Advancing lead acid batteries for grid resilience

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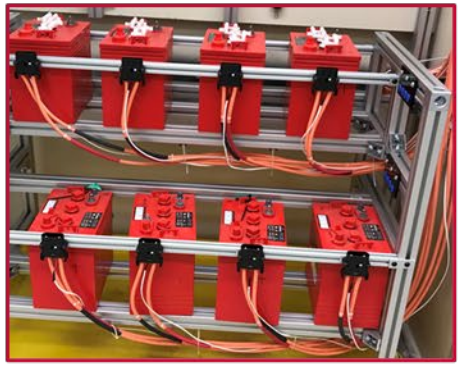
PNNL is operated by Battelle for the U.S. Department of Energy

Project Overview

- **Project Goal:** The goal of this project is to understand the failure mechanisms of lead acid batteries that are hampering its application for resilient grid scale energy storage applications and use this information to discover new additive materials and processes for improving its performance.
- **Current Practice:** Currently lead acid batteries are suitable for automotive and backup power applications owing to limited cycle life and depth of discharge. Recent research have focused on enhancing active cell components, optimizing cell geometries and designs, and integrating carbon additives to leverage complementary charge storage mechanisms without fully understanding the failure mechanisms.
- **Why PNNL:** Understanding the mechanistic details of factors limiting the performance of lead acid batteries requires a multiscale and multimodal characterization approach that combines macroscopic, microscopic, and molecular-scale analyses. PNNL (collaboration with ANL) have the required capabilities and deep expertise in solving multiscale problems using their unique in-situ and ex-situ spectroscopy, microscopy and diffraction tools.
- **Innovation:** Our innovative approach combines the top-down macromolecular scale materials characterization with the bottom-up atomic to molecular scale synthesis and characterization approaches to understand complex nucleation and dissolution processes occurring at the liquid-solid and solid-solid interfaces under applied electrochemical and chemical gradients.
- **Impact:** By enabling lead acid batteries for grid storage applications, we can establish a 100 % US based energy storage technology with abundant availability of domestic raw materials, domestic manufacturing capabilities, and mature recycling infrastructure.
- **Alignment:** This project is accelerating the development and testing of lead acid storage technology that is more cost-effective, safe, and durable, which is crucial to meeting the Administration’s goal of providing affordable, secure, and reliable energy.

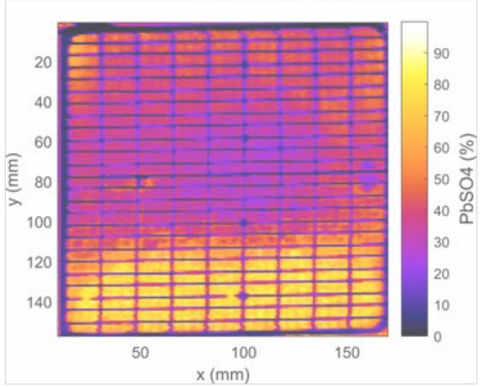
Understanding the Electrode and Electrolyte Degradation Across Length Scales

Battery pack



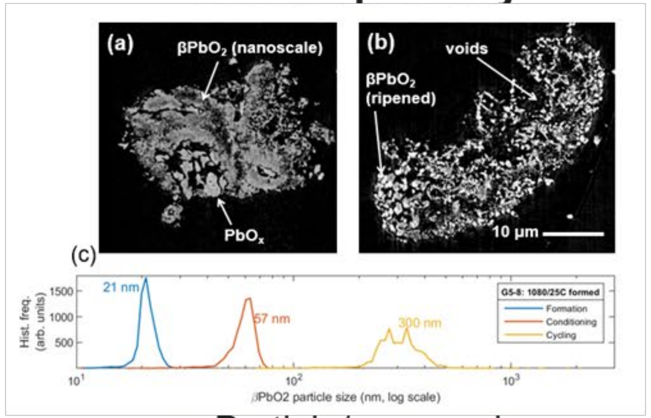
Optimized cycling parameters and electrochemical signatures for emerging failure modes

Electrodes



~mm: Continuum level challenges: diffusion, stratification, impedance

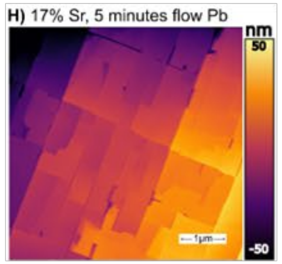
Particle/porosity



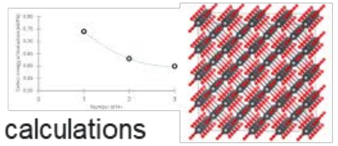
~µm: Particle/pore scale changes: surface area, tortuosity, local pH/ solubility

Atomistic

AFM during $PbSO_4$ growth on $(Ba,Sr)SO_4$ 210

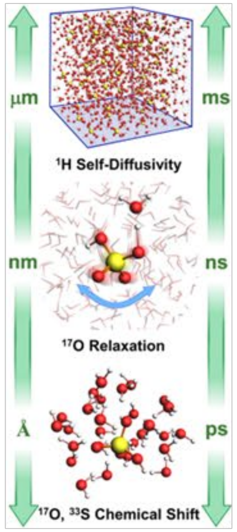


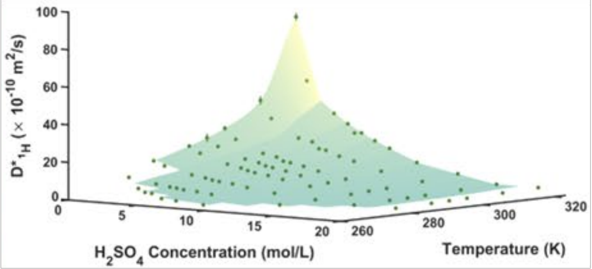
Lattice constant changes and DFT calculations

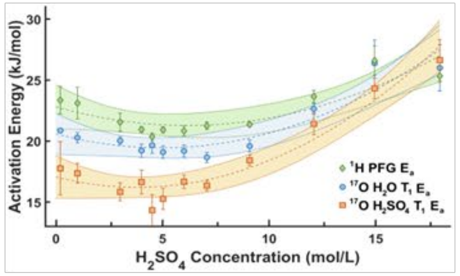


~nm: Interfacial nucleation, lattice defects, adsorption

Electrolyte

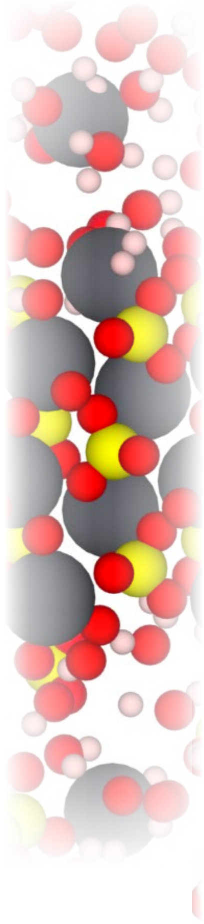






~Å – µm and ms – ps (time scale): Continuum level challenges: diffusion, stratification, impedance

Building Molecular-scale Framework: Past and Present Publications



2021 – Bazak 2021: NMR of sulfuric acid, J Phys Chem B

2022 – Kinnibrugh 2022: x-ray scattering - structure of sulfuric acid solution; J. Phys Chem B

2023 – Legg 2023: $PbSO_4$ nucleation on $BaSO_4$ 001; ACS App. Mat. Interfaces

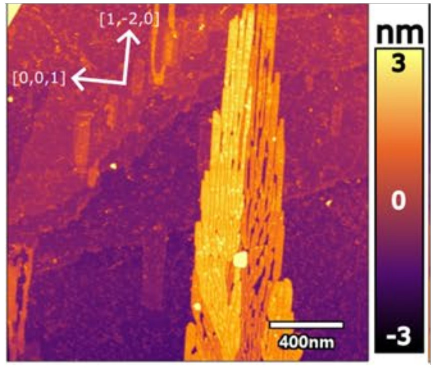
2024 – Knehr 2024: Role of $Pb/PbSO_4$ morphology on DCA; J. Elec. Society

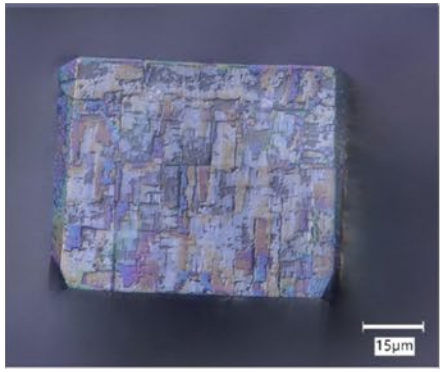
Kinnibrugh 2024: Pb_2O_3 and Pb_3O_5 crystal structure, spectroscopy; J Inor. Chem

2025 – Campbell 2025 $(Ba,Sr)SO_4$ materials, 210 surface; Small

Garcia 2025 (submitted): DFT of lattice defects in α, β PbO_2

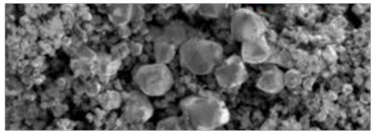
FY2025: Research Focus is on Designing and Evaluating High-performance Electrodes



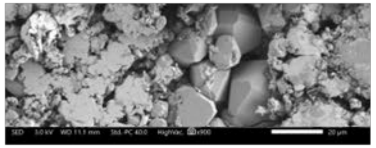


Designing new barite expander and performance testing by Industry partner

NAM Top



NAM Bottom



Evaluating electrode paste formulations for deep cycling using spectroscopic and microscopic analysis

Surface nucleation

Bulk sulfation

Electrodes

Cells/batteries

Sub-micron to microscopic scale

Macroscopic to sub-micron scale

Bottom up

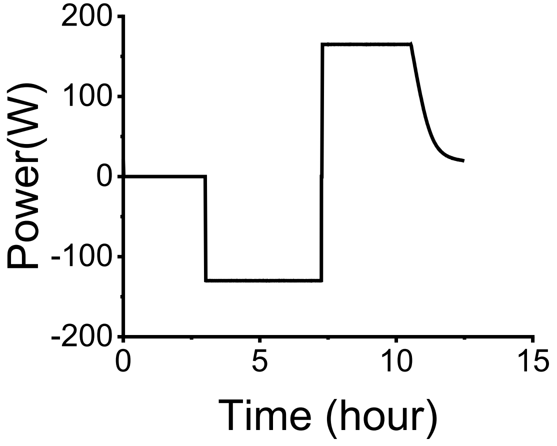
Top down

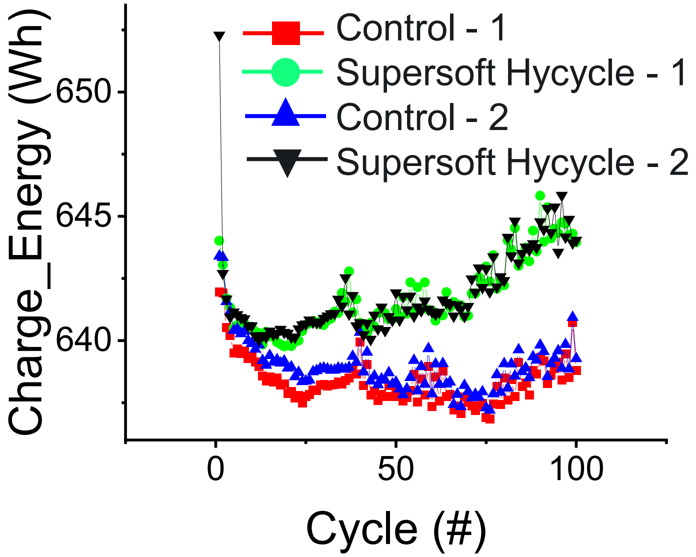
Deep-cycle Testing of Paste Formulations

