MULTISCALE CHARACTERIZATION OF LEAD ACID BATTERIES

FY26: Effect of positive electrode additives on formation and cycling

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PROJECT PROFILE

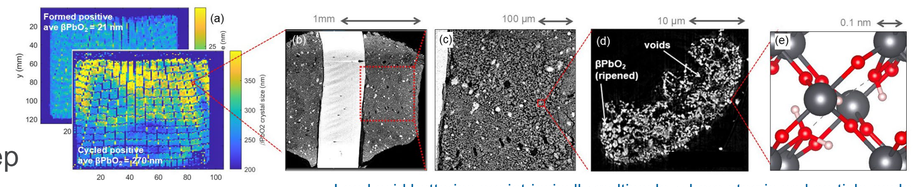
Topic: Zinc and Lead Batteries | Vertical: Materials and Systems Innovation
Strategic Pathway: Grow grid capacity, stabilize grid services
Project start and finish: FY2022 - present

MOTIVATION

Lead-acid batteries have been in use for over a century, but the mechanisms driving performance and cycle life were largely driven by trial-and-error, post-mortem studies. Moreover, lead-acid has largely been developed for high power applications, not cycle life.

Using high energy synchrotron x-ray characterization, we capture reactions in real battery environments and during cycling – connecting particle scale changes with macroscale reactivity. This will accelerate the development of additives, cell architectures, and models to translate lead-acid to stationary storage applications.

FY26 focus: understand the effect of additives that improve performance in deep cycle applications.

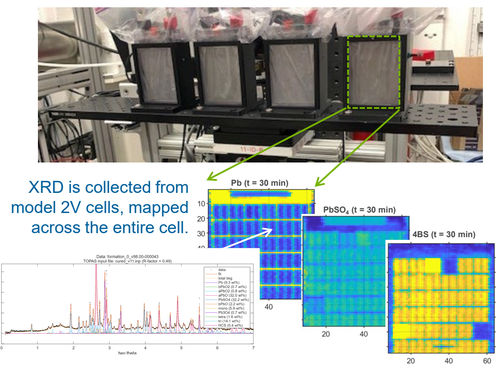


Lead acid batteries are intrinsically multiscale, where atomic and particle-scale changes can lead to macroscale reactivity across battery electrodes.

APPROACH

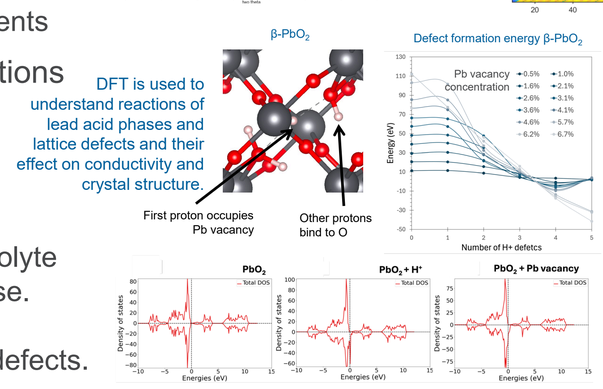
Experimental Approach: High energy synchrotron diffraction provides unique information in the evolution of positive active material.

- Refinements: electrode and acid speciation
- Lattice constants: affected by crystallographic defects and deviations from stoichiometry
- Line shape: related to morphology and crystal domain size (ripening mechanisms)
- Mapping: charge acceptance, local currents



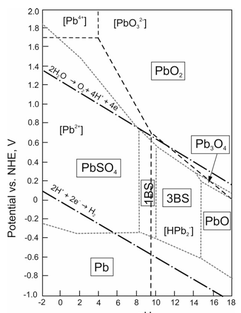
Modeling Approach: atomistic simulations and physics-based models connect reactions with a cell's electrochemical response.

- Continuum modeling: porous electrode model connecting local electrode/electrolyte speciation with electrochemical response.
- Atomistic: Density functional theory to understand role of dopants and lattice defects.



