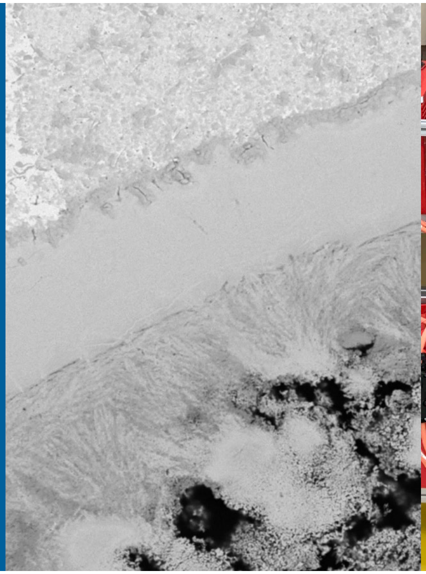
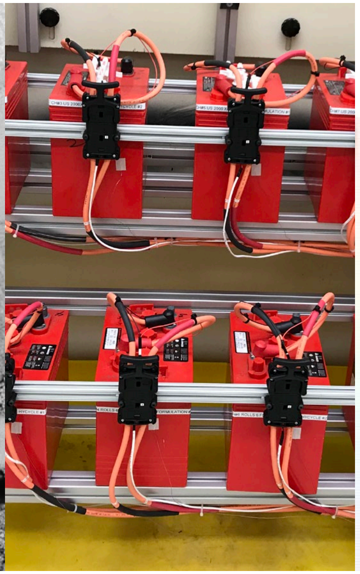
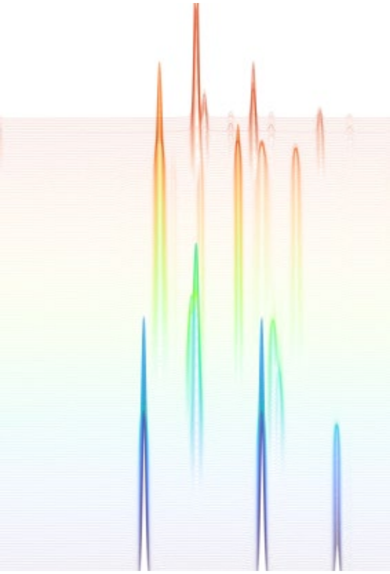
OE Energy Storage Peer Review
October 12, 2022
Presentation #701

X-RAY ANALYSIS OF NONSTOCHIOMETRIC OXIDES IN LEAD ACID BATTERIES







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U.S. DEPARTMENT OF ENERGY
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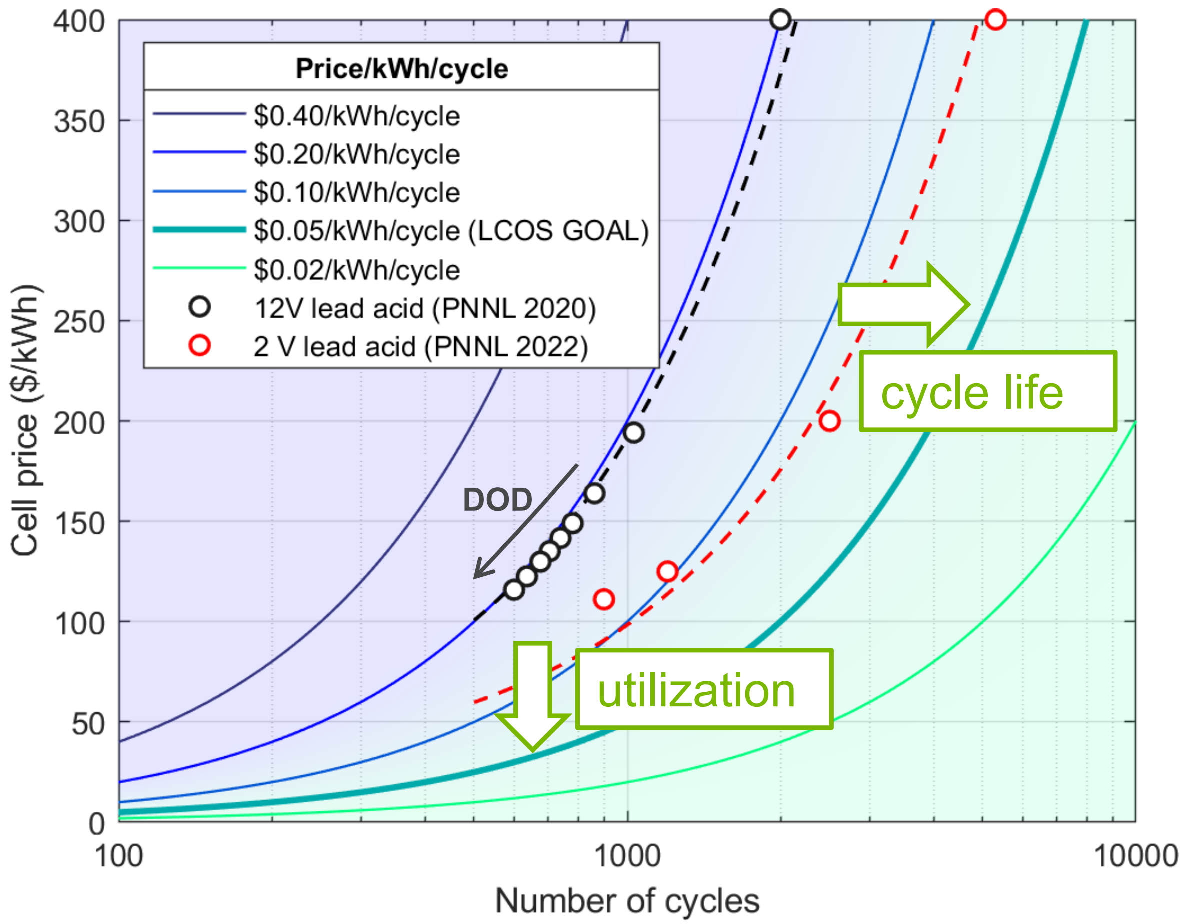
OVERVIEW OF ANL AND PNNL PROGRAMS

LEAD ACID FOR STATIONARY

Beyond SLI batteries

Advantages of lead acid batteries:

- **Stable supply chains**: 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.
  - Note recent shift in DOE numbers with switch to 2V single cell architectures.
- And despite being a mature technology, there is still significant **room for growth** in utilization and cycle life in lead acid, which has largely been optimized for motive applications.



LEAD ACID IN OE

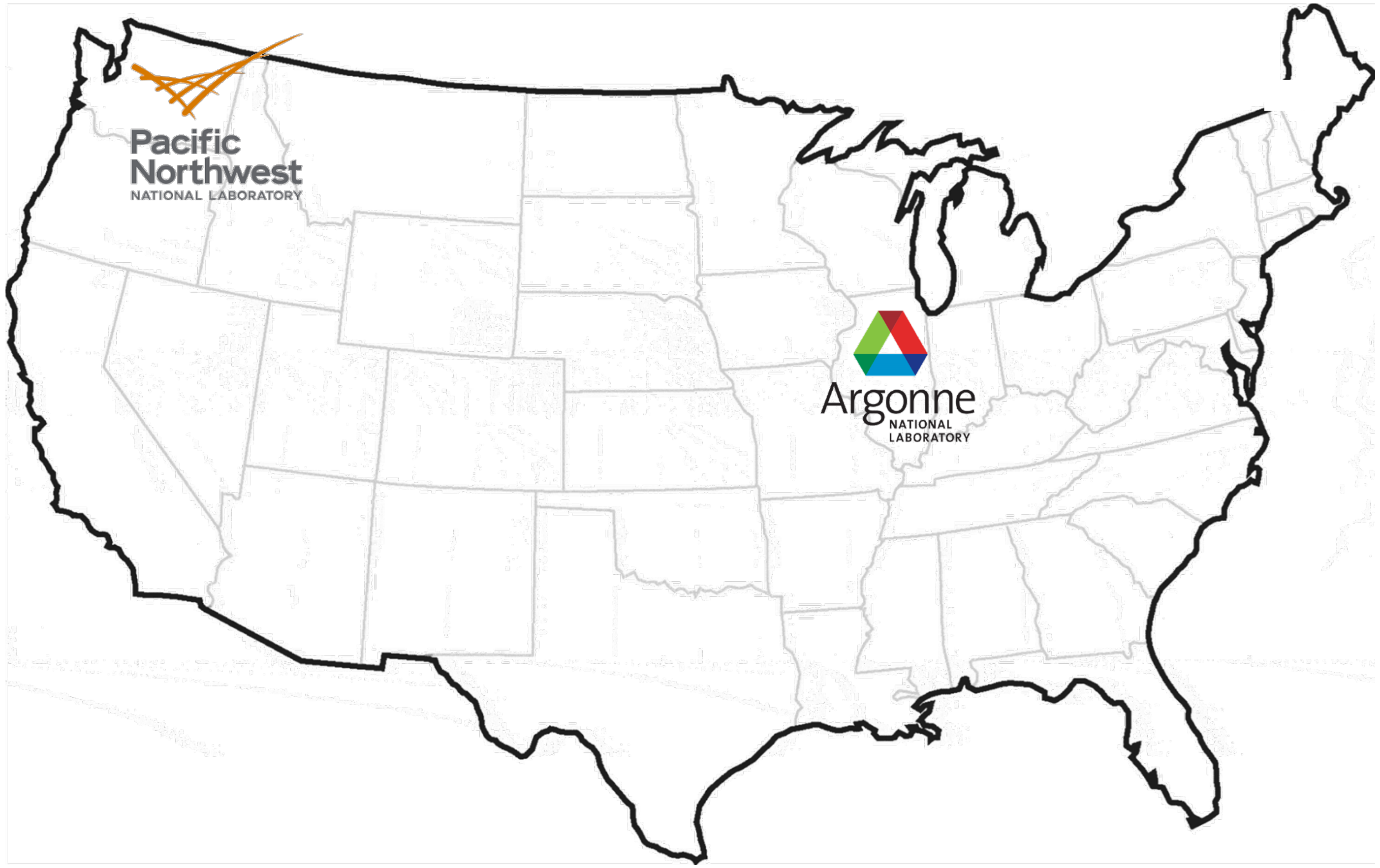
DOE collaboration

Advanced Characterization, testing: Biweekly meetings between PNNL and ANL; shared samples and resources.

- PNNL: EMSL (NMR), large scale battery testing lab
- ANL: Advanced Photon Source, cell prototyping and testing lab (FY23)

Workshops

- April 5-6 (Argonne): DOE Lead Battery Research Technical Advisory Meeting: 50 participants from DOE, national labs and industry.