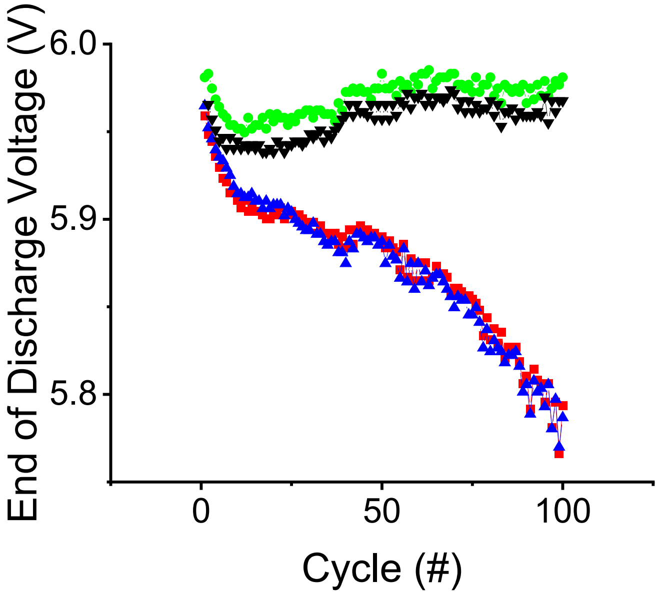
Pacific Northwest NATIONAL LABORATORY

ecobat

Cell Testing and Materials Analysis of Industry-Developed Electrodes







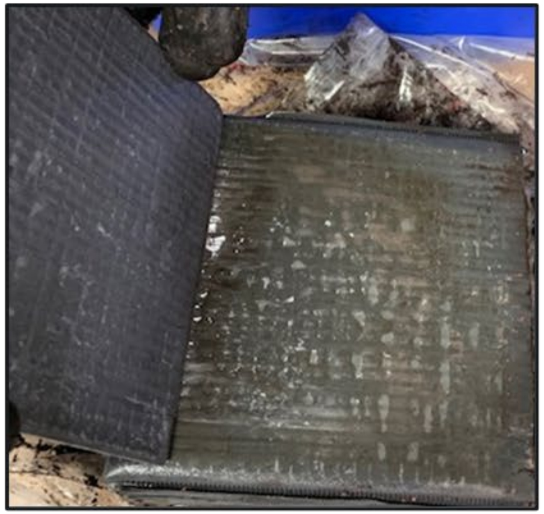
Production batteries from OEMs were subjected to aggressive deep-cycling protocols

Both control batteries and those with a paste formulation specialized for deep cycling – 'SuperSoft Hycycle' (SSHC) were tested

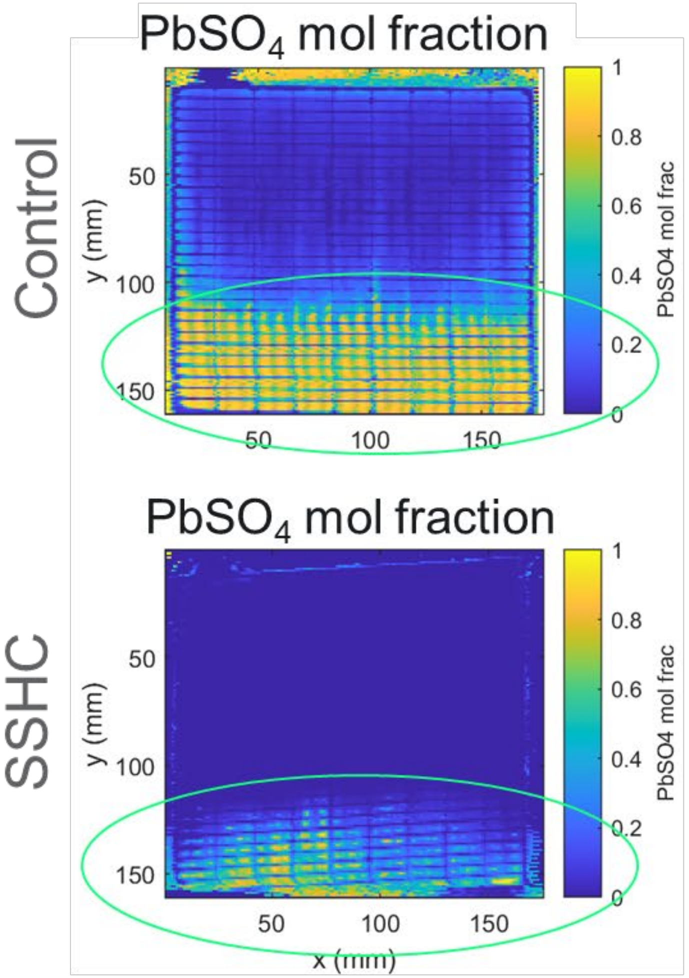
Supersoft Hycycle shows better overall performance with stable discharge, voltage and current characteristics

We are focusing on mechanistic understanding of these commercial grade paste formulations

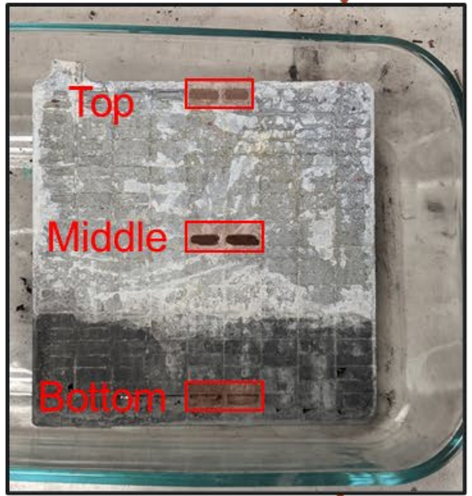
End of Life Phase Distribution in Negative Electrode: High Resolution X-ray Diffraction Maps



Post-mortem disassembly yielded electrode plates at ANL which were analyzed with XRD diffraction mapping (ANL) and NMR, XPS and SEM (PNNL)

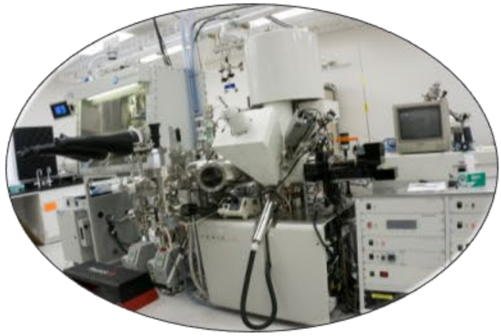


ANL

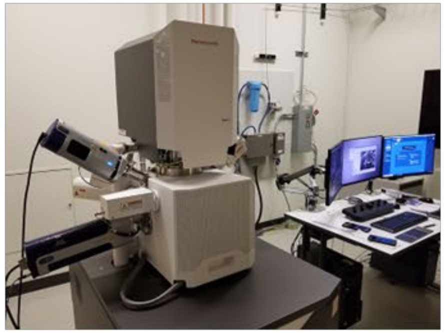


Short range structure ~Å to nm

Surface chemistry < 5 nm



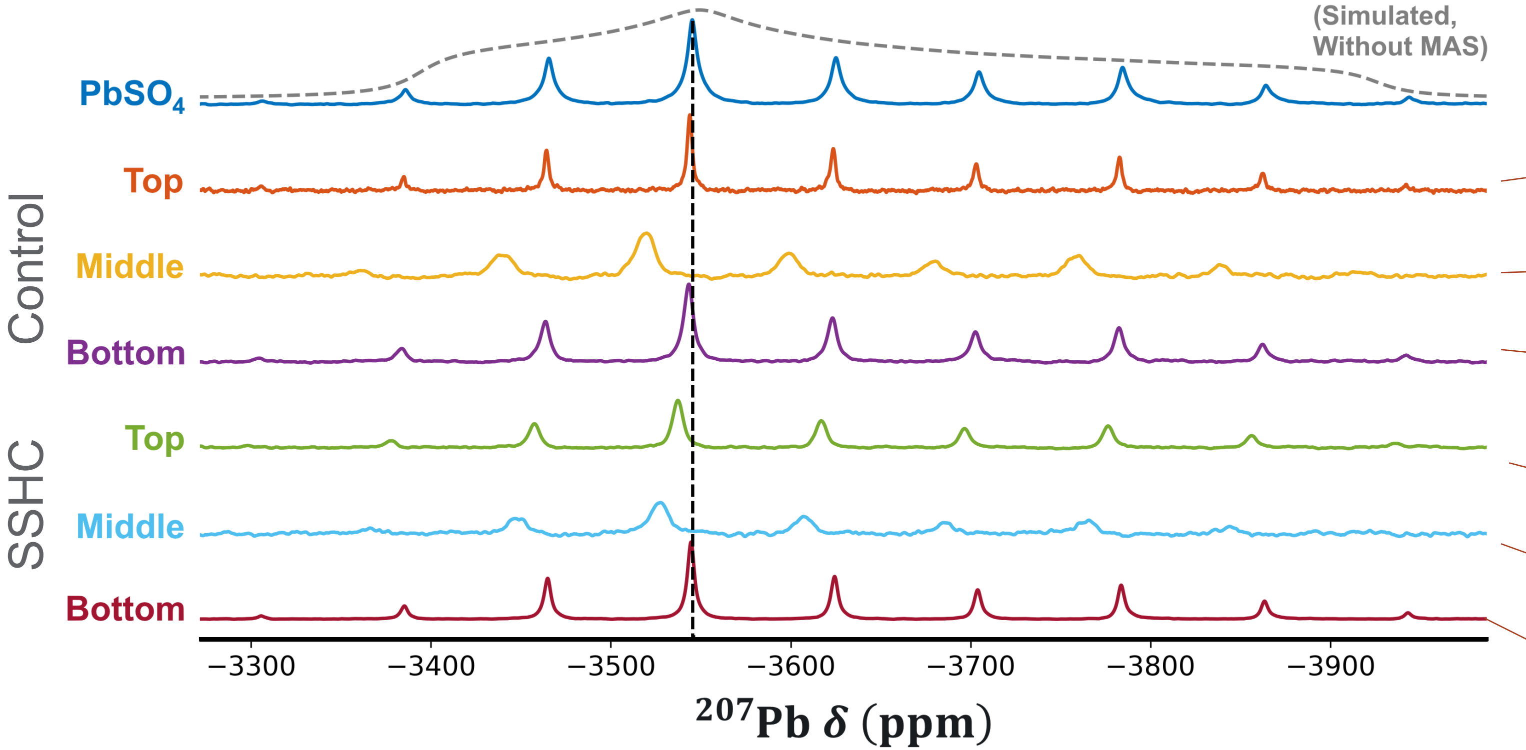
Surface morphology < nm - µm

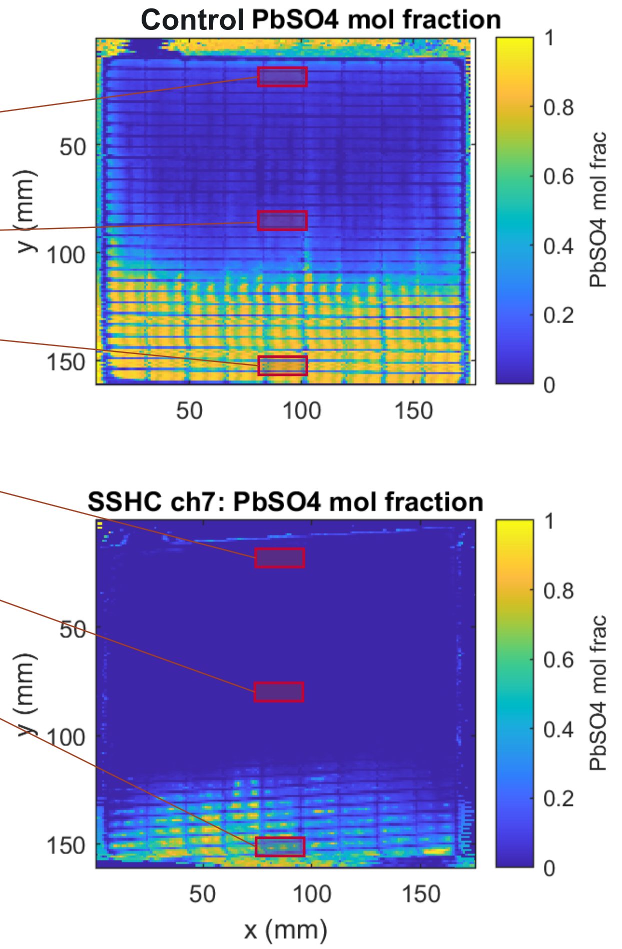


Diffraction mapping reveals large, ordered $PbSO_4$ domains which depict higher stratification in control sample and better performance in Supersoft Hycycle (SSHC)

Deep cycle sulfation: Local structural order by NMR

^{207}Pb solid-state NMR reveals disordered $PbSO_4$ phase typically invisible to X-ray diffraction mapping



