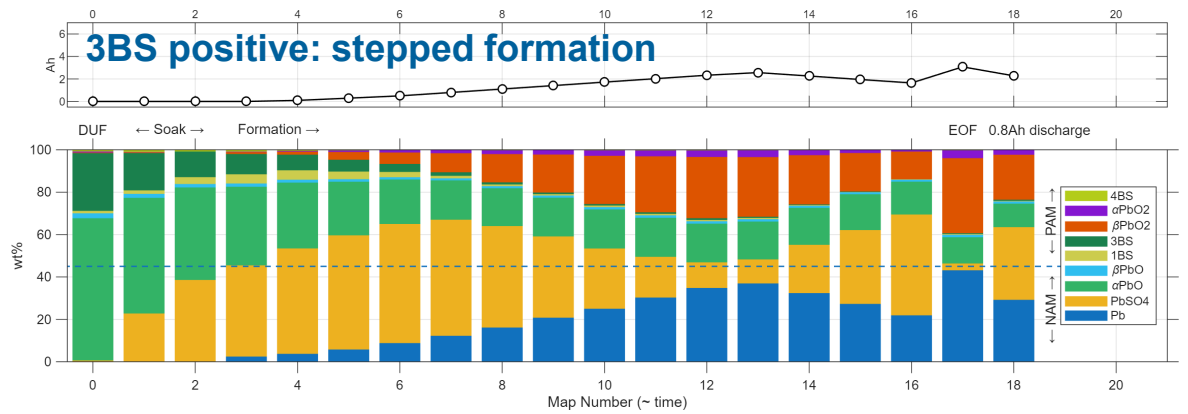
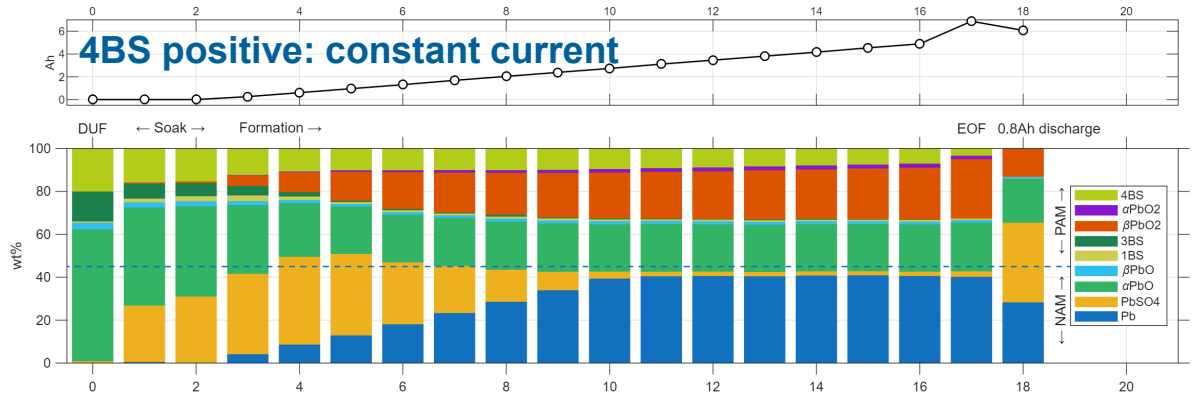
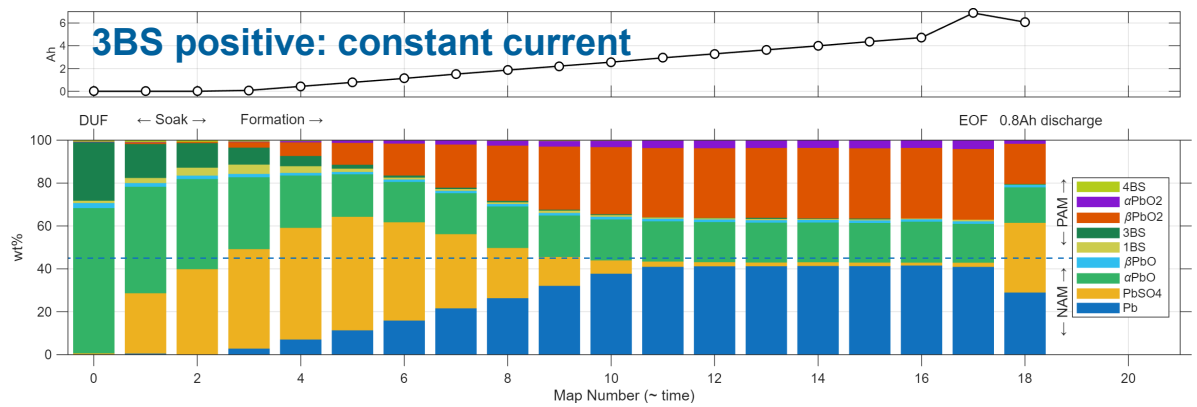




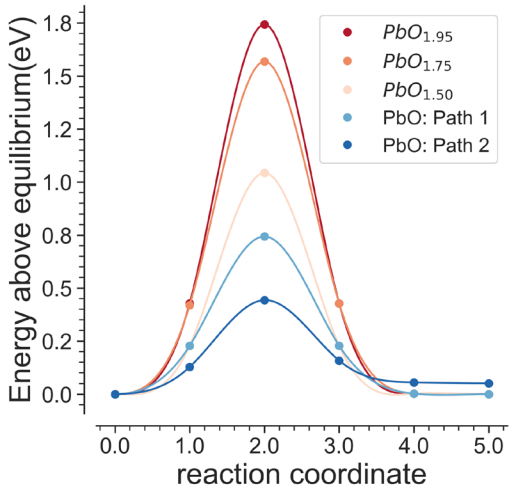




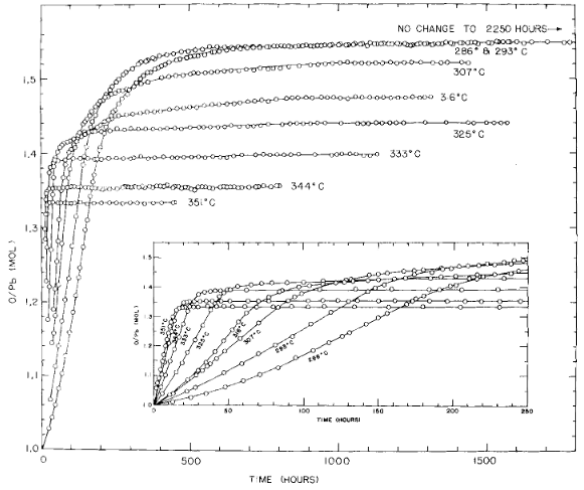
MECHANISM

PbO: an active species?

