# Demystifying Additives and Expanders in Lead-Acid Batteries

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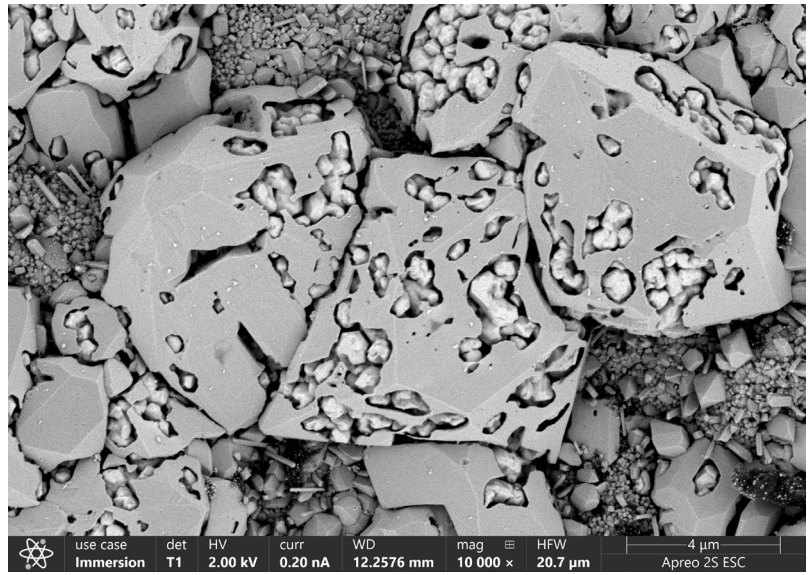



Presentation ID#: 1003

DOE OE Energy Storage Peer Review & Annual Meeting, 2026

# Project Overview

- **Project Goal:** The goal of this project is to understand the failure mechanisms of lead acid batteries which are hampering its application for resilient grid scale energy storage applications and use this information to discover new additive materials and processes for improving performance.
- **Current Practice:** Currently, lead acid batteries have limited grid storage application owing to limited cycle life and active material usage. Research on active cell components, geometries and designs, along with carbon additives, is increasing capacity and cycle life. However, limited understanding of the failure mechanisms and role played by each material in the paste hampers improving the desired performance.
- **Why PNNL:** Isolating the mechanistic details of different modes of failure and the impact of additives on overcoming these requires a multiscale and multimodal characterization strategy which isolates and identifies the mechanisms by combination of both bottom-up and top-down approaches. PNNL (collaboration with ANL) has the required capabilities and deep expertise to solve multiscale problems by bridging electrochemical process parameters with fundamental mechanisms using unique in-situ and ex-situ characterization tools.
- **Innovation:** Our innovative approach combines top-down, macromolecular-scale materials characterization with bottom-up atomic- to molecular-scale synthesis and characterization techniques to understand complex nucleation and dissolution processes occurring at the liquid-solid and solid-solid interfaces under applied electrochemical and chemical gradients.

# Project Overview

- **FY 2026 (multiple since FY 2021)**

  **Presentation**

  - Karakoti et al, MRS 2026

  **Manuscript**

  - 1 accepted in Angewandte Chemie, 2026
  - Lapson et al, Multimodal post-mortem analysis of lead electrodes, submitted

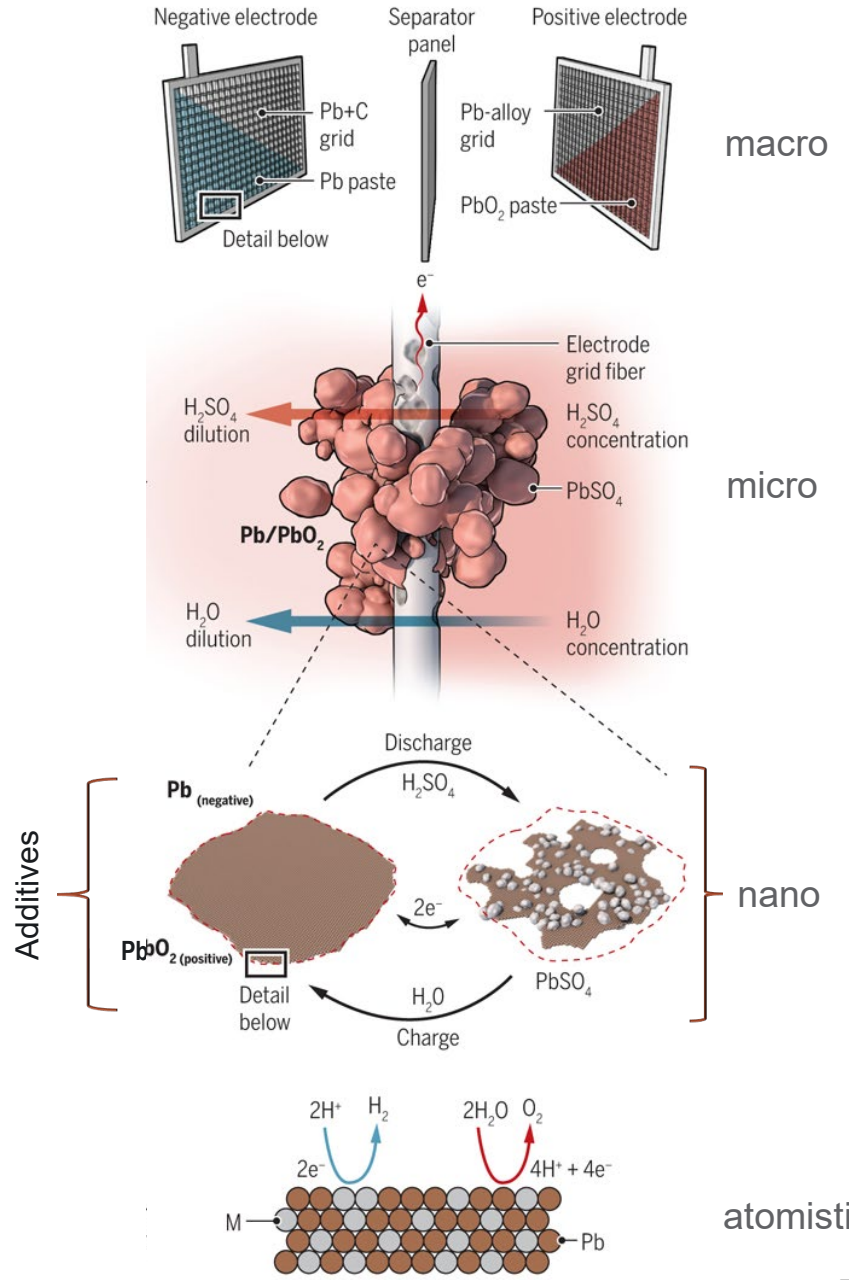
- **Impact:** Our research has shown that barite may not be the best $PbSO_4$ nucleating agent; doped forms of barite are currently being tested in collaboration with East Penn Manufacturing. Our studies have added to the understanding of $PbSO_4$ coarsening and $PbO_2$ phase evolution applicable in most failure modes.
- **Vertical/Investment Area:**

  ✓Materials and Systems Innovation

- **Alignment:** This project is accelerating development and testing of lead acid storage technology that is 100 % US-based, could become cost-effective, safe, and durable, and which is crucial to meeting the Administration's goal of optimizing grid services and growing grid capacity.

# Problem

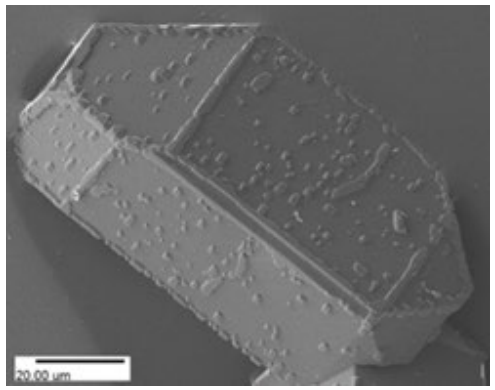
- Pivoting lead-acid batteries toward LDES and deep-cycling for frequency regulation and load-levelling requires improved electrode design to prevent degradation mechanisms such as sulfation and shedding due to gas evolution
- Complicated multiscale changes during charge-discharge process require addition of expanders to manage phase transitions
- Lignin and barites are well established expanders used by lead acid battery industry
- The role of expanders in enhancing the performance of lead acid batteries, especially how they promote Pb-$PbSO_4$ reaction, remains unknown



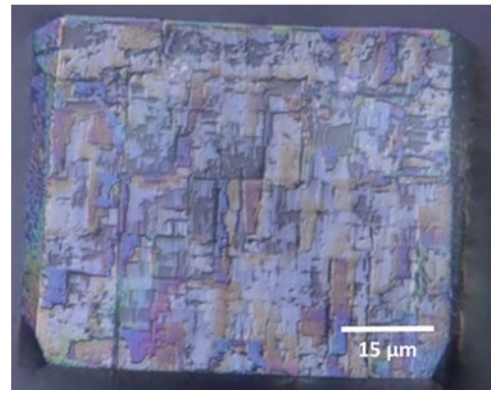

***SCIENCE,*** 2020, 369, 923-924

# What is the Role of Expanders in Lead Acid Batteries?

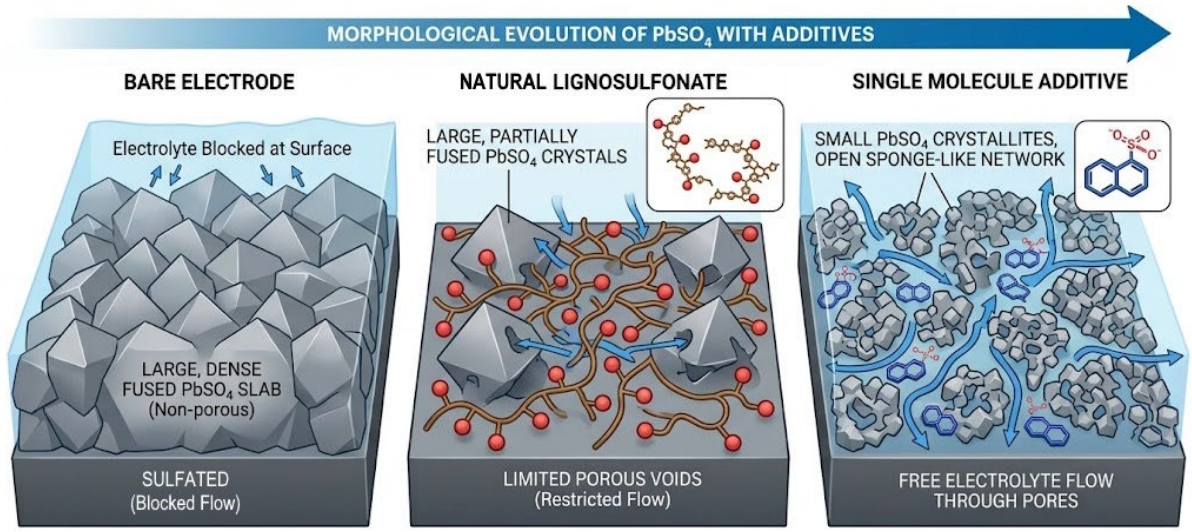
- Two main components with expander role:
  - Barite
    - $PbSO_4$ nucleation and rapid growth for cyclability and rate capability
    - Sr incorporation reduces lattice mismatch for improved growth
  - Lignin
    - Growth modulation to prevent throttling of kinetics and capacity fade by the formation of large, hard $PbSO_4$ crystals
    - Natural product with high heterogeneity, batch-to-batch variability



