OVERVIEW OF ANL AND PNNL PROGRAMS
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 PbSO₄ and acid concentration leading to stratification
PbSO₄ NUCLEATION

Solution species, nucleation,

- FY21 science goals: analyze nucleation of PbSO₄ on BaSO₄, DFT modeling of PbSO₄ surface energies
- Real world applications:
  - Discharge power density
  - Negative sulfation

![Diagrams and figures related to PbSO₄ nucleation](image)

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From Benjamin Legg et al ACS AM&I (submitted): *In situ* AFM during first monolayer growth of PbSO₄ on BaSO₄ (001)

Sang Soo Lee: X-ray scattering from PbSO₄ growth on BaSO₄ (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 ($\alpha/\beta$-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 complicate cycling of lead acid batteries:

- Issues with negative: not enough charging
  - Sulfation (PbSO₄ 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-PbO₂)
  - Active material shedding (OER)
  - Grid corrosion

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.

Procedure:
Discharge 10 A to 90 Ah (50% DOD);
Recharge 104%, with 7.3 V voltage limit
Capacity check every 100 cycles
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.

![Graph showing discharge capacity and voltage over cycles for baseline and modified charging](image)

![Graph showing end of discharge current over cycles for baseline and modified charging](image)

6V 200 Ah battery cycling (Ed Thomsen)

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

PbSO₄ ‘tide line’ develops from higher concentration acid at bottom of battery, which inhibits charging due to lower Pb²⁺ solubility.
XRD MAPS

Positive plates

- Clear evidence of paste softening: conversion $\alpha$-PbO$_2$ to $\beta$-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 $\alpha$-PbO$_2$ near positive grid architecture: necessary to hold active $\beta$-PbO$_2$ species to grid.
IMPROVING PASTE ADHESION

Corrosion layer species

- Positive failure mechanisms are often tied to the interface between the Pb current collector (grid) and the PbO₂ active material.

- This region, the “corrosion layer,” is thought to have PbO or PbOₓ (x = 1-2) phases that chemically bond Pb and PbO₂.

Note that Pb, PbO, and PbO₂ have a common lead sublattice, providing a natural epitaxy between these phases.
IMPROVING PASTE ADHESION

Corrosion layer species

- Positive failure mechanisms are often tied to the interface between the Pb current collector (grid) and the PbO₂ active material.
- This region, the “corrosion layer,” is thought to have PbO or PbOₓ (x = 1-2) phases that chemically bond Pb and PbO₂.
- These nonstoichiometric PbOₓ phases have been identified by SEM, thermal gravimetric analysis, and color, but the crystal structure is not known.
CORROSION LAYER STUDIES

X-ray absorption, x-ray diffraction

- Below: High resolution XRD maps of battery cross-section showed enhanced $\alpha$-PbO$_2$ signal near the grid, like previous x-ray maps.
  - An additional phase (similar to PbO) was also found at the interface.

- 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\textsubscript{x}

Kinetically unstable

- Isolating PbO\textsubscript{x} is challenging since its structure continues to lose oxygen during a low-T hold, eventually forming Pb\textsubscript{3}O\textsubscript{4}.

- Overall structure matches tet-PbO, but additional peaks may suggest multiple phases, like Pb\textsubscript{x}O\textsubscript{19} (Pb\textsubscript{12}O\textsubscript{19}, Pb\textsubscript{12}O\textsubscript{17}, Pb\textsubscript{14}O\textsubscript{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.
**PbO<sub>x</sub> 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.

![Diagram of PbO, PbO<sub>x</sub>, and PbO<sub>2</sub> with energetics](image)

$E_r = 0.78 \text{ eV/atom} \quad (-0.19 \text{ eV from unstrained})$

- DFT was used to look for PbO<sub>x</sub> intermediates.
- Several metastable phases were identified and strain between PbO and PbO<sub>2</sub> 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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