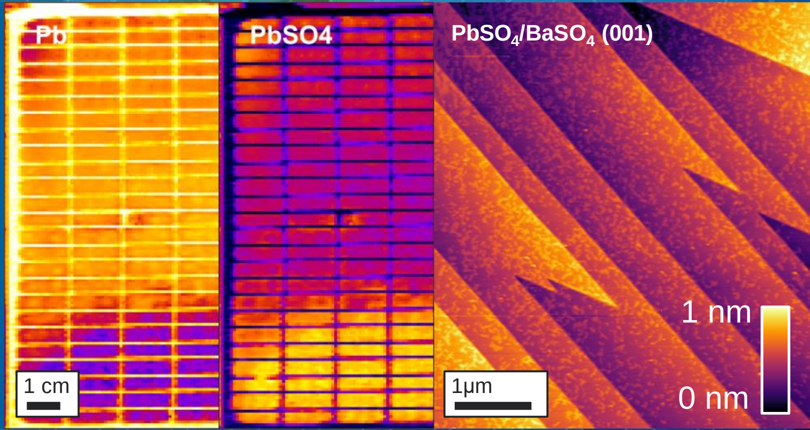
OE Energy Storage Peer Review
October 27, 2001

IMPROVING CYCLE LIFE AND UTILIZATION IN LEAD ACID BATTERIES: A MULTISCALE APPROACH



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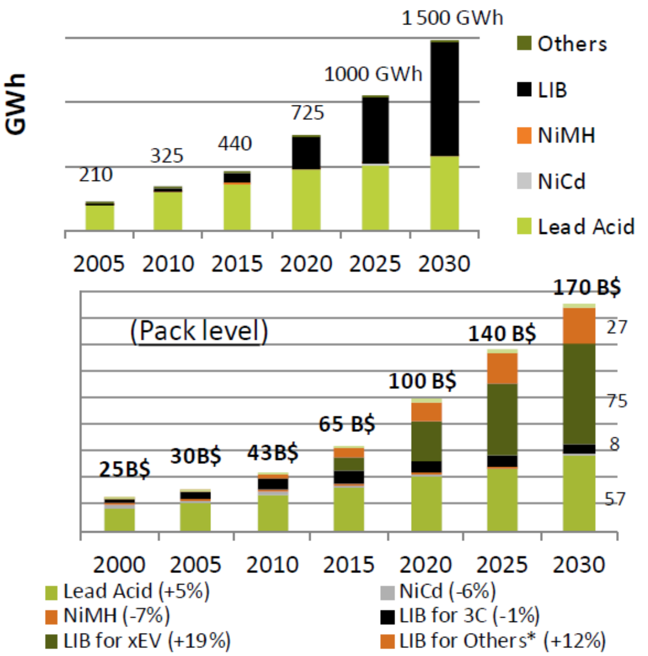
WHY LEAD ACID BATTERIES?

Lead acid continues to be a large market

- Lead acid continues to be a large part of the secondary battery market, with a large domestic manufacturing presence.
  - BUT: lead acid will likely need to diversify from transportation sectors in the future.
- Lead acid has cheap up-front costs (Pb = $2/kg) and is easy to recycle.
- Lead acid is **nowhere near its theoretical energy density** (~200 Wh/kg)
  - Theoretical specific capacity of PbO_2 = 223 mAh/g = 2100 mAh/L
- Current SLI technology designed for high power applications without voltage control; **lifetime could be substantially improved** for stationary applications with a BMS.

Contender for stationary storage?

Avicenne forecast (2020 AABC)



IMPROVING UTILIZATION, CYCLE LIFE

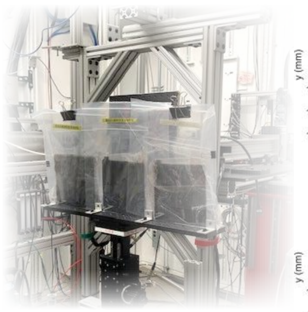
Lead acid: multiscale, liquid-solid interactions

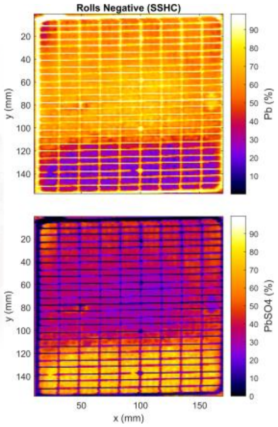
Improving utilization and lifetime is a multiscale problem involving **solid** and **liquid** species.

- Pack level issues: electrolyte stratification, grid corrosion, paste shedding/softening
- Particle level issues: sulfation/pore clogging, diffusion/tortuosity limitations for e^- and SO_4^{2-}
- Atomic level issues: $PbSO_4$ nucleation, Pb^{2+} solvation, acid dissociation, additives/dopants

Pack level (~mm)

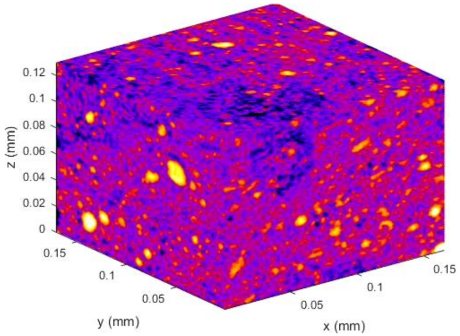
Example: cycling at PNNL and XRD from EOF battery plates





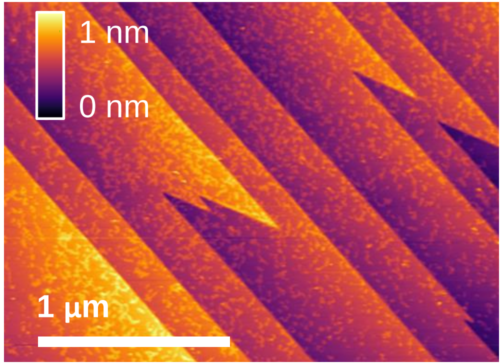
Particle level (~µm)

Example: Reconstructed volume from CT scan of a paste electrode (color = density)



Atomic level (~nm)

Example: monolayer growth of $PbSO_4$ on barite 001.