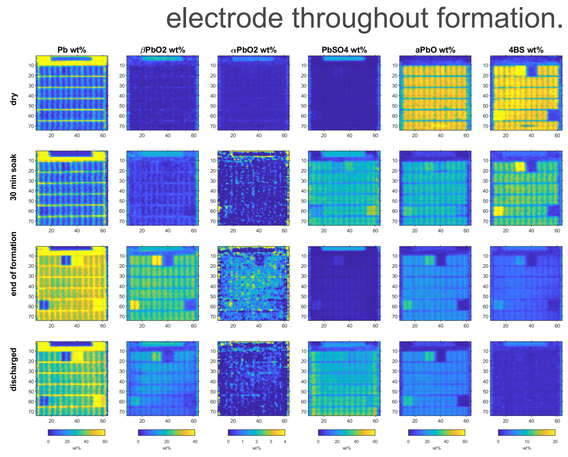
FORMATION: EVOLUTION OF "ALKALINE" SPECIES

Positive electrodes consist of βPbO_2 that is active in acidic conditions, supported by "alkaline species" including αPbO_2 and PbO_x phases. Positive shedding results from loss of these phases over repeated cycles and is a primary cause of failure.

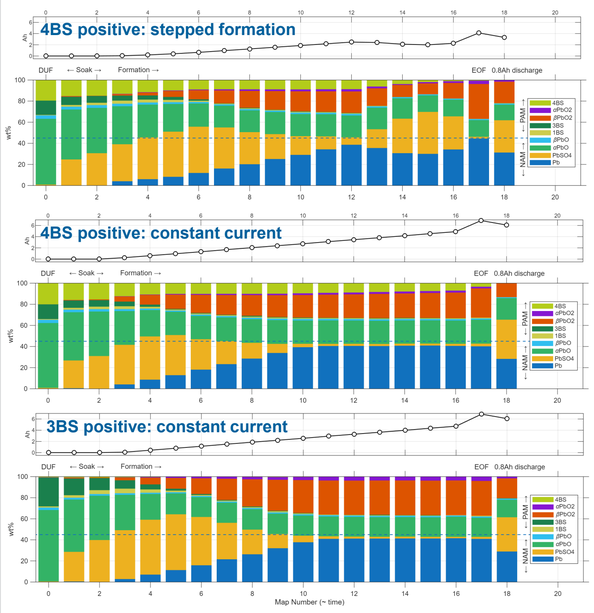


Lead acid Pourbaix diagram

In cured electrodes, tetrabasic lead sulfate (4BS) is used to provide a "reticular backbone" for the positive active material. Contrary to popular wisdom, we find that 4BS is consumed during discharge; however PbO remains in the positive electrode throughout formation.

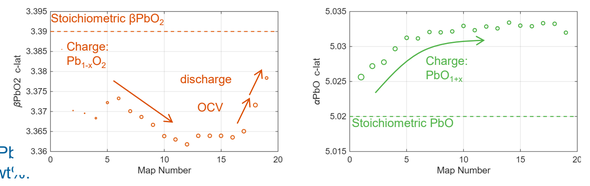


XRD maps collected during formation. Windows that help isolate pos/neg species.



Above: Change in average cell speciation for different formation profiles and positive compositions

Following changes in lattice constants, we find that the PbO is oxidized (to PbO_{1+x}) during charging, preventing its conversion to $PbSO_4$ and βPbO_2. In contrast PbO in the negative is consumed within 6 hours of formation.

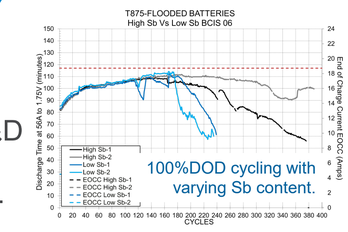


Right: change in lattice constant for βPbO_2 and αPb species. Marker size is proportional to wt%.