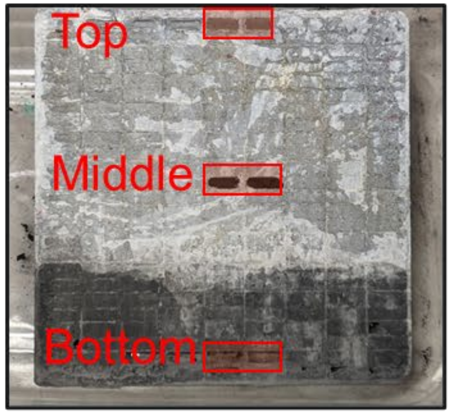


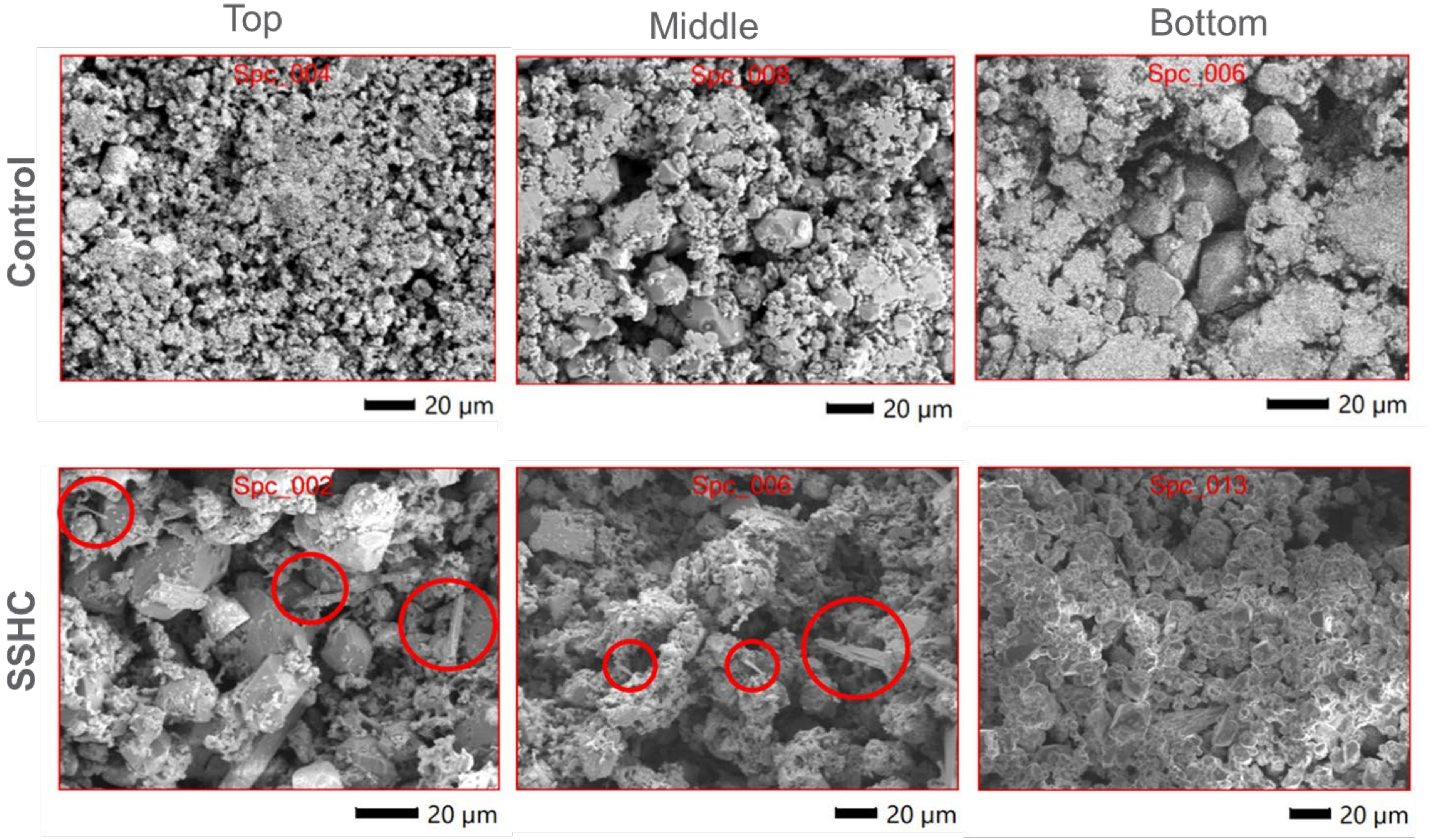
Diffraction Maps (ANL)

- $PbSO_4$ is detected even where the diffraction maps are blank
- Deviation from the 'ideal' $PbSO_4$ line shape indicates more disordered/ smaller sulfation domains
- SSHC yields less – and smaller domain – $PbSO_4$ than the baseline samples at the top and middle of the plate; strong tideline formation evident in bottom indicating stratification

Deep cycle sulfation: Morphological characteristics by SEM

Negative Electrode

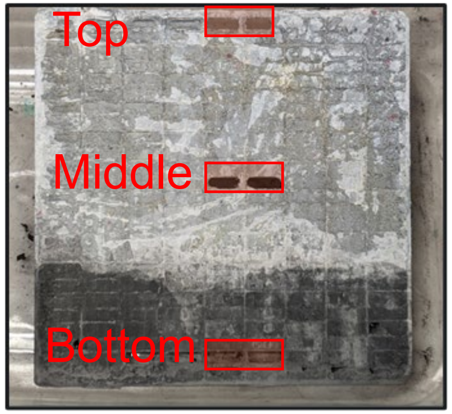


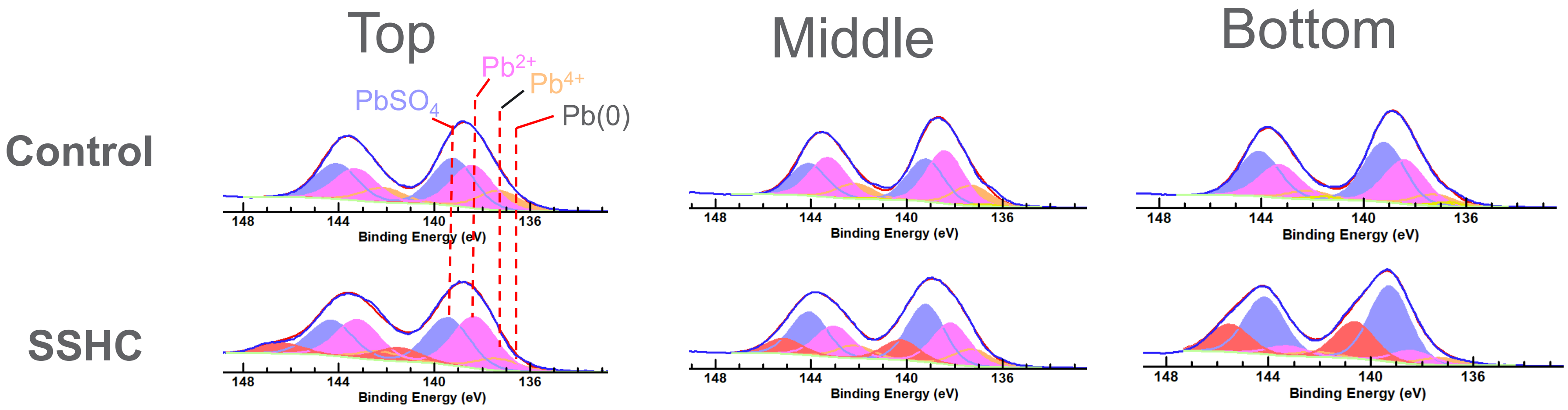


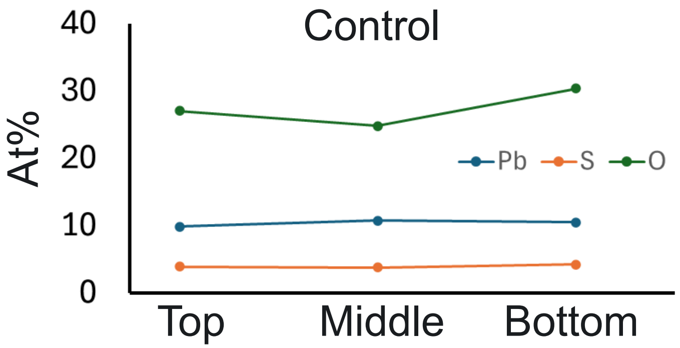
Morphology of particles in negative electrodes show smaller crystals at the bottom of the plate along with spiky features not observed in control samples

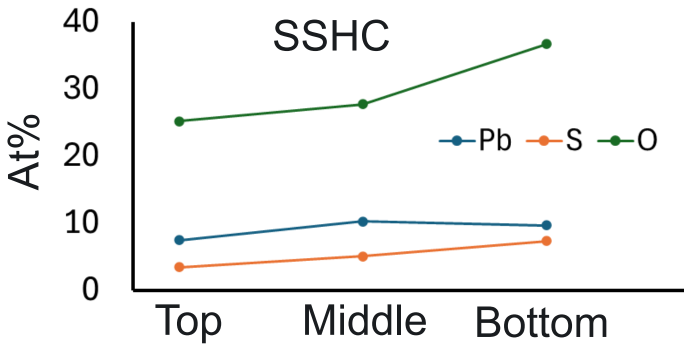
Deep cycle sulfation: Elemental Speciation by XPS

Negative Electrode





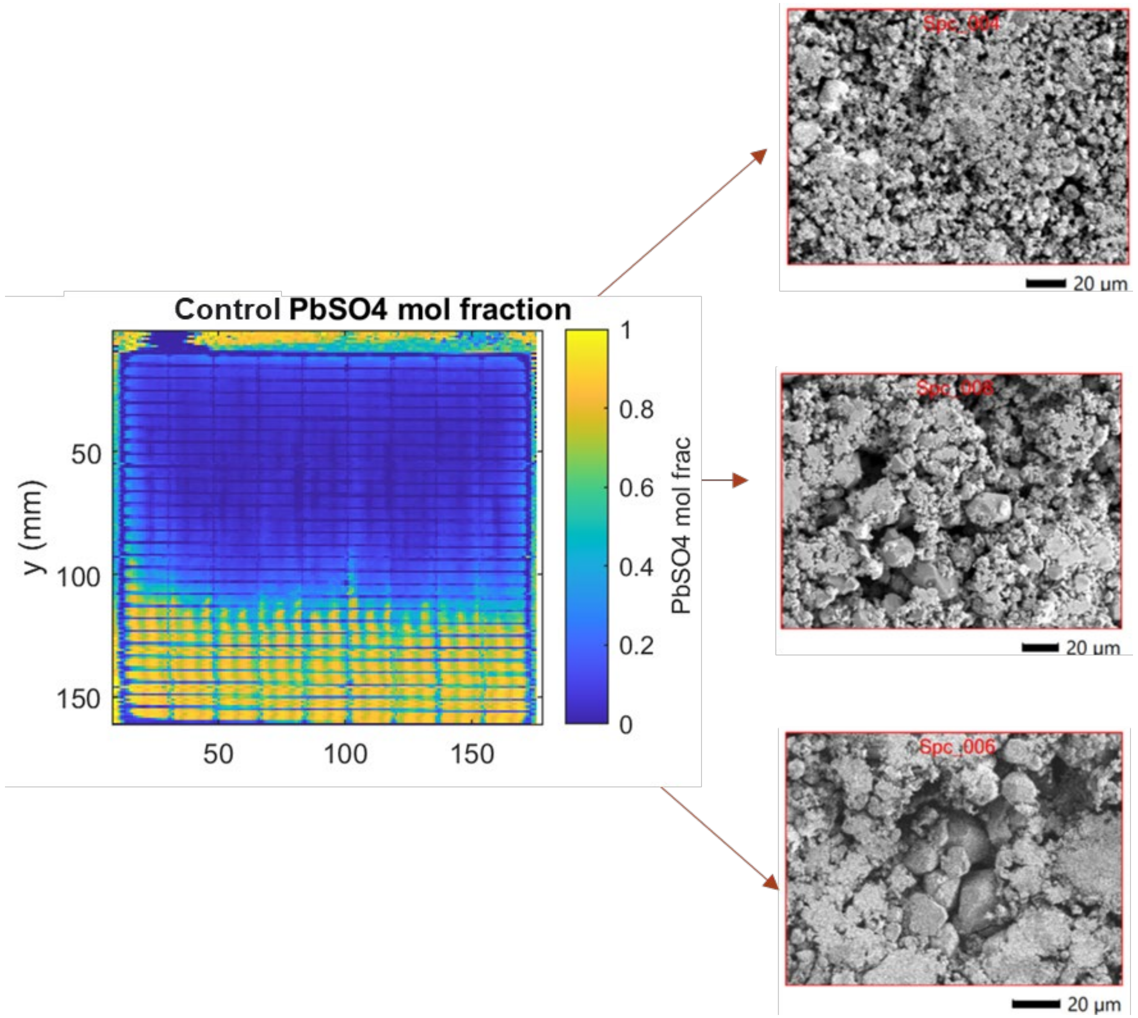




- XPS confirms the presence of $PbSO_4$ in all locations in agreement with NMR
- $PbSO_4$ speciation higher in bottom of all electrodes; unidentified form of Pb at higher binding energy in SSHC
- Minor changes in surface atomic composition, co-existence of complicated phases of PbO, PbO_2, $PbSO_4$ and others