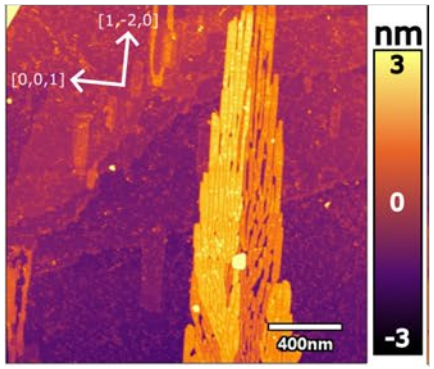
Island like nucleation and growth

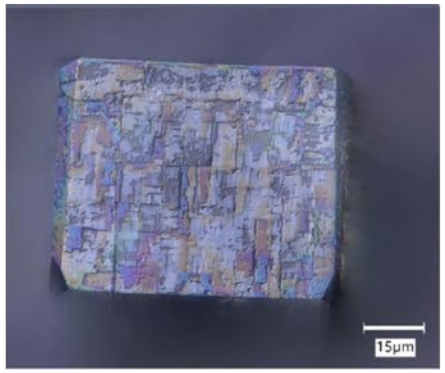



Layer-by-layer growth

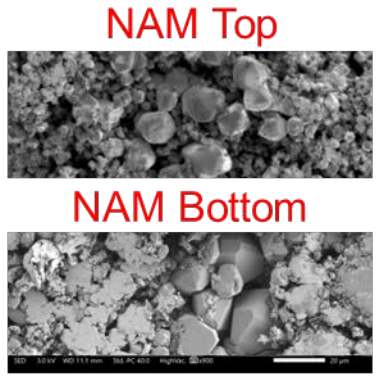


# Previous Research Focus




Designing new barite expander and performance testing by industry partner




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

Surface nucleation

Bulk sulfation

Electrodes

Cells/batteries

Sub-micron to microscopic scale

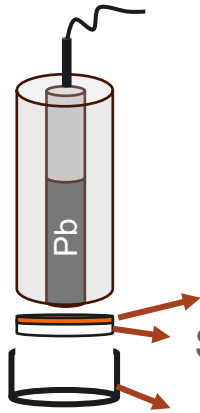
Macroscopic to sub-micron scale

Bottom up

Top down

# Challenge in Performance of New Expander Tested by Industry Partner – East Penn Manufacturing

Paste level performance of barites




Paste mix composition

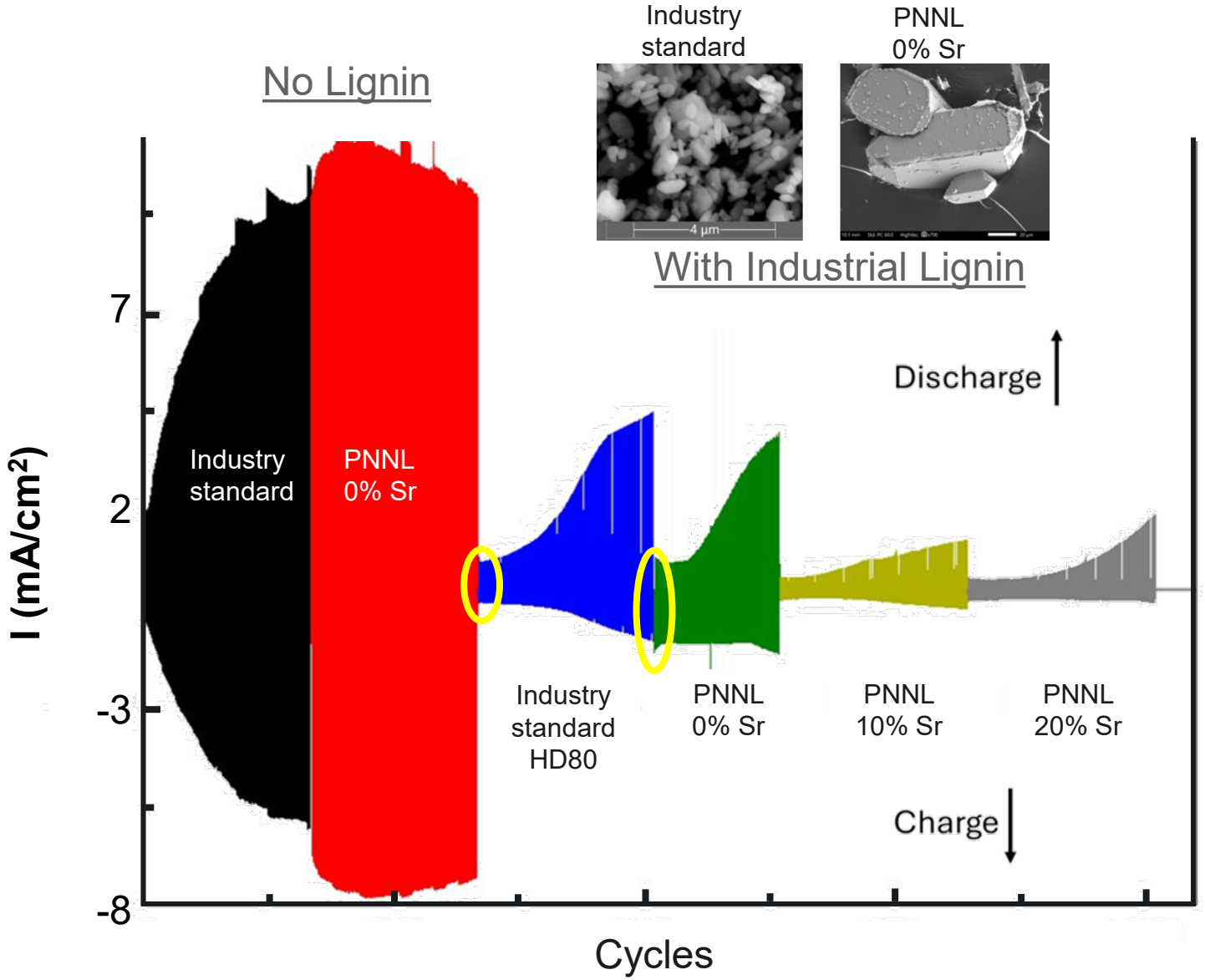
PbO + Carbon + additives

Paste-mix

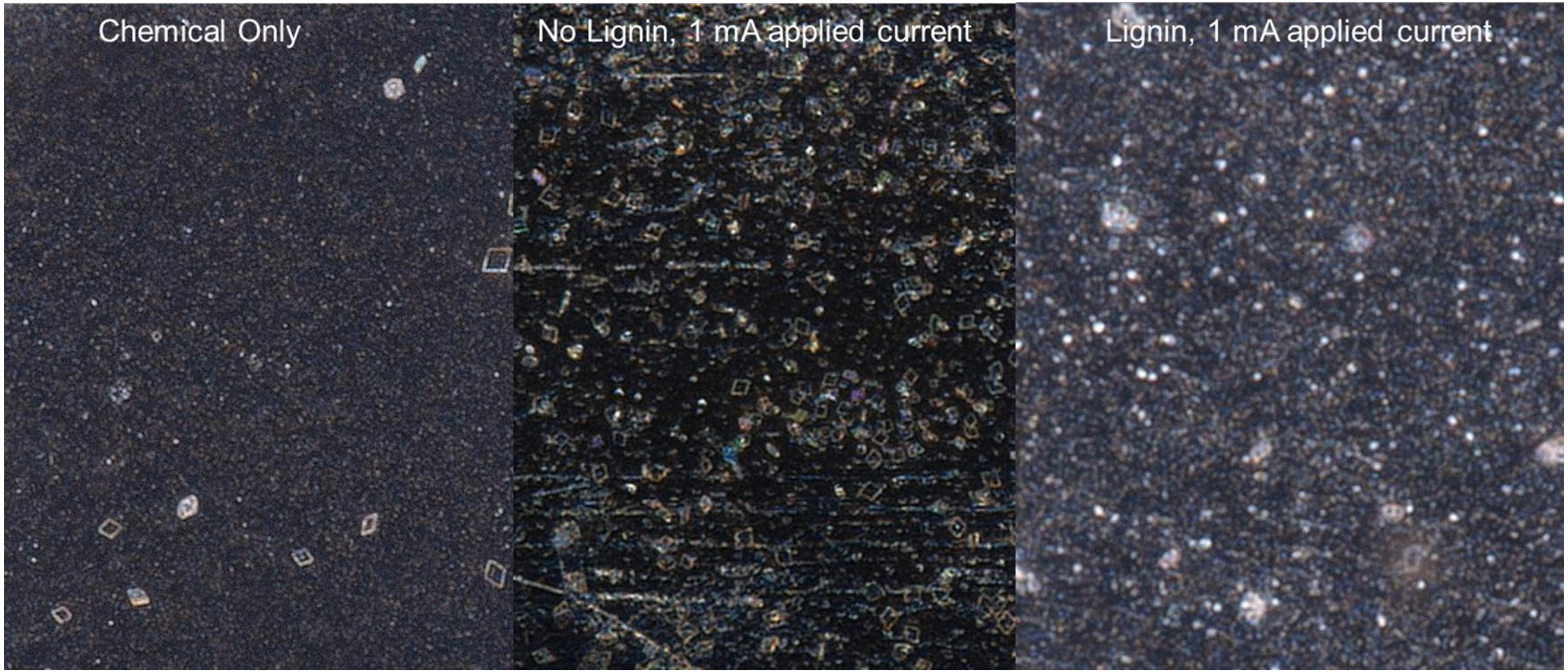
Separator

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

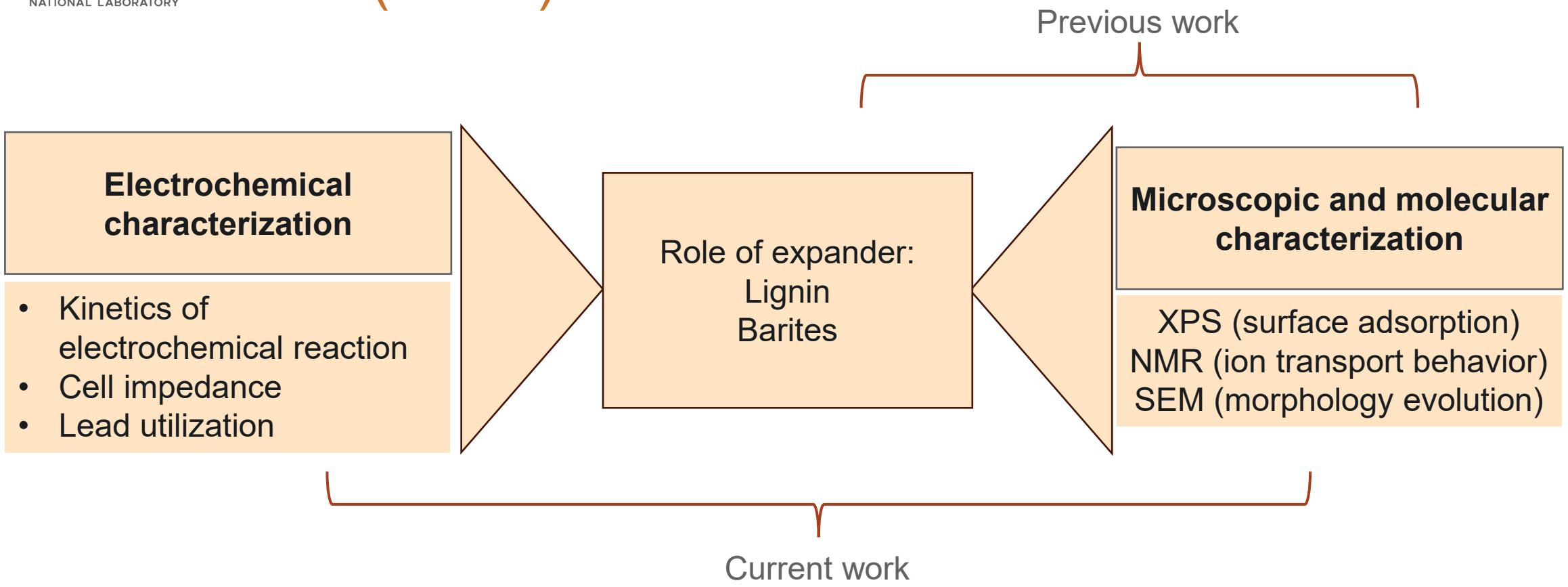


# In-situ Observations of $PbSO_4$ Growth

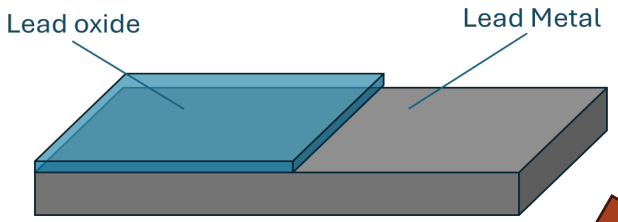



Motivation: Results are great, now explain what is happening with lignin

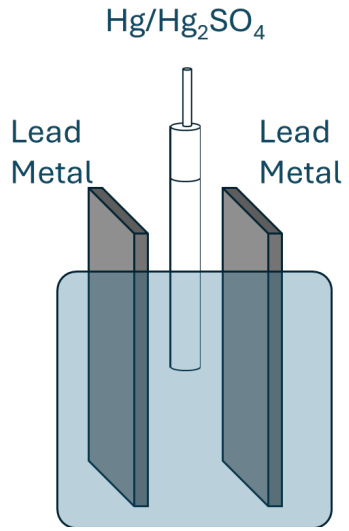
# Approach (Methods) - Observe One-factor-at-a-time (OFAT)



# Testing Methods: Cycling Lead Metal Anode in Presence and Absence of Lignin Sulfonate

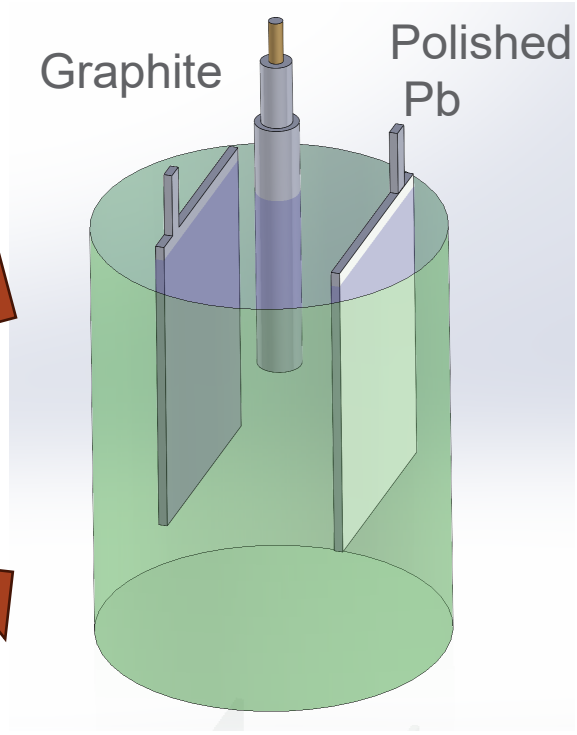



Physical polishing



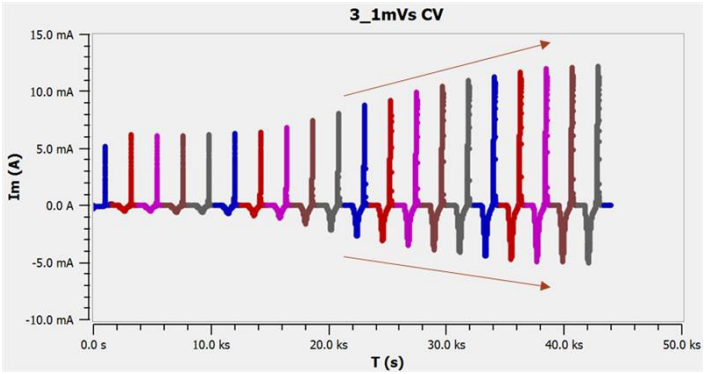

Electrochemical polishing

Hg/$Hg_2SO_4$

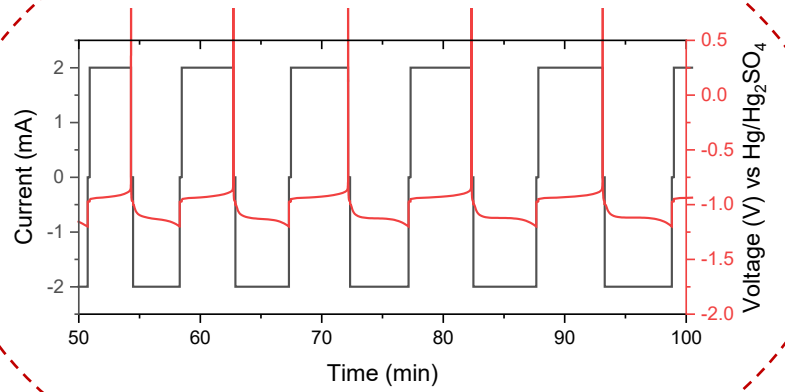



Beaker Cell (50 ml)

Cyclic voltammetry



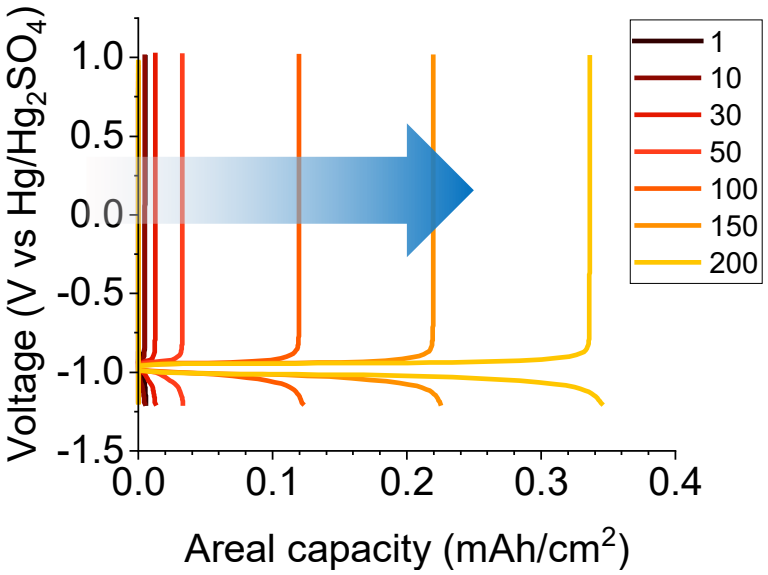

Galvanostatic cycling

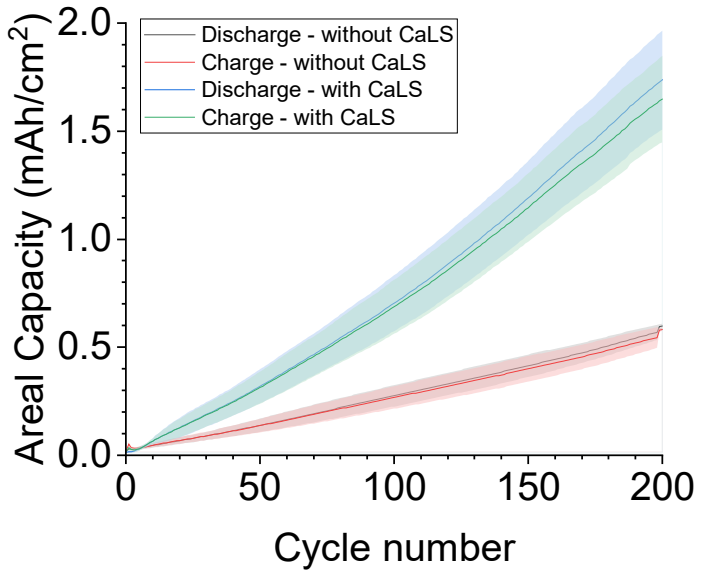


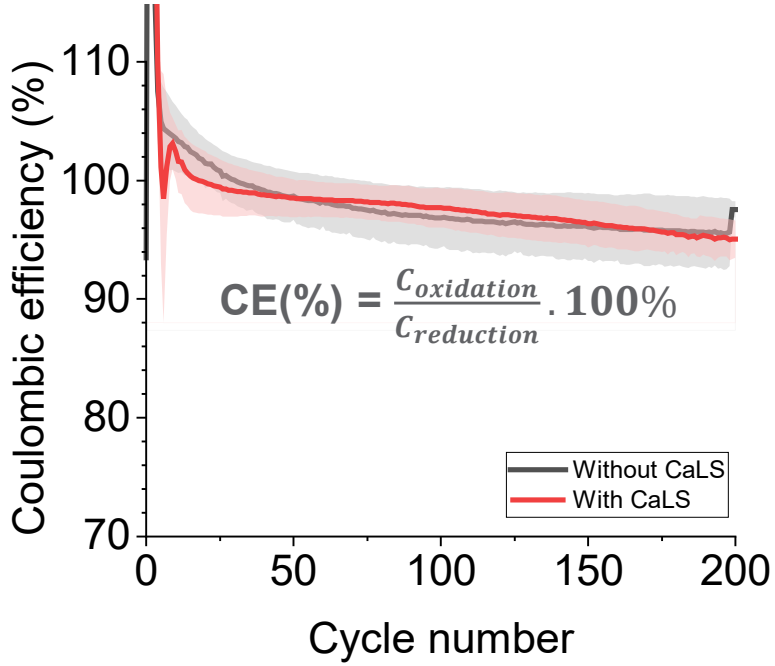

Electrolyte: 1M $H_2SO_4$ or 5 M $H_2SO_4$
Additives: with and without CaLS

# Understanding the Effect of Lignin on Lead Metal Anode in 1M $H_2SO_4$

Galvanostatic cycling (Constant current-voltage limit)