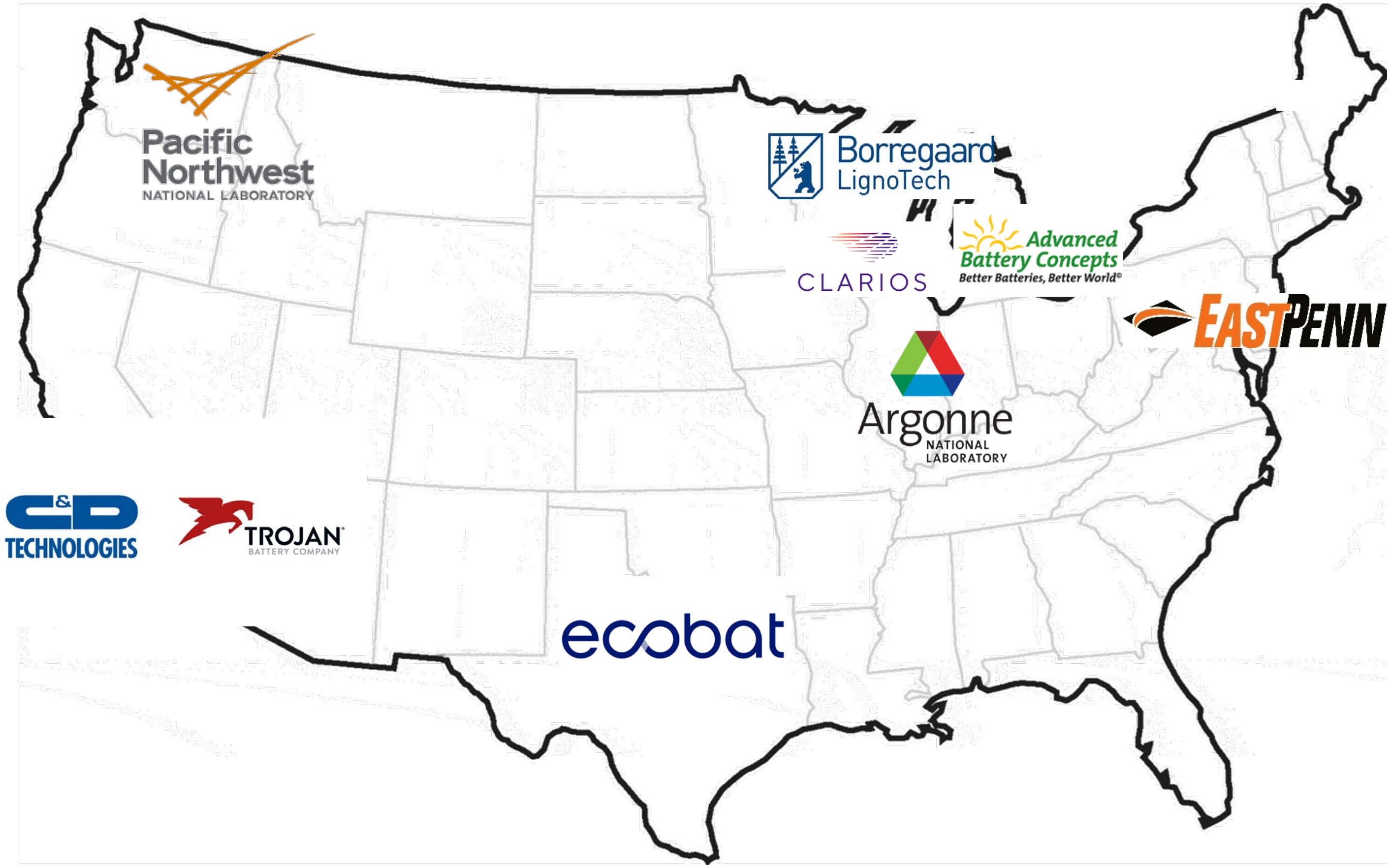


LEAD ACID IN OE

DOE + Industry

Industrial collaboration (FY22):

- Ecobat: 6V 200Ah batteries
- Clarios: Battery teardowns
- East Penn: model 2 V cells.
- Borregaard: lignins
- C&D Trojan: PAM cross sections
- Advanced Battery Concepts: model bipolar cells.



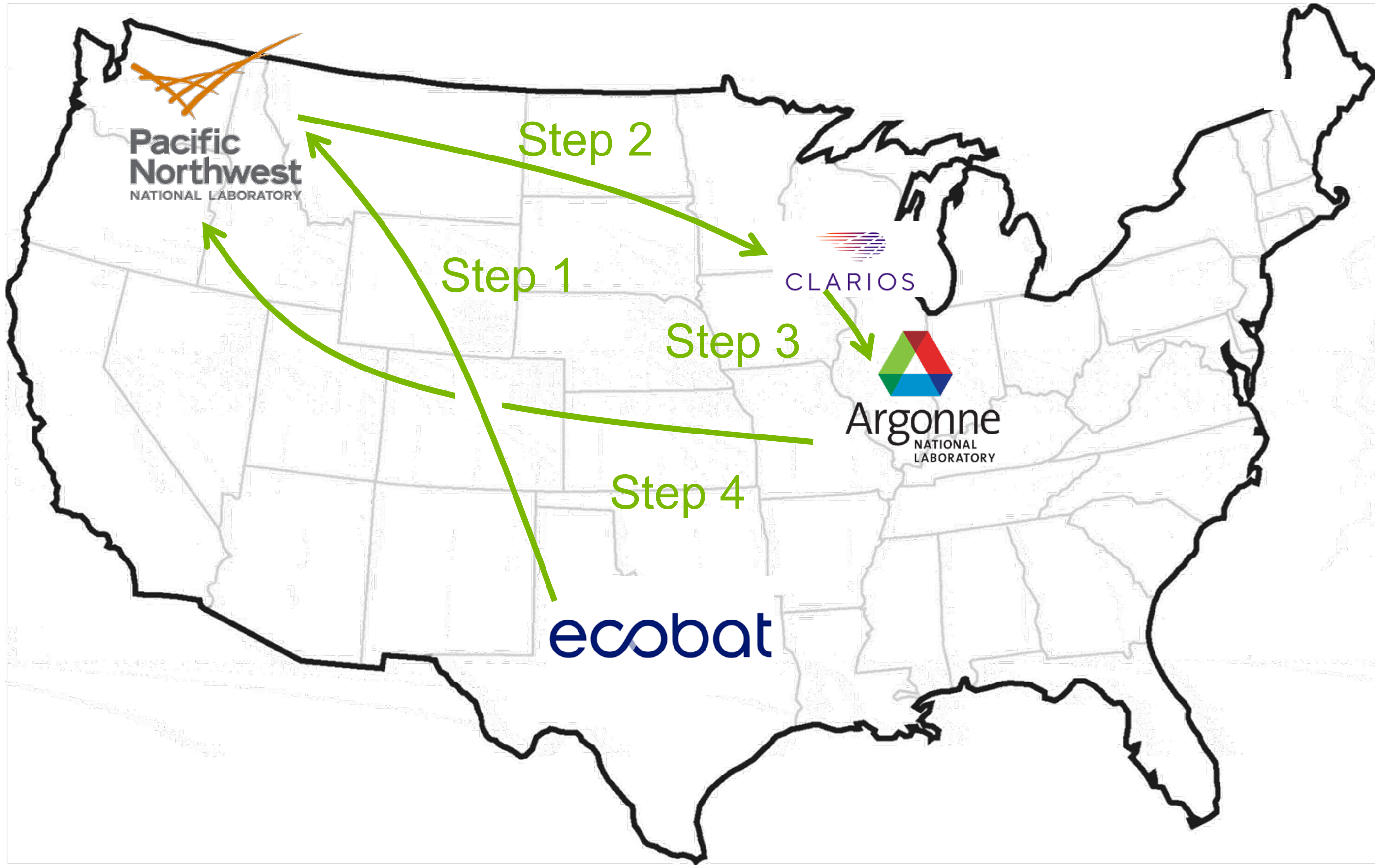
LEAD ACID IN OE

DOE + Industry

Industry collaboration (FY22)

Example:

1) Batteries supplied by Ecobat shipped to PNNL for cycling.
2) End-of-life batteries shipped to Clarios for disassembly.
3) Plates analyzed at Argonne at APS
4) Plates shipped back to PNNL for further analysis

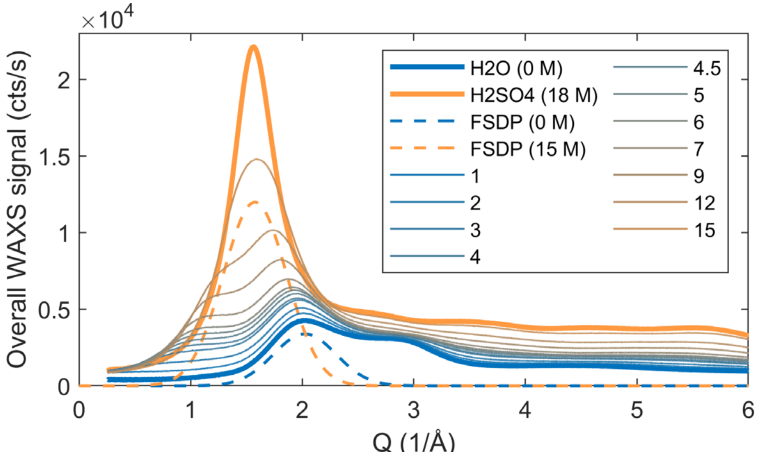


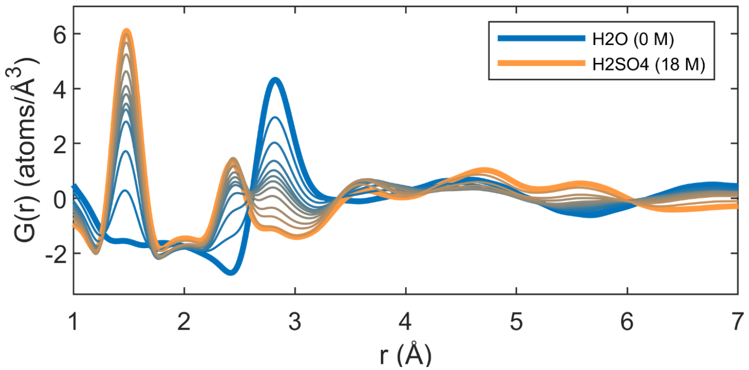
SOLUTION STRUCTURE

Solution species

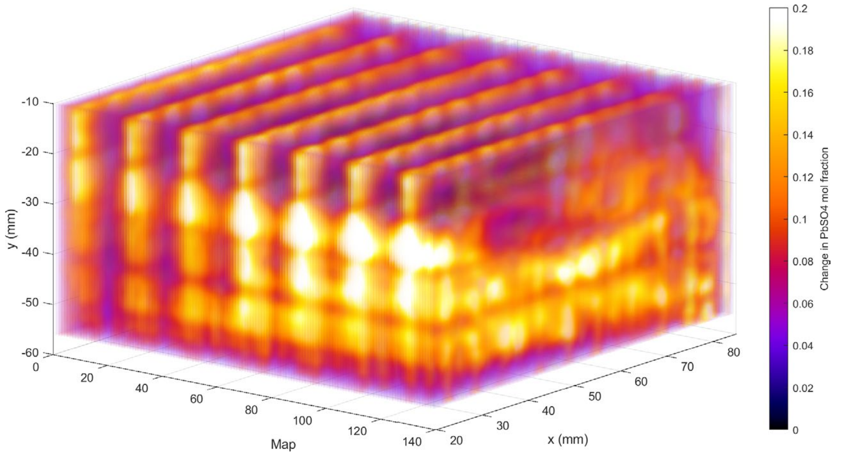
- FY20 science goals: measure solution structure with NMR, PDF, XAS.
  - Co-refinement of electrode *and* electrolyte species during formation and cycling!
- Real world applications:
  - Operation at low temperature
  - Stratification
  - Formation bottlenecks.

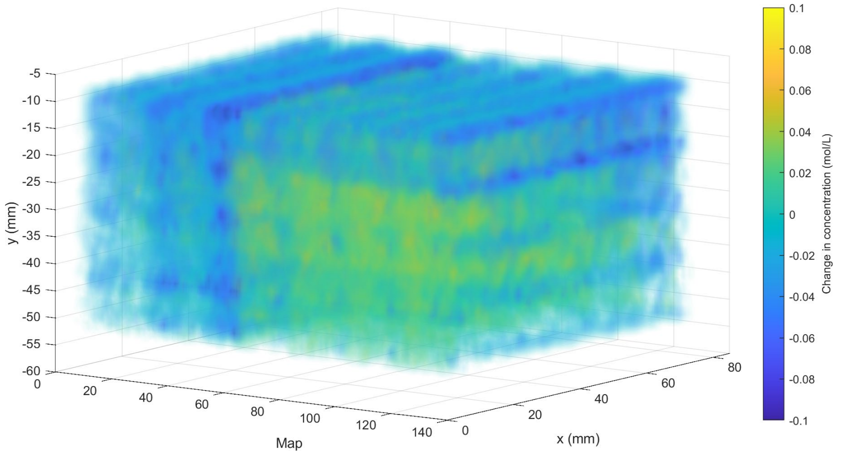
X-ray scattering and PDF of sulfuric acid with varying concentration (Kinnibrugh and Fister JPCB 2022)





XRD data during C/2 cycling: changes in $PbSO_4$ and acid concentration leading to stratification