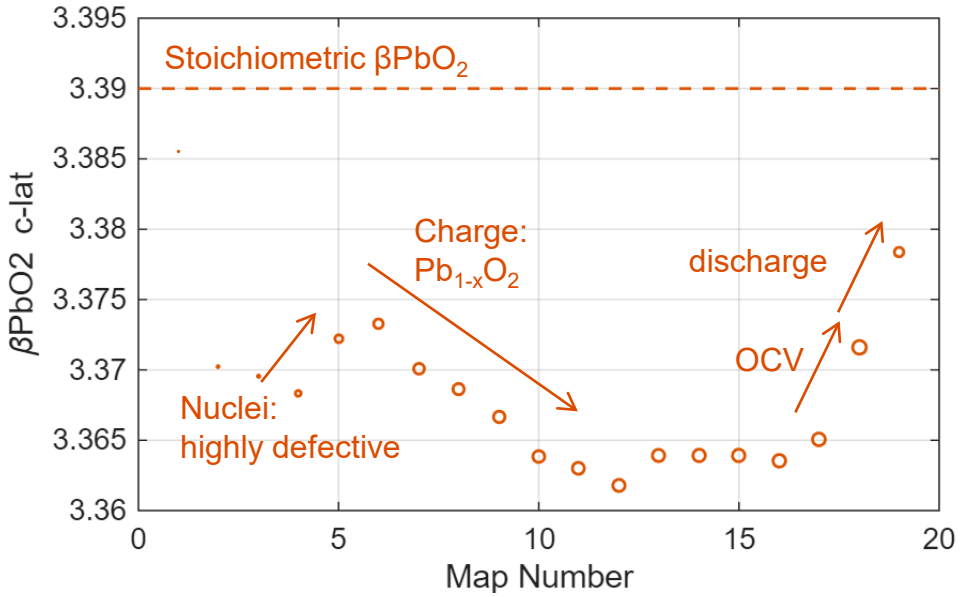
- During ***soak***, PbO reacts similarly in pos and neg.
  - $PbO \rightarrow PbSO_4$, 1BS
- During ***charge***, PbO in pos stops dissolving and lattice constant increases, consistent with PbO oxidation that stops conversion to $PbSO_4$
  - $PbO \rightarrow PbO_{1+x}$, $PbSO_4 \rightarrow \alpha, \beta PbO_2$
- βPbO_2 also sees changes consistent with H^+ incorporation on Pb site (see FY25 talk).

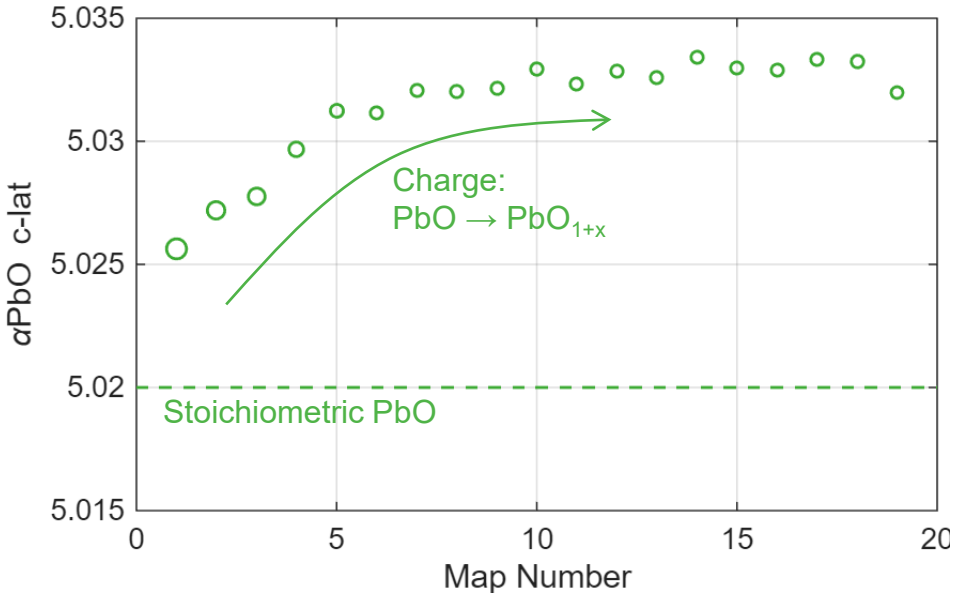


Oxygen transport is highly favorable in PbO (Garcia/Iddir/Fister submitted 2026)



Thermal oxidation of PbO was previously measured (Sorrell, 1973).





The change in PbO_2 and PbO lattice constants is consistent with cation defects in PbO_2 and oxygen interstitials in PbO, as discussed in previous peer review presentations.

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GRID ALLOYS: ROLE OF ANTIMONY