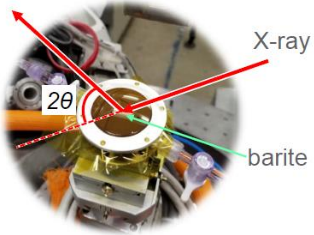


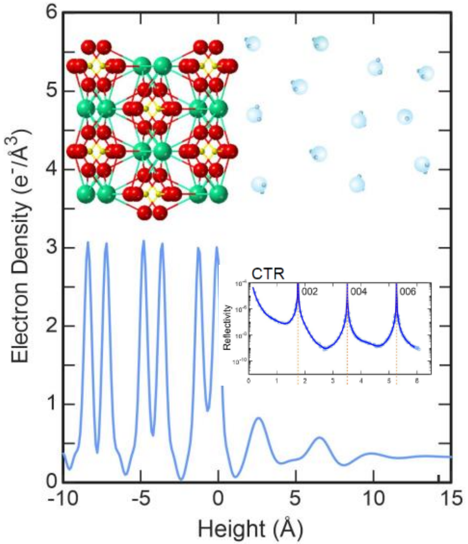
ATOMIC SCALE: INTERFACIAL AND SOLUTION SPECIES

INTERFACIAL STRUCTURE

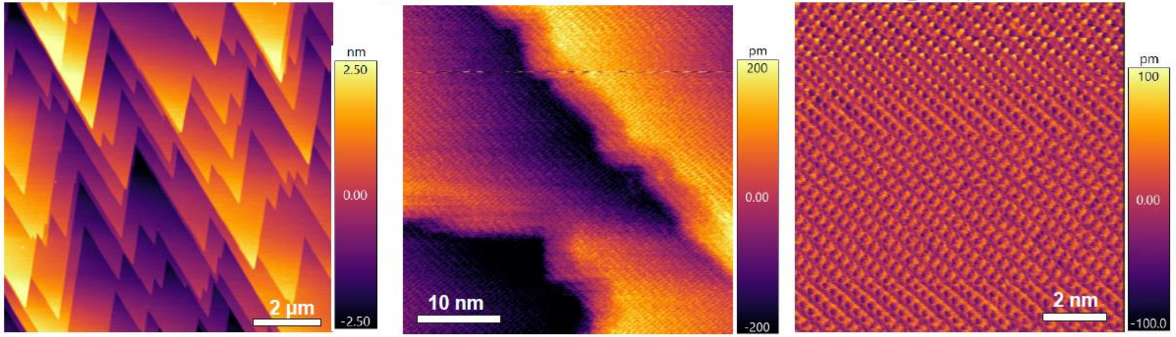
$PbSO_4$ growth on $BaSO_4$ 001

- $BaSO_4$ is a common nucleation agent in lead acid batteries.
- $BaSO_4$ crystals cleave on 001 and 210 planes, providing an ideal model surface for studying growth/dissolution by atomic force microscopy (AFM) and surface x-ray scattering.





Barite (001) cleavage plane imaged with AFM in 100 mM H_2SO_4



Terrace/step morphology of cleaved barite 001 surface

Detailed view of step-edge and lattice (double-step)