Summary

- Multiscale characterization of the cycled battery allows better analysis of the failure modes
- Sulfation of negative electrode and electrolyte stratification was higher in control samples
- NMR and XPS shows sulfation throughout the electrode even where diffraction maps were blank
- Top and bottom electrodes show disordered and smaller domain sizes of $PbSO_4$, respectively indicating that ordered $PbSO_4$ may be inactive or less active in comparison



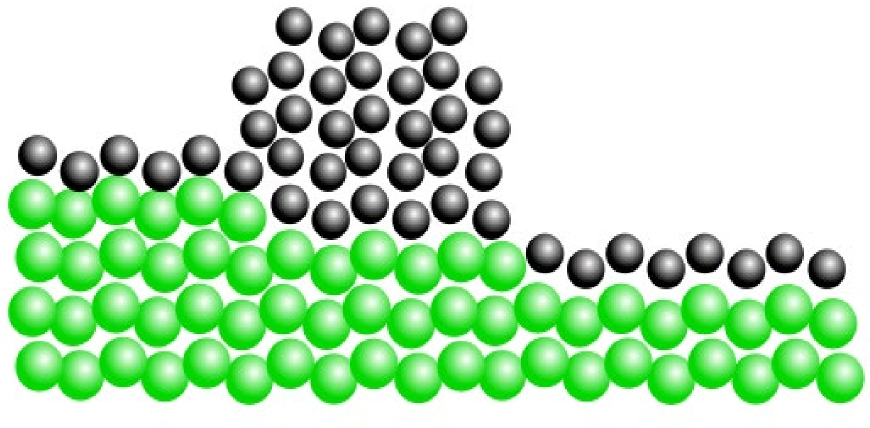
Controlling reversible sulfation

A bottom-up approach

Stranski Krastanov Growth

(Frustrated islands over monolayer)

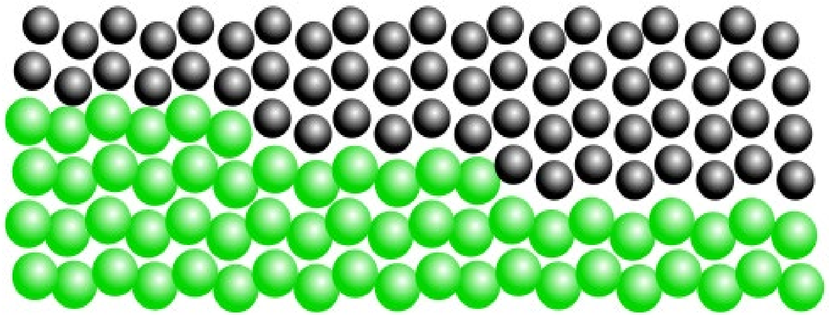
High strain (traditional barite)



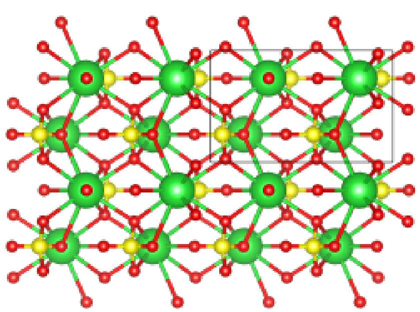
Frank-Van der Merwe Growth

(Layer by layer)

Low strain (engineered barite)

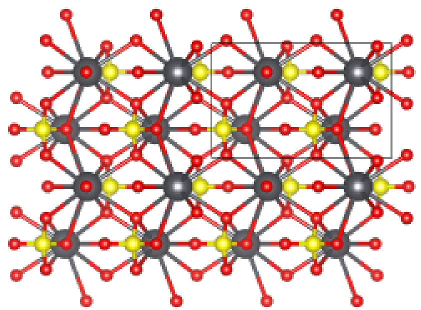


Pb-Acid Battery Technical Challenges at Negative Electrode



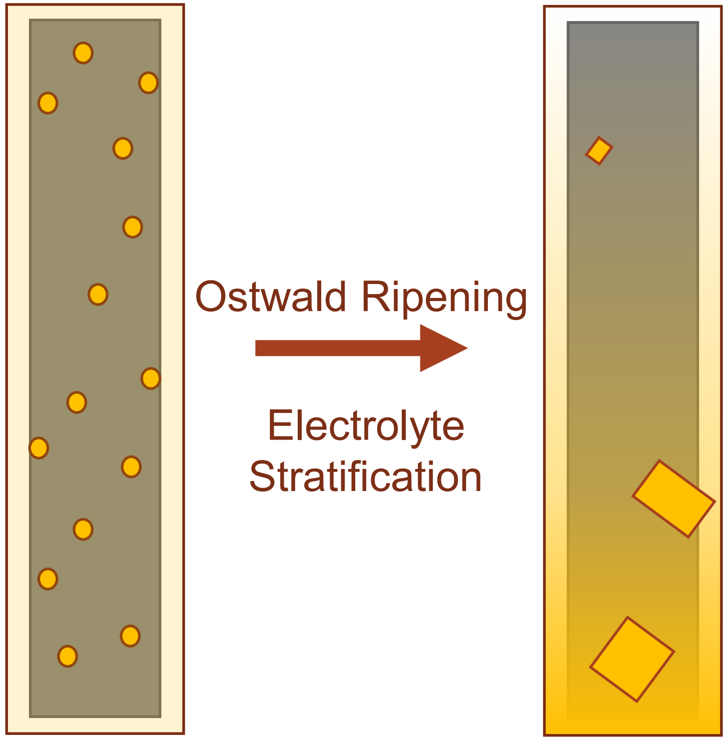
Barite ($BaSO_4$)

a = 8.88 Å
b = 5.46 Å
c = 7.16 Å



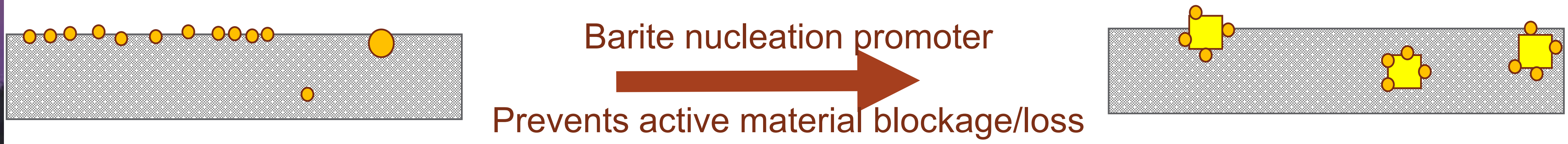
Anglesite ($PbSO_4$)

a = 8.48 Å (4.7% misfit)
b = 5.40 Å (1.1% misfit)
c = 6.96 Å (2.8% misfit)



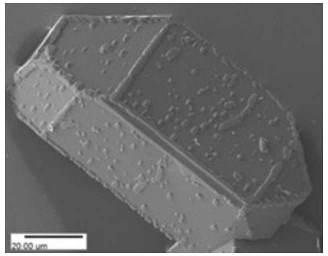
- Sulfation!
  - Electrolyte stratification
  - PSoC storage/use
  - DoD limitations

- **For grid scale storage applications, need to better address sulfation, extend cycle life**

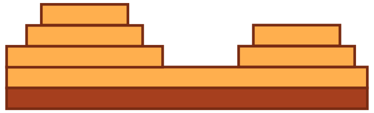


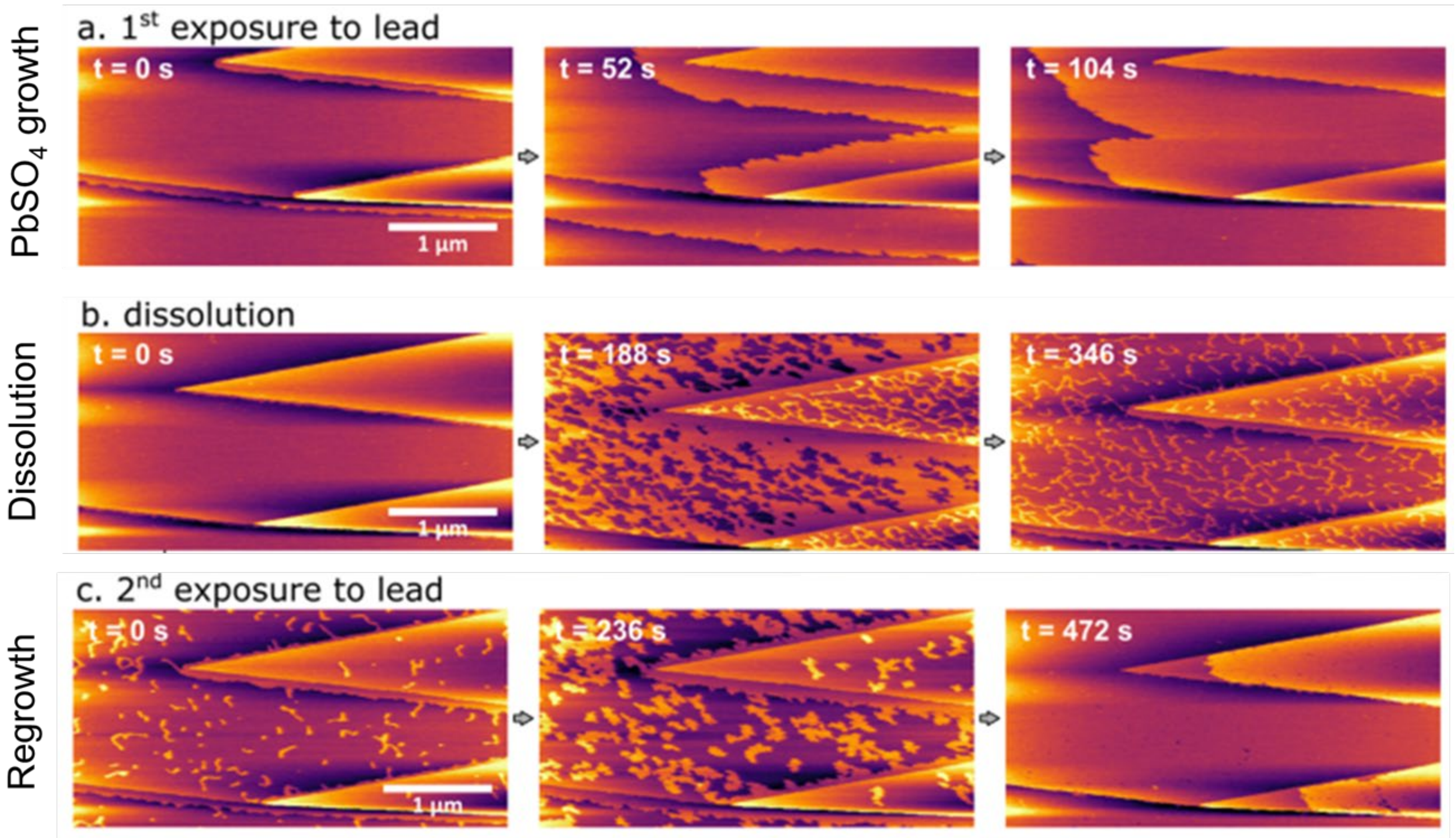
Nucleation and Growth of $PbSO_4$ on Cleaved Barite

- Cleaved natural barite sample
  - Monolayer film growth in response to 9 μM $Pb(NO_3)_2$ and 100 mM H_2SO_4
  - Subsaturated solution!