COLLABORATION WITH C&D TROJAN

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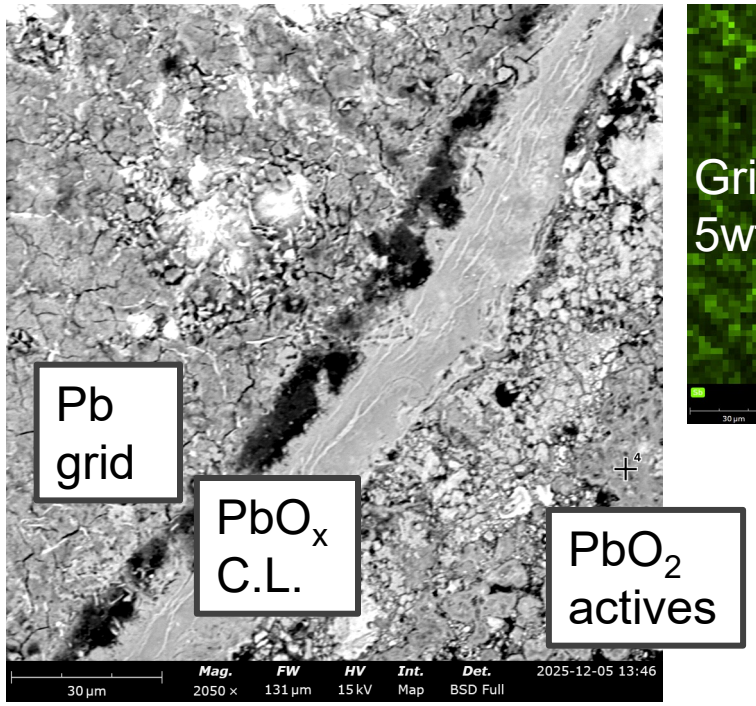
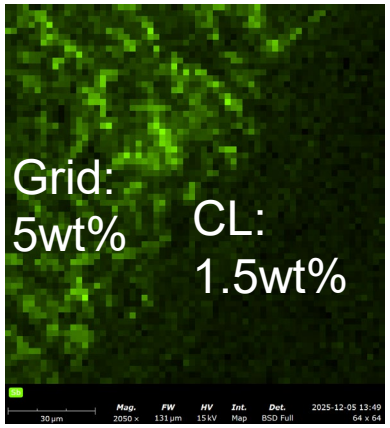
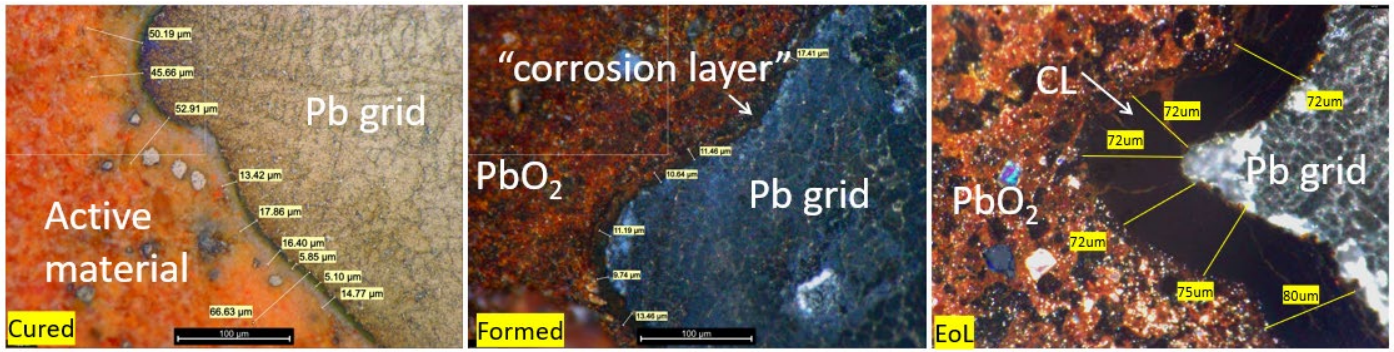
ANTIMONY

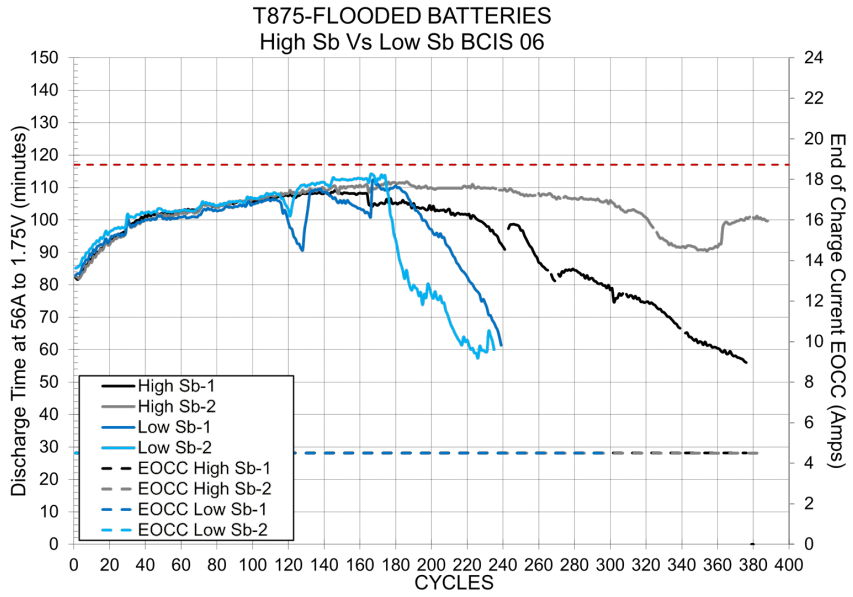
Grid dopant engineering

- Antimony-doped grids (5-10% Sb) are commonly used in deep-cycle applications.
- Sb is seen as essential for cycle life, but mechanisms are unclear.
- Recent increases in the cost of Sb has reopened the question: what is the role of antimony in lead acid batteries?







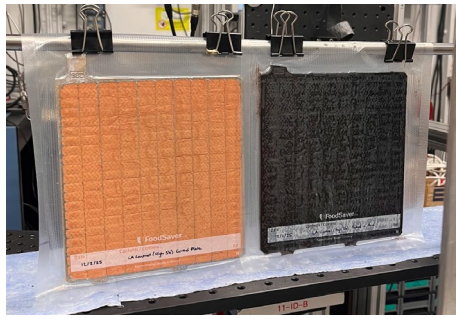


XRD MAPS

After formation

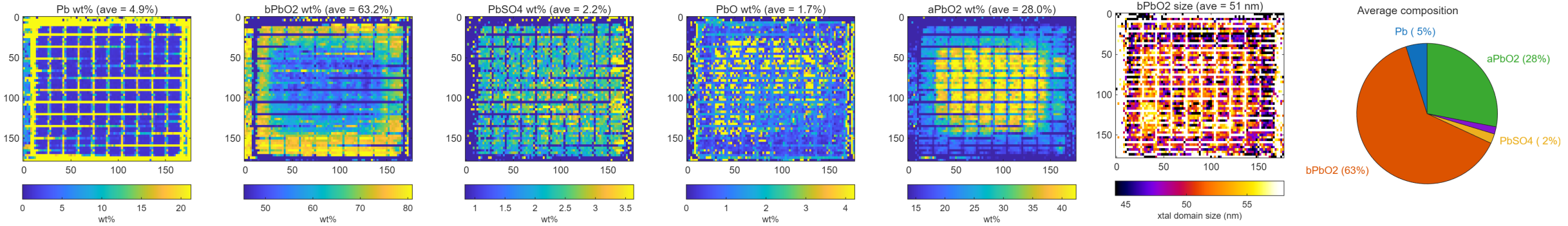
Cured, formed and cycled electrodes studied.

- After formation: not much difference between positives with high and low Sb content in the grid.