Crystal lattice of barite 001 surface

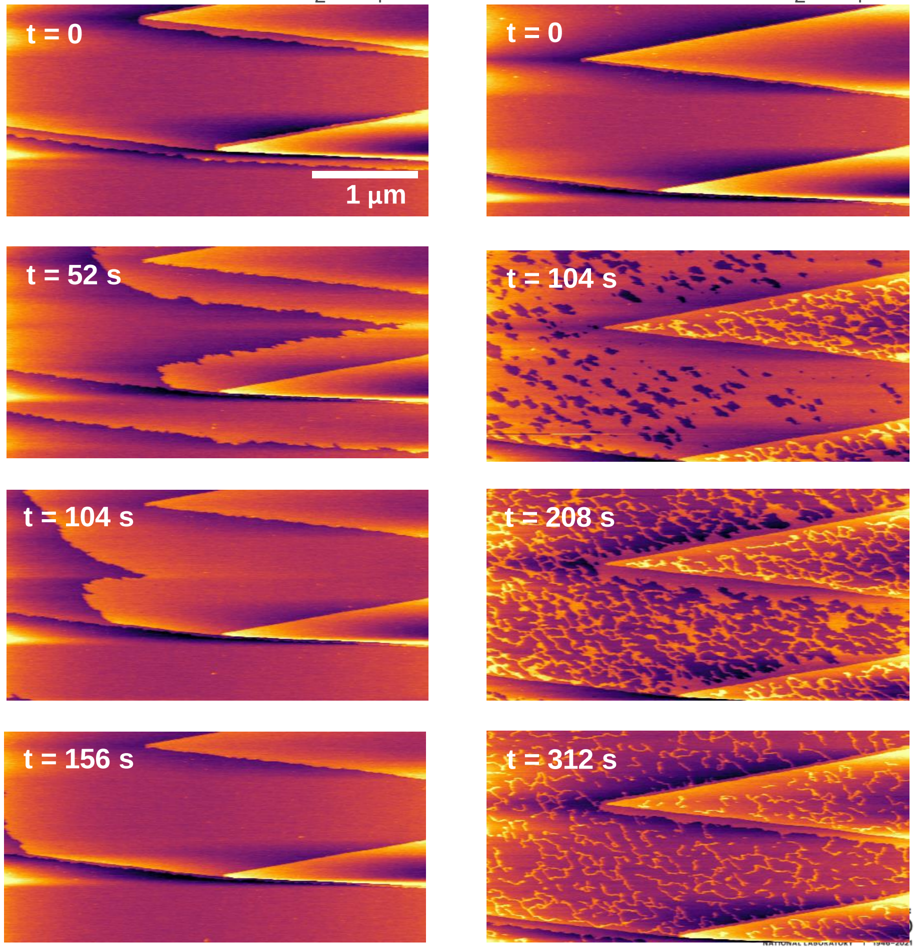
OPERANDO AFM

$PbSO_4$ on $BaSO_4$ 001

- First exposure to $PbSO_4$-saturated solutions: rapid growth of a single monolayer of $PbSO_4$ propagating from $BaSO_4$ step edges.
- Dissolution in undersaturated (Pb-free) solutions is patchier and slower.

1st exposure to lead
9 uM Pb, 100 mM H_2SO_4

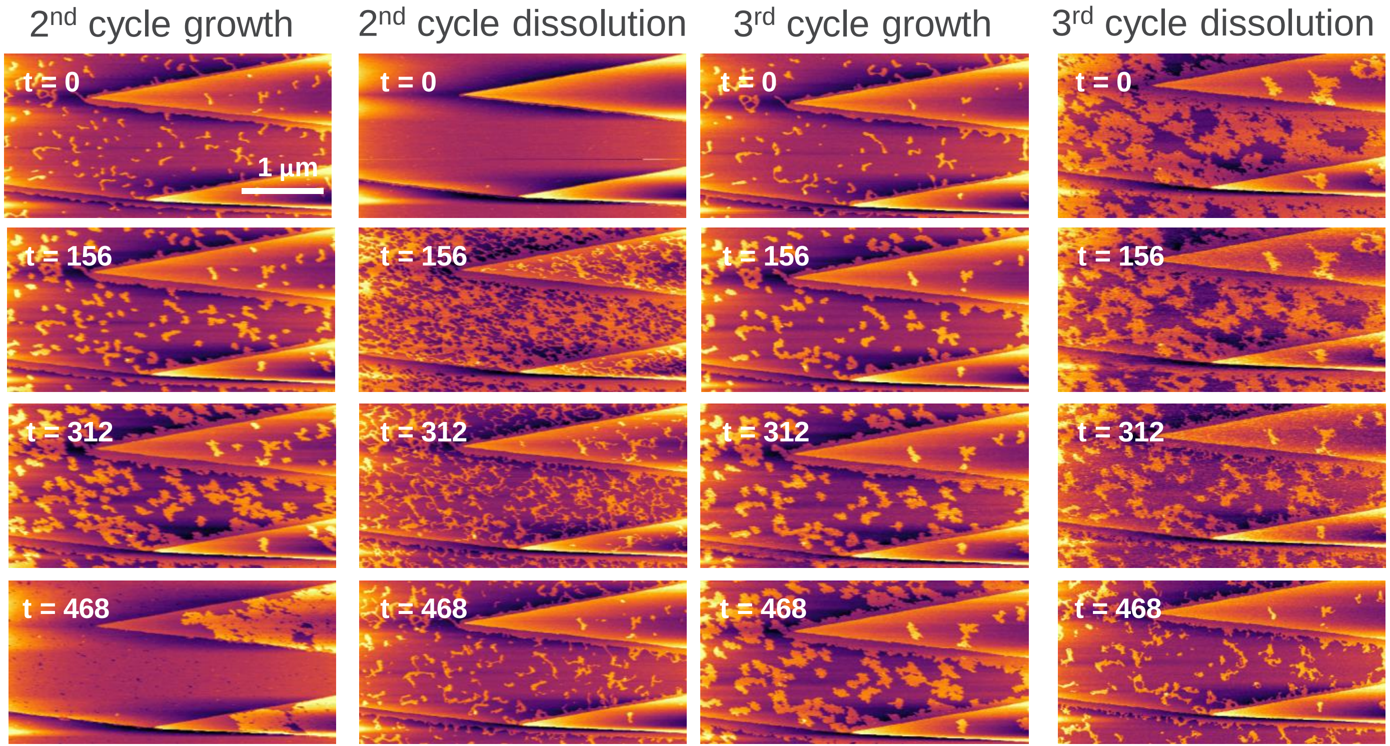
1st dissolution
Pb-free 100 mM H_2SO_4



OPERANDO AFM

$PbSO_4$ on $BaSO_4$ 001

- Subsequent cycles: growth propagates from residual $PbSO_4$ nucleation sites.
- Stepflow growth resumes after dissolution in nitric acid (which removes both $PbSO_4$ and $BaSO_4$ layers).