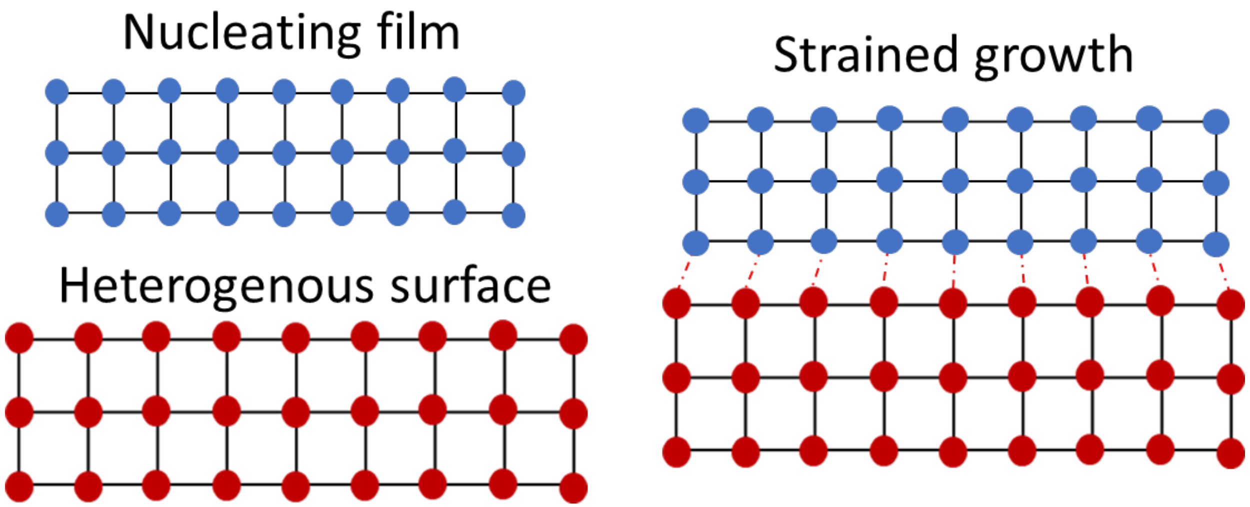
Stranski-Krastanov

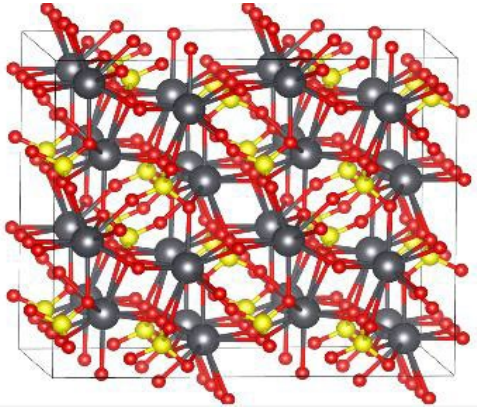




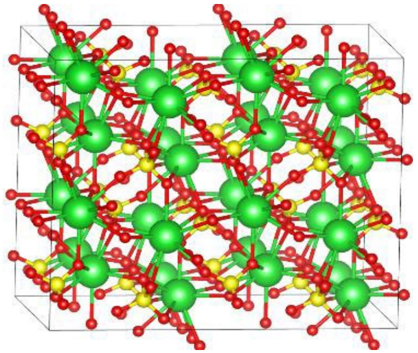
ACS applied Materials and Interfaces 2023

Strain Engineering to Control $PbSO_4$

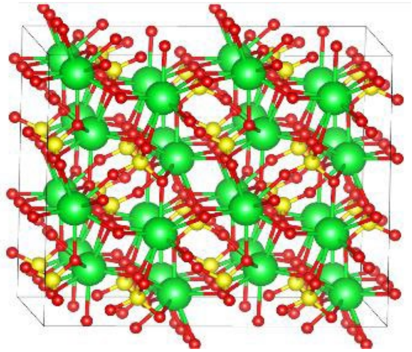




Anglesite ($PbSO_4$)
a: 8.48 Å, b: 5.40 Å, c: 6.96 Å



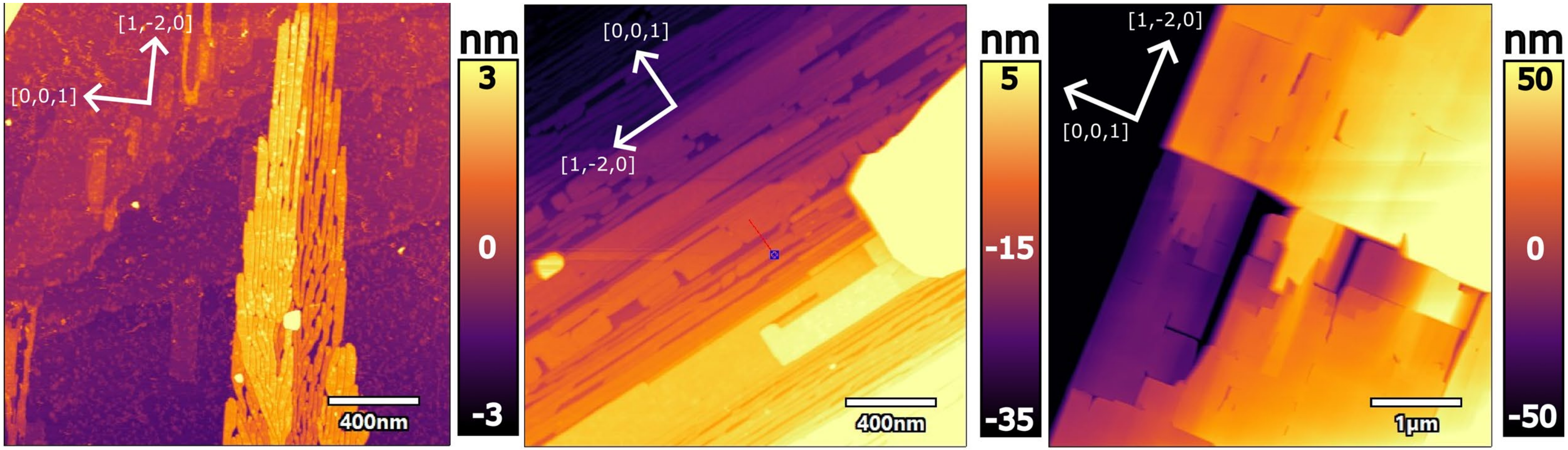
Barite ($BaSO_4$)
a: 8.88 Å **(+4.8% mismatch)**, b: 5.46 Å **(+1.1%)**, c: 7.16 Å **(+2.9%)**



Celestite ($SrSO_4$)
a: 8.37 Å **(-1.3%)**, b: 5.36 Å **(-0.8%)**, c: 6.87 Å **(-1.3%)**

Doped Sr:$BaSO_4$ – Dopant Concentration Dependent Growth

$BaSO_4$ | 6% Sr-$BaSO_4$ | 17% Sr-$BaSO_4$



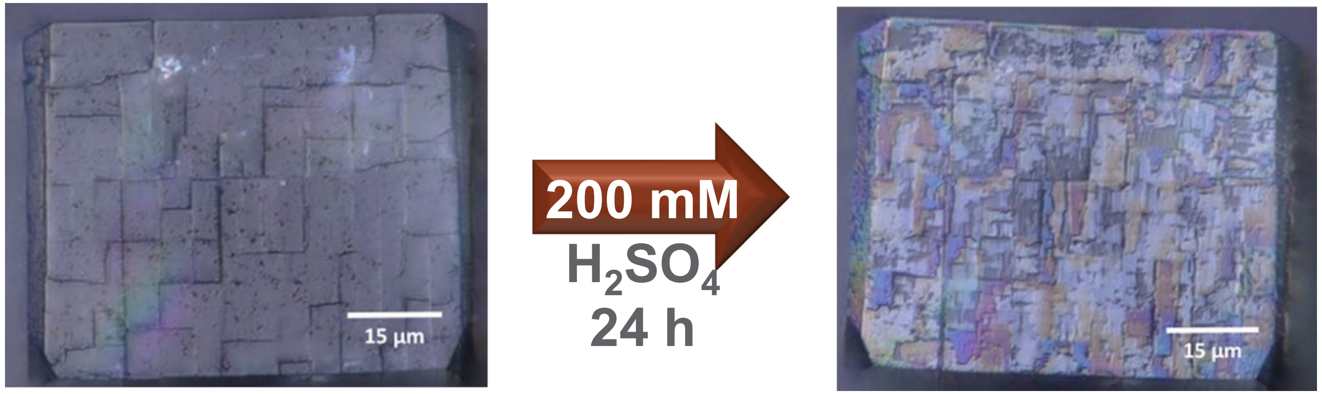
In –situ AFM images shows a drastic difference in the film growth behavior over pure and doped barite surfaces

Small 2025

Atomic Scale to Macroscopic Scale

- Ex-situ optical microscopy confirms the layer-by-layer growth of PbSO4 on Sr doped barite compared to island growth on barite

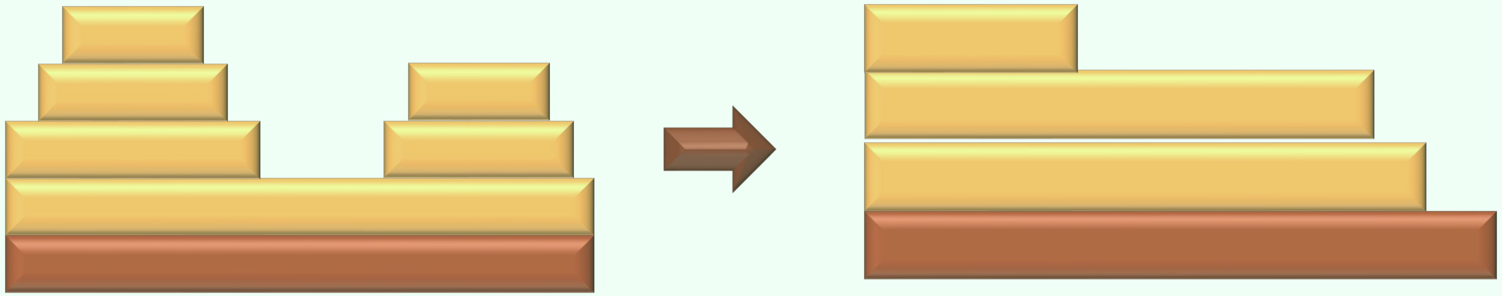
Ex- situ optical microscopy



17%Sr-$BaSO_4$ | $PbSO_4$ on 17%Sr-$BaSO_4$

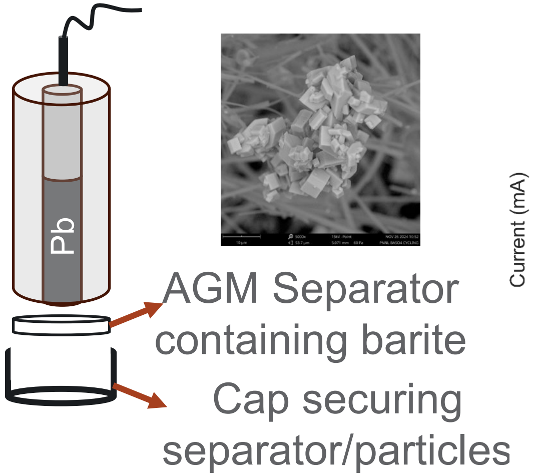
- Strain engineering by doping is able to change the growth behavior from Stranski-Krastanov to Frank van-der-Merve

Stranski-Krastanov | **Frank van-der-Merwe**

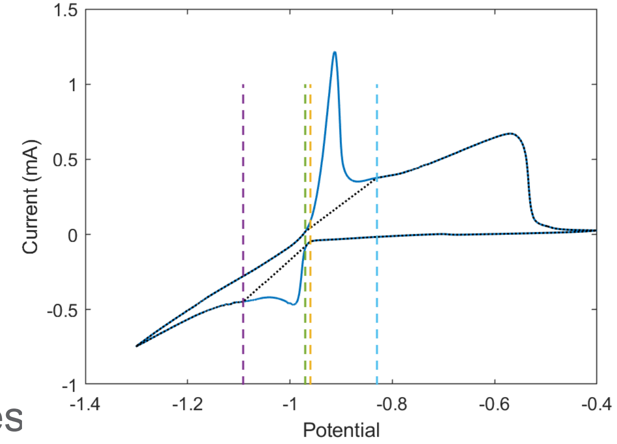


Testing PNNL Samples by Industry Partner – East Penn Manufacturing

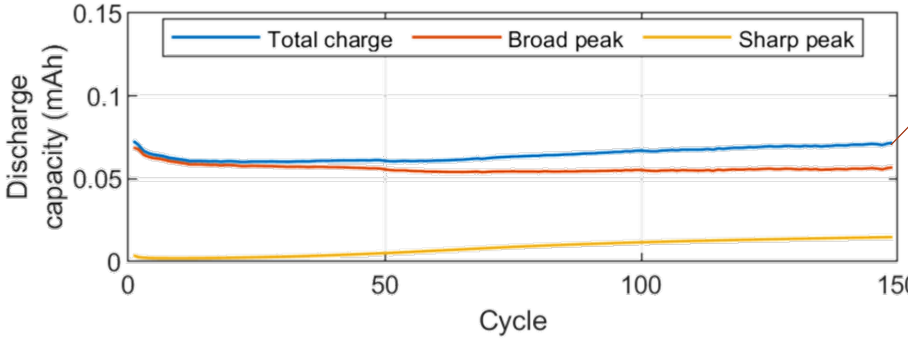
Component level testing of barites ($BaSO_4$): New test set up