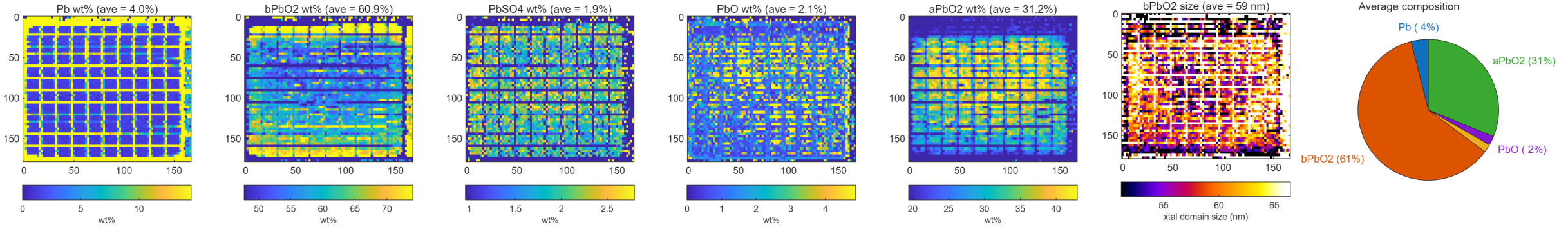


Cured and formed electrodes from C&D Trojan

Low-Sb positive: after formation (cycle 0)



High-Sb positive: after formation (cycle 0)



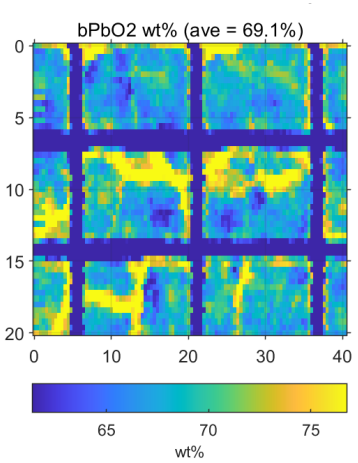
XRD MAPS

After cycling

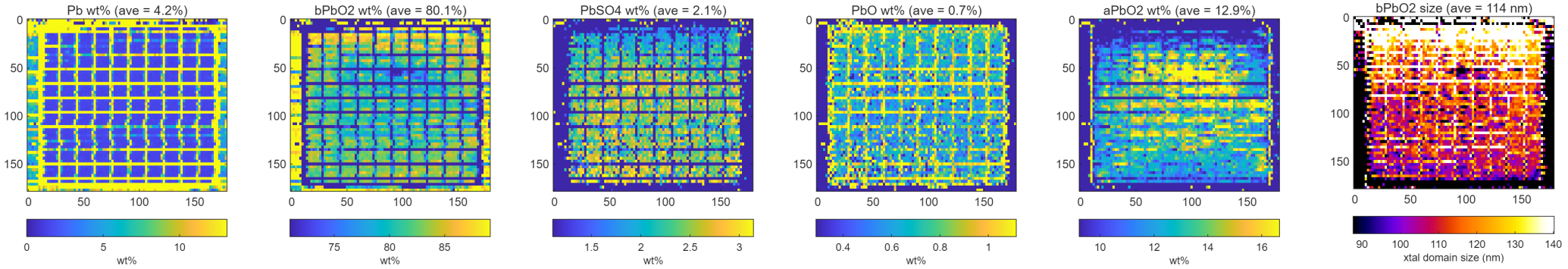
After 50 cycles: we can see differences in α/β-PbO_2 content and average PbO_2 crystal size.

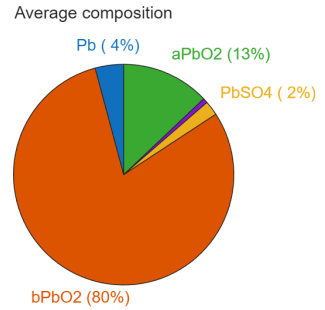
- High-Sb sample has more αPbO_2 and smaller crystals, both features associated with longer cycle life.
- Higher resolution maps: veins of high βPbO_2 content/cracks – origin of PAM shedding?

High res βPbO_2 map

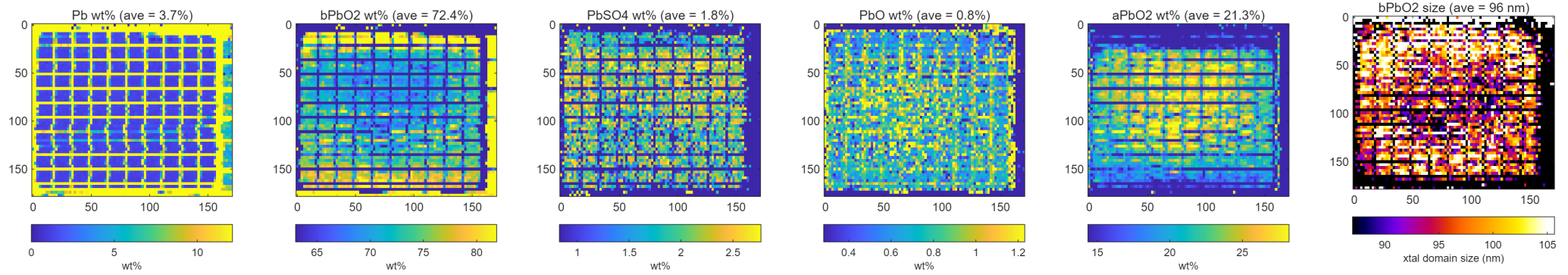


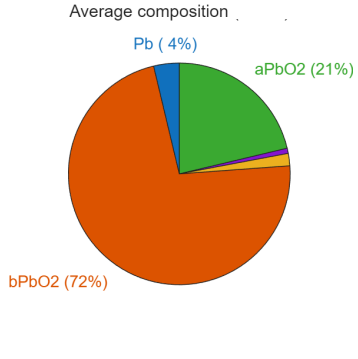
Low-Sb positive: after formation (cycle 50)





High-Sb positive: after formation (cycle 50)