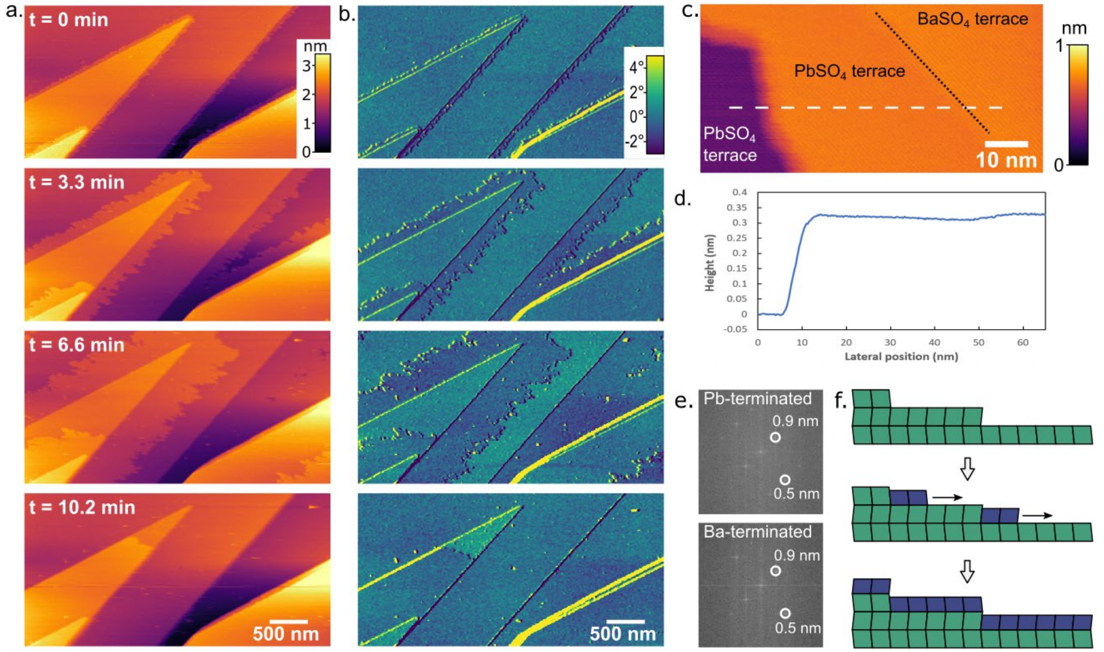




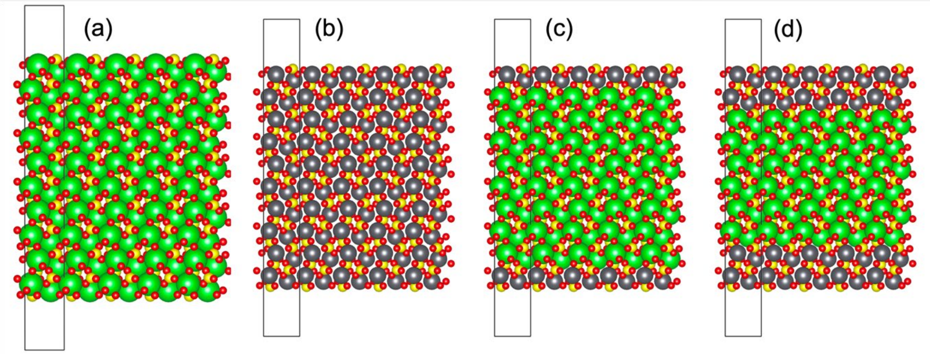
$PbSO_4$ NUCLEATION

Solution species, nucleation,

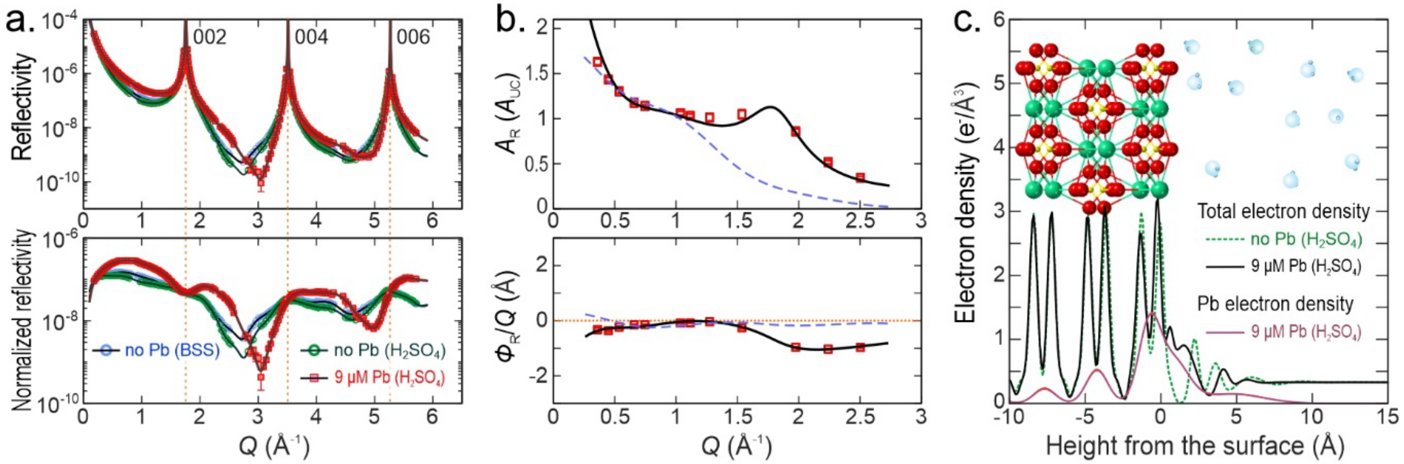
- FY21 science goals: analyze nucleation of $PbSO_4$ on $BaSO_4$, DFT modeling of $PbSO_4$ surface energies
- Real world applications:
  - Discharge power density
  - Negative sulfation



From Benjamin Legg et al ACS AM&I (submitted): *In situ* AFM during first monolayer growth of $PbSO_4$ on $BaSO_4$ (001)



Garcia/Iddir: DFT modeling of interfacial energy barriers for continued $PbSO_4$ growth

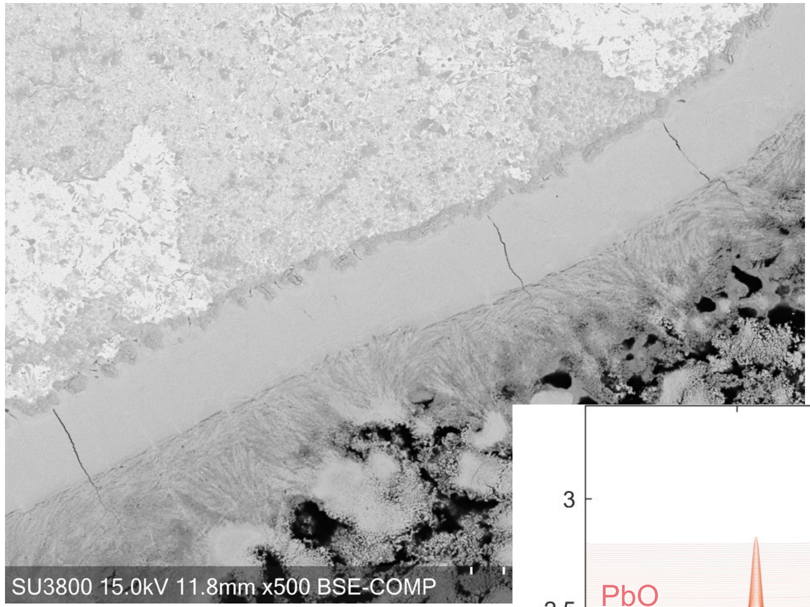


Sang Soo Lee: X-ray scattering from $PbSO_4$ growth on $BaSO_4$ (001): sub-surface lead incorporation

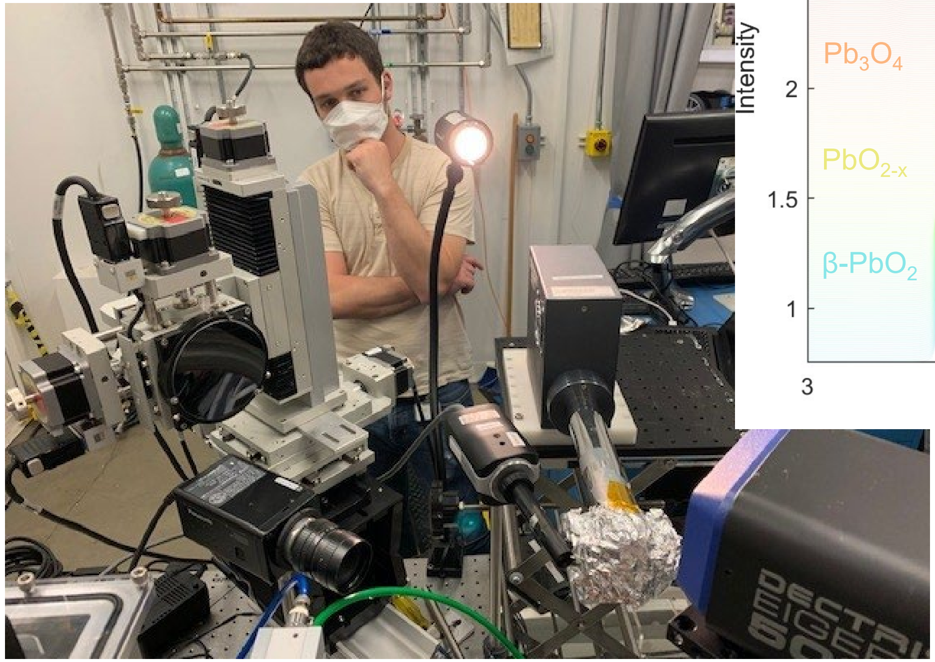
POSITIVE ELECTRODE

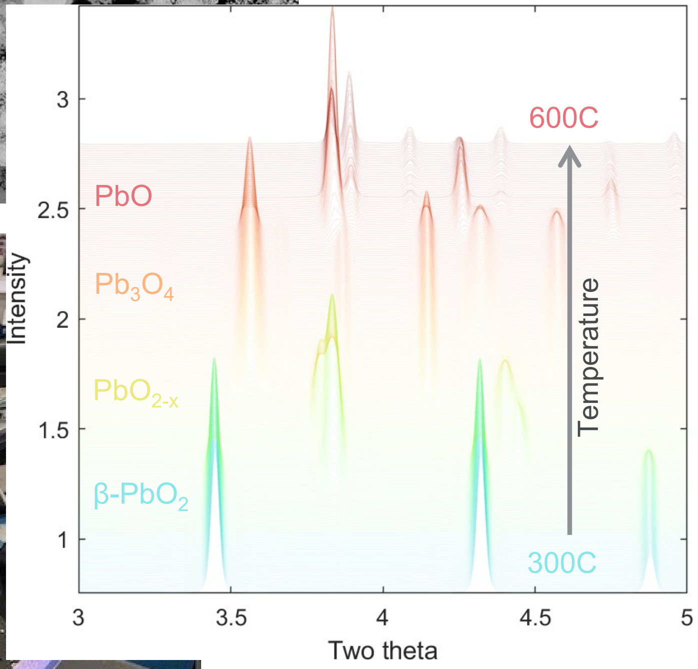
Corrosion layer species

- FY22 science goals: positive electrode material composition, especially at PbO_2/Pb interface
- Real world applications:
  - Positive active material softening (α/β-PbO_2)
  - PAM shedding (managing the corrosion layer)
  - Positive grid corrosion



Left: SEM of "corrosion layer" in positive electrode cross-section (M. Verde, C&D Trojan)





Above: Kinnibrugh: isolating PbO_x intermediates by thermal decomposition of PbO_2.