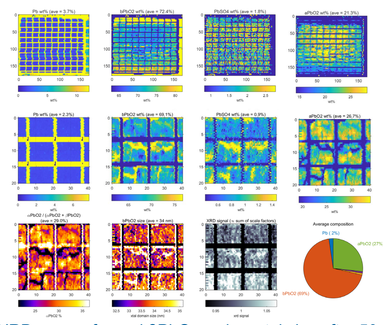
Like the corrosion layer, this PbO_{1+x} phase is a necessary 'glue' for positive active material. Ongoing studies with Clarios are looking at the evolution of these phases during cycling.

POSITIVE GRID ADDITIVES: ROLE OF ANTIMONY

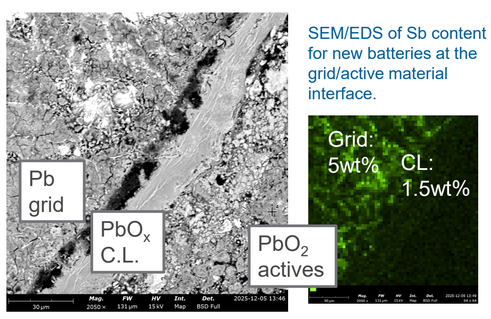
Antimony is known to improve cycle-life but its mechanism is unclear. In collaboration with C&D Trojan, we find that Sb helps maintain α-PbO_2 and reduces β-PbO_2 crystal ripening.



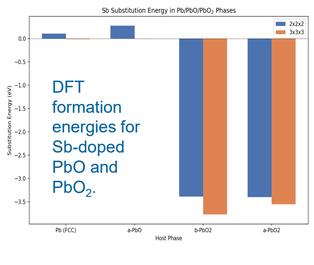
100%DOD cycling with varying Sb content.



XRD maps of α and βPbO_2 and crystal size after 50 cycles. Cracks correlate with high βPbO_2 content



SEM/EDS of Sb content for new batteries at the grid/active material interface.

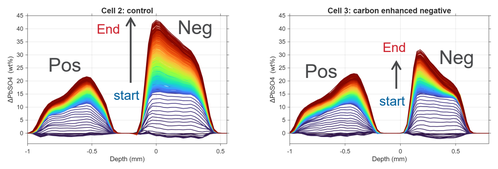


DFT formation energies for Sb-doped PbO and PbO_2.

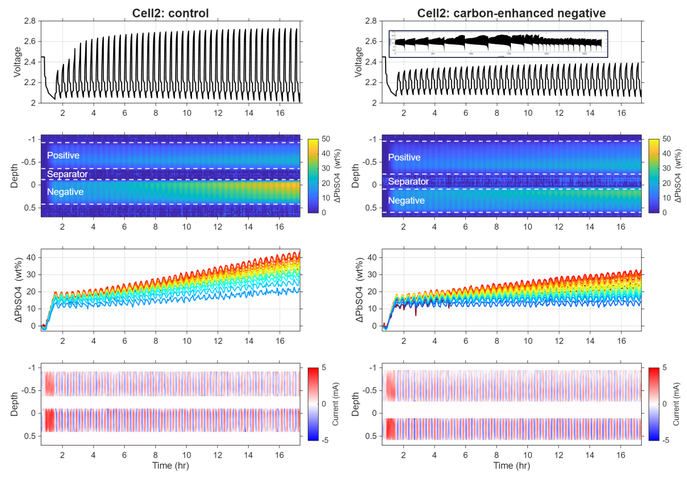
DFT shows that Sb is readily incorporated into PbO_2 phases (Sb^{5+}). Sb is not incorporated into PbO phases, leading to an oxidized PbO_x ($x > 1$) corrosion layer that is more conductive.