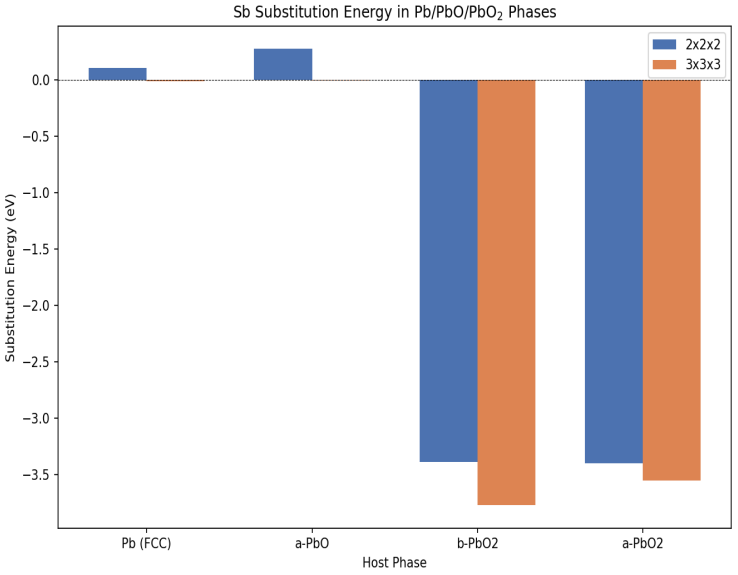


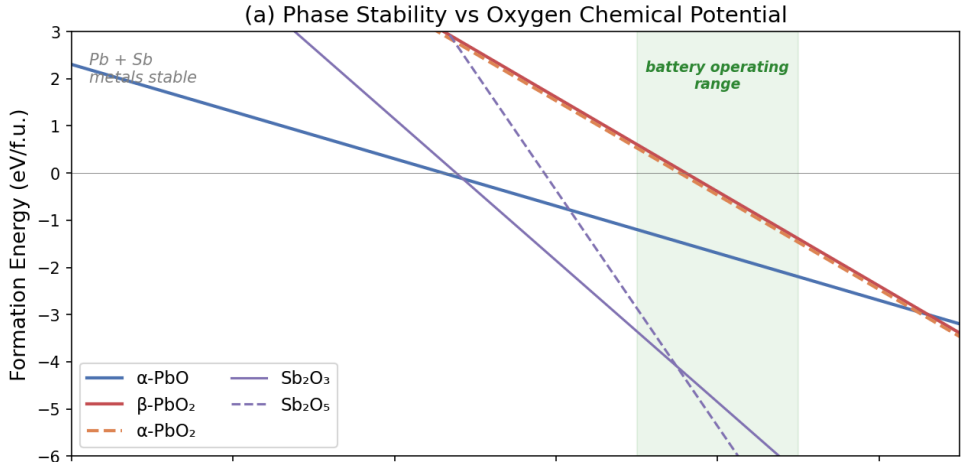


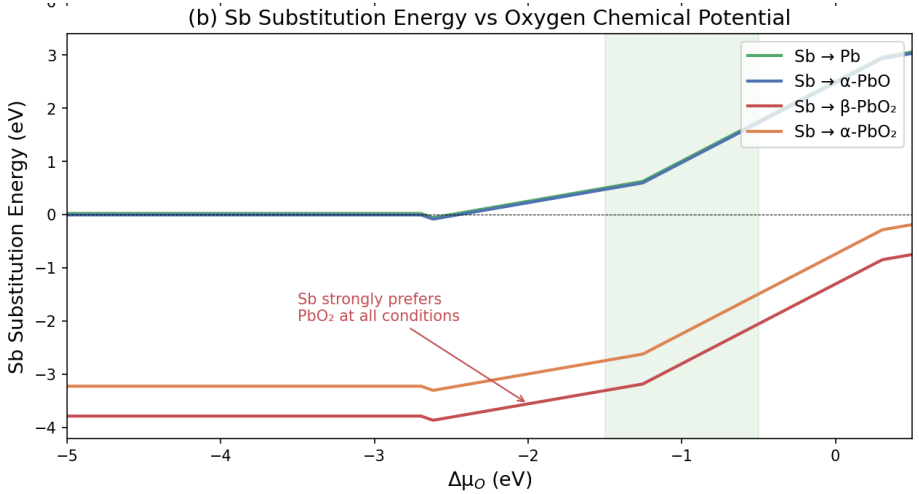
DENSITY FUNCTIONAL THEORY

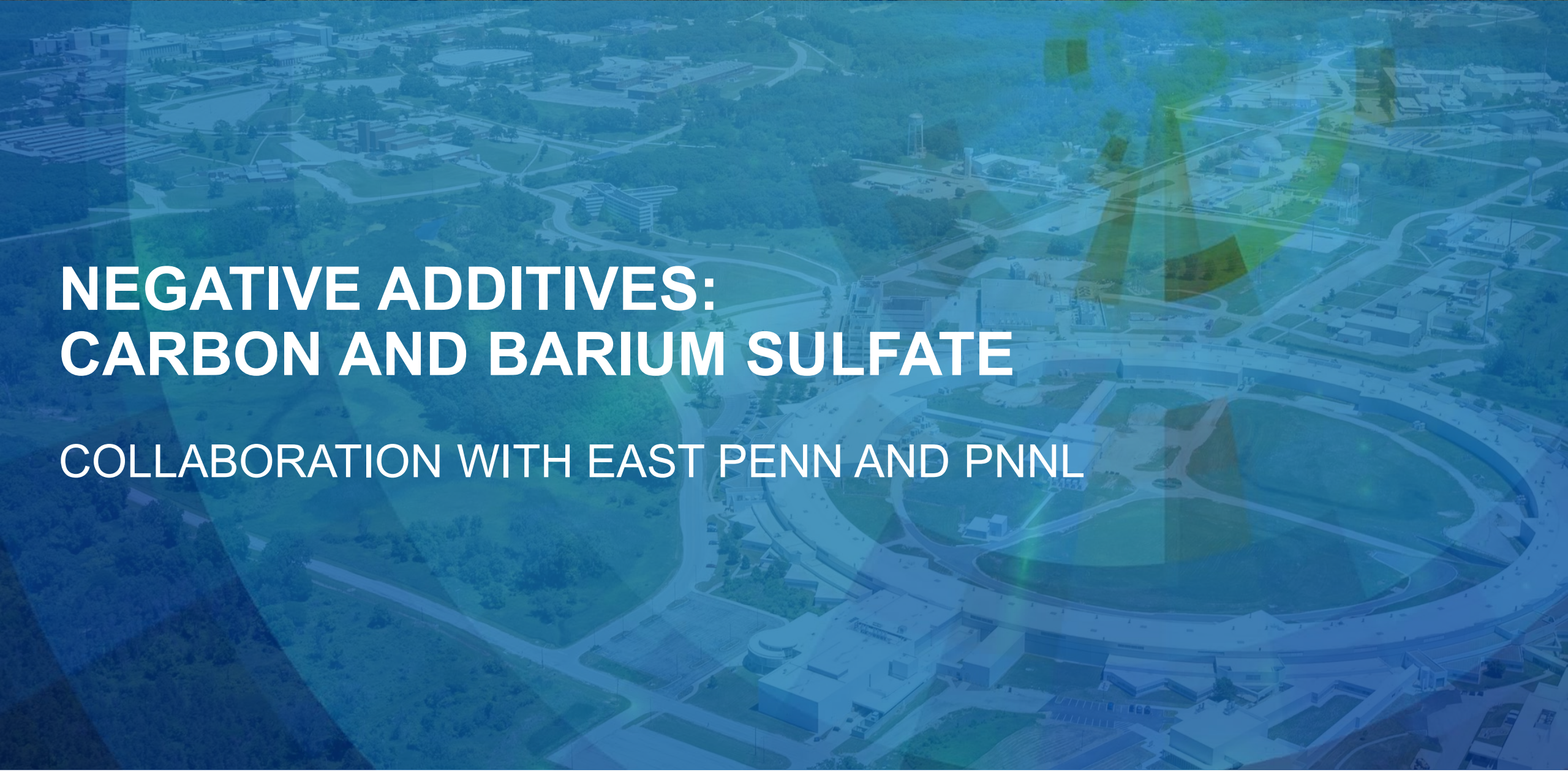
Mechanisms

- Density functional theory: Sb incorporation is unfavorable in PbO or Pb, but ***highly*** favorable in PbO_2.
  - Sb^{5+} can be accommodated by Pb vacancy or H^+ interstitial.
    - These types of defects could inhibit PbO_2 ripening
  - Sb in corrosion layer likely enhances PbO_x stoichiometry, increasing its electrical conductivity
  - Higher resolution (sub-μm) mapping planned for 2026.