Left: Wolfman's microprobe + HERFD experiment: lots of detectors

FY22: POSITIVE FAILURE MECHANISMS AND CORROSION LAYER SPECIES

FAILURE MODES

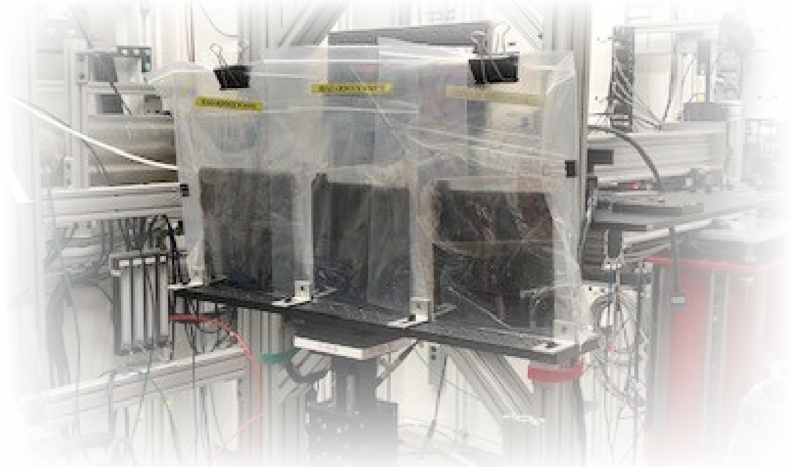
Competing mechanisms

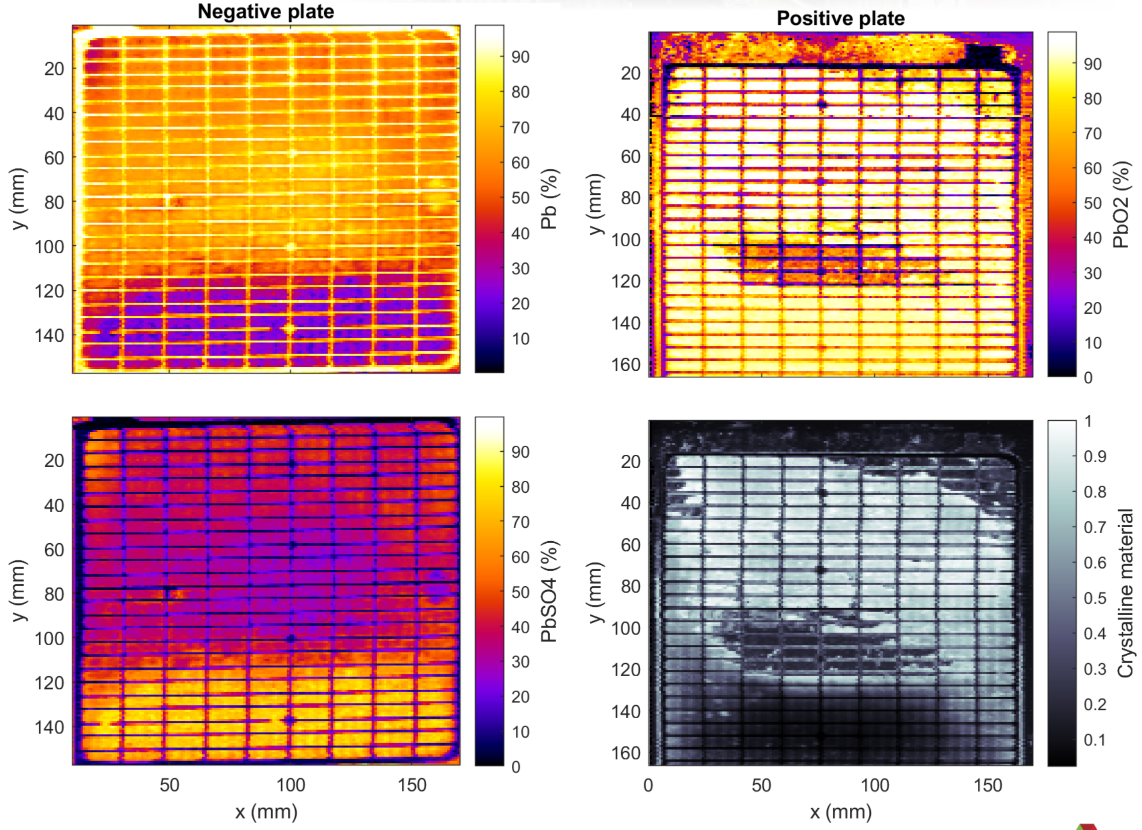
Competing mechanisms complicate cycling of lead acid batteries:

- Issues with negative: not enough charging
  - Sulfation ($PbSO_4$ ripening), pore-clogging at surface (ORR)
  - Imbalanced cell state-of-charge
  - Not enough overcharge: electrolyte stratification
- Issues with positive: too much charging
  - Positive active material softening (α/β-PbO_2)
  - Active material shedding (OER)
  - Grid corrosion

XRD mapping of battery plates extracted from batteries cycled at PNNL.

Plates are kept in acid for the measurement.





Bottom of negative plate heavily sulfated due to acid stratification.

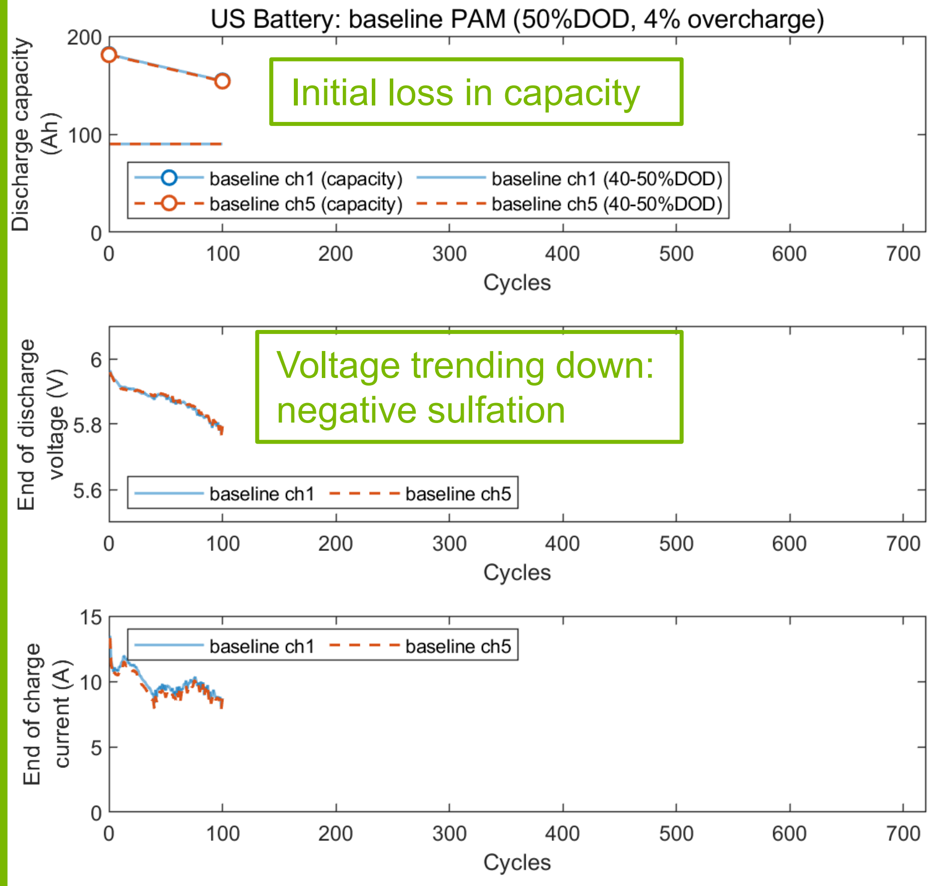
Paste shedding is prevalent in positive electrodes.

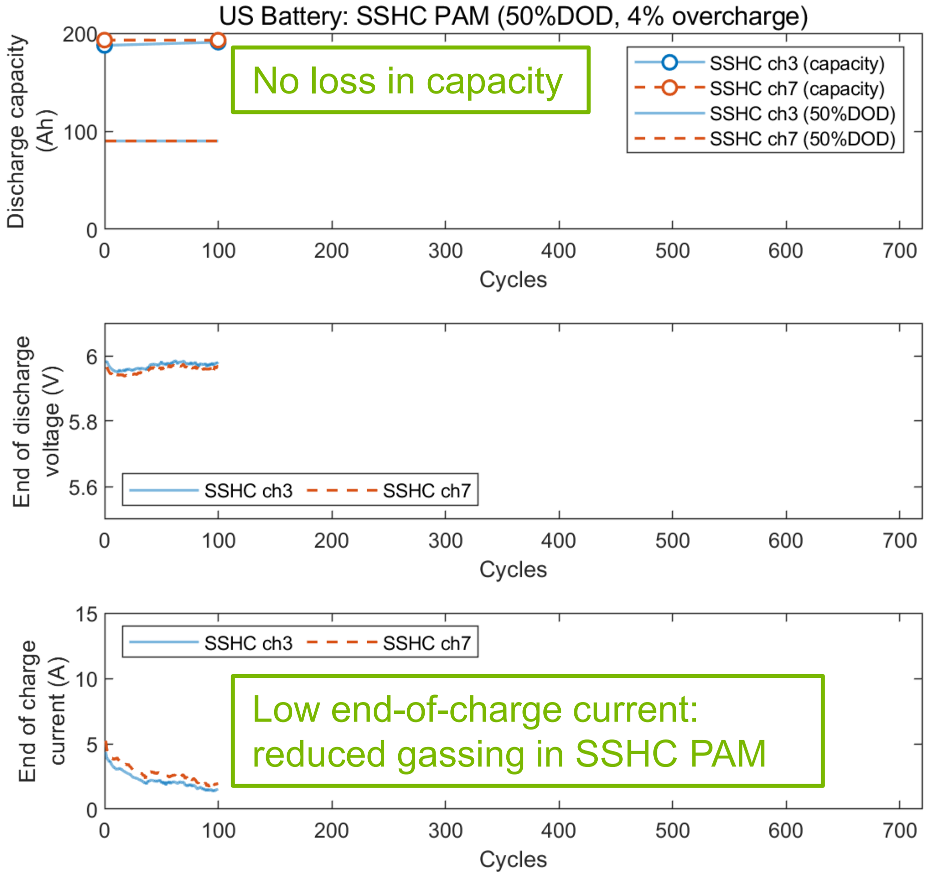
CYCLING AND XRD MAPS

Failure modes due to deep discharge

- Batteries cycled at PNNL (right) compared effects of positive active material (PAM) doping: SuperSoft HyCycle (SSHC) from Ecobat.
  - SSHC: much lower gassing currents = efficient charging.
  - First 100 cycles: control batteries rapidly lose capacity.

Golf cart batteries in testing rack at PNNL





6V 200 Ah battery cycling (Ed Thomsen)

Procedure: Discharge 10 A to 90Ah (50% DOD); Recharge 104%, with 7.3V voltage limit