Cyclic voltammetry

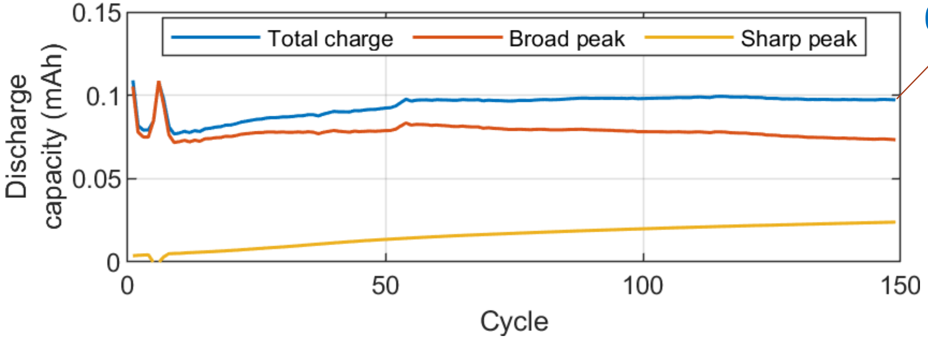


Industry Standard



0.05

PNNL (20%Sr)

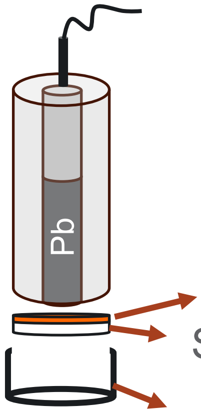


0.10

Approximately twofold capacity increase with PNNL 10% and 20% Sr $BaSO_4$ compared to the industry standard.

Testing PNNL Samples by Industry Partner – East Penn Manufacturing

Paste level performance of barites



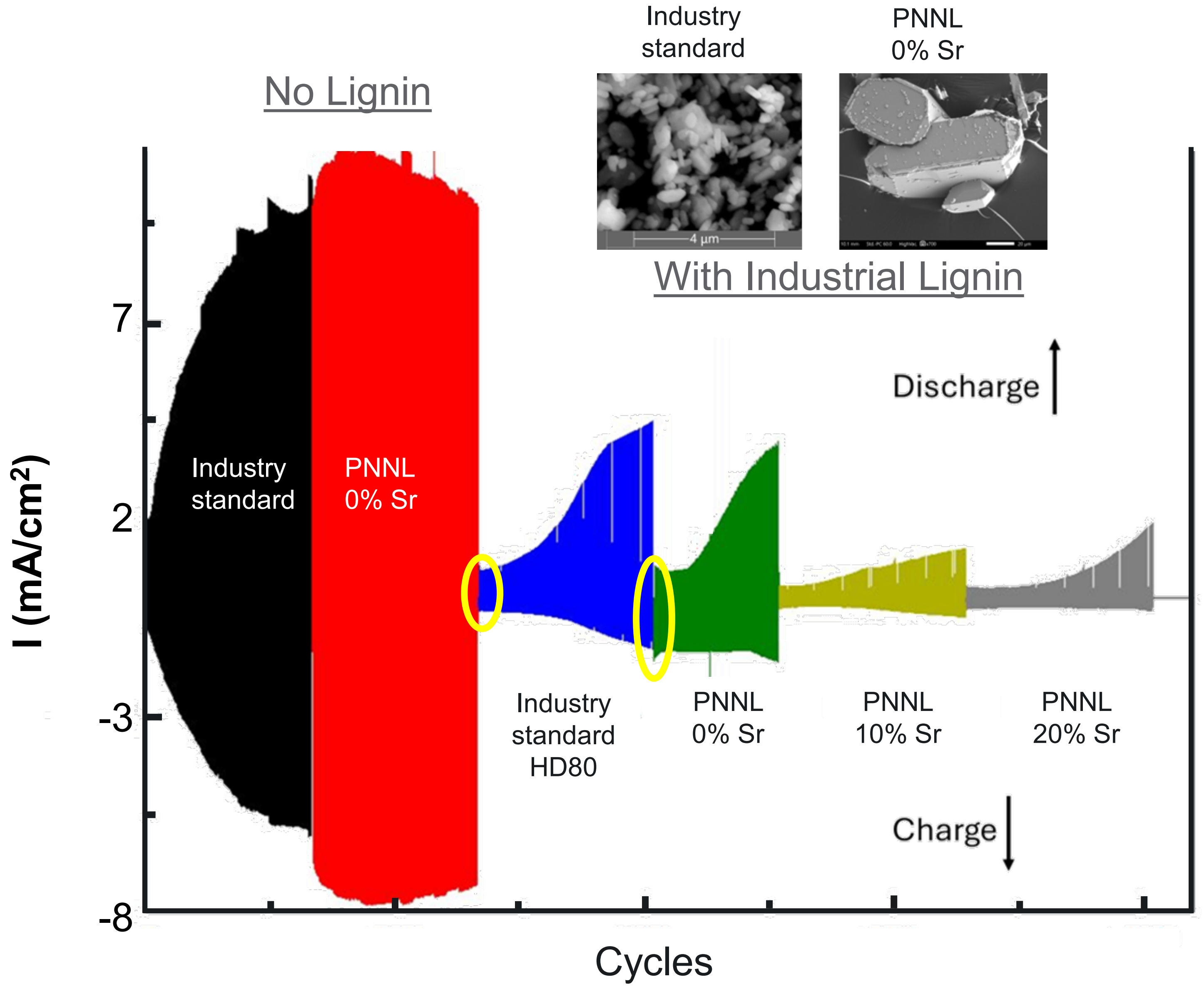
Paste mix composition

PbO + Carbon + additives

Paste-mix

Separator

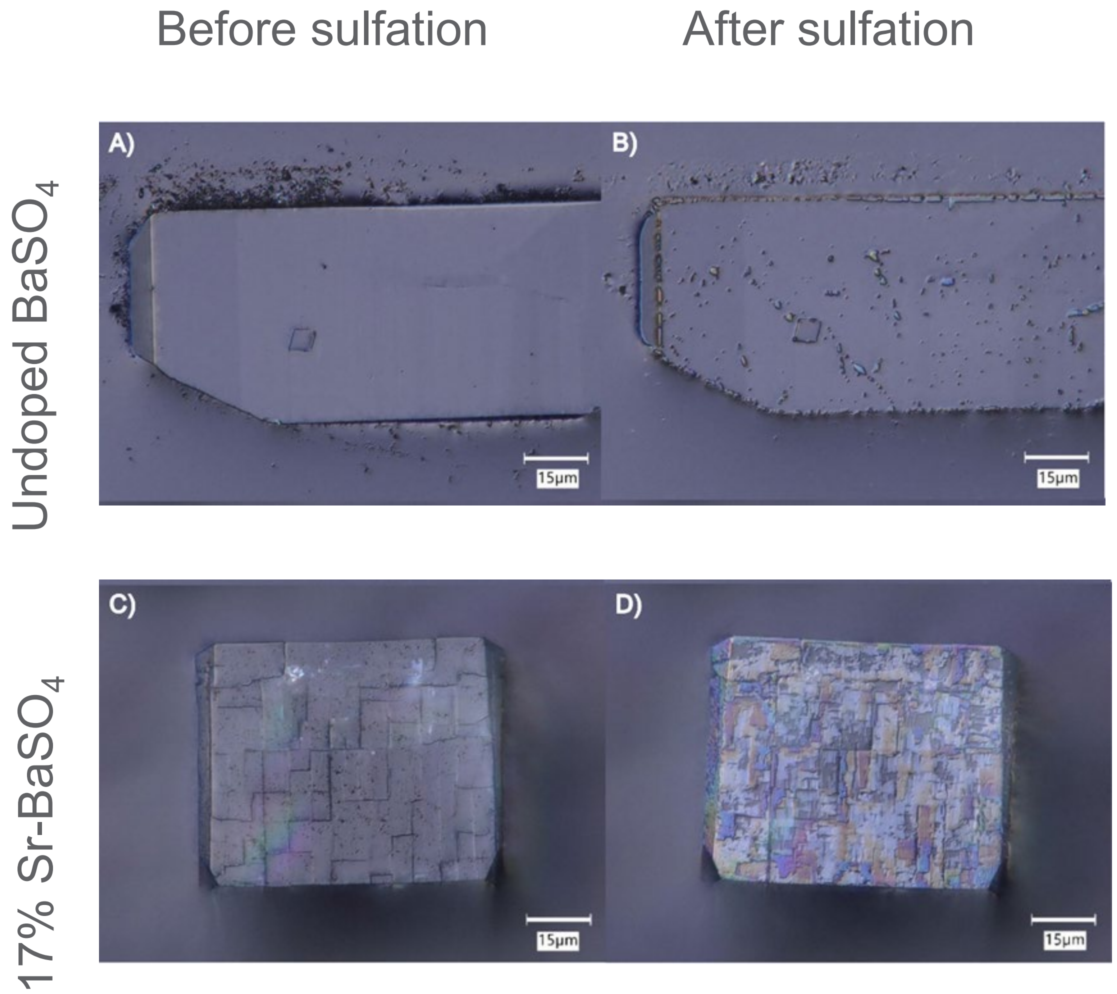
Cap securing separator/particles



Understanding the difference in performance in presence and absence of lignin is critical and could solve potential problems with sulfation of negative electrodes.

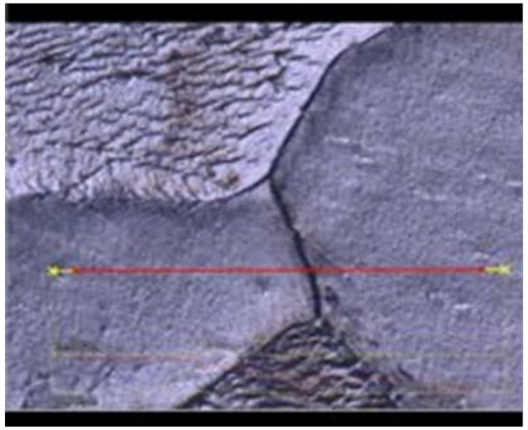
Summary

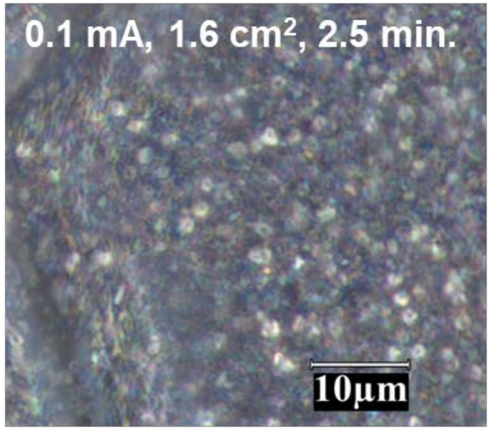
- Interfacial strain engineering by Sr doping in BaSO4 could promote nucleation of PbSO4
- Doping with Sr reduces strain energy by nearly 35% for the (001) and (210) surface
- Sample tested by industry partner East Penn Manufacturing showed tremendous promise upon testing at component level
- Presence of lignin leveled the doping advantage

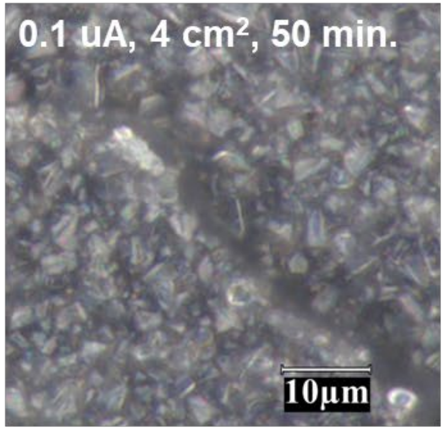


Current Studies - Understanding the Role of Lignin: Correlated Microscopy and Spectroscopy Studies