NEGATIVE ADDITIVES: CARBON AND BARIUM SULFATE

COLLABORATION WITH EAST PENN AND PNNL

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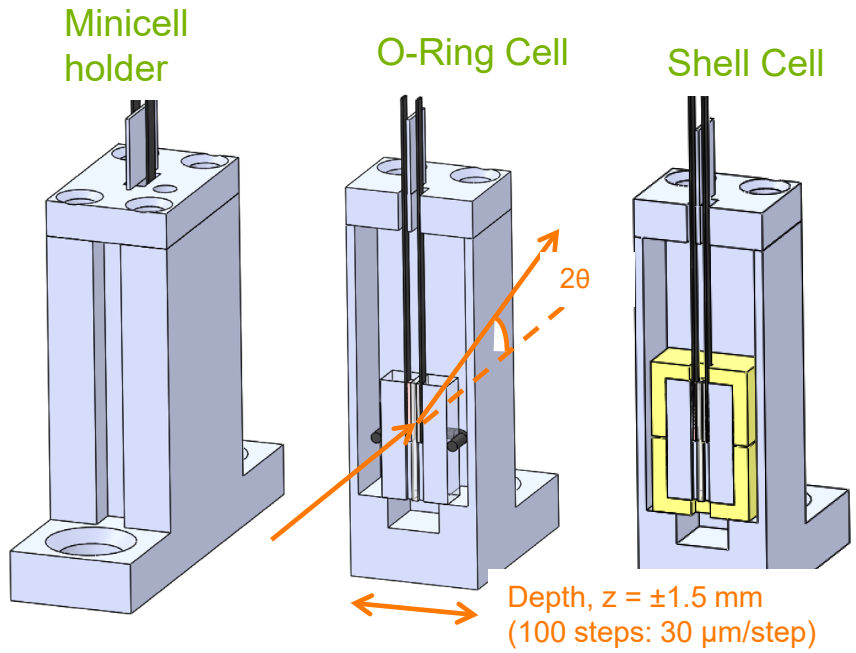
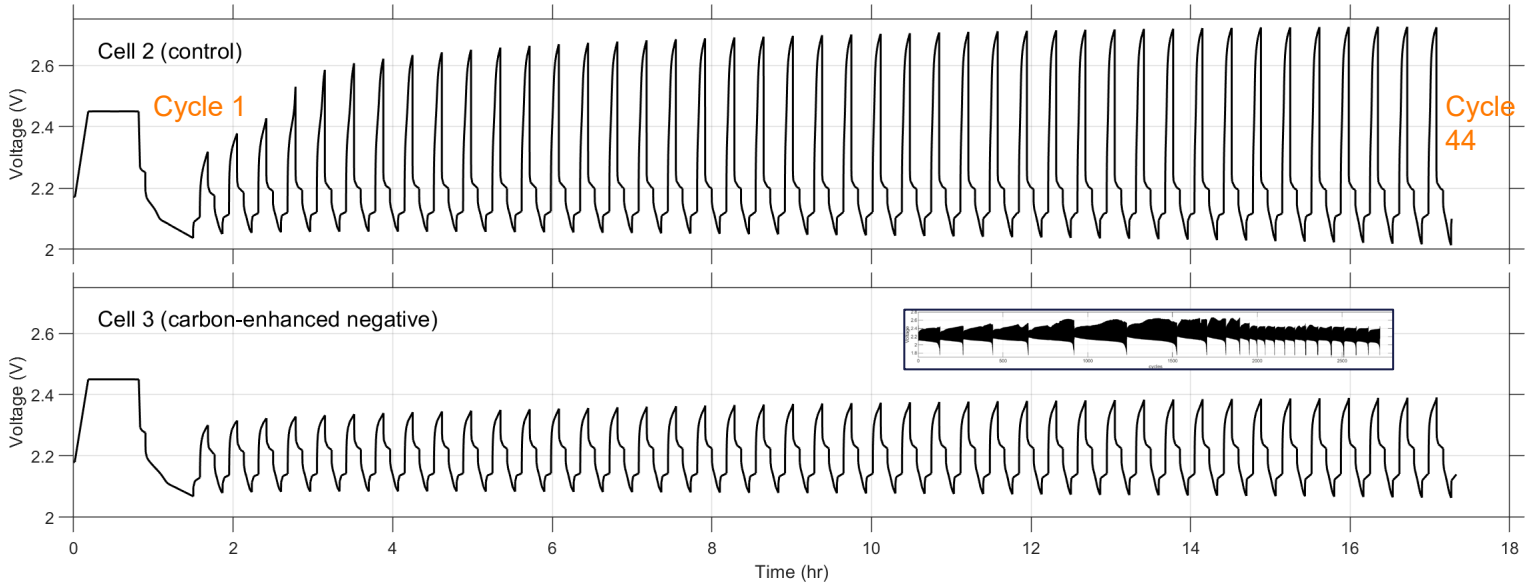
EAST PENN MINICELLS

Depth profiling lead acid batteries

- "Minicells" developed at East Penn and Argonne for x-ray depth profiling.
  - Pasting defined within small acrylic fixtures.
  - Sample is scanned horizontally through beam.