Capacity check every 100 cycles

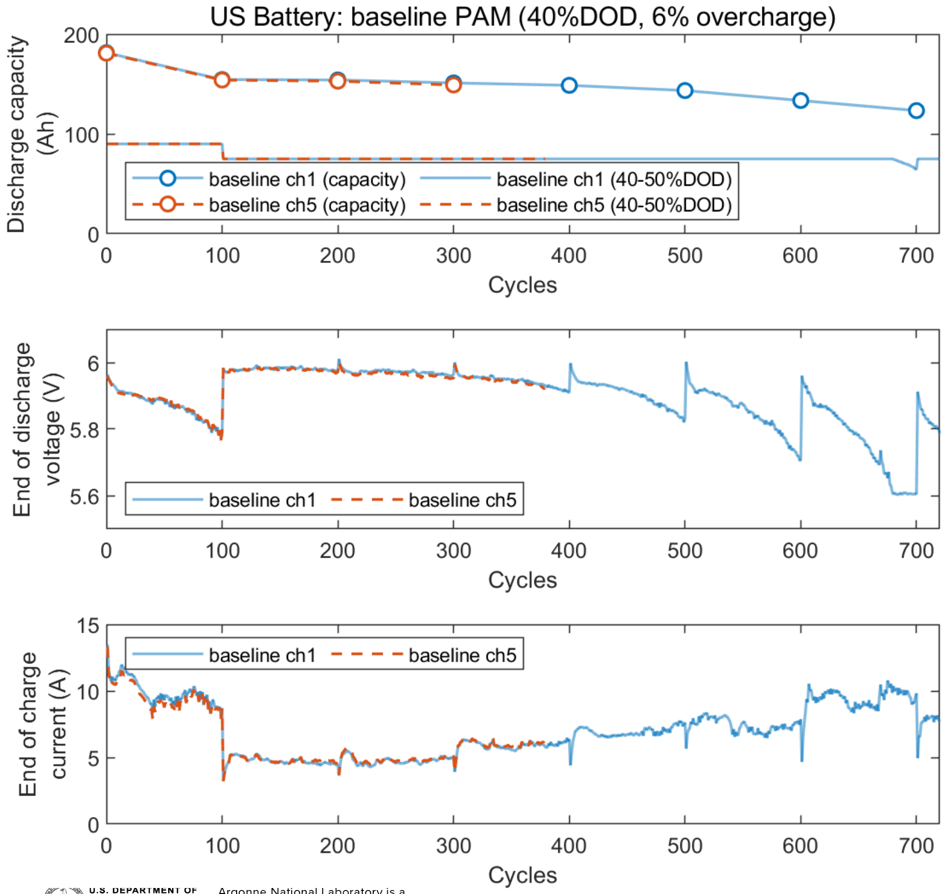
Argonne NATIONAL LABORATORY

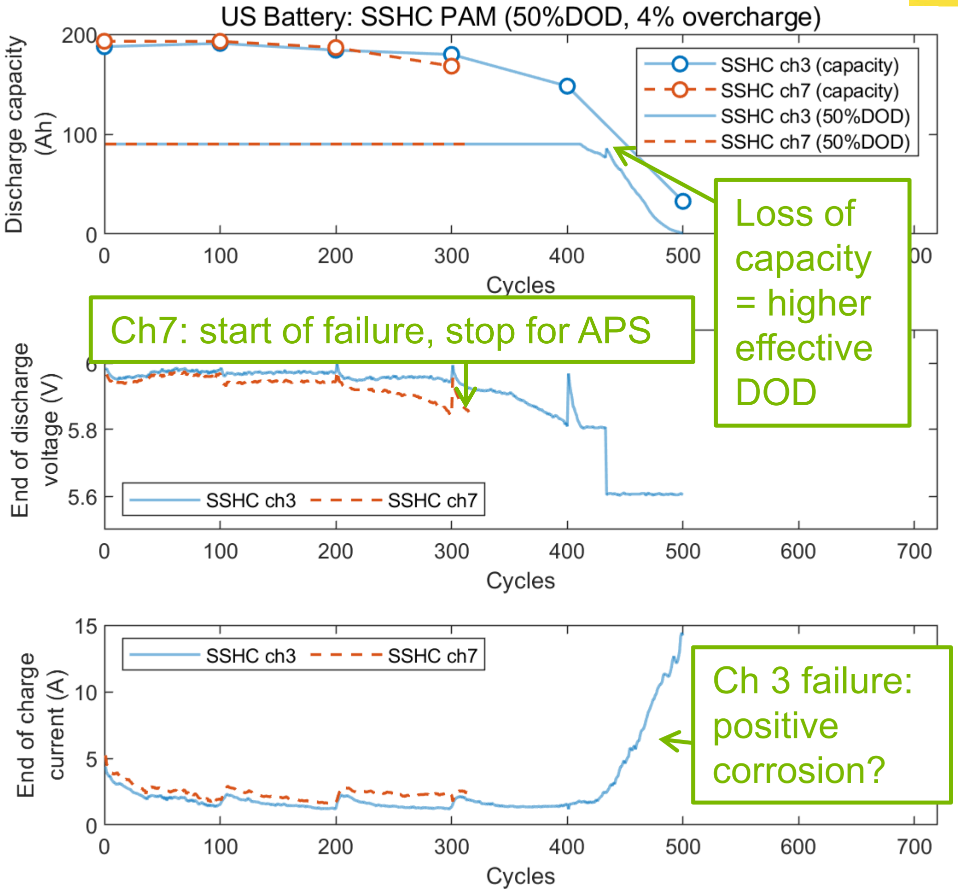
CYCLING AND XRD MAPS

Failure modes due to deep discharge

- Modified control charging to preserve battery: 40%DOD, 6% overcharge
  - Control maintained capacity at shallower DOD, while SSHC failed 420 cycles.
  - Channel 1 and 7 were stopped at ~300 cycles for XRD analysis.

Golf cart batteries in testing rack at PNNL





6V 200 Ah battery cycling (Ed Thomsen)

Procedure: Discharge 10 A to 90Ah (50% DOD); Recharge 104%, with 7.3V voltage limit

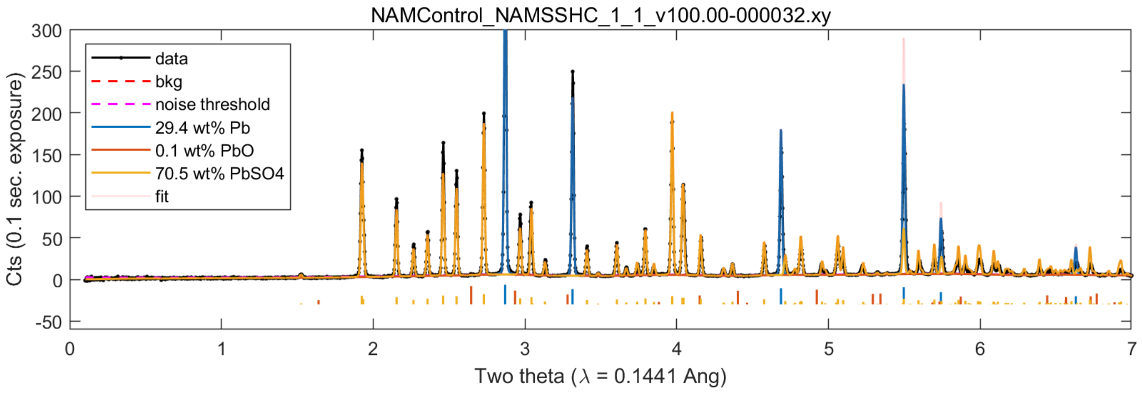
Capacity check every 100 cycles

XRD MAPS

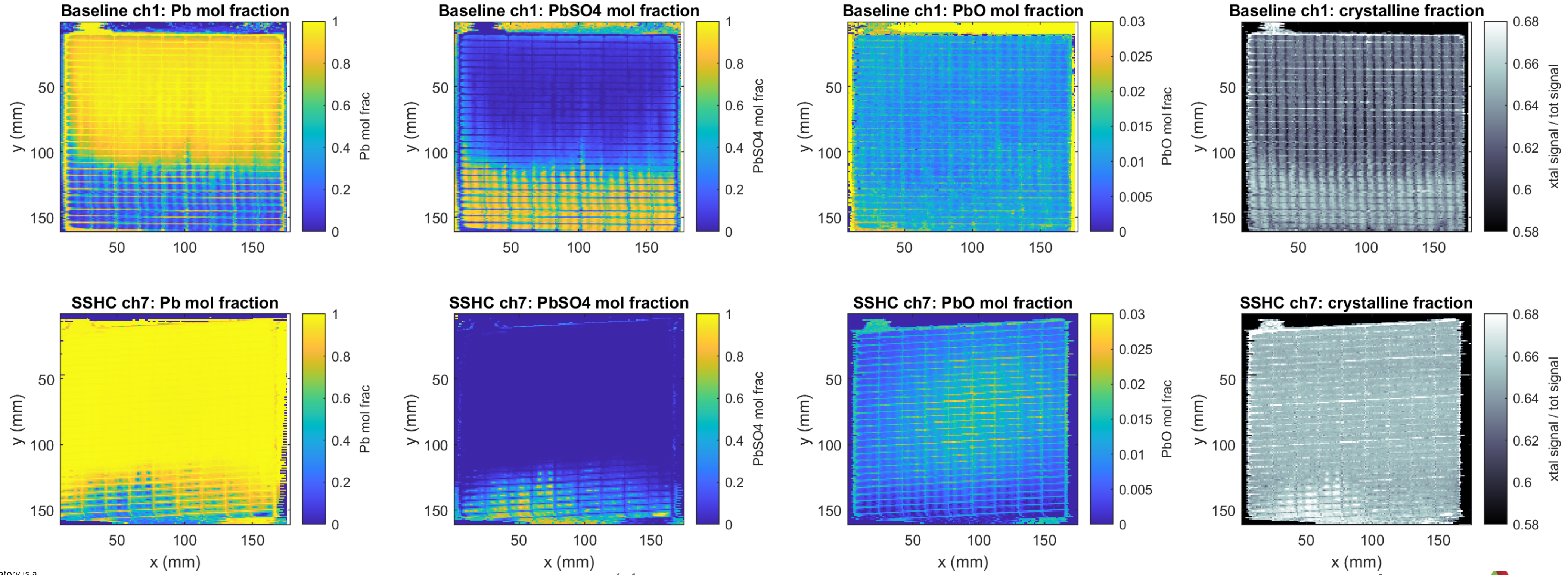
Negative plates

- Clear evidence of stratification/sulfation.
- Less sulfation on SSHC battery, consistent with lower end-of-charge current.

Each map has 30,000 XRD patterns, like the one below.



$PbSO_4$ 'tide line' develops from higher concentration acid at bottom of battery, which inhibits charging due to lower Pb^{2+} solubility.

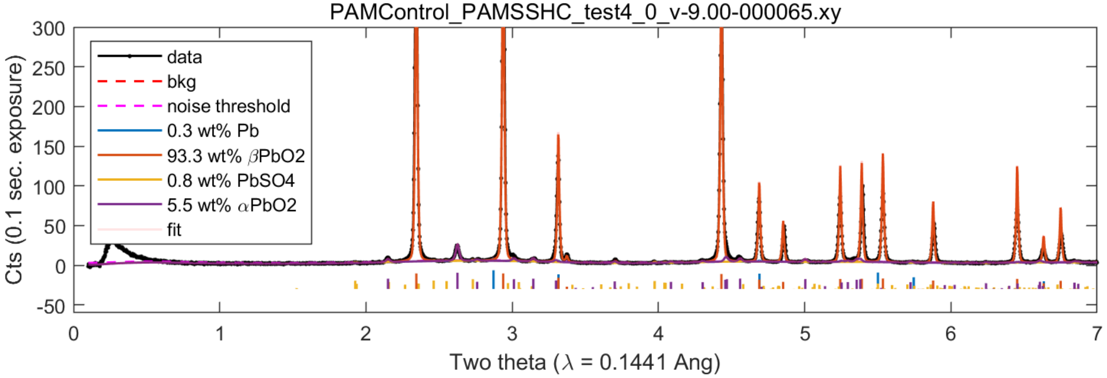


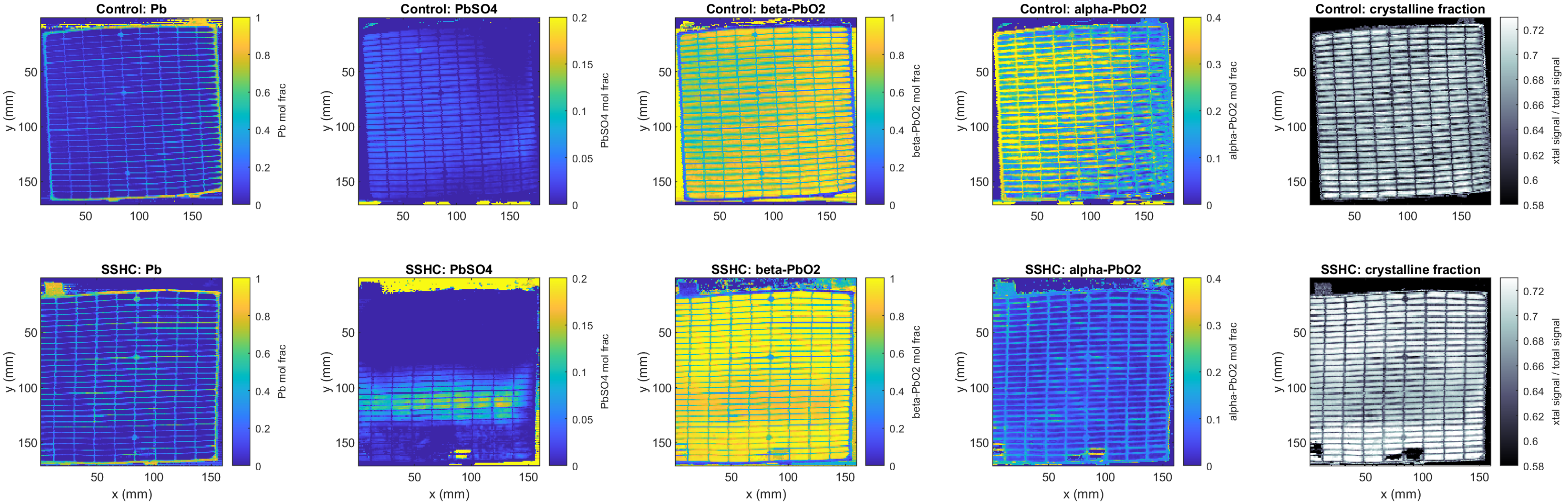
XRD MAPS

Positive plates

- Clear evidence of paste softening: conversion α-PbO_2 to β-PbO_2.
  - During disassembly: SSHC had poor paste adhesion, some grid corrosion in 50% DOD battery (SSHC).

Each map has 30,000 XRD patterns, like the one below.