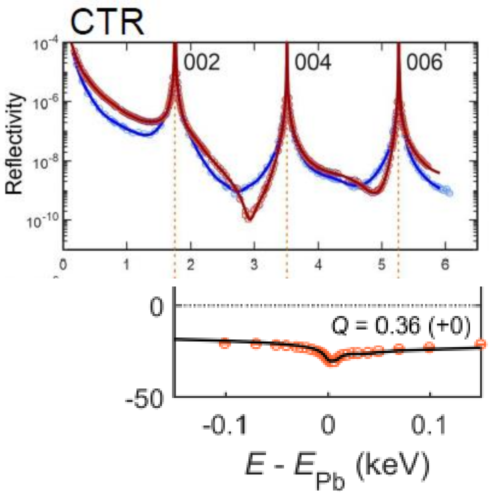


X-RAY ANALYSIS

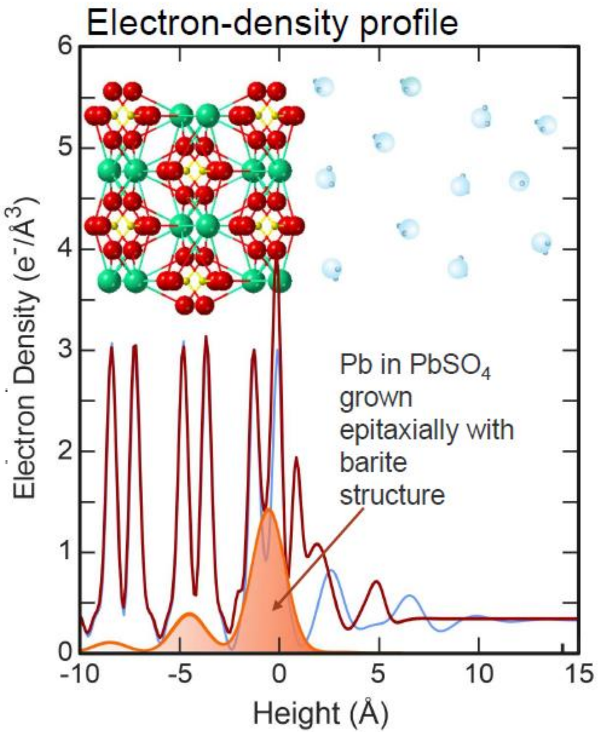
$PbSO_4$ on $BaSO_4$ 001

Similar measurements performed using surface diffraction/resonant scattering.

- Large change in $BaSO_4$ (001) crystal truncation rod (CTR) upon exposure to Pb solution.
- Combined with resonant scattering, these x-ray results show a similar monolayer of $PbSO_4$ on barite surface AND Pb incorporation deeper into the subsurface layers.



Top: CTR and resonant scattering data
Right: analysis of data shows Pb incorporation into $BaSO_4$ surface



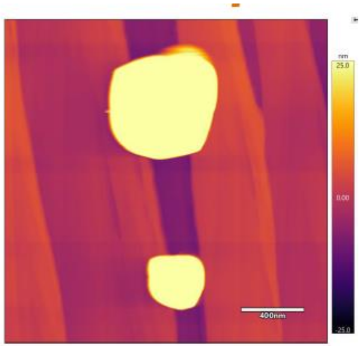
Red: CTR of Pb-exposed surface
Orange: RAXR of Pb-exposed surface

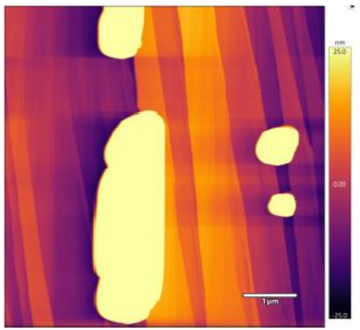
- Pb incorporation affects $BaSO_4$/$PbSO_4$ interfacial strain, possibly leading to modified growth modes observed by AFM.

NUCLEATION

Other facets

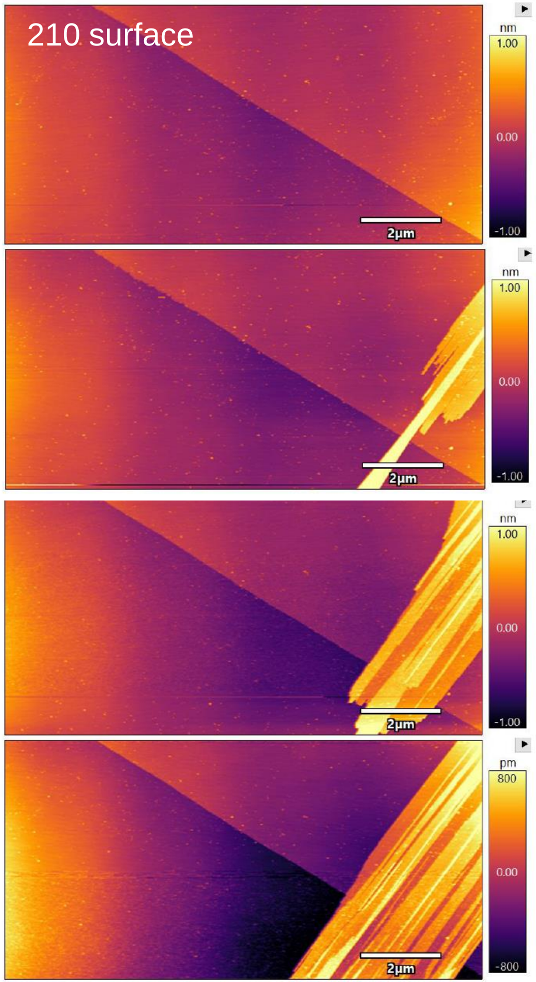
- Unoriented particles also nucleate at step edges but show continuous growth/dissolution.





- Multilayer growth found on 210 surface, possibly due to smaller misfit strain.