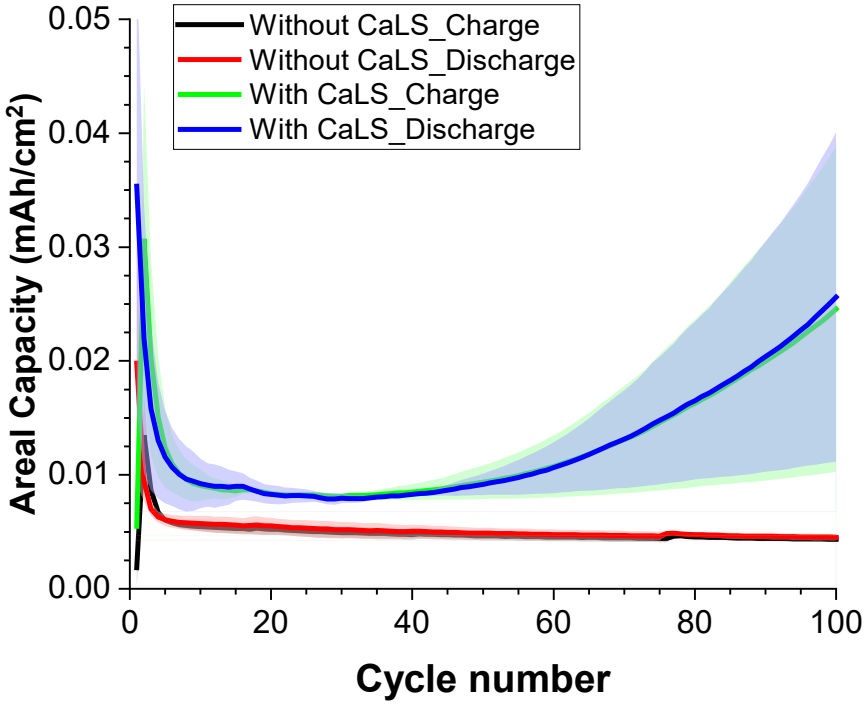



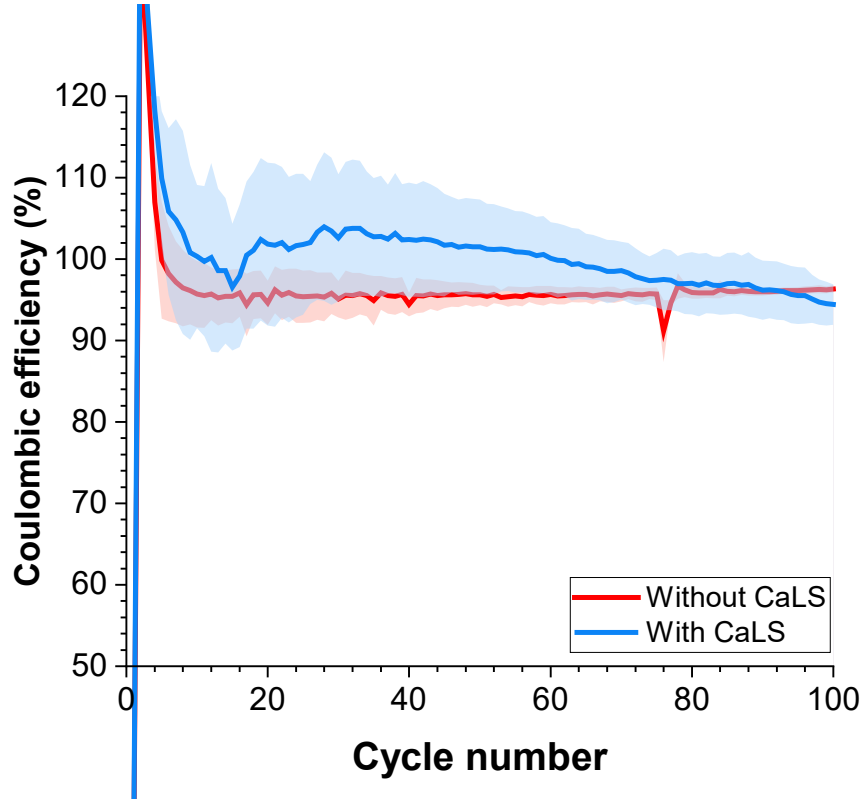




- CaLS enhanced lead activation with cycle number and delivers higher Coulombic efficiency

# Understanding the Effect of Lignin on Lead Metal Anode in 5M $H_2SO_4$

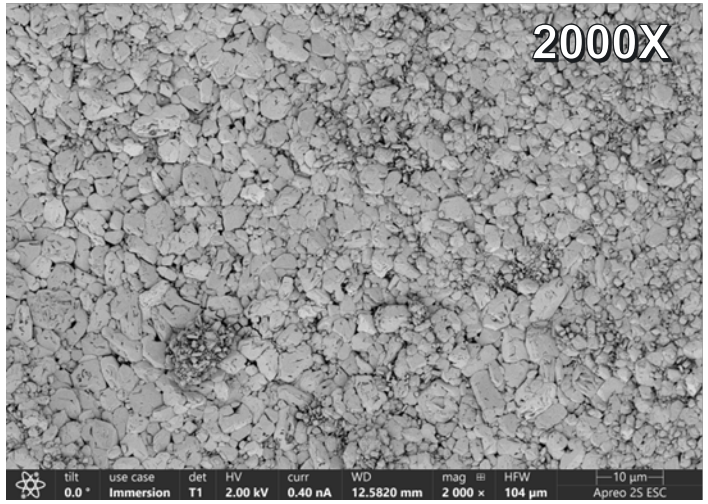
Lead / Graphite
5M $H_2SO_4$ with / without CaLS
4 mA/cm$^2$ Cut-off: -1.2 – 1.0V vs $Hg/Hg_2SO_4$