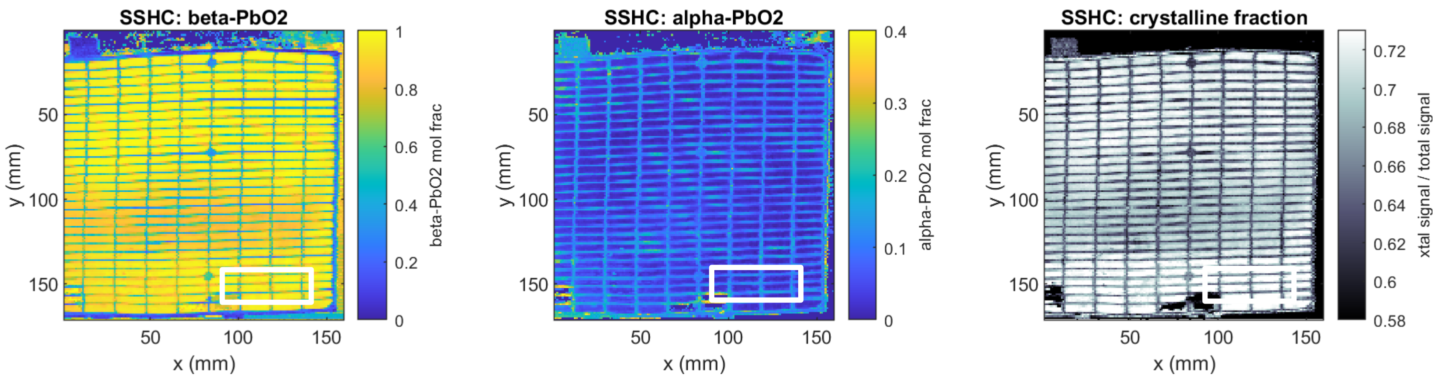


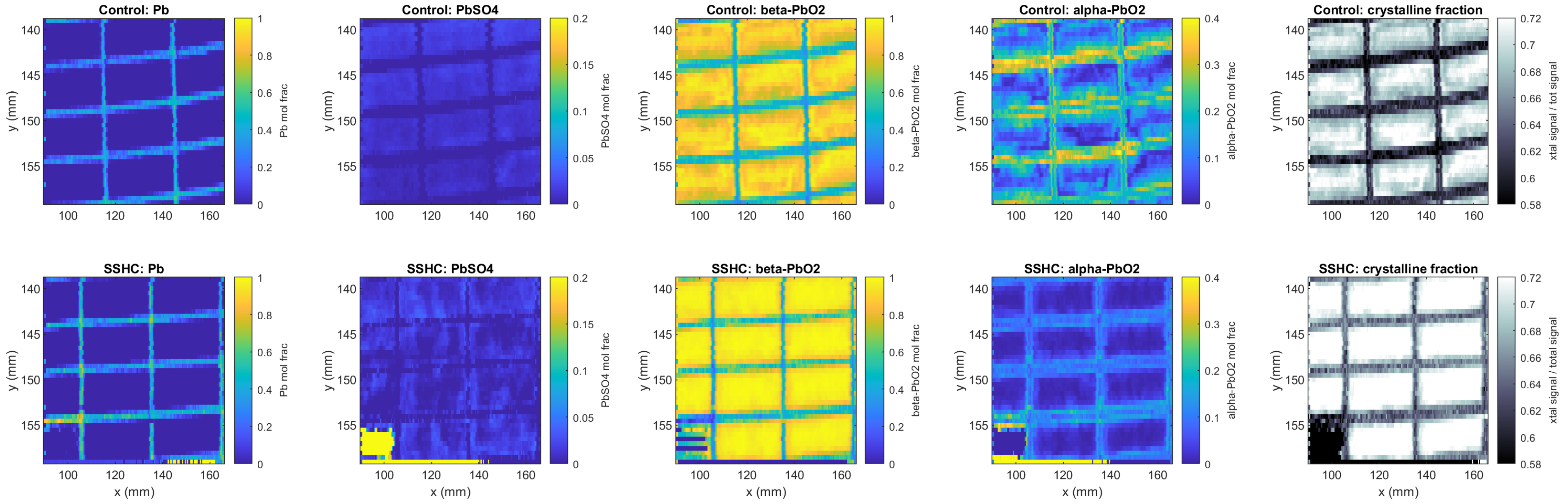
XRD MAPS

Positive plates

- Finer scale map: presence of α-PbO_2 near positive grid architecture: necessary to hold active β-PbO_2 species to grid.

Inset from previous maps

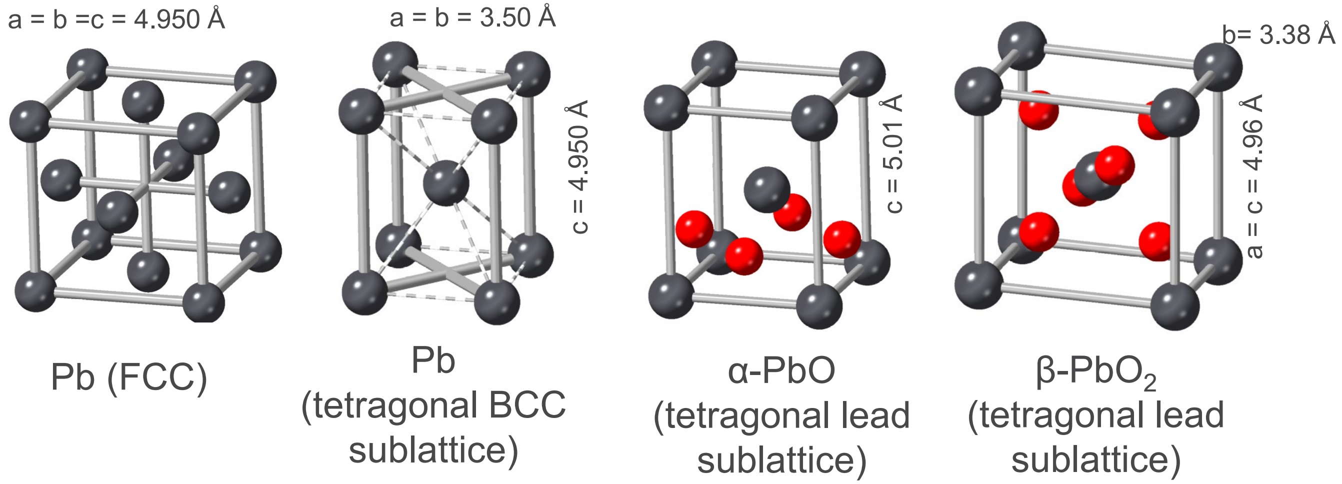




IMPROVING PASTE ADHESION

Corrosion layer species

- Positive failure mechanisms are often tied to the interface between the Pb current collector (grid) and the PbO_2 active material.
- This region, the "corrosion layer," is thought to have PbO or PbO_x (x = 1-2) phases that chemically bond Pb and PbO_2.



Note that Pb, PbO, and PbO_2 have a common lead sublattice, providing a natural epitaxy between these phases.

IMPROVING PASTE ADHESION

Corrosion layer species

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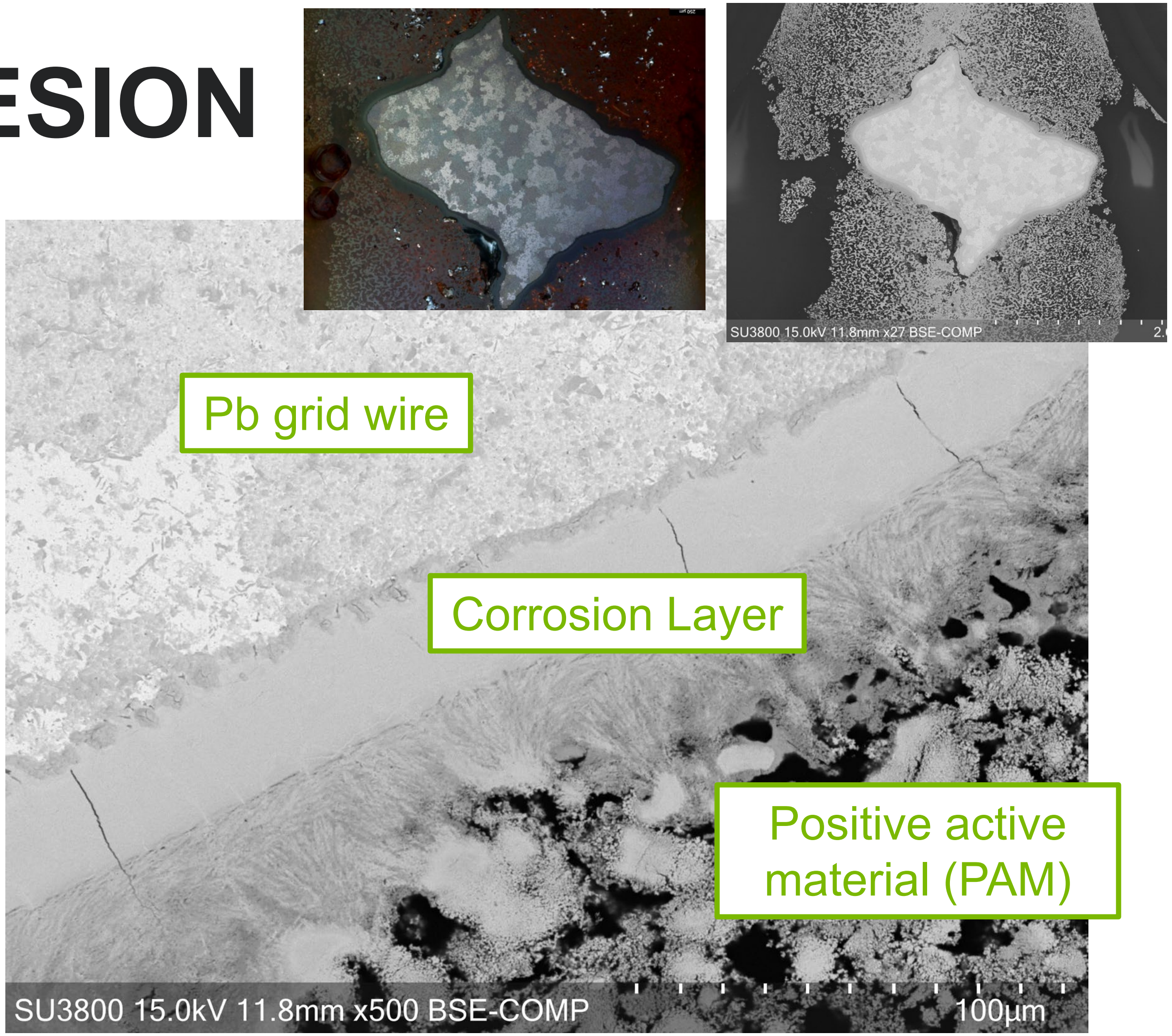
- This region, the "corrosion layer," is thought to have PbO or PbO_x (x = 1-2) phases that chemically bond Pb and PbO_2.
- These nonstoichiometric PbO_x phases have been identified by SEM, thermal gravimetric analysis, and color, but the crystal structure is not known.

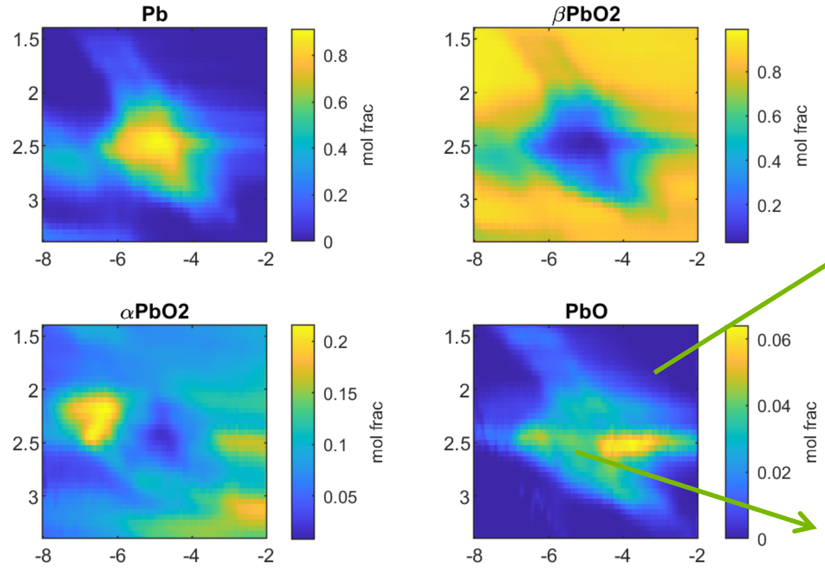


M. Verde (C&D Trojan): optical microscopy and SEM of PAM cross-section near grid

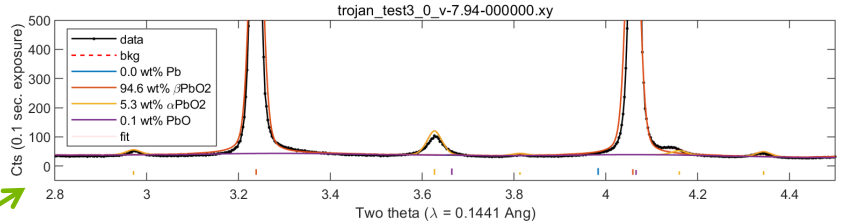
CORROSION LAYER STUDIES

X-ray absorption, x-ray diffraction

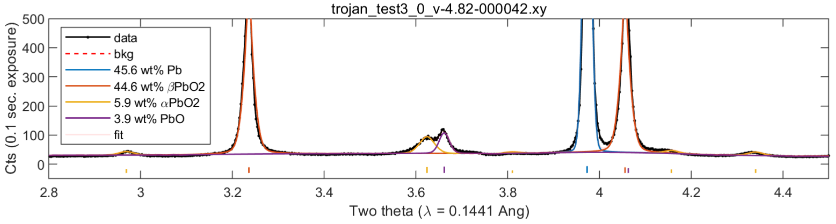
- Below: High resolution XRD maps of battery cross-section showed enhanced α-PbO_2 signal near the grid, like previous x-ray maps.
  - An additional phase (similar to PbO) was also found at the interface.