Conclusion: $PbSO_4$ nucleation, growth, and dissolution is facet-dependent. Tailoring $BaSO_4$ and $PbSO_4$ crystal habit could lead to higher power batteries. Future work will incorporate DFT/AIMD to understand heterogeneous nucleation processes.

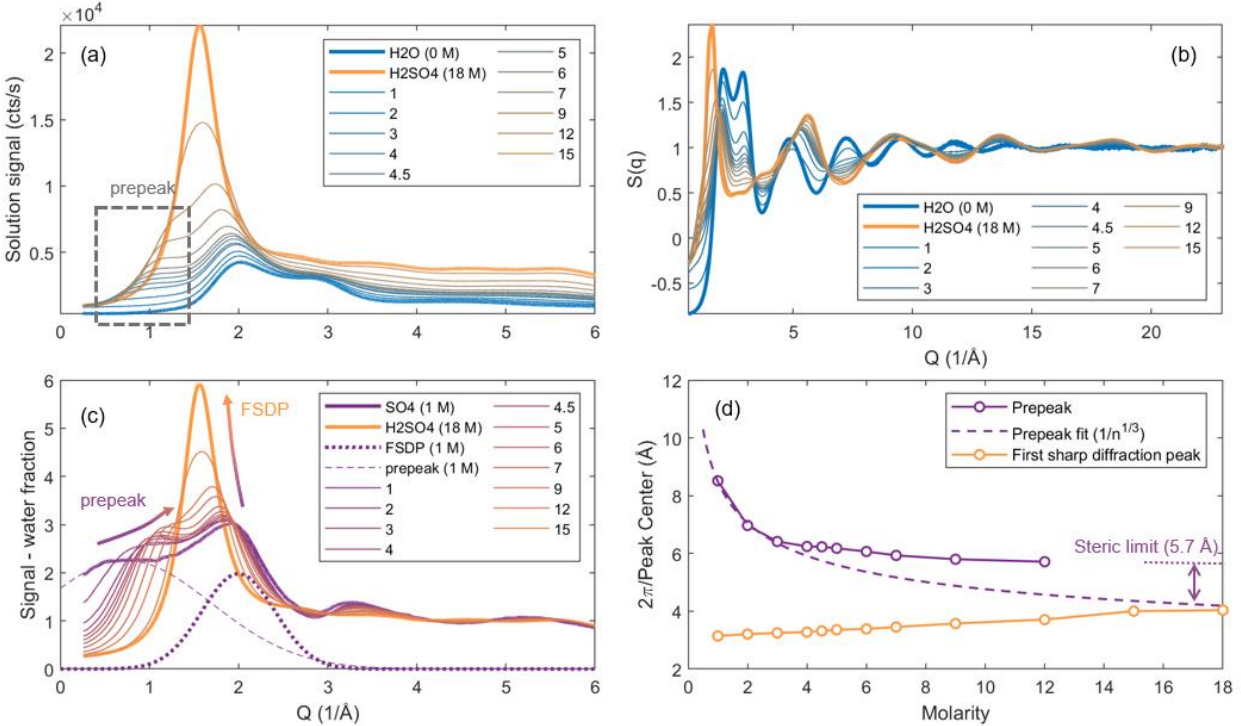


SOLUTION STRUCTURE

Hydration and mesoscale ordering

- Building from previous NMR results,[1] sulfuric acid was measured by x-ray scattering over full concentration range.[2]
- SAXS/WAXS: Clear signatures of H_2O, SO_4^{2-}, and H_2SO_4: can measure acid concentration in working battery…
- Hydrated sulfates quickly reach steric limit.

1. Bazak et al JPCB 2020. 2. Kinnibrugh, Fister in review



Top: (a) Overall scattering PDF structure factor from sulfuric acid. (c,d) Analysis of sulfate contribution.