NEGATIVE ACTIVE MATERIAL ADDITIVES: CARBON

Continued work with East Penn: depth-profiling "mini-cells" with XRD during PSOC cycling regimes. Negative electrodes are prone to runaway $PbSO_4$ growth in this regime, especially at surface. Carbon helps reduce the rate of surface sulfation.



Comparison of low carbon and high carbon $PbSO_4$ content in "mini cells" during HRPSOC cycling

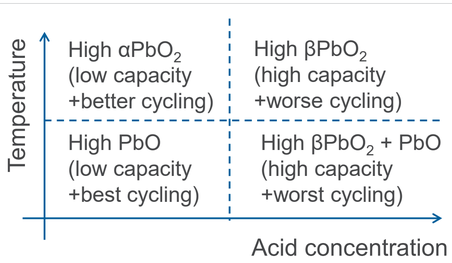


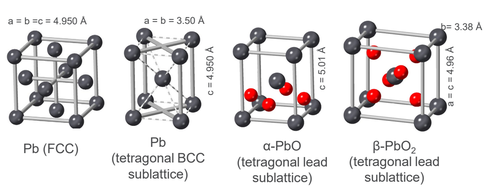
Electrochemistry and $PbSO_4$ concentration during first 44 cycles of HRPSOC procedure

CONCLUSIONS AND IMPACT

Alkaline phases are key to the long-term cyclability of positive electrodes. Understanding their evolution during formation guides strategies for cycling.

- FY25: high temperature, high pH → αPbO_2
- FY26: low temperature: PbO stabilized during charge
- FY26: Grid dopants (Sb, Sn, etc) can be incorporated in active material.





The common sublattice between Pb and related oxides helps stabilize PbO_x intermediates.

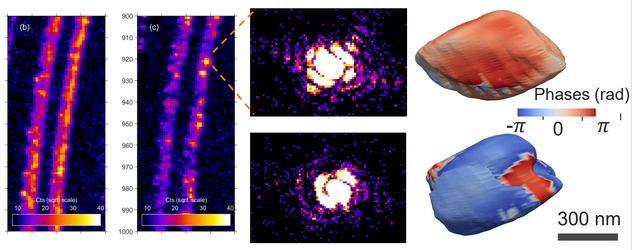
FY26 manuscripts and patents

- Garcia, Iddir, Fister, "Role of defects on PbO2 structure, conductivity and phase stability: insights from DFT calculations" in review J. Phys Chem
- Two more in preparation for FY26.
- US12567599, "Pumping charge & discharge electrolytes" (2026)
- US20240186592A1: "Electrode Manufacturing" (2026)
- IN-26-014 (provisional): "Acoustics signatures…" (2026)

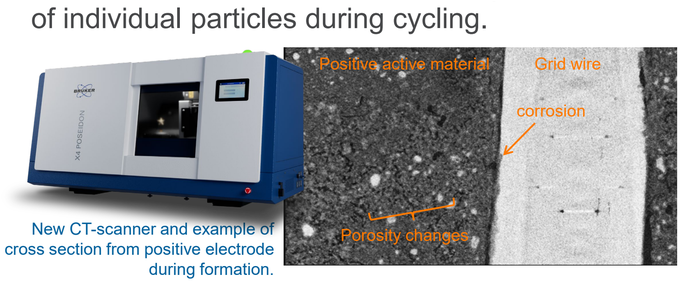
NEXT STEPS

APS-Upgrade provides smaller beams and coherent x-rays: we will connect particle-scale changes with macroscale reactivity.

- Coherent diffraction imaging (CDI) is used to reconstruct the size and shape of individual particles during cycling.



Inset of XRD powder lines. Right: example of CDI during dissolution of a single $PbSO_4$ particle.



New CT-scanner and example of cross section from positive electrode during formation.

- New micro-CT system will allow direct measurement of changes in active material density/porosity and grid corrosion. Unlike APS studies, we can track electrodes over their entire service life.

U.S. DEPARTMENT of ENERGY

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