Kinnibrugh, Fister: XRD maps in positive electrode cross-section

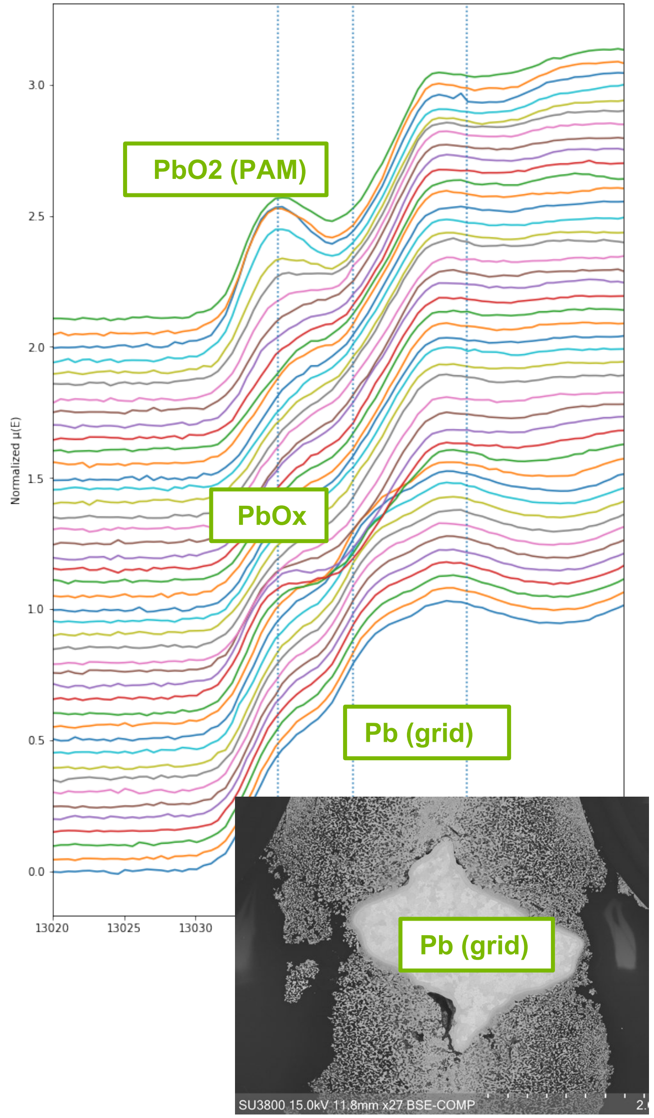


XRD in PAM



XRD in corrosion layer

Wolfman: HERFD-mode XANES through corrosion layer region

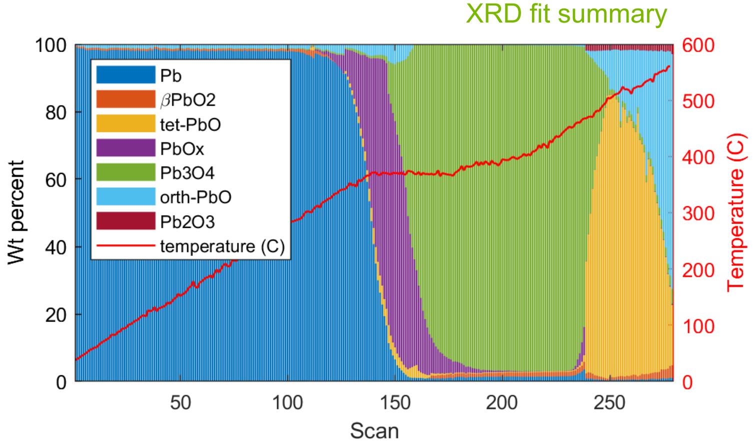


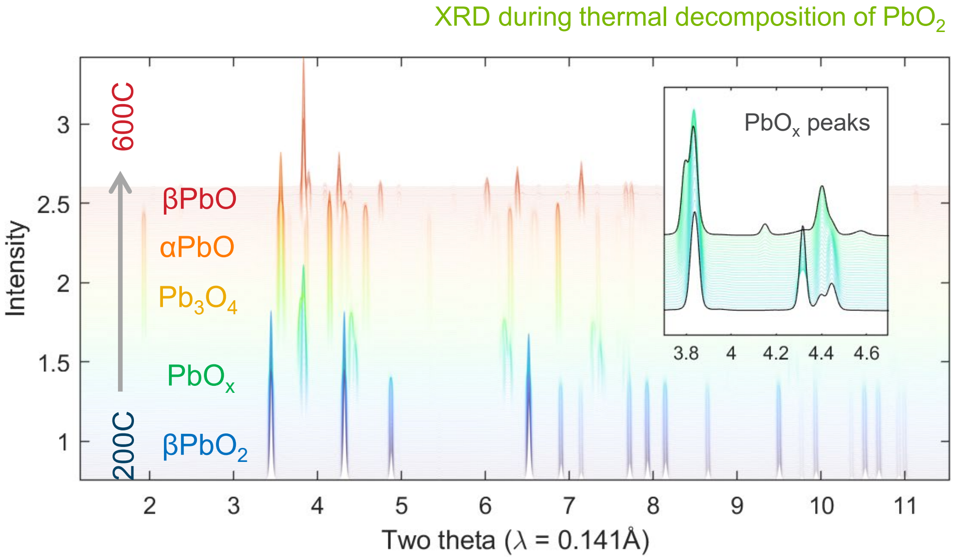
- Right: micro-focused x-ray absorption (HERFD mode) on same sample identified intermediate composition species within the corrosion layer.

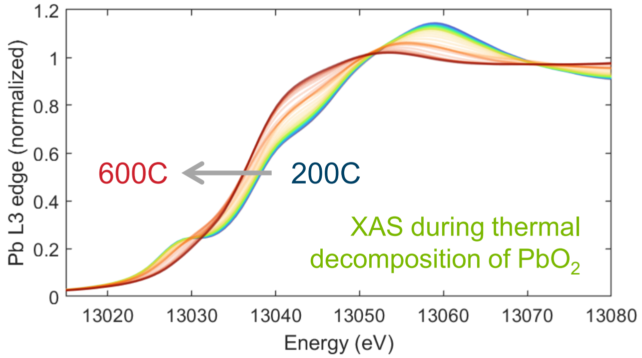
ISOLATING PbO_x

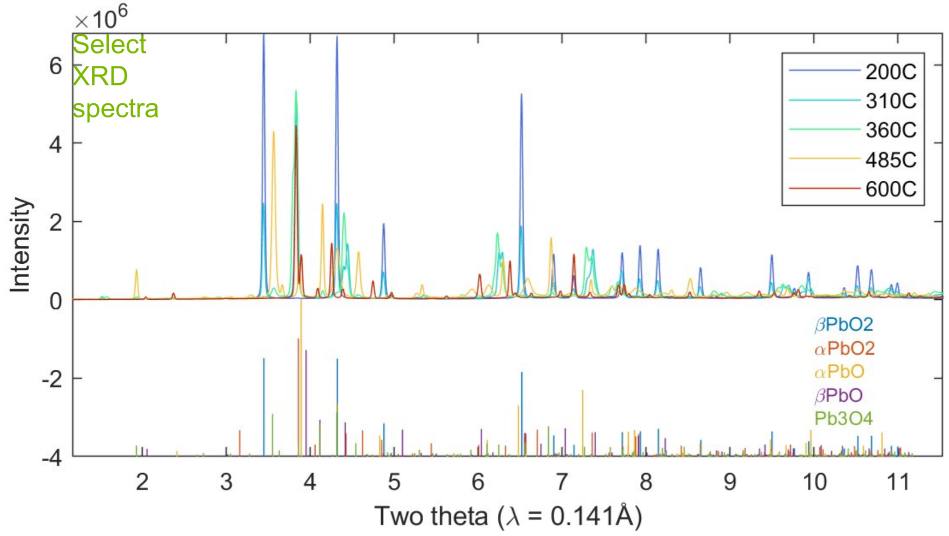
Thermal studies

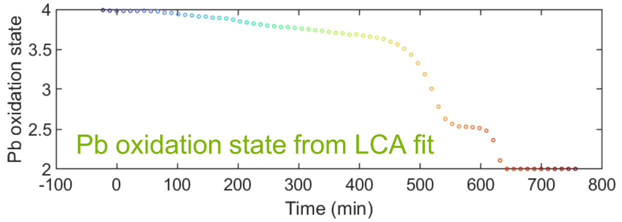
- PbO_2 undergoes a well-known reduction to Pb_3O_4 and PbO at elevated temperature.
- XRD shows the presence of these phases and a new PbO_x phase which resembles tet-PbO.
- XAS shows similar phase change, and provides independent measure of oxygen stoichiometry.









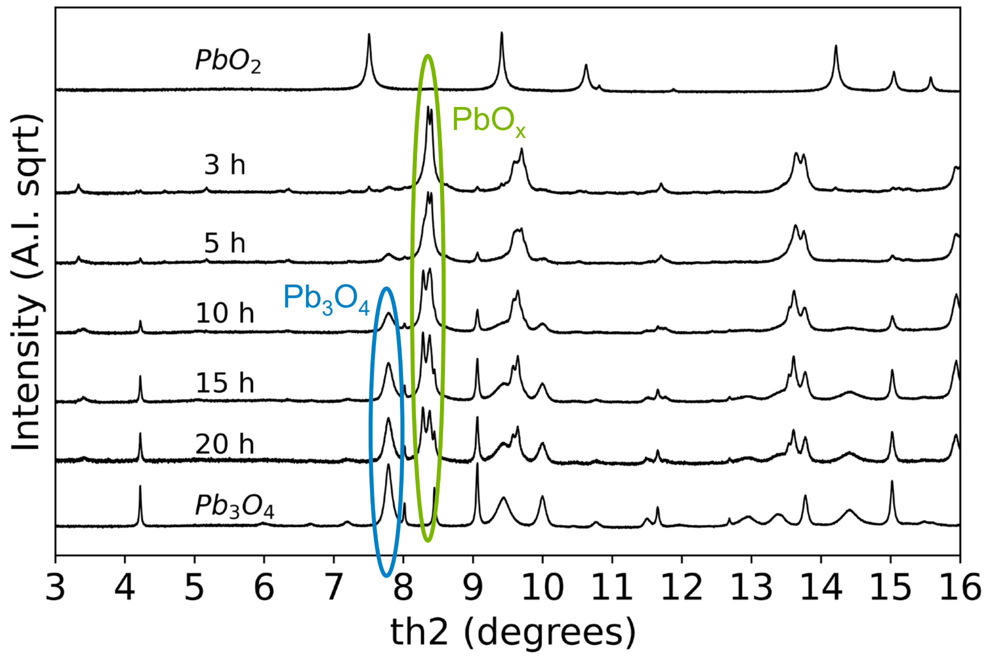


ISOLATING PbO_x

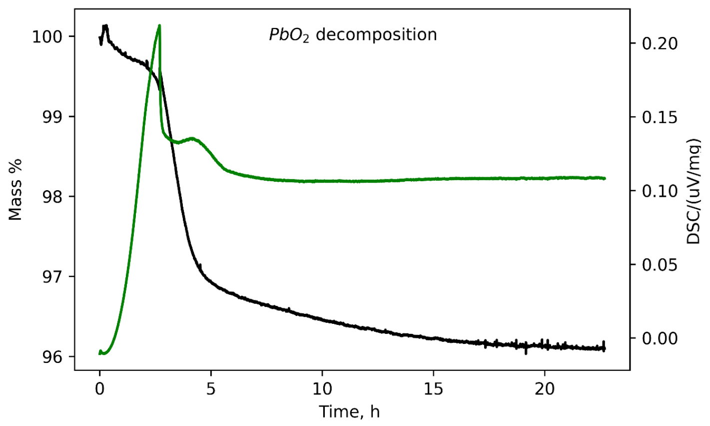
Kinetically unstable

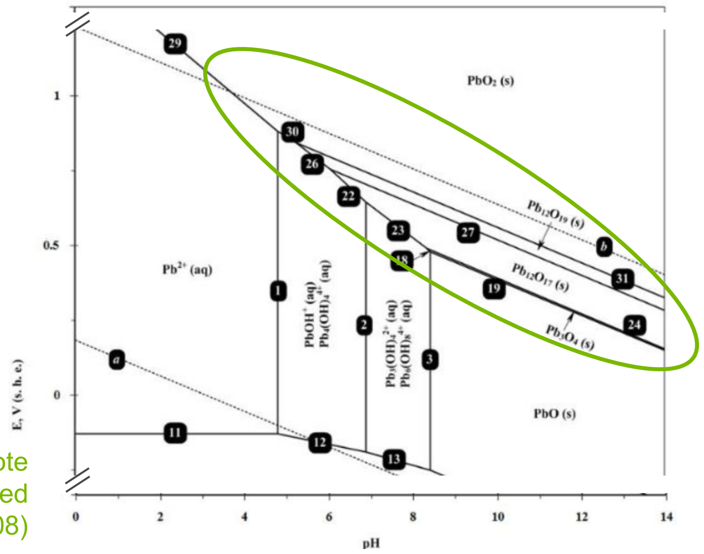
- Isolating PbO_x is challenging since its structure continues to lose oxygen during a low-T hold, eventually forming Pb_3O_4.
- Overall structure matches tet-PbO, but additional peaks may suggest multiple phases, like Pb_xO_{19} ($Pb_{12}O_{19}$, $Pb_{12}O_{17}$, $Pb_{14}O_{19}$, etc), that have been predicted in previous literature.
- These phases could arise in manufacturing during leady oxide production, paste curing, or even early stages of formation where battery briefly approaches alkaline conditions.