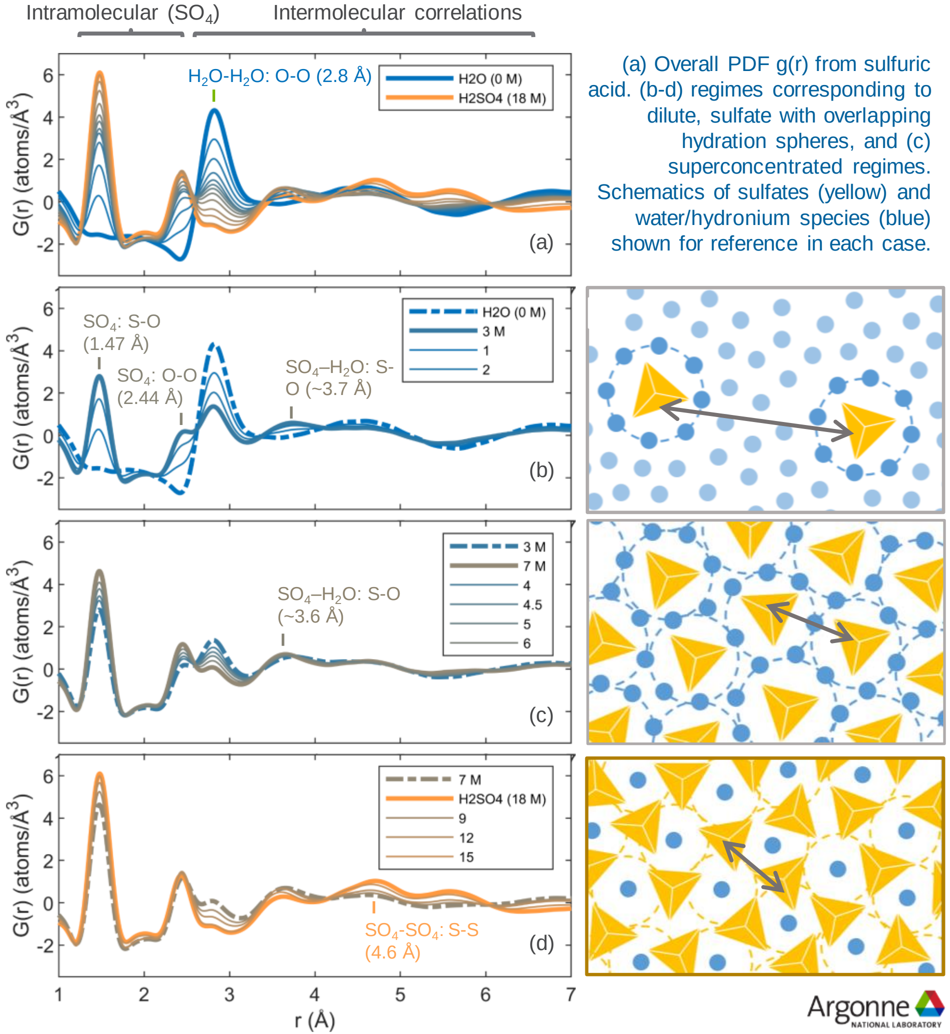
SOLUTION STRUCTURE

Hydration and mesoscale ordering

Pair distribution function (PDF) analysis shows transition from:

- 0-3 M: noninteracting octahydrated sulfates
- 3-9 M (b,c): overlapping sulfate coordination spheres with decreasing hydration
- 9-18 M: a water-in a salt regime where isolated waters are coordinated by polymerizing sulfate species.

The solution structure leads to rheological changes and deep eutectic points associated with suppressed freezing temperature.



(a) Overall PDF g(r) from sulfuric acid. (b-d) regimes corresponding to dilute, sulfate with overlapping hydration spheres, and (c) superconcentrated regimes. Schematics of sulfates (yellow) and water/hydronium species (blue) shown for reference in each case.

MACROSCALE: PACK LEVEL FEATURES

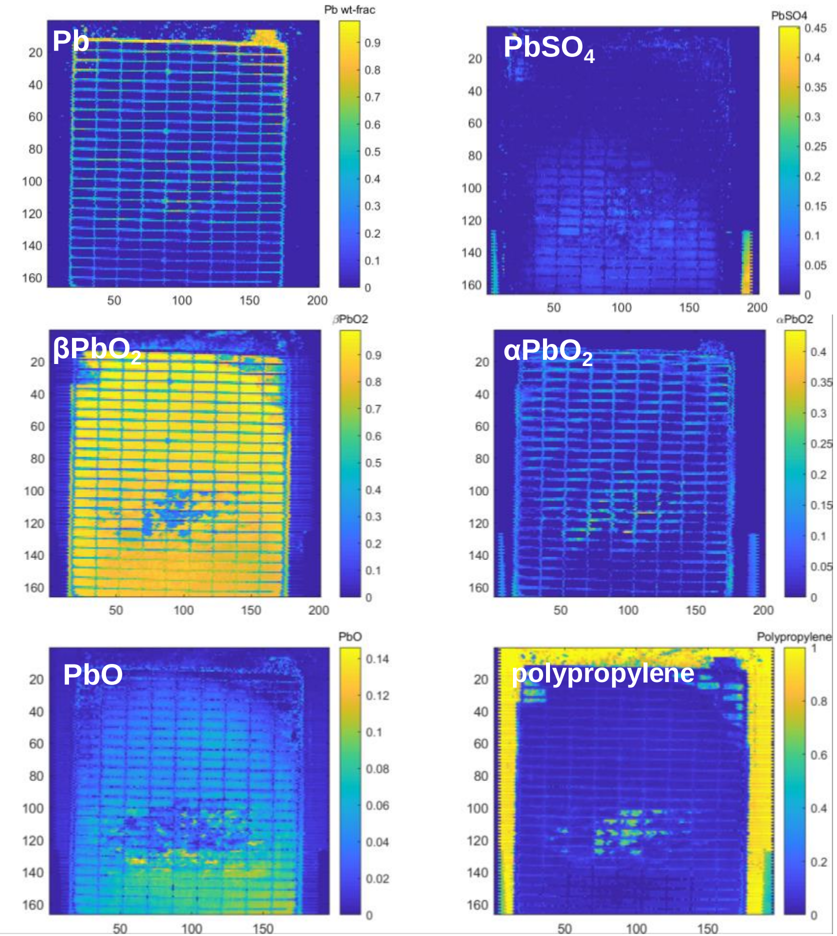
TESTING AND ANALYSIS

Identifying failure modes

- PNNL conducting tests on industrial batteries with varying build parameters and Pb-alloy composition.
- Batteries are shipped to ANL and are then analyzed using high energy XRD at APS in acid. Current failure modes being studied:
  - PAM paste softening/shedding
  - NAM stratification
- Further analysis performed by PDF, XAS, and NMR.

200Ah batteries being tested at PNNL. Right: XRD maps of PAM plate species after 258 cycles. Note paste shedding at center of electrode.