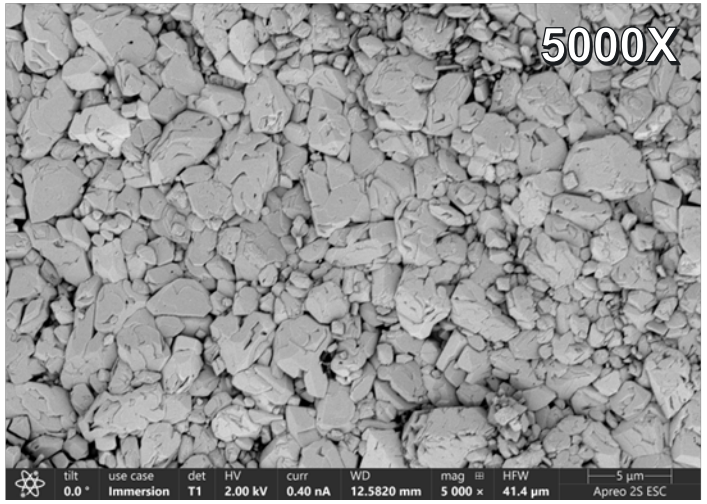


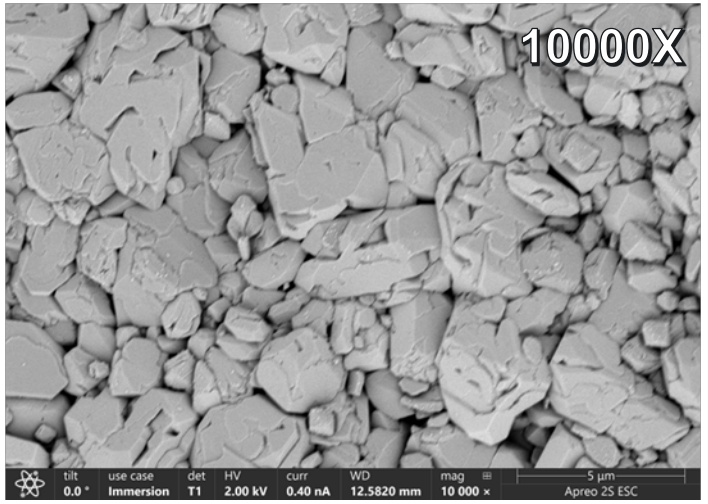



# 1 M $H_2SO_4$ with and without CaLS

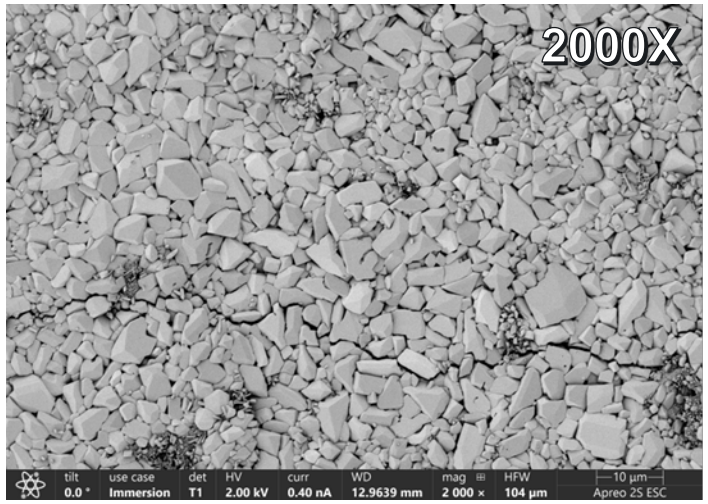
**With CaLS**

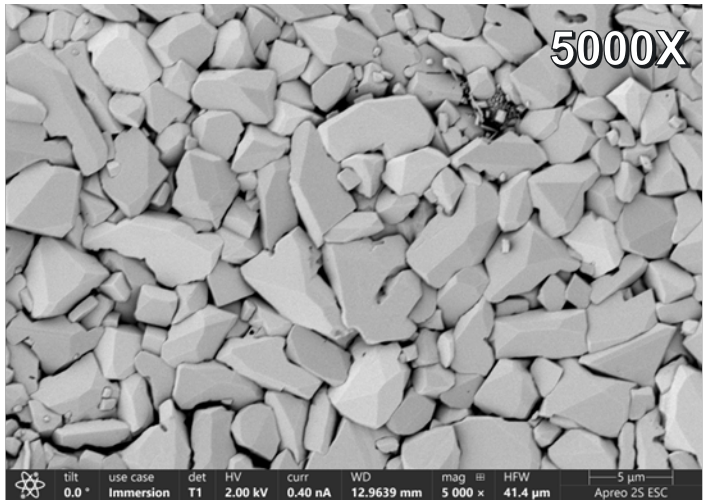


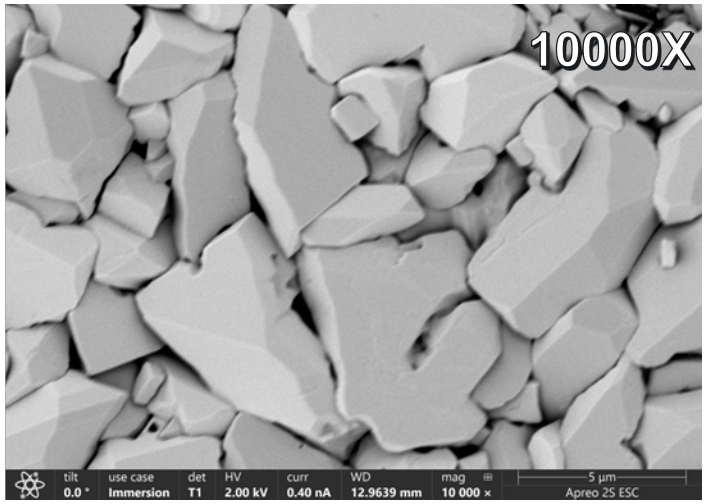



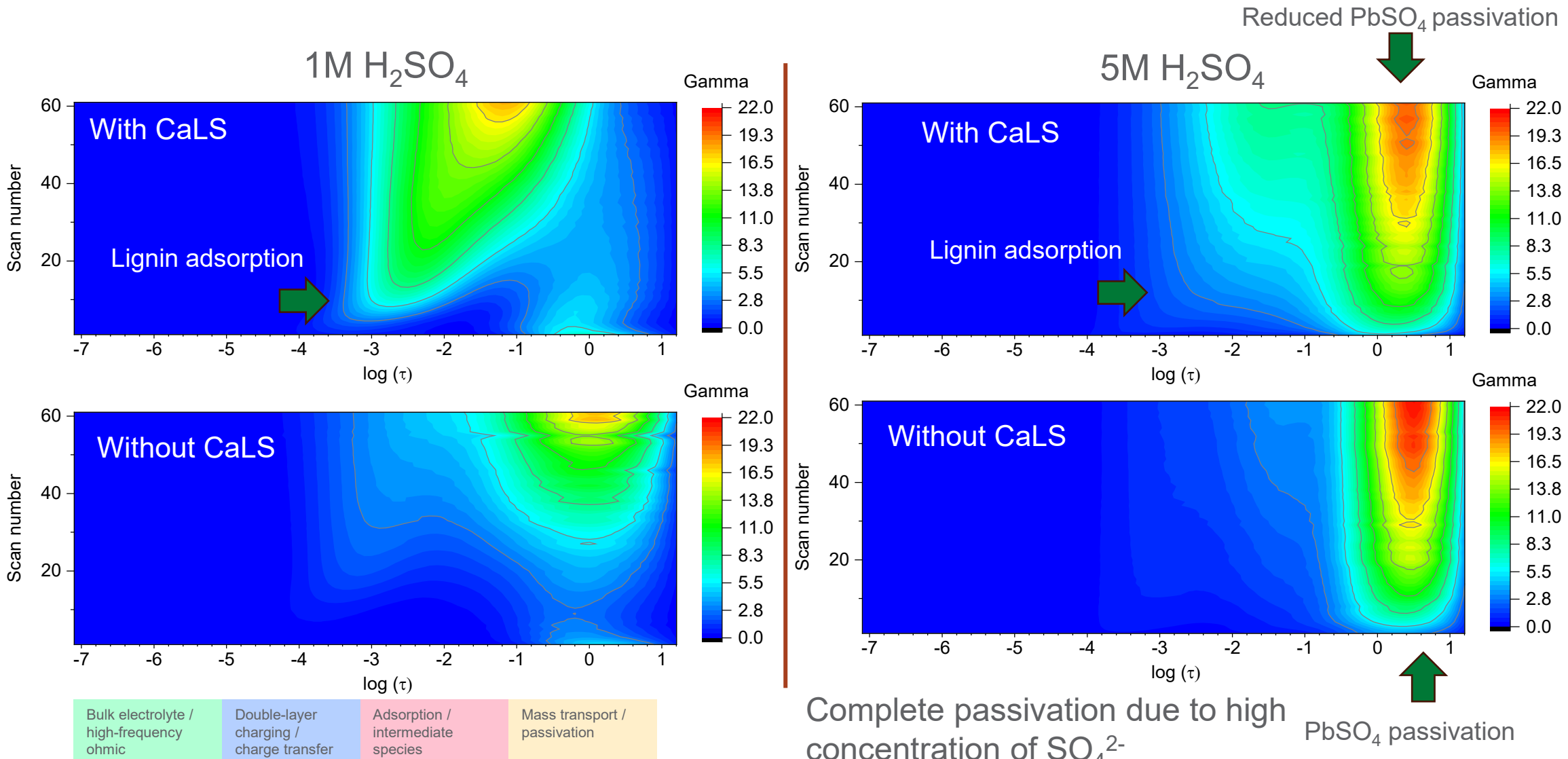

**Without CaLS**



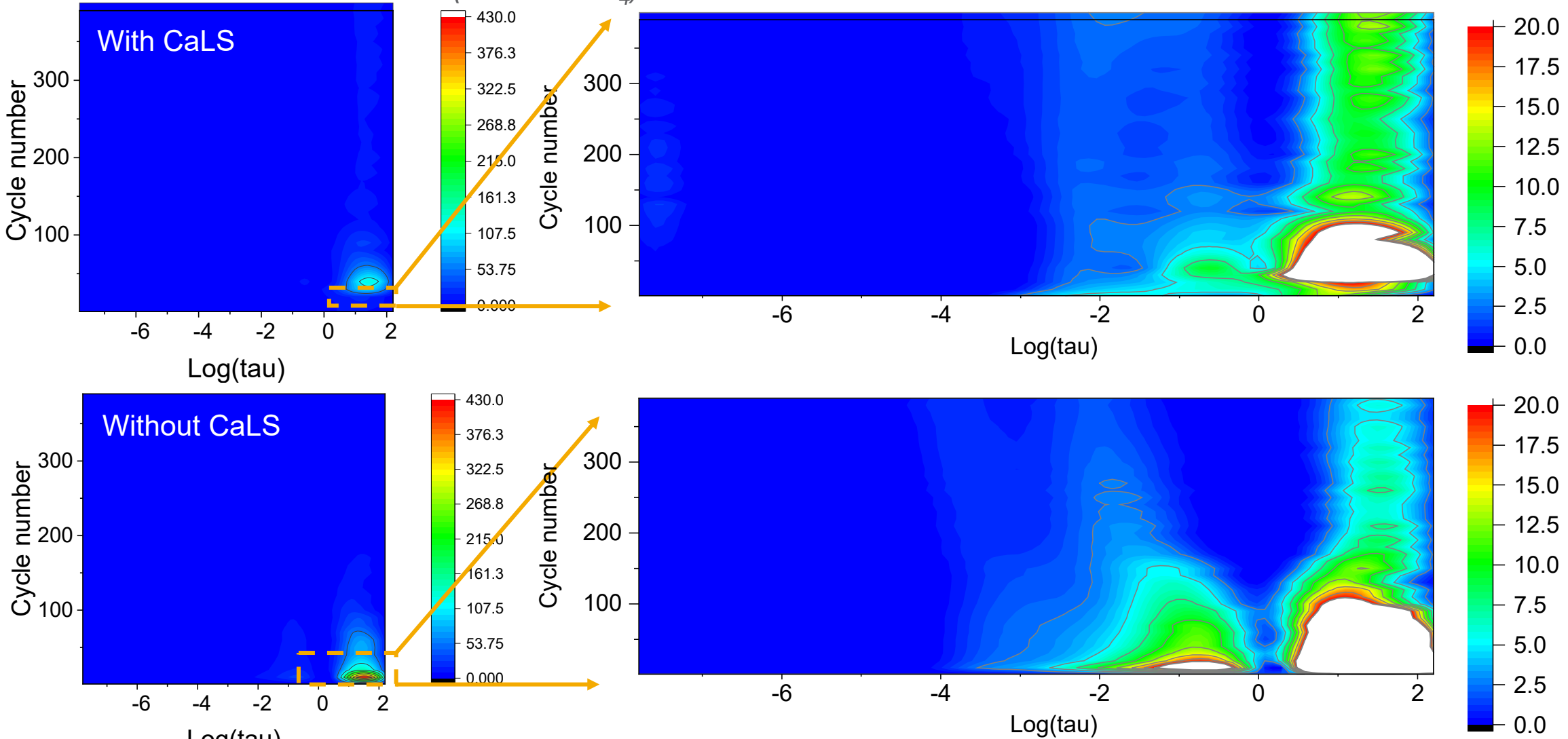
# Lignin Surface Adsorption Reduce Passivation



# Lignin Surface Adsorption Reduce Passivation

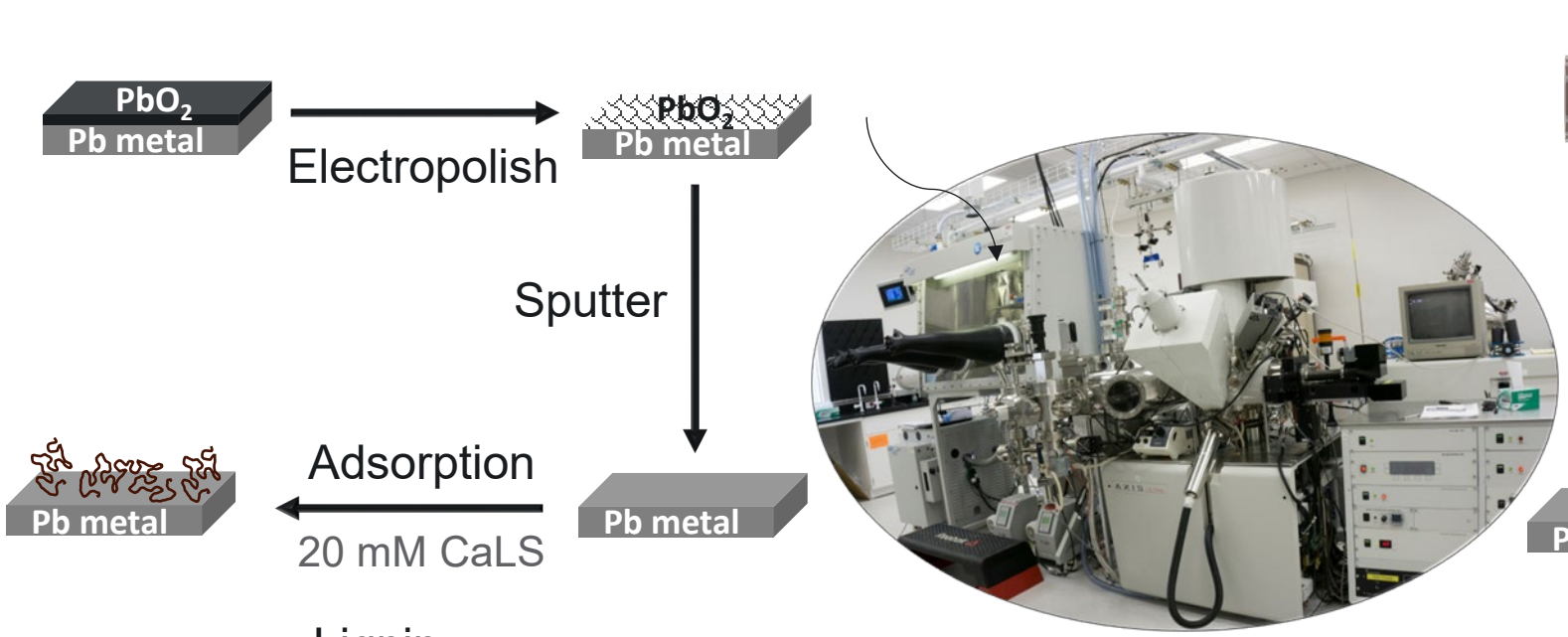
*Measured at oxidized state (Pb→$PbSO_4$)*

Consistent $PbSO_4$



# In-situ XPS: Lignin Adsorption Delays Sulfation

## Semi in-situ lignin adsorption study





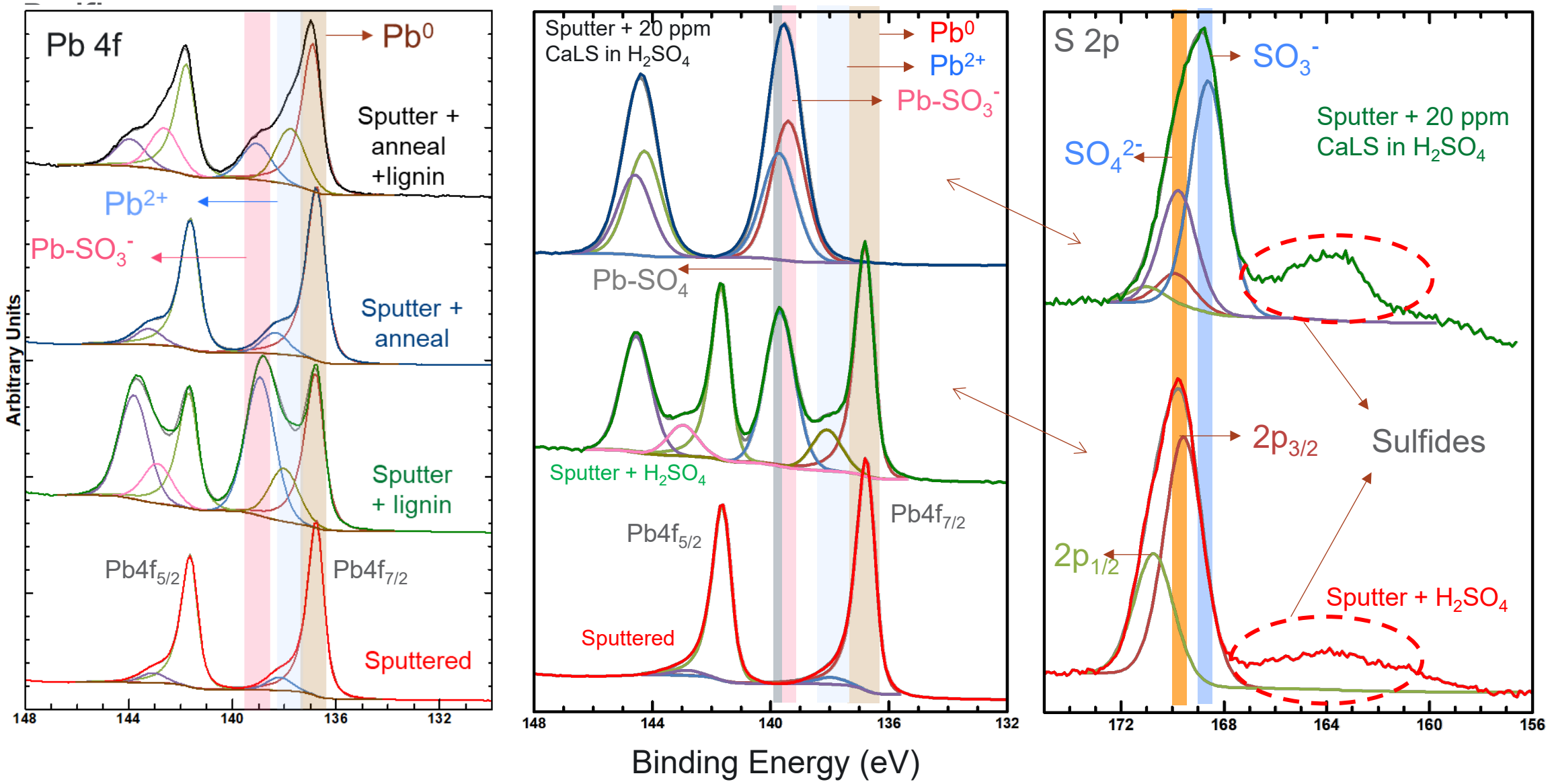




AIP Advances, 2021, 11(6):065024

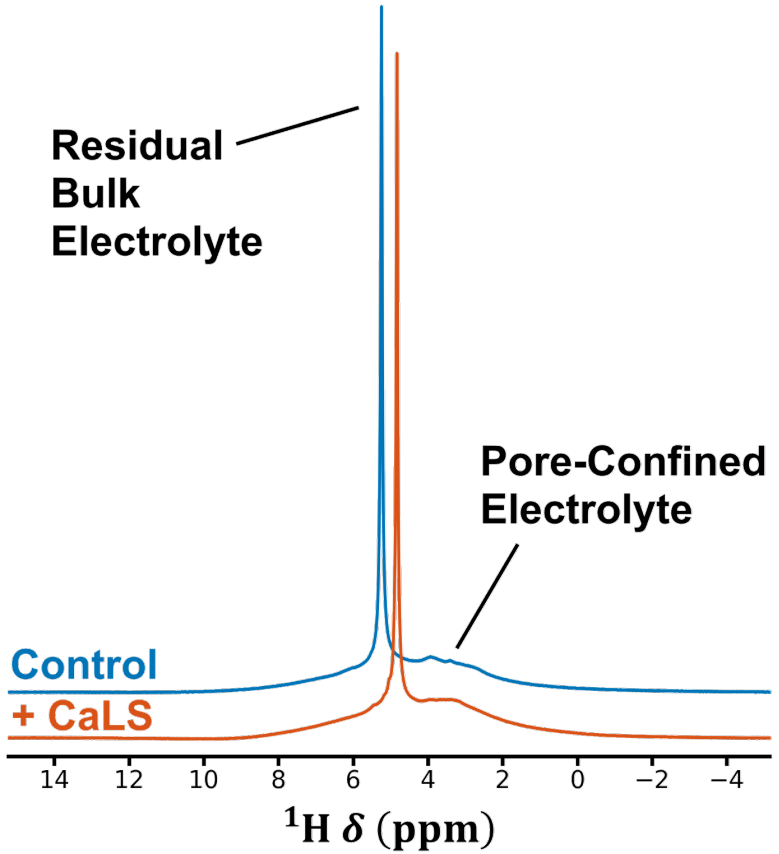
Cryo –XPS measurements

# In-situ XPS to Understand Lignin Surface Adsorption




Lignin binds strongly to lead metal surface; lignin reduces lead sulfate formation

# Porous Solvent Diffusion in Pb Oxidation Layer



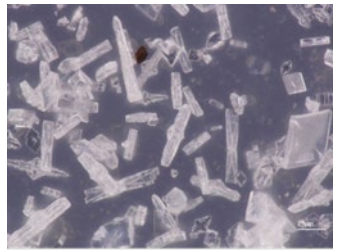

| | Control | | | | + CaLS | | | |
|---|---|---|---|---|---|---|---|---|
| | Bulk | Δ (%) | Pores | Δ (%) | Bulk | Δ (%) | Pores | Δ (%) |
| $^1$H $T_1$ (ms) | 193 | 2.4 | 62 | 0.9 | 301 | 0.2 | 212 | 0.3 |
| $^1$H $T_2$ (ms) | 14.1 | 0.9 | 4.0 | 2.0 | 26.9 | 0.6 | 13.1 | 0.6 |
| **$^1$H $D^*$ (x $10^{-10}$ m$^2$/s)** | **17.1** | **0.2** | **10.6** | **0.2** | **18.1** | **0.1** | **15.9** | **0.3** |
| $k_{1H}$ ($s^{-1}$) | 556 | | | | 39.7 | | | |
| **$\tau_{1H}$ (ms)** | **1.8** | | | | **25.2** | | | |

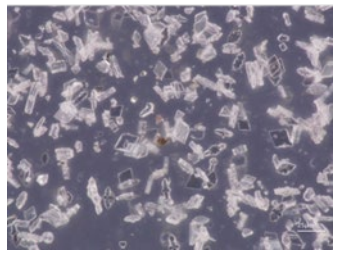
- Comparison of long-cycled (300+) Pb foil in $H_2SO_4$ with CaLS (20 ppm loading) and without ('Control')
- $^1$H Linewidths differentiate residual bulk electrolyte and pore-confined electrolyte ($PbSO_4$ growth)
- Multiple dynamical/transport markers show that CaLS produces looser, more porous oxidation layer with longer in-pore residence time, pointing to reduced sulfation in long-term cycling