Kinnibrugh: High resolution powder diffraction from samples held at 345C with varying time



TGA of PbO_2 held at 345C for 20 hr



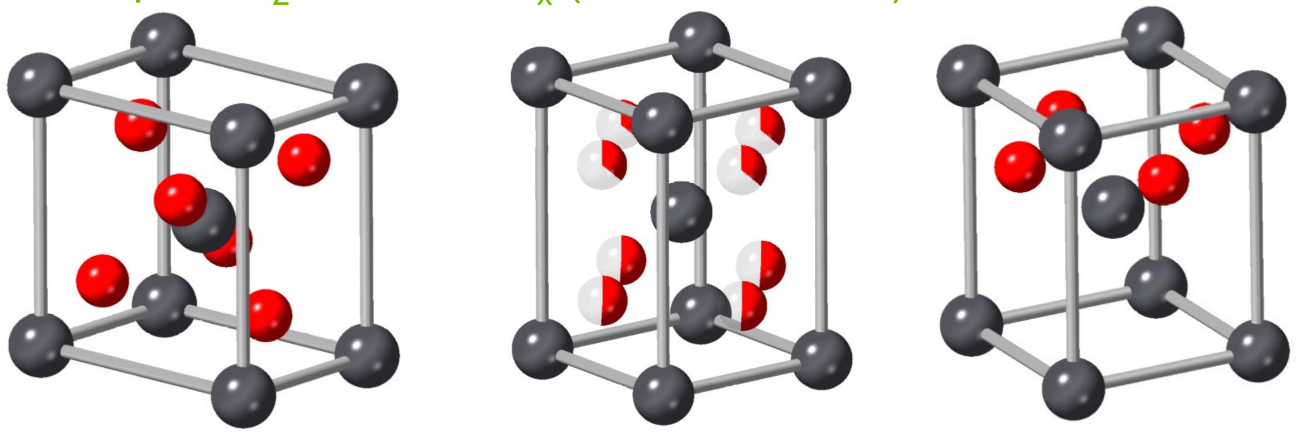


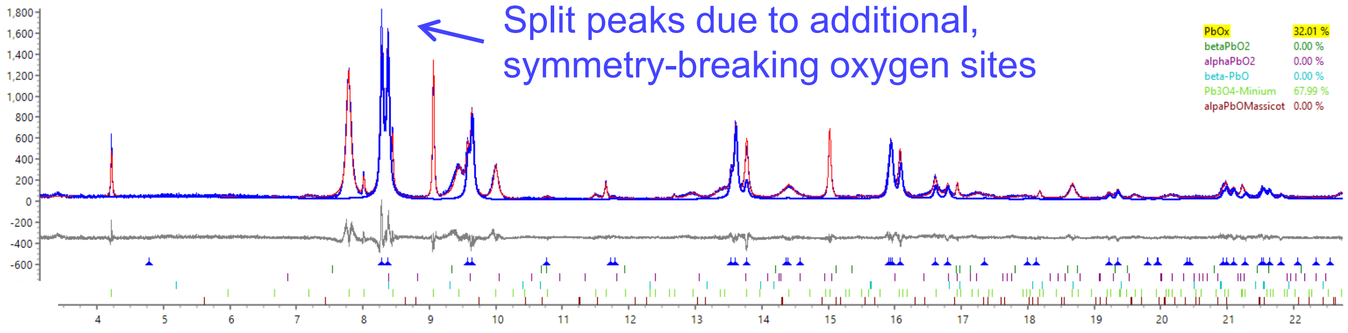
Calculated Pb Pourbaix diagram: note cluster of PbO_x intermediates (adapted from DOI10.2478/auoc-2018-0008)

PbO_x STRUCTURE

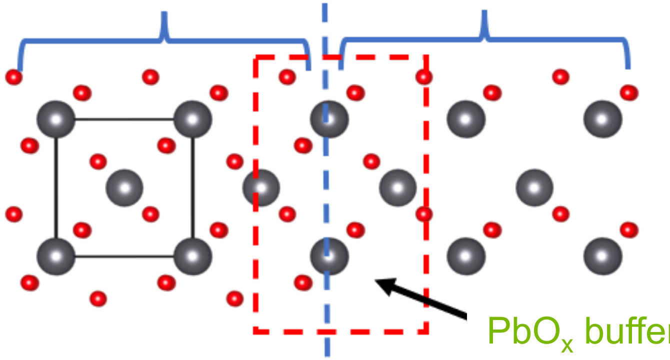
Rietveld refinement and energetics

- High resolution powder diffraction used analyze TGA samples.
- Structure is similar to PbO, but with additional, low-occupancy oxygen sites.





Kinnibrugh: Rietveld refinement of PbO_x crystal structure



E_f = 0.78 eV/atom (-0.19 eV from unstrained)

PbO_x buffer region relaxes strain at the interface

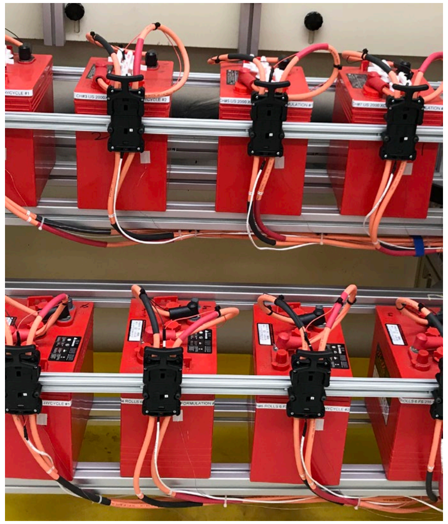
Garcia/Iddir: Schematic of interfacial DFT calculation

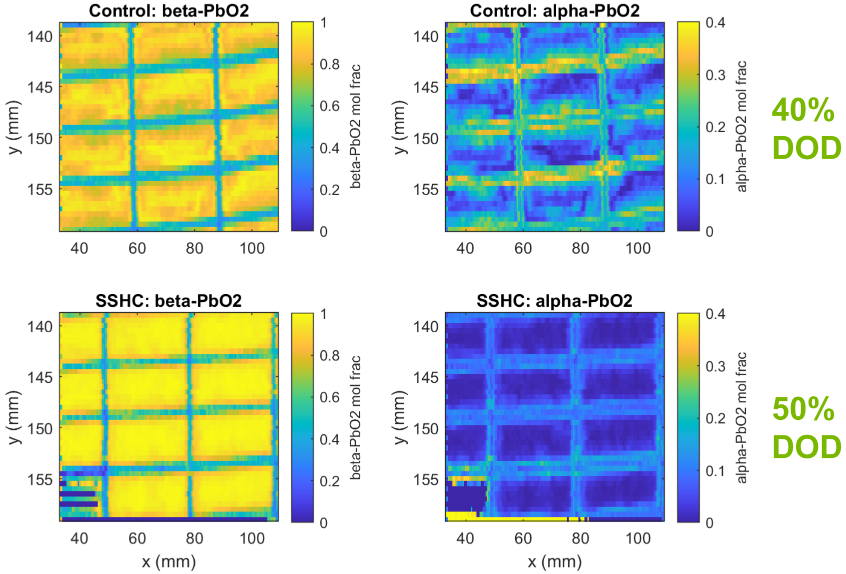
- DFT was used to look for PbO_x intermediates.
- Several metastable phases were identified and strain between PbO and PbO_2 was also found to lower the energy of these phases.

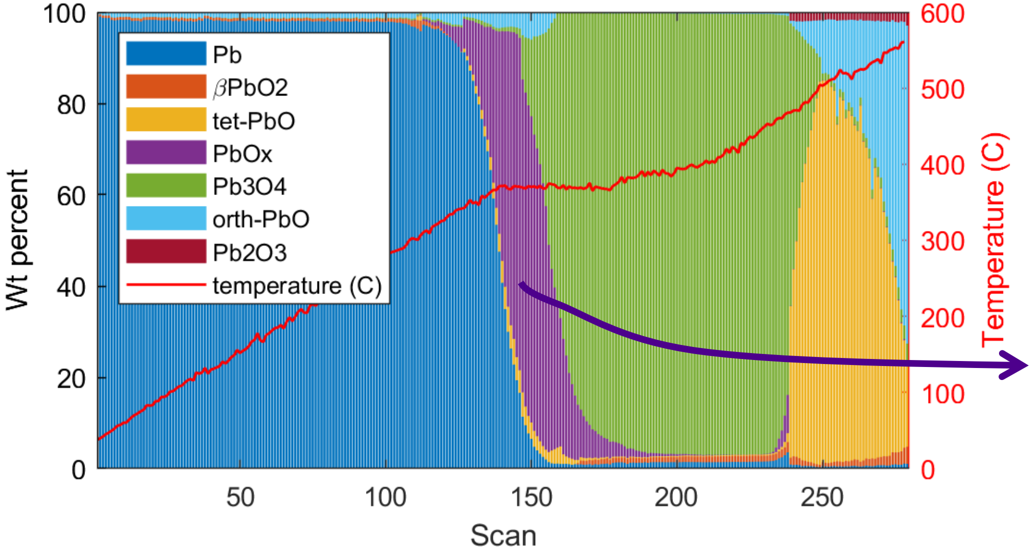
SUMMARY

Positive failure modes and speciation

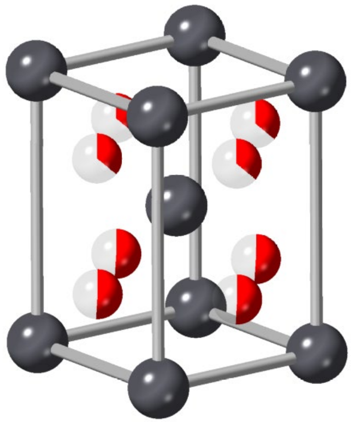
- Greater depth of discharge accelerates positive failure, eliminating ‘alkaline phases’ like PbO_x and α-PbO_2 for β-PbO_2.
- Preserving these phases requires a deeper knowledge of their structure and origin.
  – XRD and XAS used to isolate species in corrosion layer.
  – Thermal studies used to isolate and identify the crystal structure of PbO_x.







PbO$_x$ (x = 1.4-1.55)



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DOE, OFFICE OF ELECTRICITY: IMRE GYUK

ANL/PNNL: PATRICK BALDUCCI, DAVID REED, VINCE SPRENKLE

INDUSTRY: TRAVIS HESTERBERG (ECOBAT); MICHAEL VERDE, SHAWN PENG, JON ANDERSON (C&D TROJAN); JULIAN KOSTACKI, MATTHEW SPENCE (CLARIOS); SUBHAS CHALASANI, JACK SCOTT, KEVIN SMITH (EAST PENN MANUFACTURING)

APS: SECTORS 10BM, 20ID, 11ID, 11BM