XRD maps (weight fractions)



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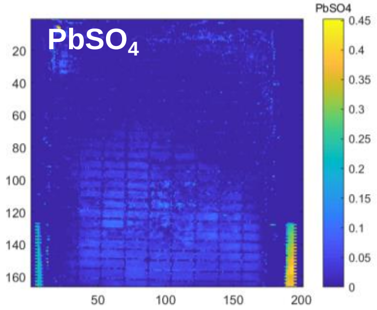
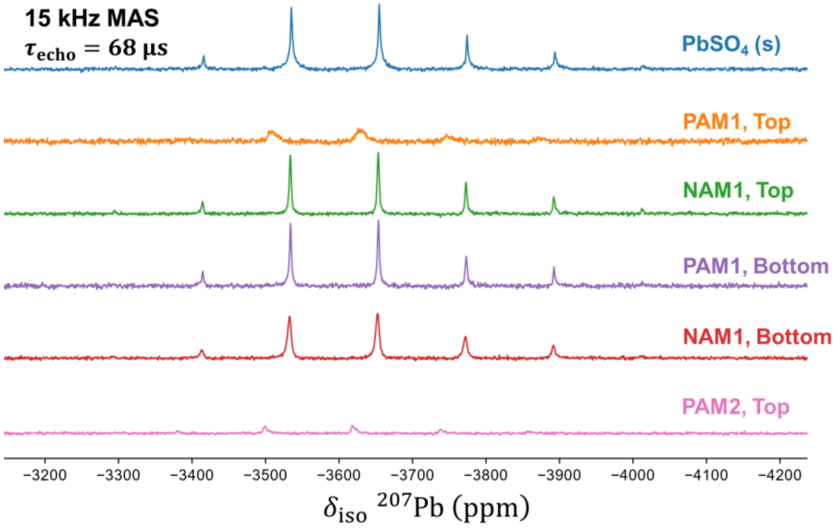


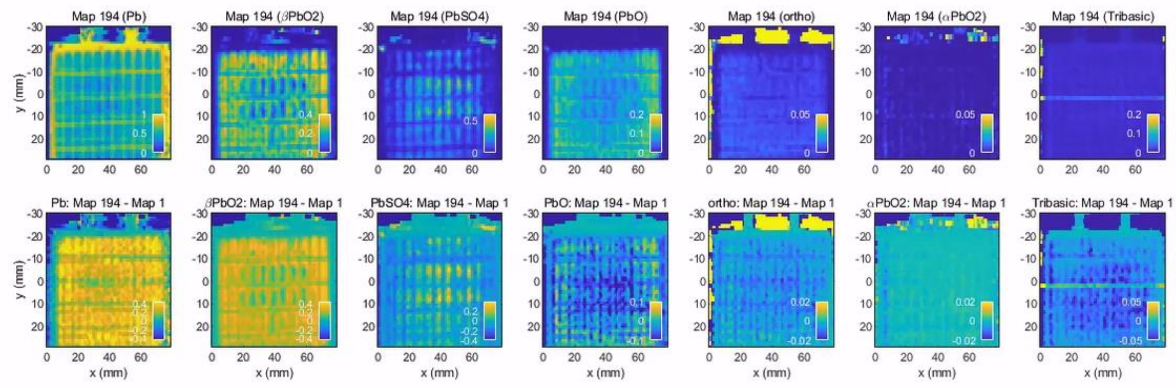


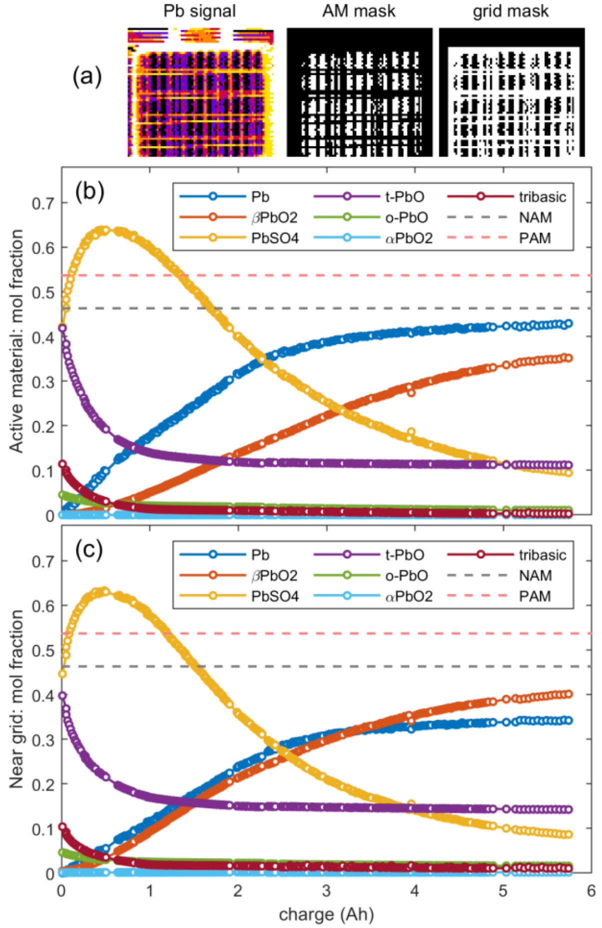
Differences in Pb NMR signal suggests varying $PbSO_4$ morphology between batteries and at different points in each plate.

FORMATION

XRD from electrode *and* electrolyte species

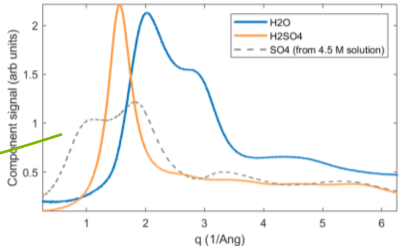
- XRD can also be used to study electrodes during operation.
- Example: formation on 2V electrodes provided by industry. Analysis shows that negative and positive form heterogeneously and at different overall rates.