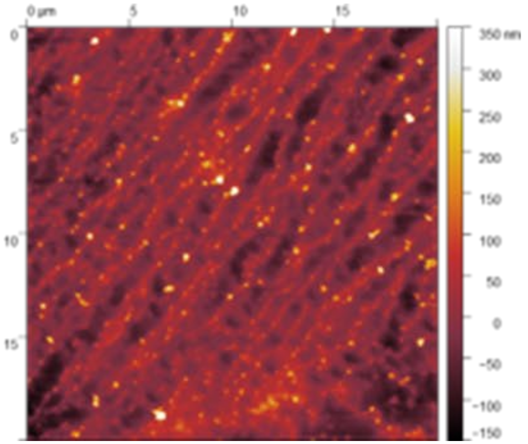
Optical microscopy
10s of μm

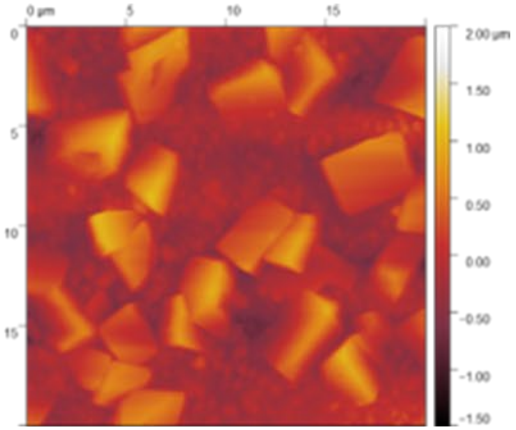


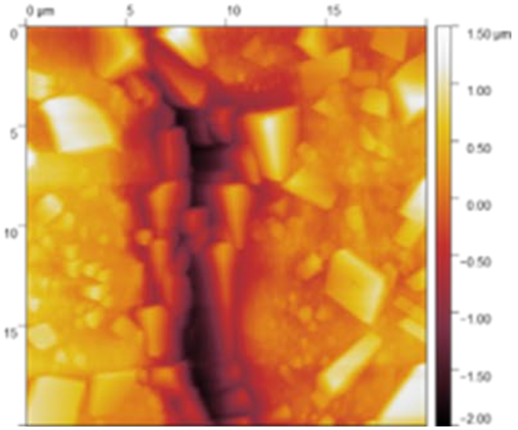




AFM microscopy
10s – 100s of nm







Ex-situ studies show correlative microscopy possible at different length scales to study sulfation of lead electrodes

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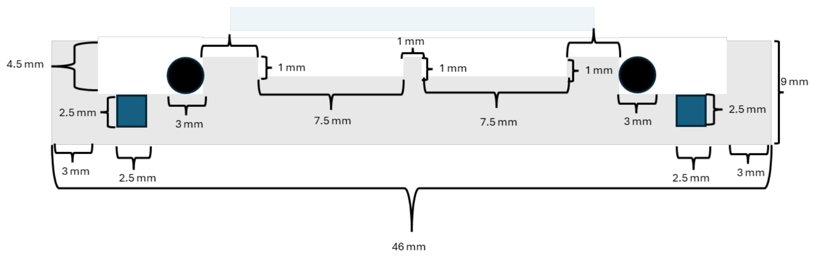
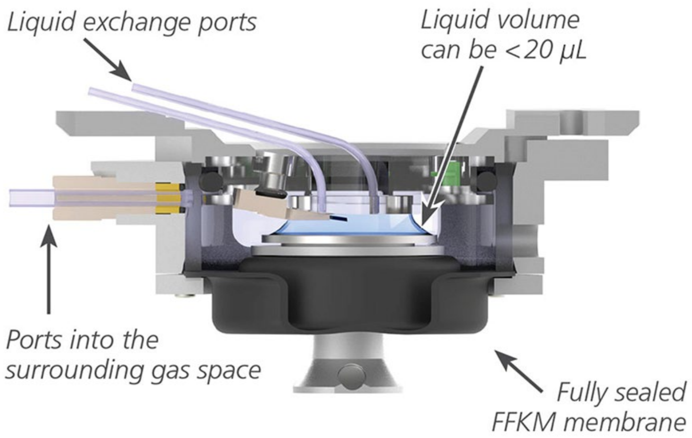
Current Studies - Understanding the Influence of Lignin: In-situ Optical and Atomic Force Microscopy studies

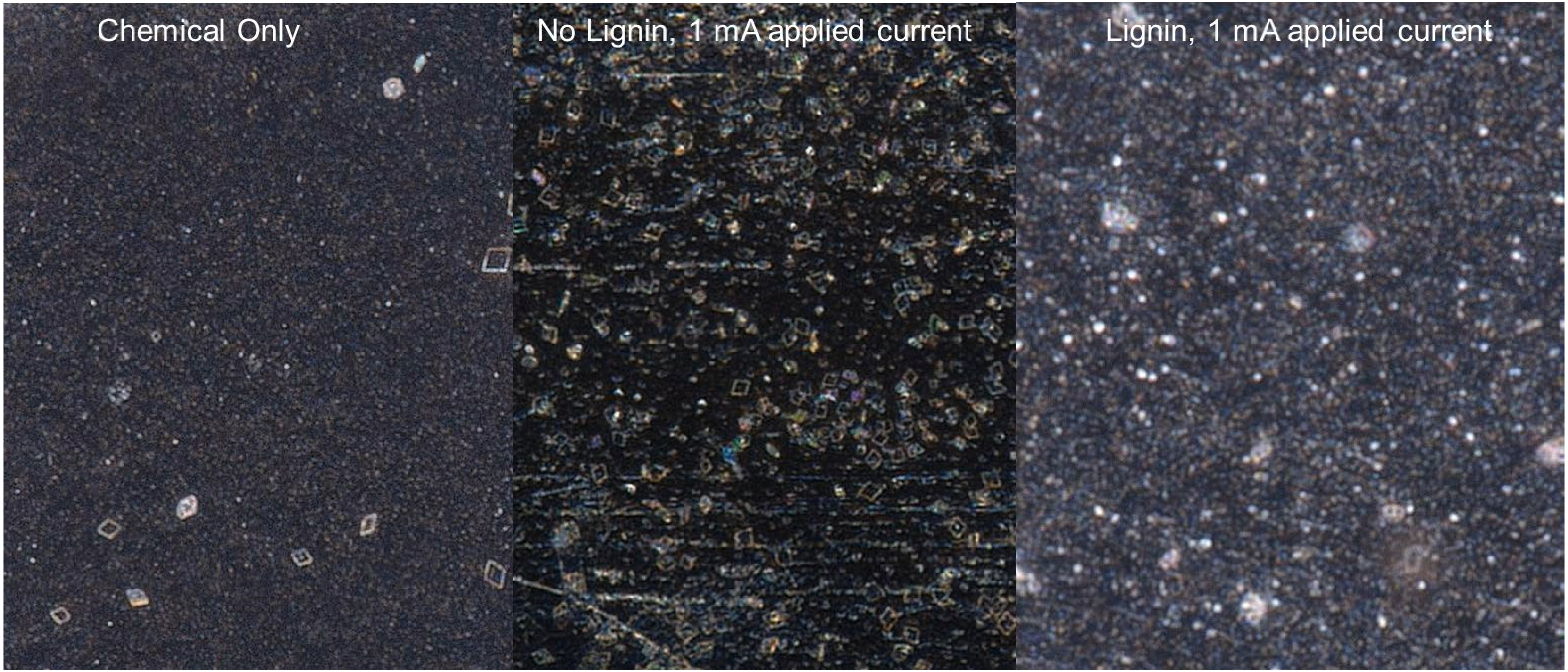
In-situ optical cell



In-situ electrochemical AFM cell

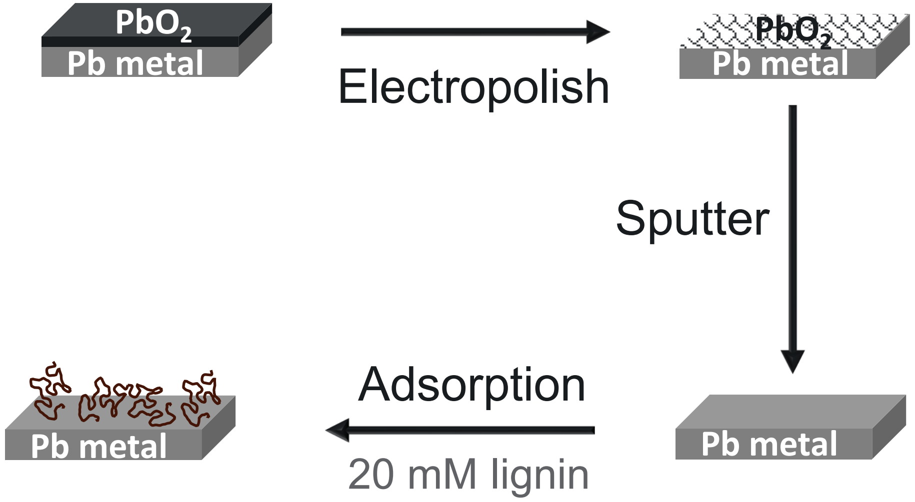


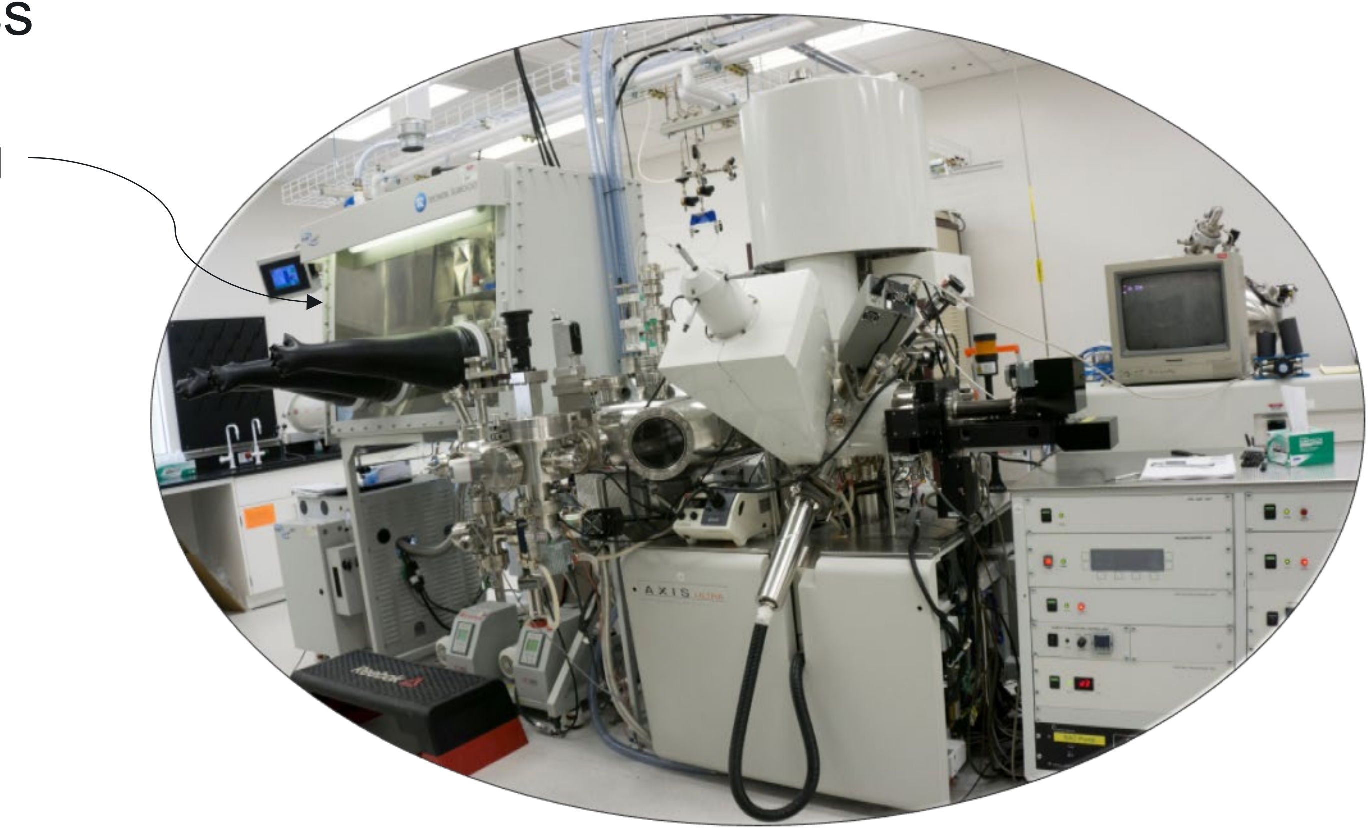
In-situ Observations of $PbSO_4$ Growth



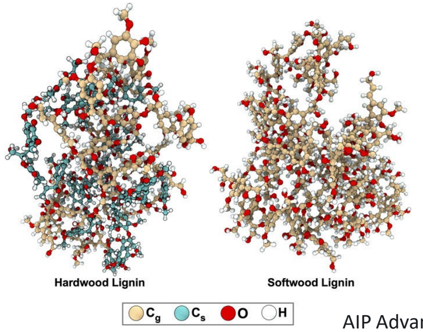
In-situ XPS Studies of Lignin Adsorption