# Broadening Effects in $^{207}$Pb Linewidths Indicate Heterogeneity or Disorder

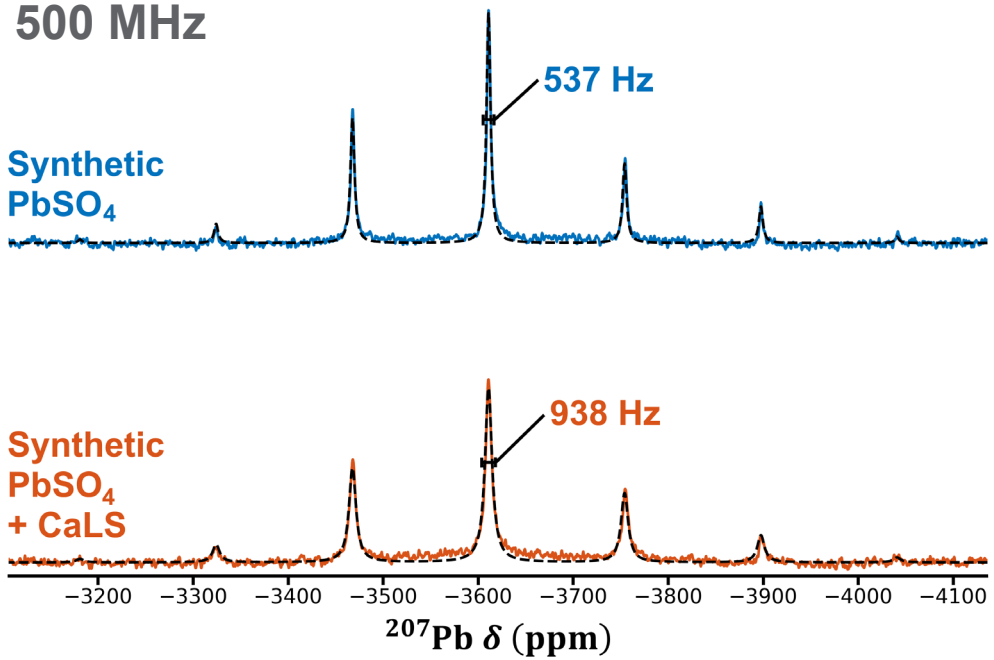
Pacific Northwest NATIONAL LABORATORY

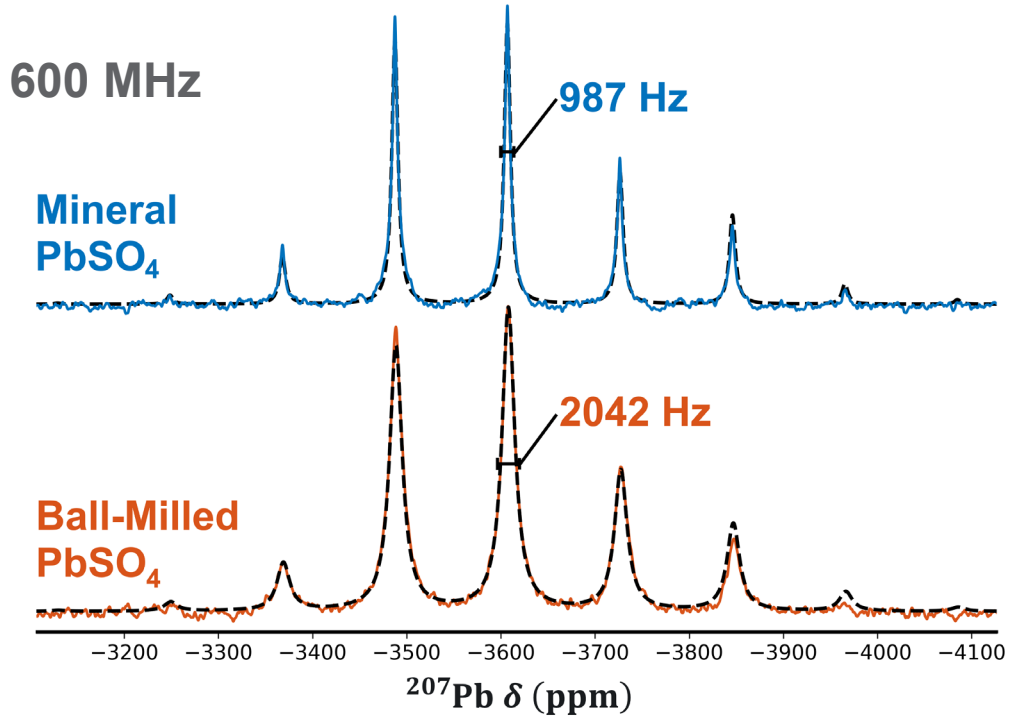
$PbSO_4$





$PbSO_4$ synthesized in presence of lignin




- Synthetic $PbSO_4$ control exhibits considerably smaller linewidth than $PbSO_4$ synthesized in the presence of CaLS, indicating a greater distribution of $Pb^{2+}$ environments (i.e. CaLS is disrupting the $PbSO_4$ crystallinity)
- Ball-milling experiments for mineral $PbSO_4$ shows that grinding-induced particle size heterogeneity also broadens the $^{207}$Pb lines

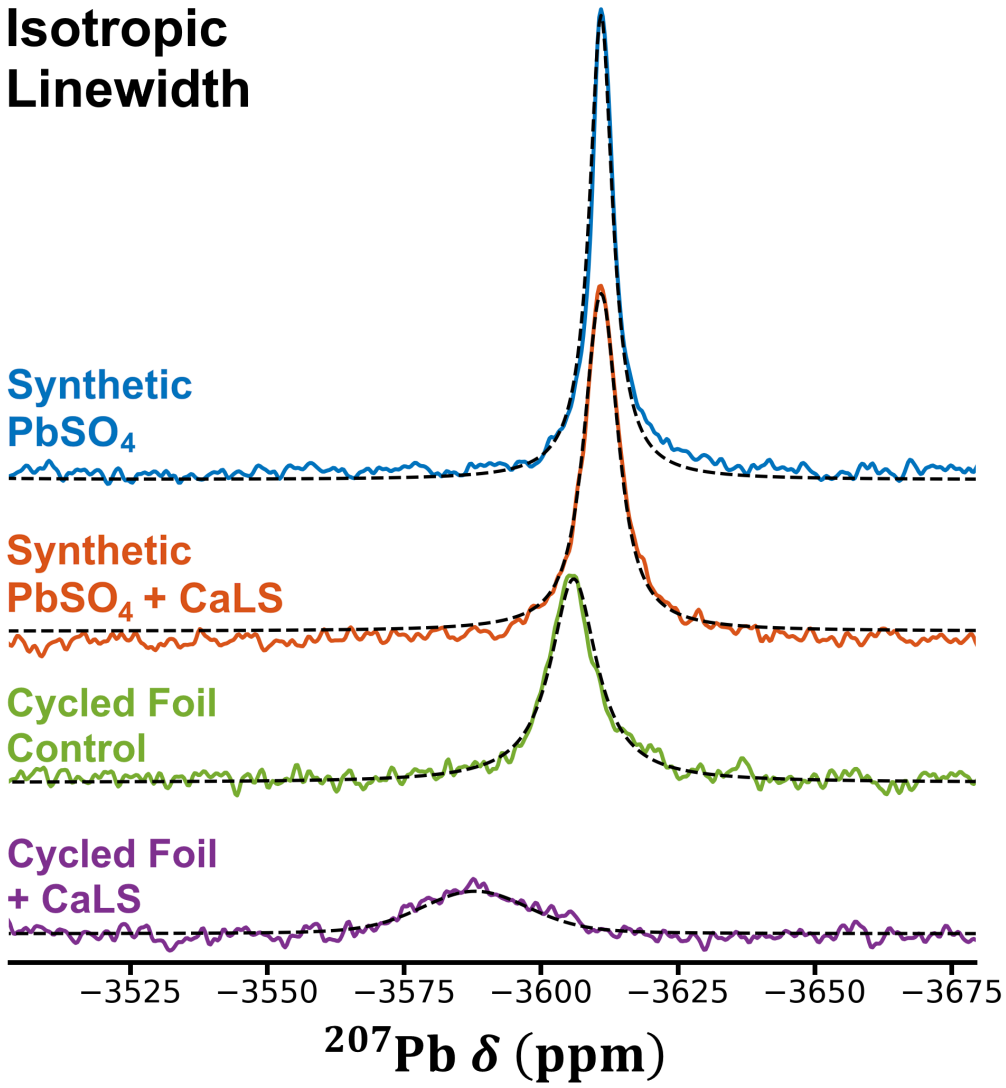
*Note: Linewidths are not directly comparable at the two different fields

| 15 kHz MAS | Syn. $PbSO_4$ | + CaLS |
|---|---|---|
| $\delta_{iso}$ (ppm) | $-3611^{+1}_{-1}$ | $-3611^{+1}_{-1}$ |
| $\Delta\delta$ (ppm) | $-310^{+10}_{-11}$ | $-308^{+11}_{-10}$ |
| $\eta$ | $0.54^{+0.13}_{-0.17}$ | $0.69^{+0.12}_{-0.13}$ |
| $\nu_L$ (Hz) | $\mathbf{537^{+43}_{-31}}$ | $\mathbf{938^{+60}_{-72}}$ |

# Broadening Effects in $^{207}Pb$ Linewidths Indicate Heterogeneity or Disorder – Contrasting with Cycled Foils

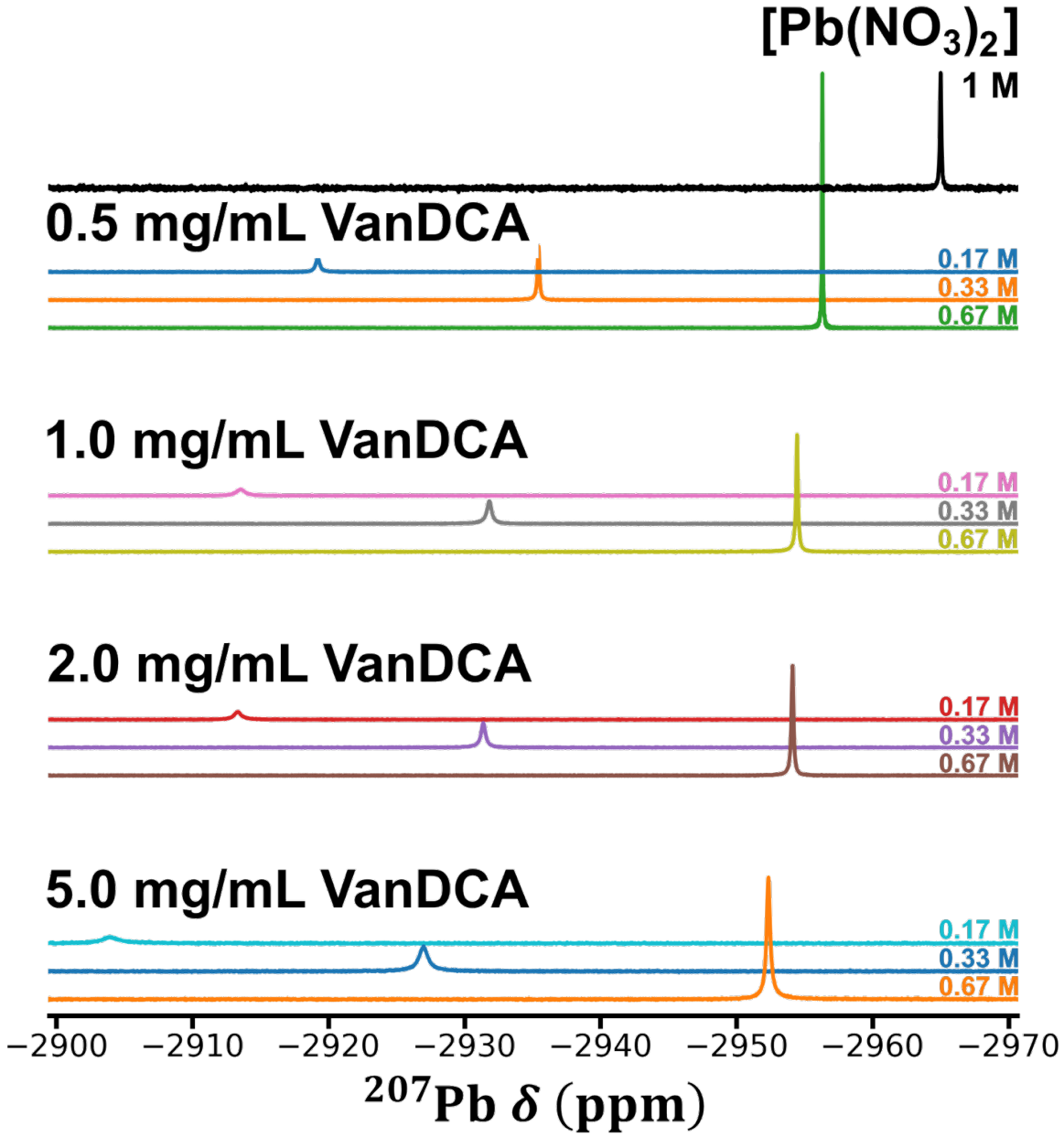
- Comparing the $PbSO_4$ signal from the dried, 300+ cycled Pb foils to the synthetic $PbSO_4$ illustrates the strong, cumulative effect of LS
- Repeated breakdown and reformation of the $PbSO_4$ leads to increased size heterogeneity, which broadens the linewidths
- Dramatically more dispersed $PbSO_4$ when cycled in the presence of LS, linking with the significantly higher porosity

| Sample | $\nu_V$ (Hz) |
|---|---|
| Synthetic $PbSO_4$ | 537 |
| Synthetic $PbSO_4$ + CaLS | 938 |
| Cycled Foil Control | 1070 |
| **Cycled Foil + CaLS** | **2453** |

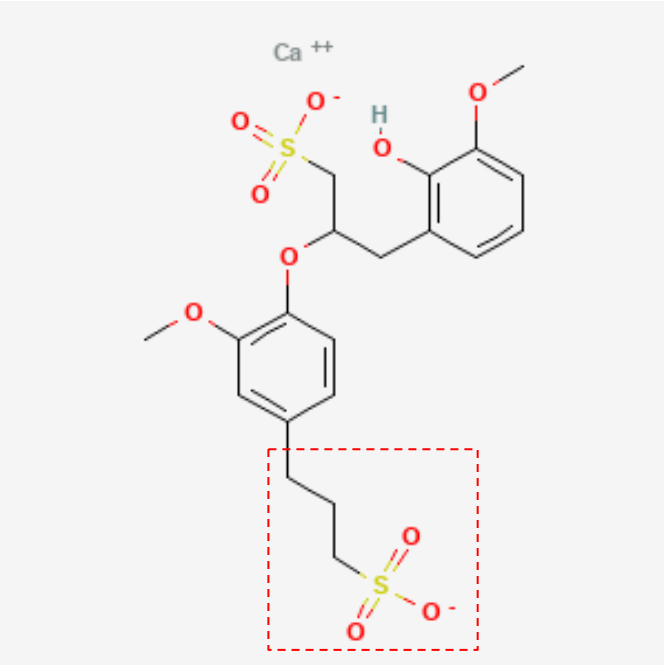


# Lignosulfonate-$Pb^{2+}$ Association in Solution

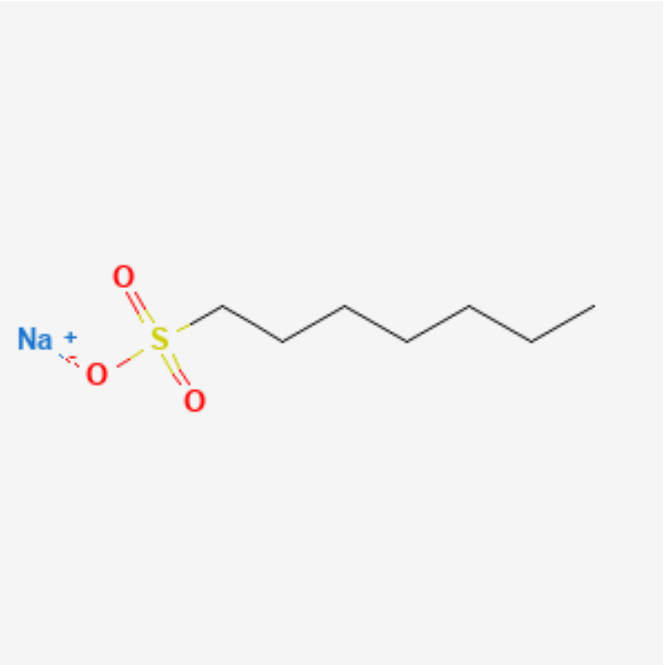
- Concentration series of VanDCA and aqueous $Pb(NO_3)_2$ showed strong (up to ~50 ppm) association effects on the $^{207}Pb$ shift
- At all LS/$Pb^{2+}$ concentration ratios, fast exchange dynamics always appear (single peak representing weighted ensemble-average ranging from pure aqueous solvation to correlation with LS moieties, *but not chelation*)
- Stronger chelation effects required to successfully identify organic-$Pb^{2+}$ association pathways (e.g. PbO dissolved in $H_2SO_4$ + Na-heptane sulfonate), as elementary step towards identifying LS association mechanism