Maps and overall trends in electrode species during formation

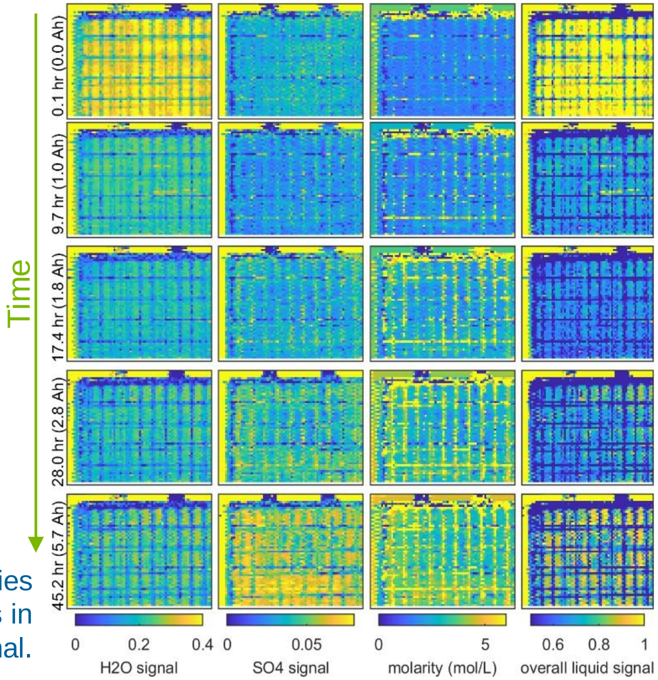
Electrolyte species used to co-refine XRD data.

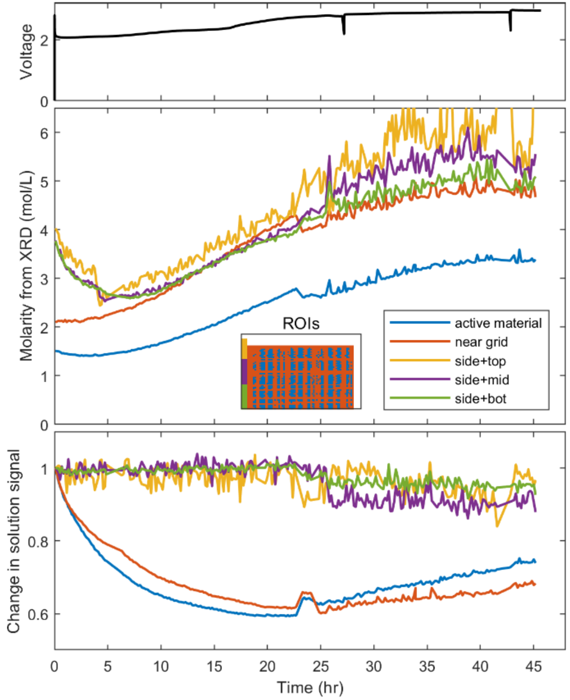


FORMATION

XRD from electrode *and* electrolyte species

- Scattering from solution species (previous slides) allowed further analysis to include changes in electrolyte species.
- This showed that both the concentration AND the amount of electrolyte changes dramatically during formation.





Select maps of *electrolyte* species during formation. Right: trends in concentration and overall signal.

SUMMARY AND FUTURE WORK

LEAD ACID RESEARCH

FY22: new research directions

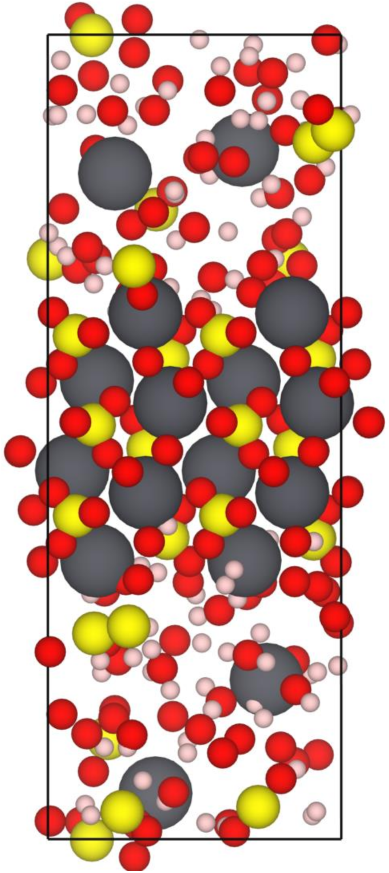
Using methods developed in previous years:

Molecular studies: improving utilization, power density

- Effect of lignins on $PbSO_4$ nucleation and growth.
- Analyze sulfuric acid with varying temperature to understand structural origins of its deep eutectic point.
- Incorporate first principles calculations into both.

Pack level: improving cycle-life

- Incorporate new industry partners (East Penn Manufacturing)
- Sulfation: analyze $PbSO_4$ morphology and size distribution in batteries at end-of-life.
- Positive failure modes: identify $Pb/PbO_x/PbO_2$ structures associated with PAM paste adhesion and the corrosion layer.



AIMD simulation of $PbSO_4$ growth in solution

ACKNOWLEDGEMENTS

- Dr. Imre Gyuk and U.S. Department of Energy’s Office of Electricity Cost-Competitive Energy Storage program (Contract no. 57558)
- DOE User Facilities
  - APS: sectors 11ID, 6ID, 33ID
  - PNNL: EMSL
- Industrial collaborators: Ecobat and East Penn Manufacturing