In-situ lignin adsorption process





Lignin



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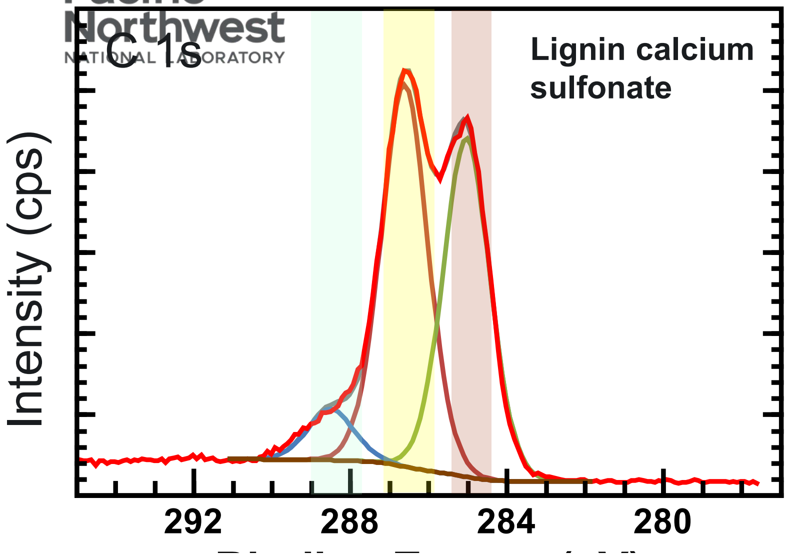
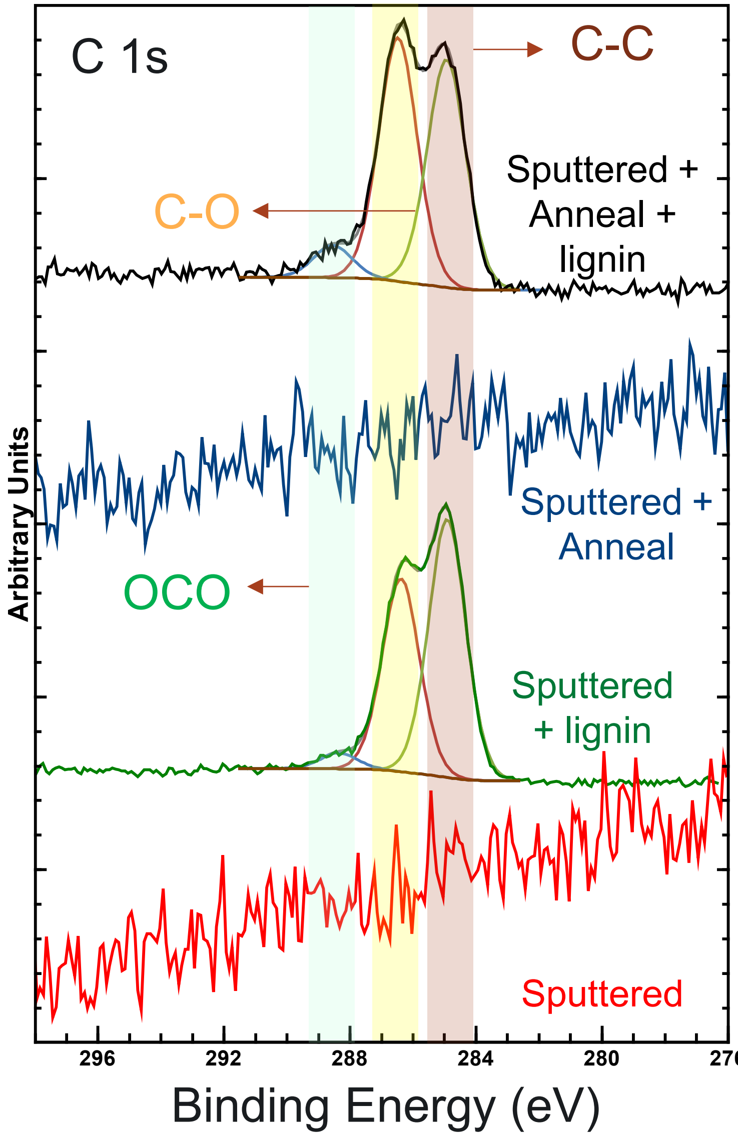
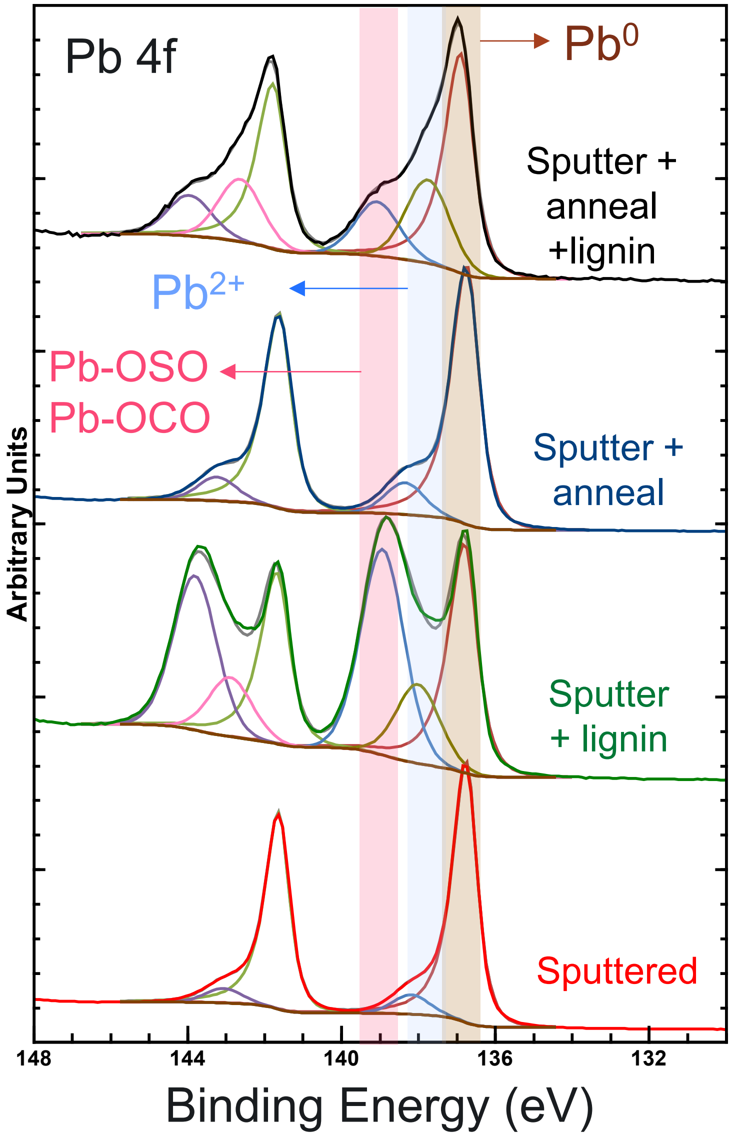
In-situ XPS Studies of Lignin Adsorption







Lignin binds strongly to lead metal surface; defects increases adsorption

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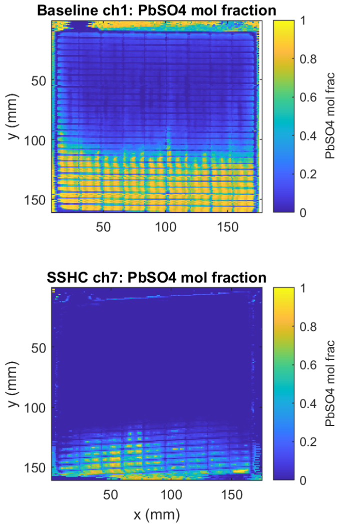
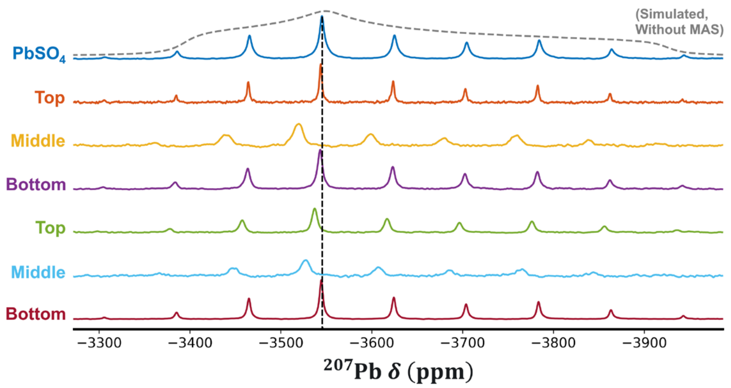
Enabling Pb-acid batteries for Grid resilience

Focused on identifying failure modes and new additive materials for enabling deep cycling of Pb-acid battery

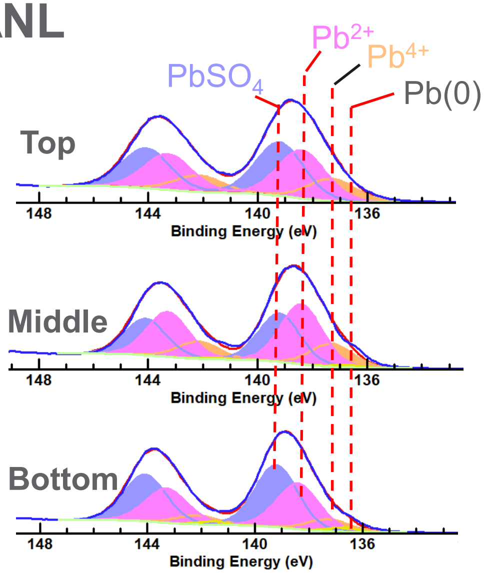
Multiscale analysis at PNNL and ANL



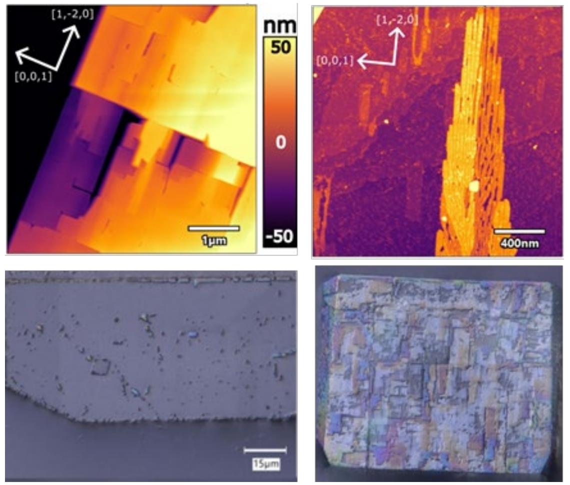
XRD maps of crystalline matter



NMR analysis of short-range order



Surface chemistry analysis



Nucleation and growth at different length scales

On-going Impactful Science for Pb-acid Technology

1. Multiscale analysis of cycled electrodes show differences in nature of $PbSO_4$ formed at different plate heights leading to different battery performance
2. Disordered and/or smaller sized $PbSO_4$ seems to be more active phase that is tied to better performance
3. Interfacial strain engineering by doping $BaSO_4$ with Sr changes the growth behavior from Stranski-Krastanov to Frank van-der-Merve leading to layer-by-layer growth improving its role as nucleating agent.

Acknowledgment

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- We acknowledge the support of our industry partners from East Penn Manufacturing for testing our materials.
- All PNNL, ANL and industry contributors

Thank you