# New Small Molecule

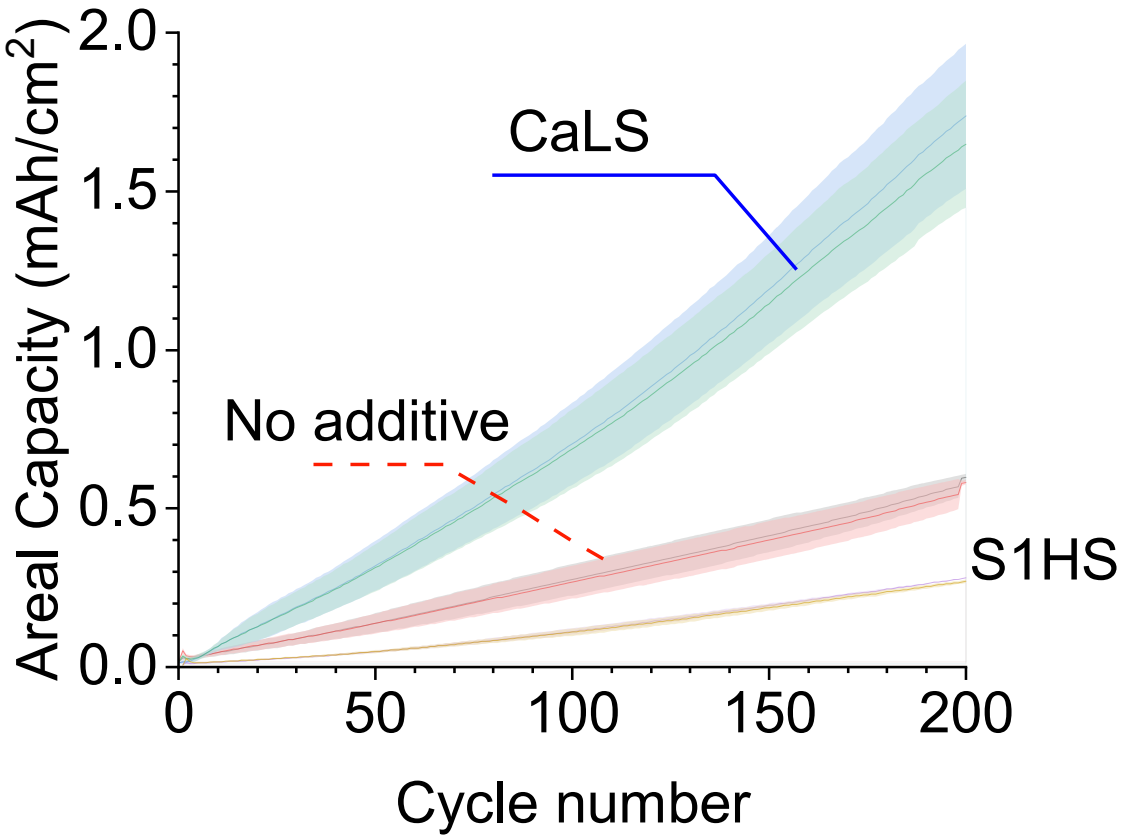


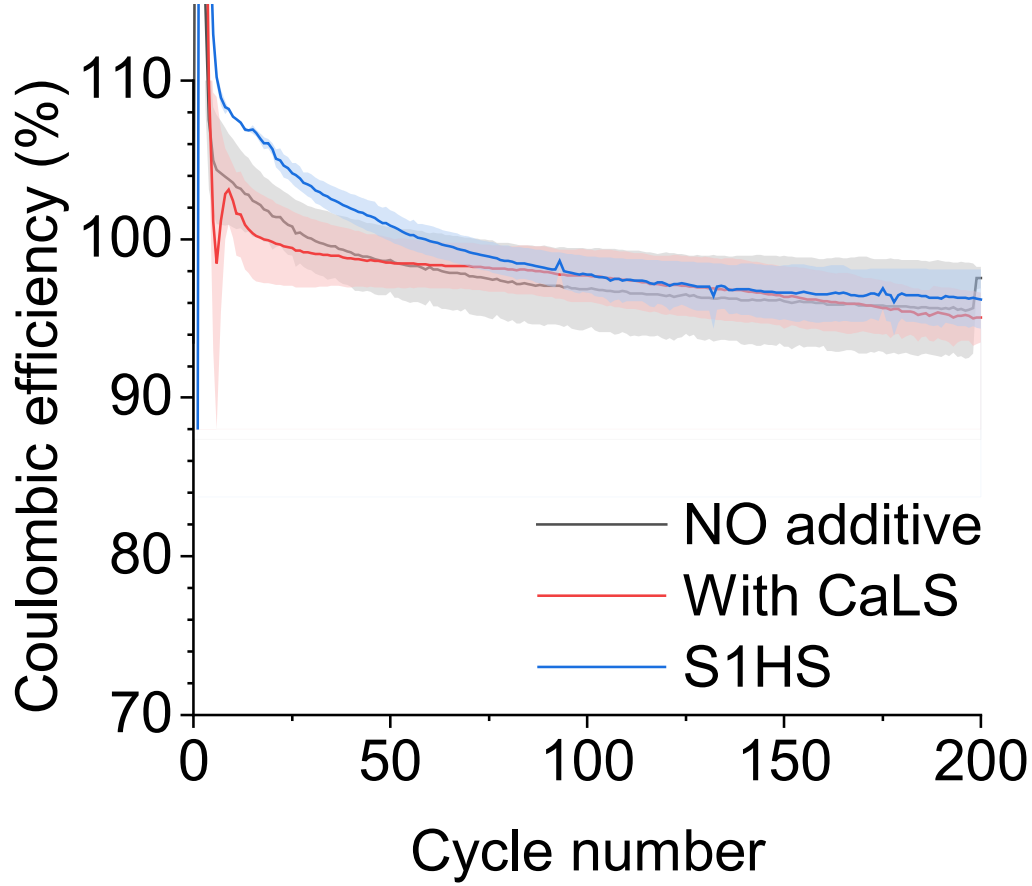

Calcium lignosulfonate (CaLS)




Sodium 1-heptanesulfonate (S1HS)

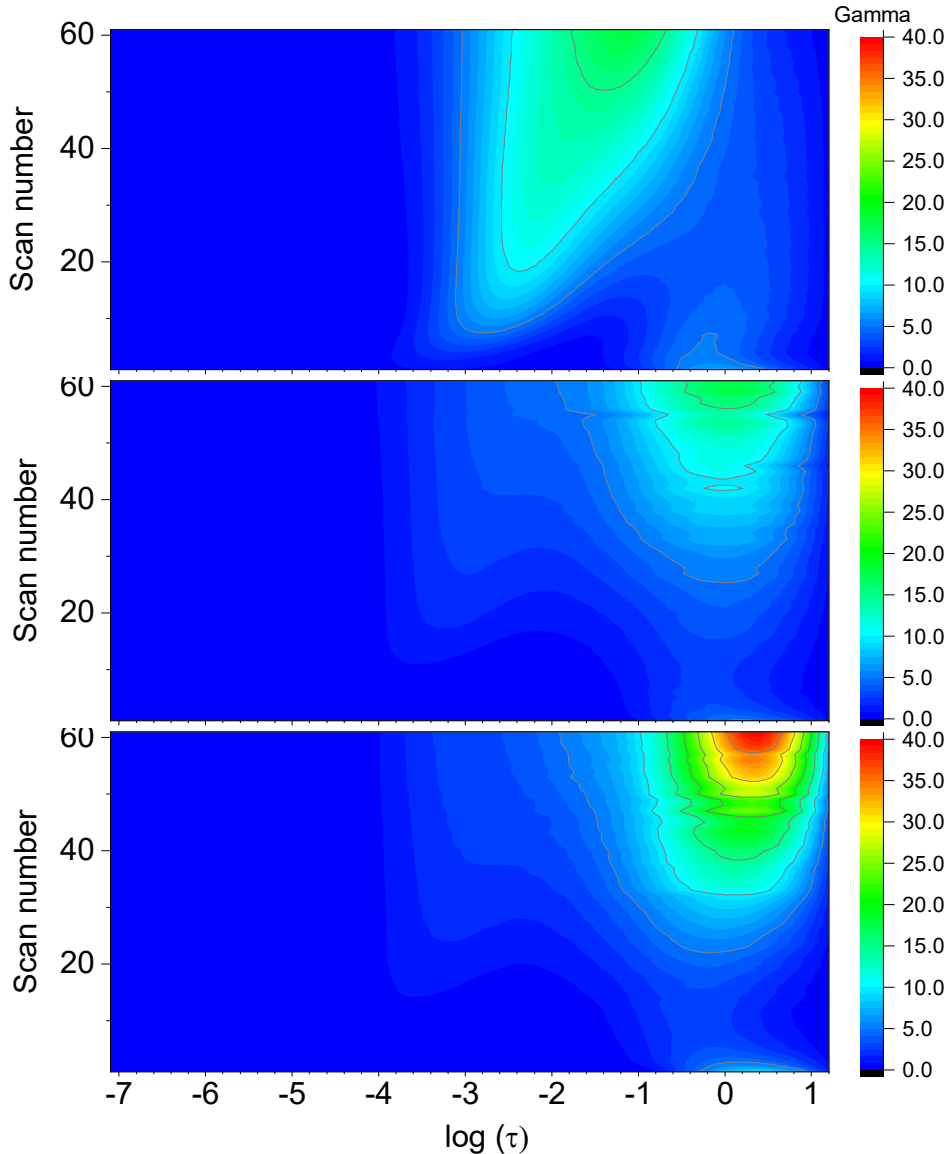
# The S1HS additive: S1HS Reduced Reactions of Lead Acid




- With adding of 20 ppm of S1HS, the lead anode shows much lower activation (less than no additive cells)

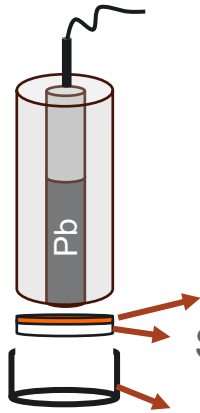
# The S1HS Additive: S1HS Increased Passivation of Pb Anode




- S1HS additive shows no effect on protection of Pb electrode against reaction with sulfate
- The S1HS seems to increase passivation of lead acid

# Testing PNNL Samples by Industry Partner – East Penn Manufacturing

Paste level performance of barites




Paste mix composition

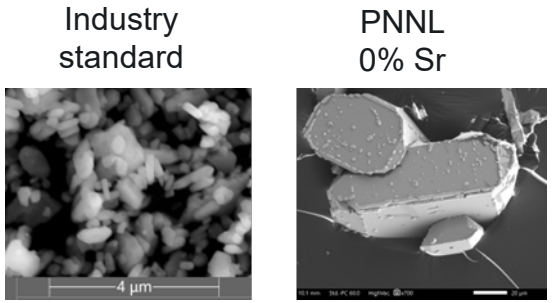
PbO + Carbon + additives

Paste-mix

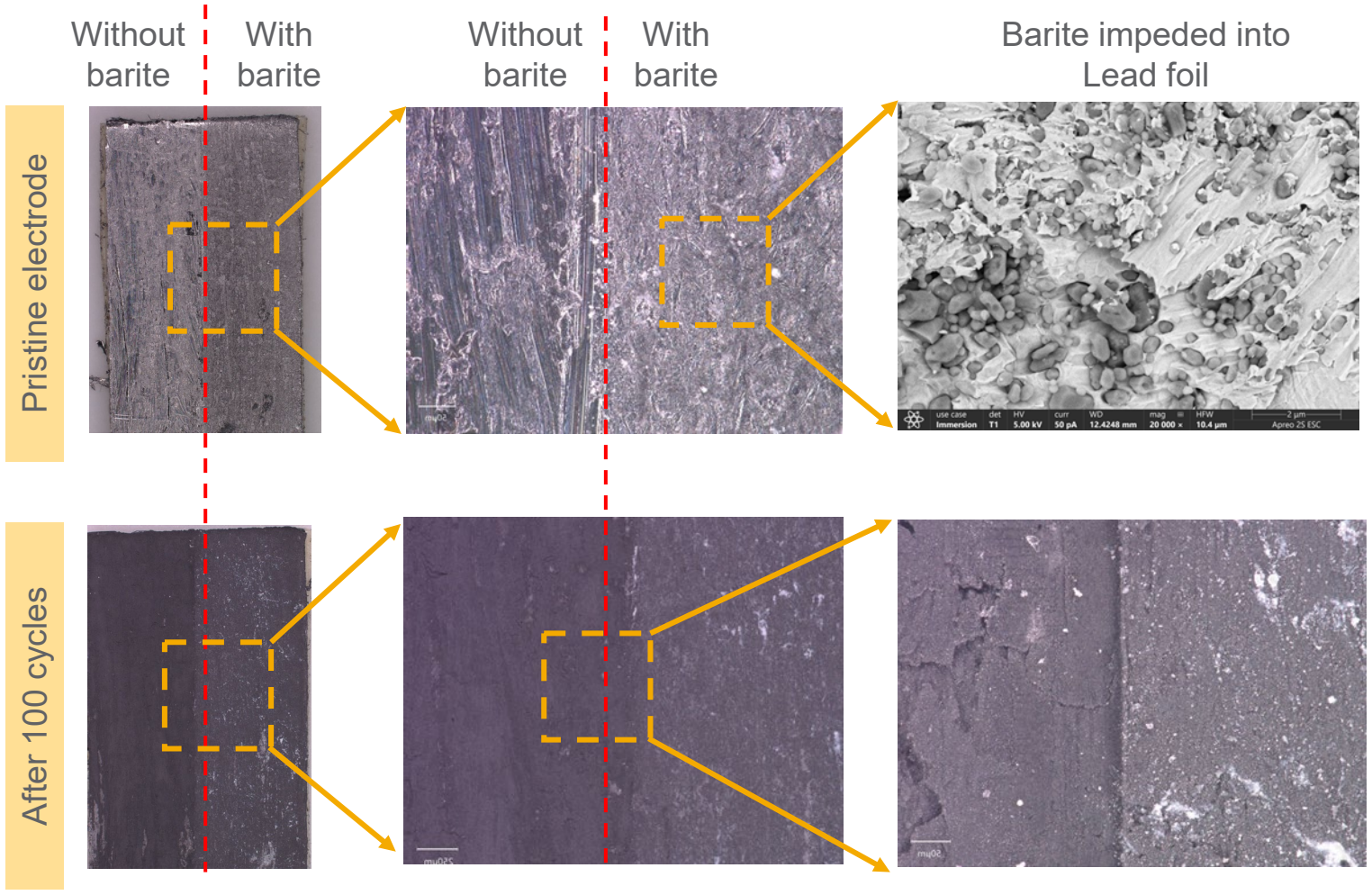
Separator

Cap securing separator/particles

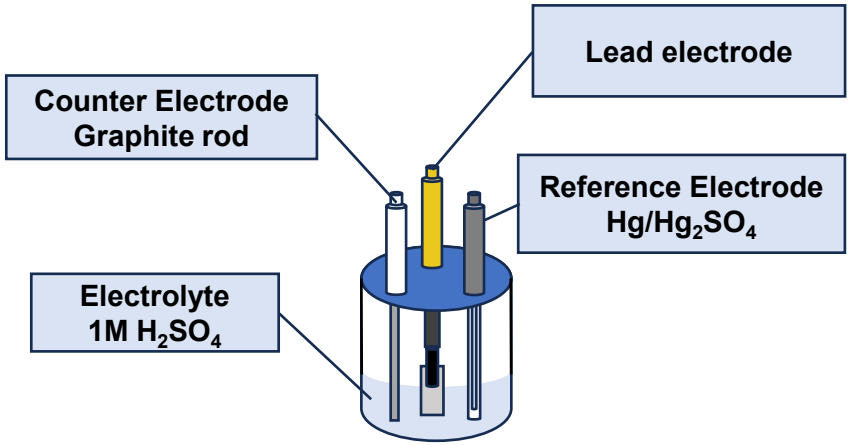
Understanding the difference in performance in presence and absence of lignin is critical and could solve potential problems with sulfation of negative electrodes



# Influence of Barite + Lignin on Nucleation and Growth of $PbSO_4$



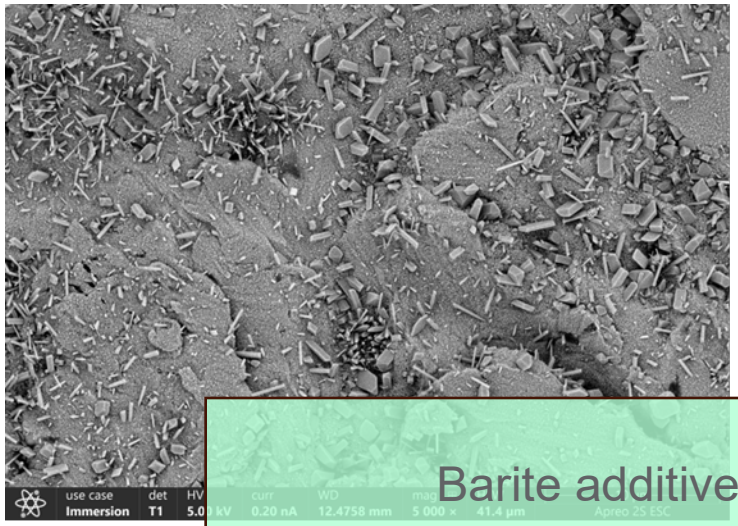

Electrolyte: 1 M $H_2SO_4$ with 20 ppm CaLS

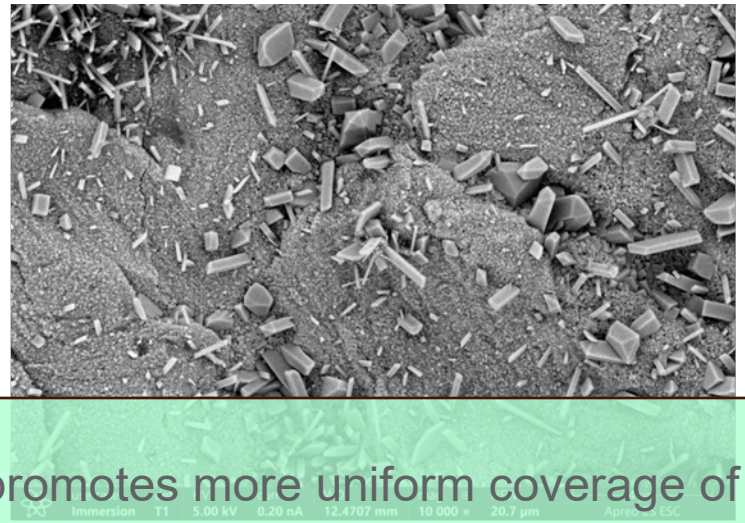


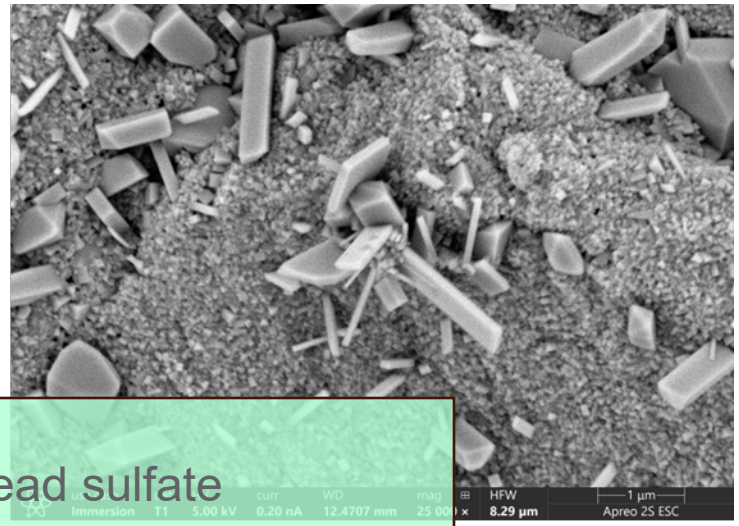
# Barite acted as a Nucleating Agent for $PbSO_4$