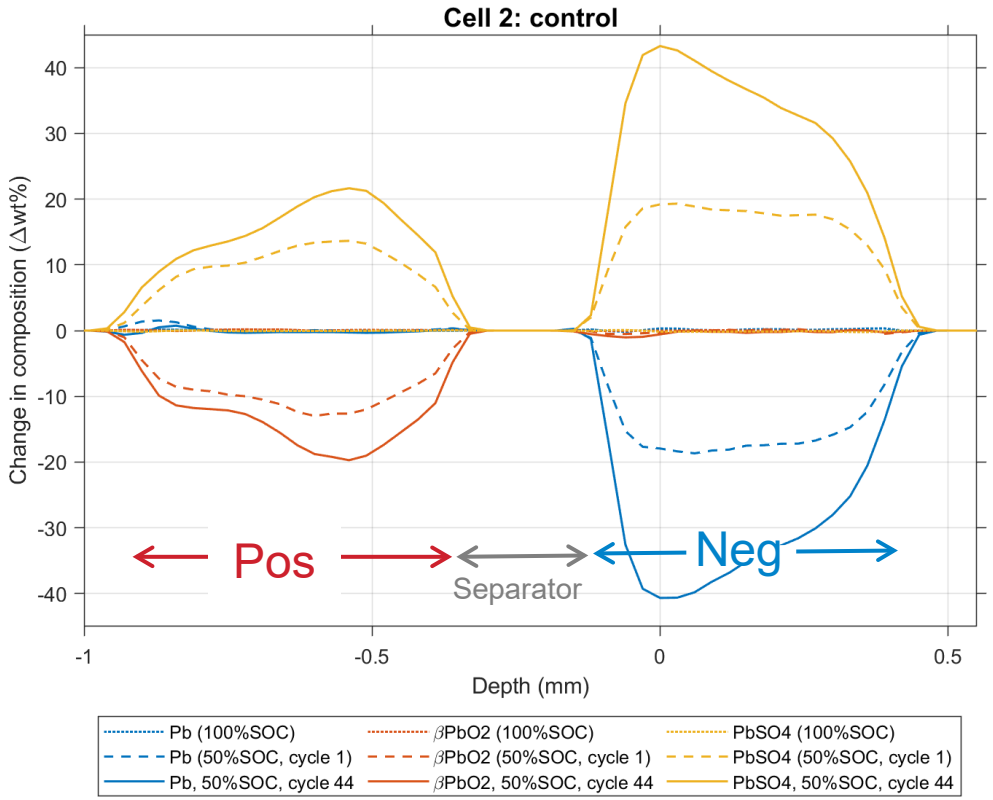
- Accelerated lifecycle test:
  - High-rate partial state of charge (HRPSOC) cycling: 50-60% SOC at 1C (3.5 mA), no overcharge
  - Carbon has significant effect on charging voltage…
  - Ran >3000 cycles after APS (inset).

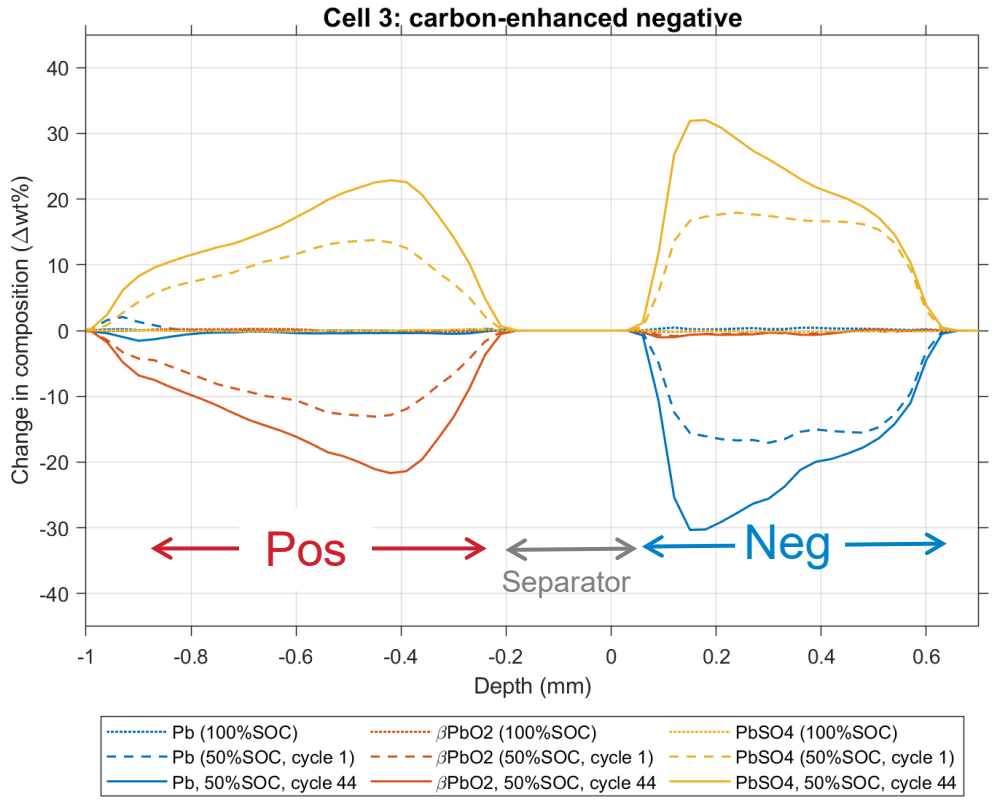


VISUALIZING CHARGE ACCEPTANCE

By looking at the change in Pb, PbO_2, and $PbSO_4$ signals, we can measure charge acceptance through the depth of the cells, directly measuring surface “sulfation” during cycling.

- Initial discharge from to 50%SOC: uniform charge acceptance in negative electrode.
- After 44 cycles: evidence of $PbSO_4$ surface sulfation for both positive and negative electrode, but accumulated $PbSO_4$ is significantly reduced in carbon-enhanced cell.