(images taken at 20th cycles)

No barite

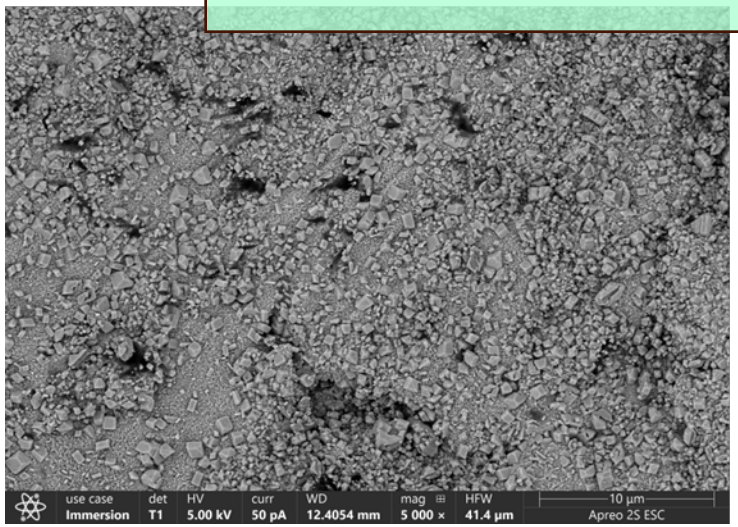


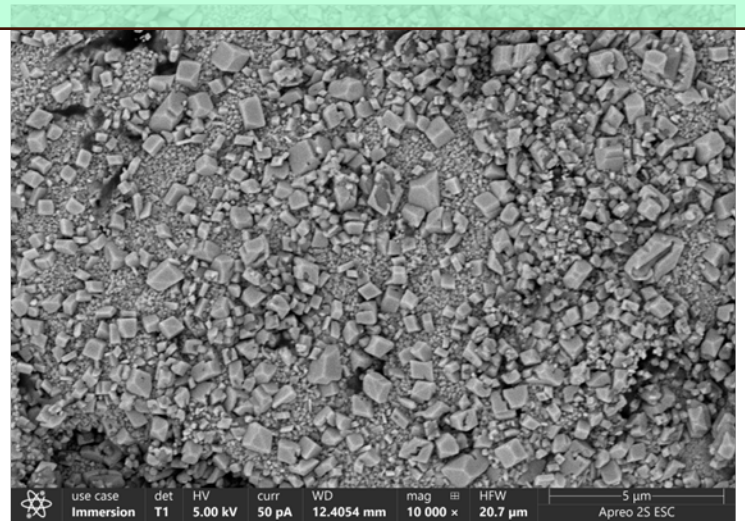



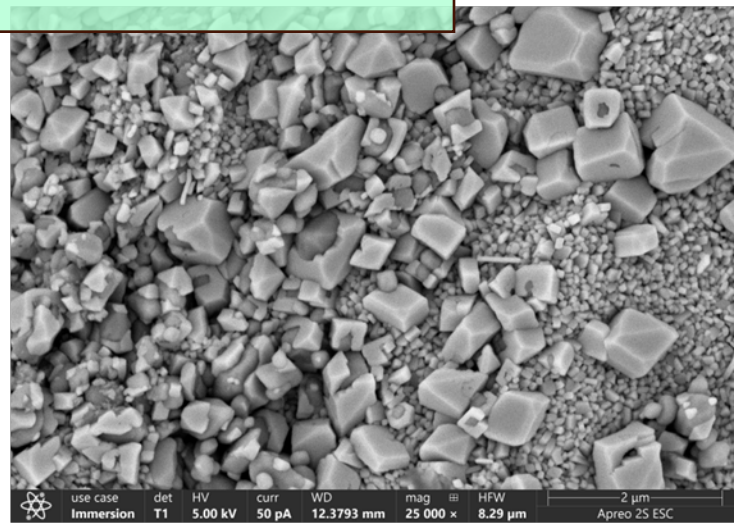




Barite additive promotes more uniform coverage of lead sulfate

With barite

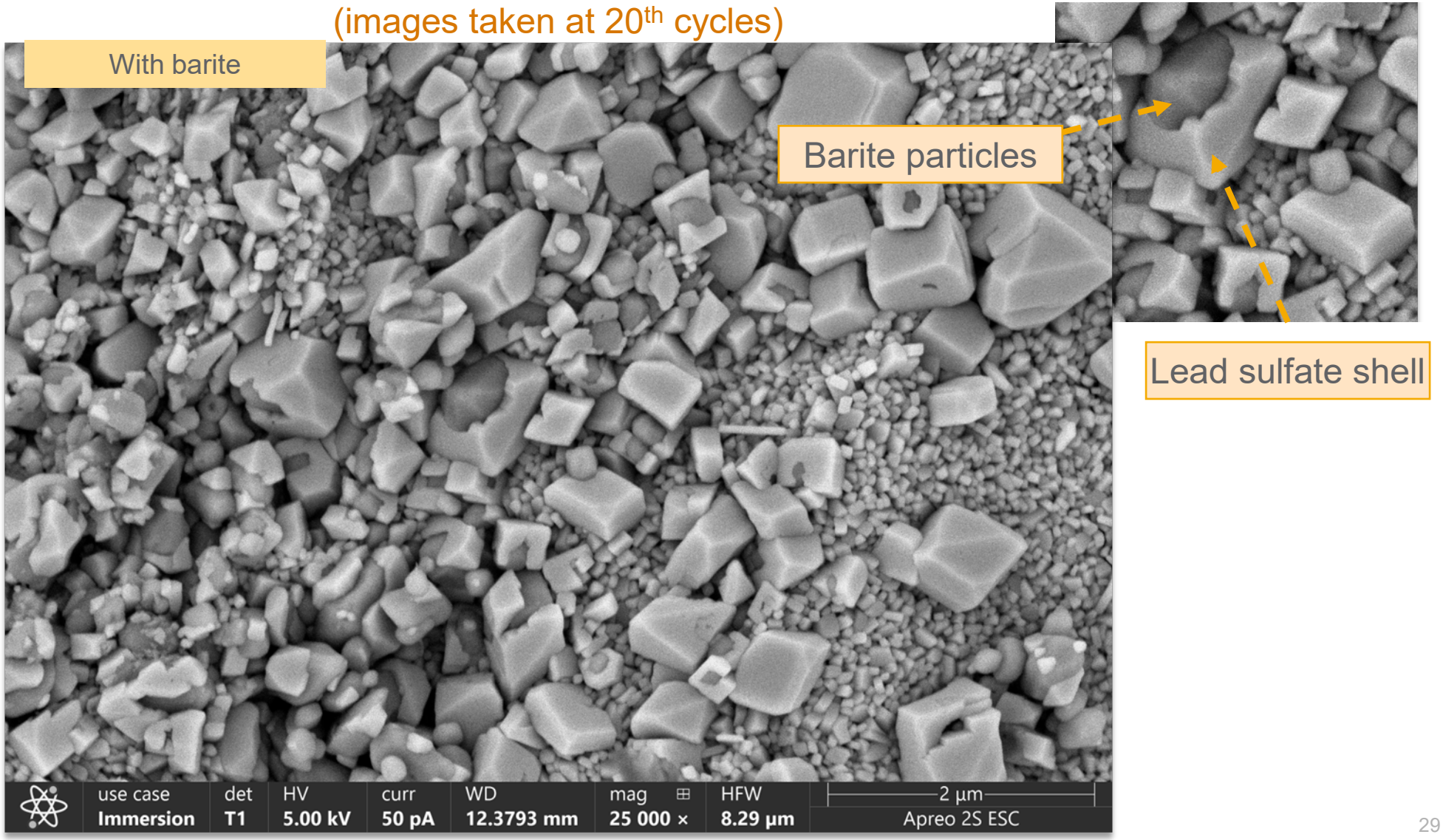


# Barite acted as a Nucleating Agent for $PbSO_4$

(images taken at 20th cycles)

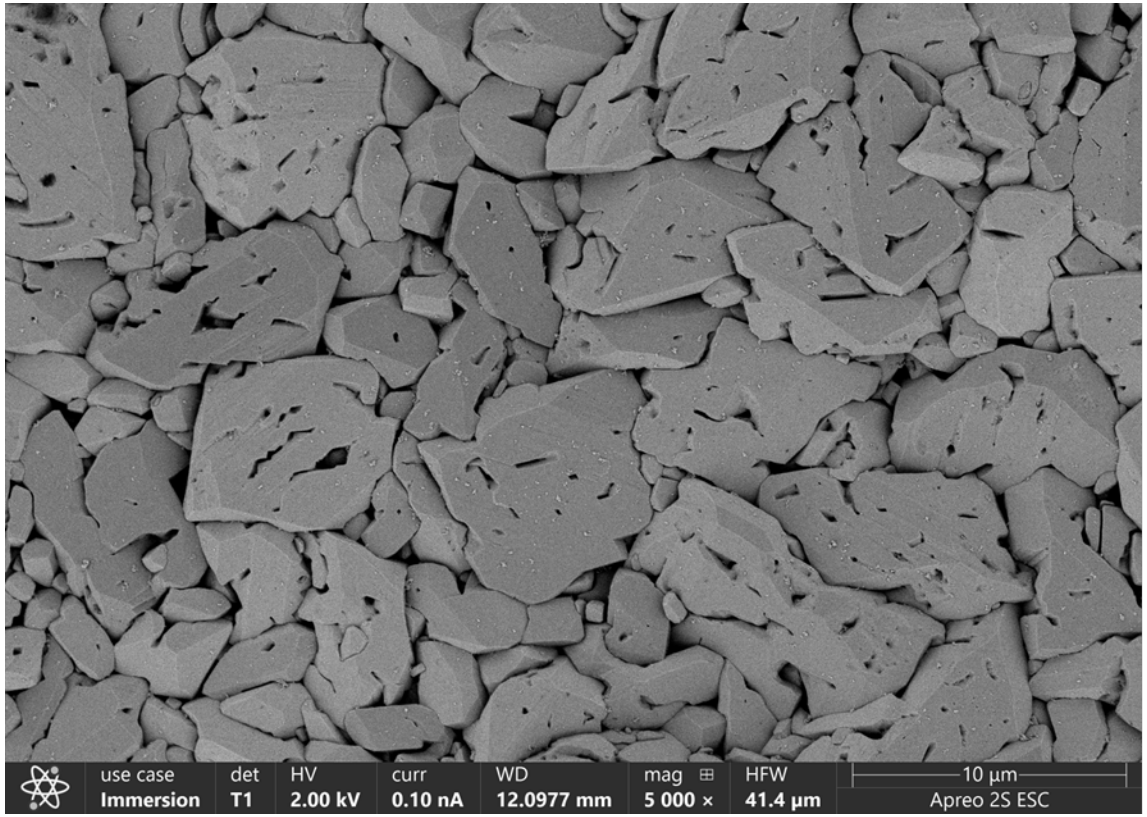


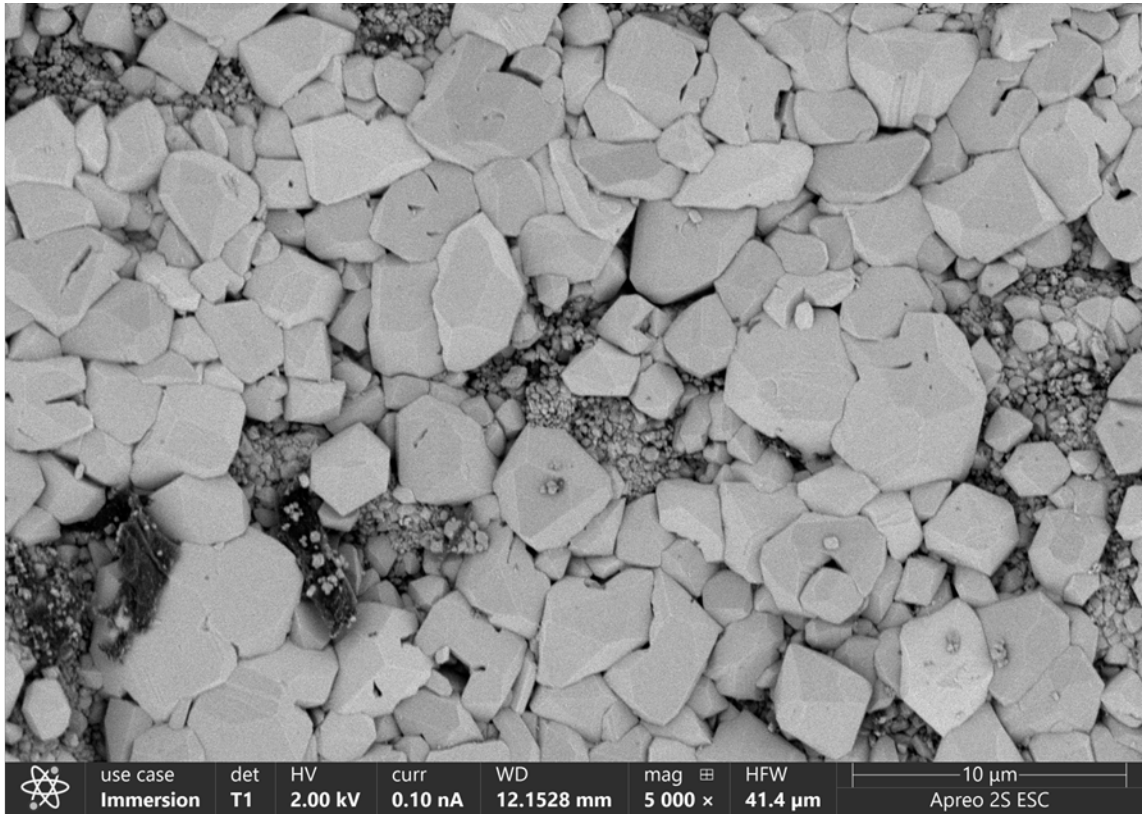
# Barite Promote Smaller $PbSO_4$ Particle Size

No barite

(images taken at 100th cycles)