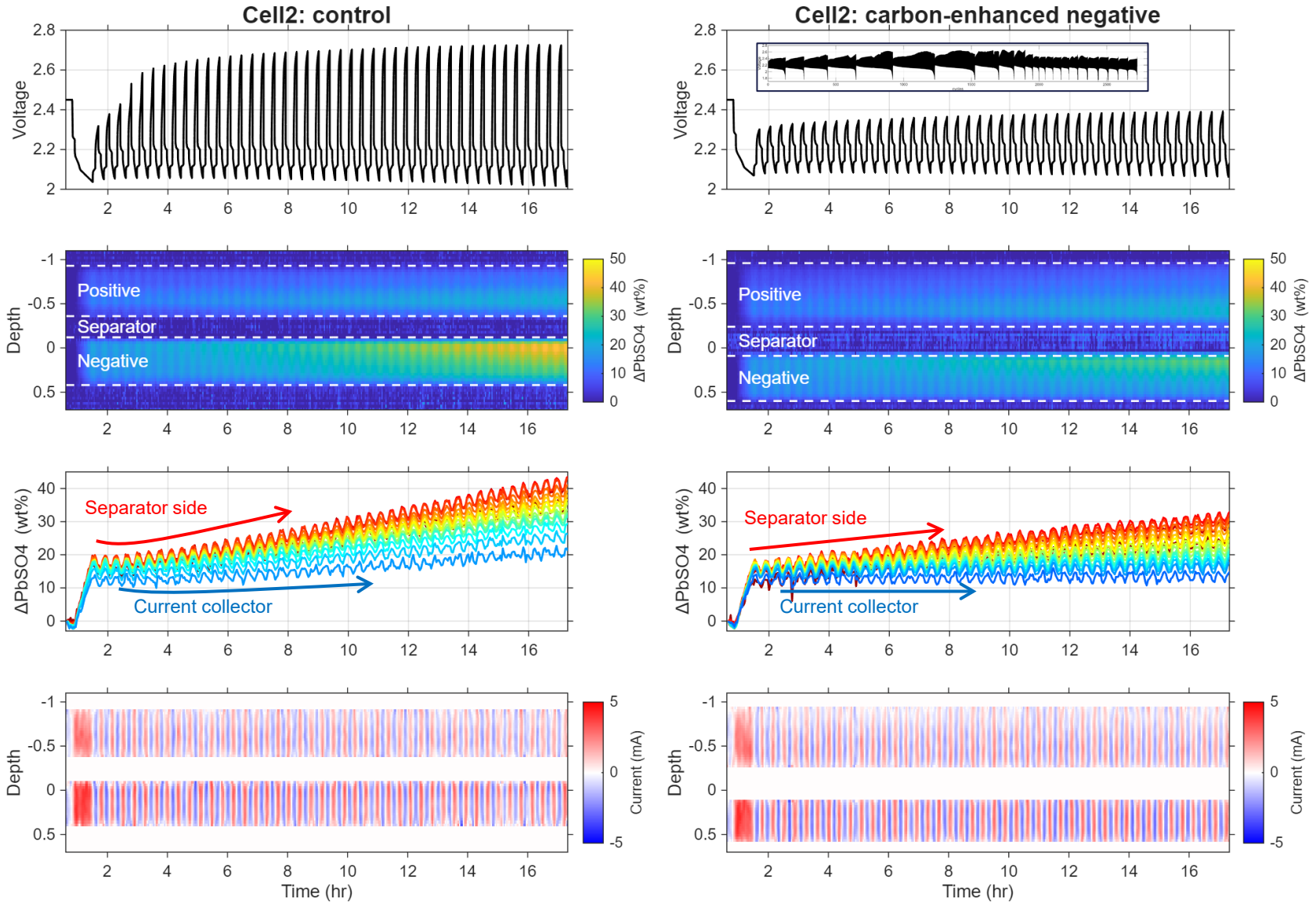




OVERALL PICTURE

Comparison with cycling

- Entire data set can be compared with cycling results.
  - Surface sulfation rates are higher in control sample.
  - Local current density measured by change in wt% and mass of electrode.
  - Comparison with continuum model in progress.

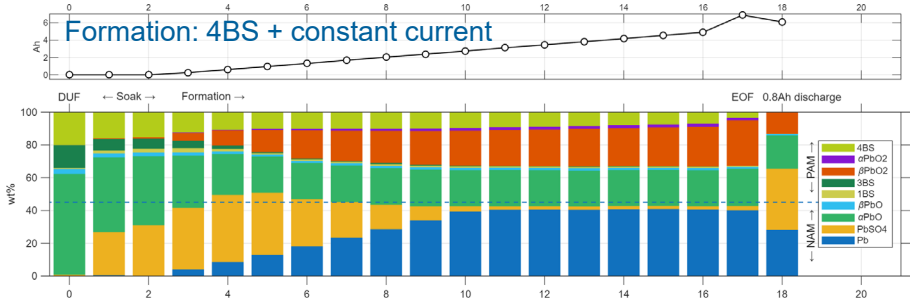


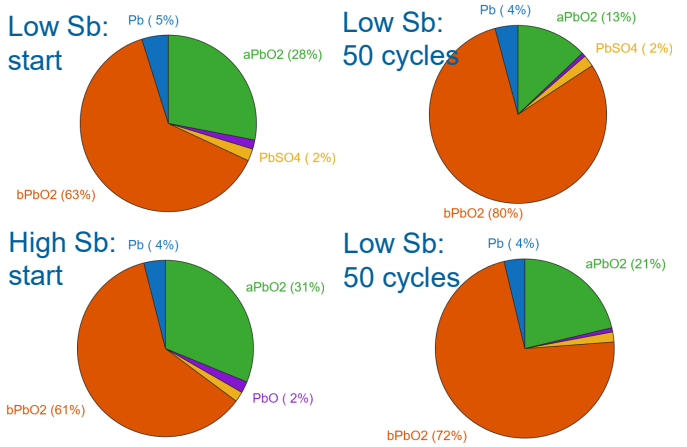
SUMMARY AND OUTLOOK

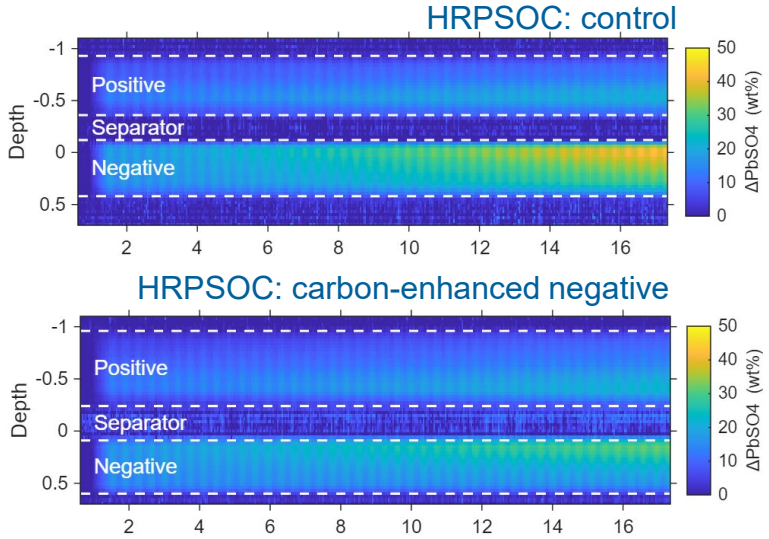
MECHANISMS DURING FORMATION AND CYCLING

Material innovations for lead acid

- 3BS vs 4BS formation: batteries are generally over-charged during formation. PbO is a reticular species (not 4BS)
  - Future: image 4BS positives with micro-CT and study at higher temperature.
  - Future: effect of Pb_3O_4 as PbO_2 nucleation agent.
- Sb-doped positives: Sb helps promote α-PbO_2 retention and slows PbO_2 ripening – both useful for cycle life. DFT shows that Sb is favorable dopant for PbO_2 and PbO_x (x > 1) phases.
  - Future: higher resolution maps. Data at higher cycle count.
- Depth profiling during micro-cycling: carbon slows surface sulfation.
  - Future: continuum modeling
  - Future: comparison to AGM and “ultra-battery” minicells.
  - Future: continued work with PNNL on (Ba/Sr)SO_4 additives.







This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.