With barite



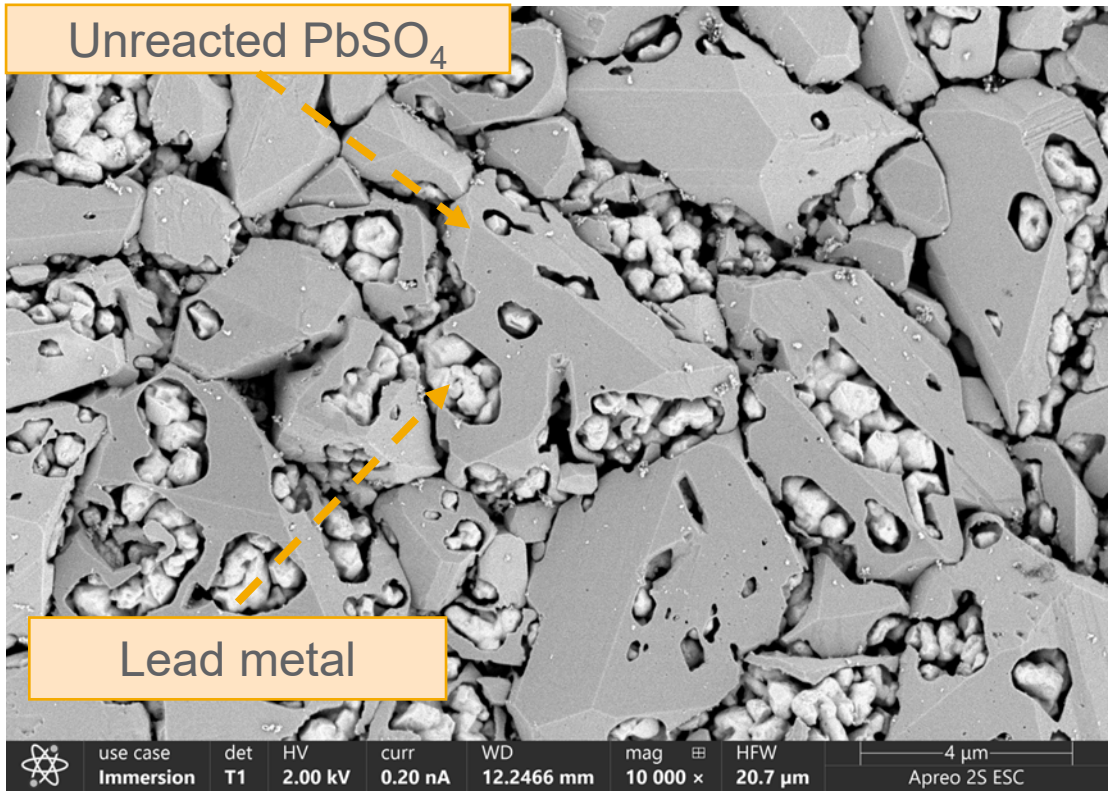



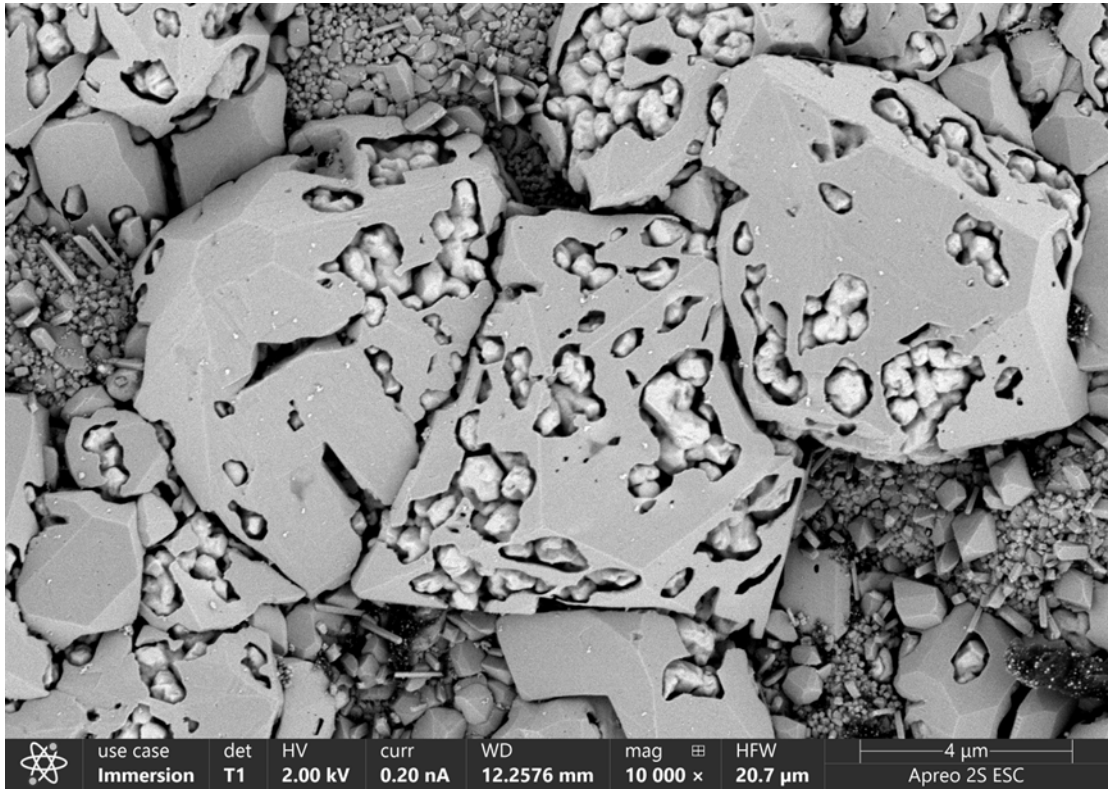

At oxidized state (Pb →$PbSO_4$)

# Impact of Barite on $PbSO_4 \rightarrow Pb$ Reduction

No barite

With barite




Mechanism of dissolution is inside out

Images taken at reduced state ($PbSO_4 \rightarrow Pb$)

# $PbSO_4$ Formation and Surface Densification after Cycling

No barite

(After 100th cycles)

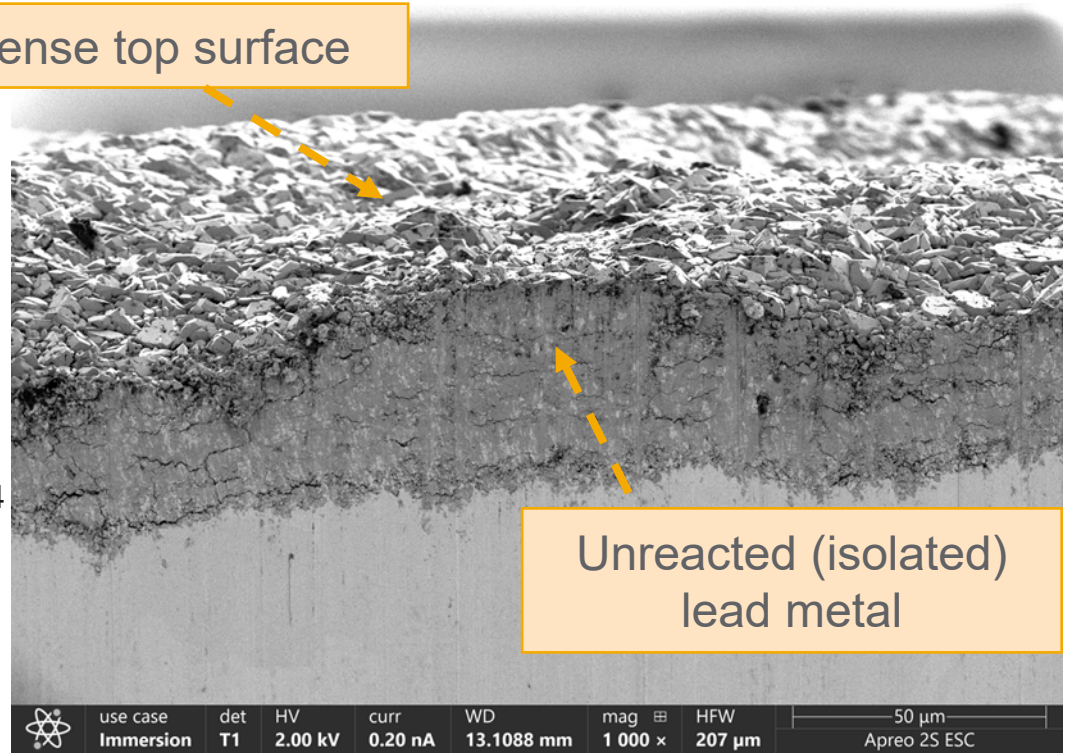
With barite

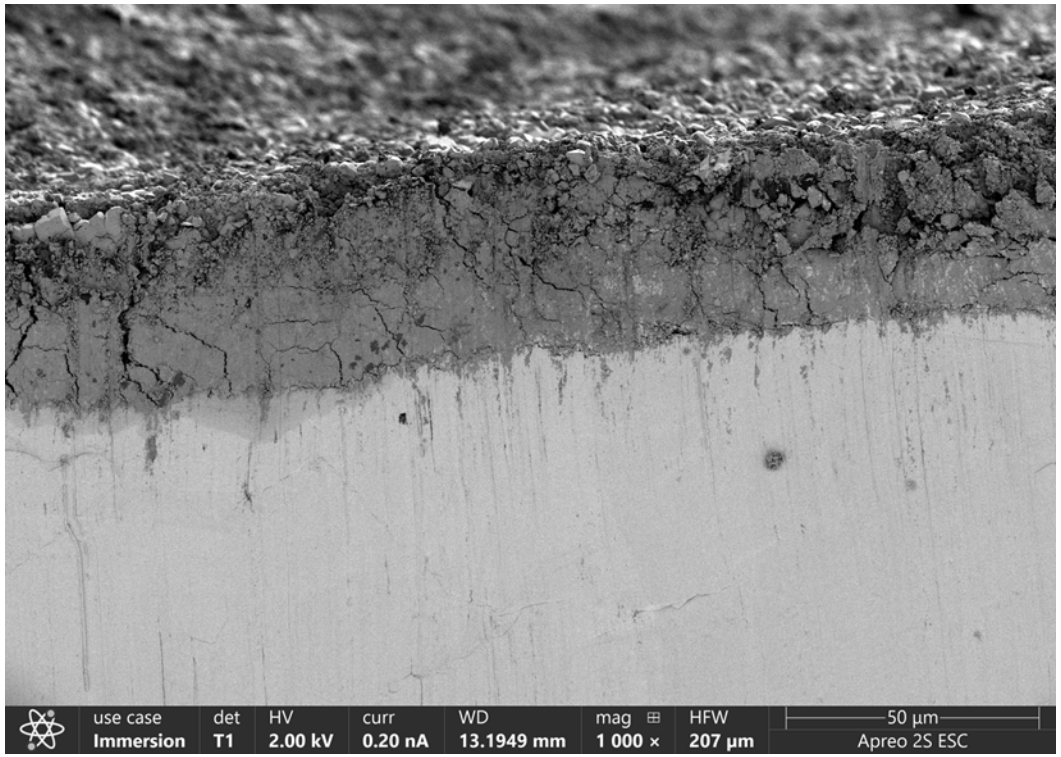
Dense top surface

$PbSO_4$

Pb + $PbSO_4$

Bulk Pb

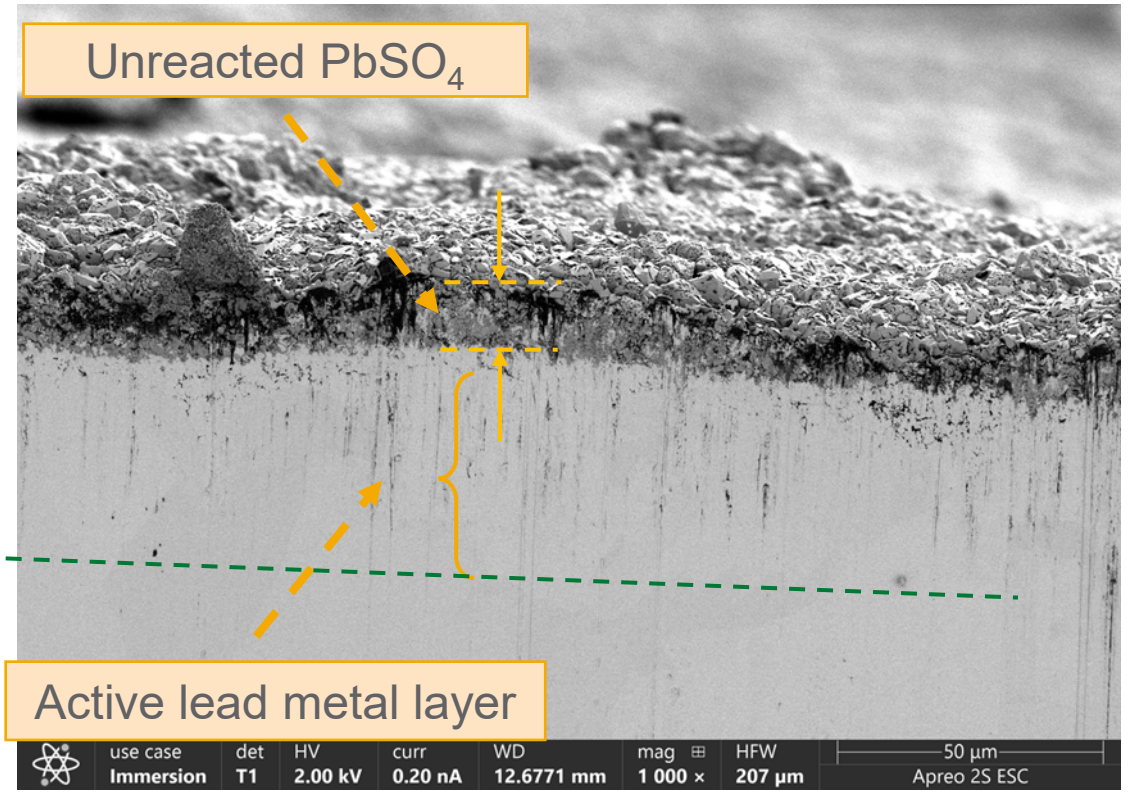


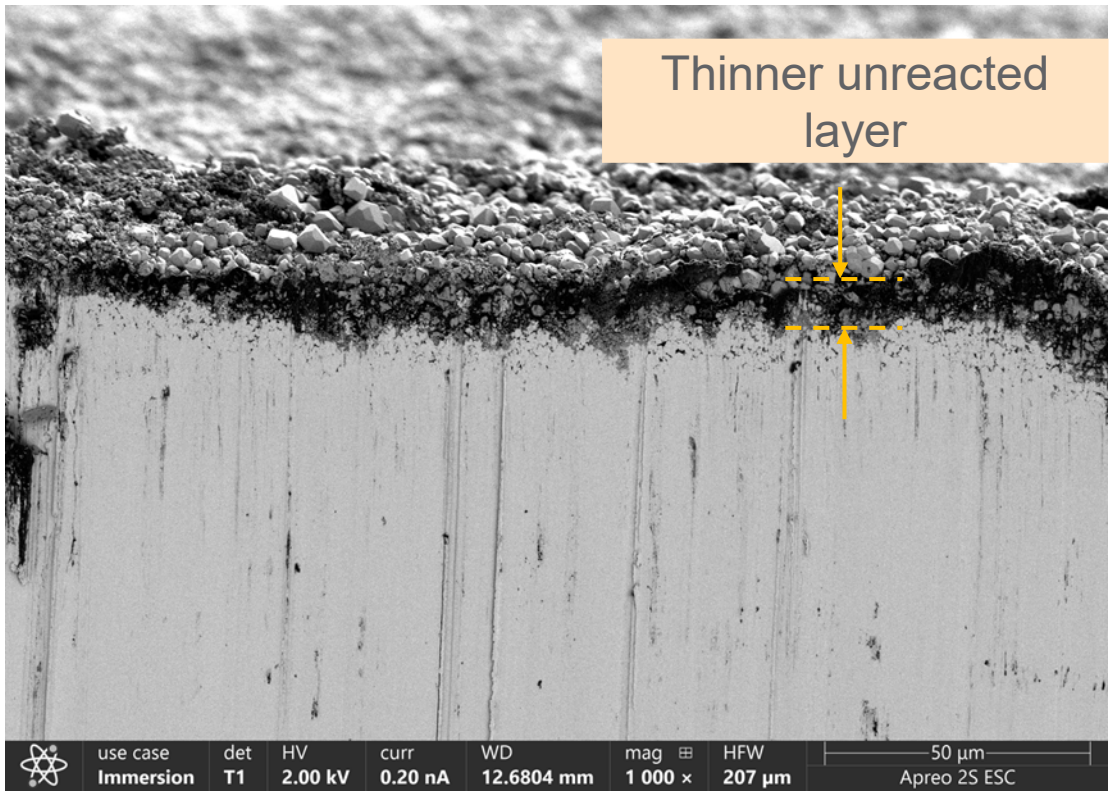

At oxidation state (Pb →$PbSO_4$)

# Impact of Barite on Unreacted Layer and Ion Transport

No barite



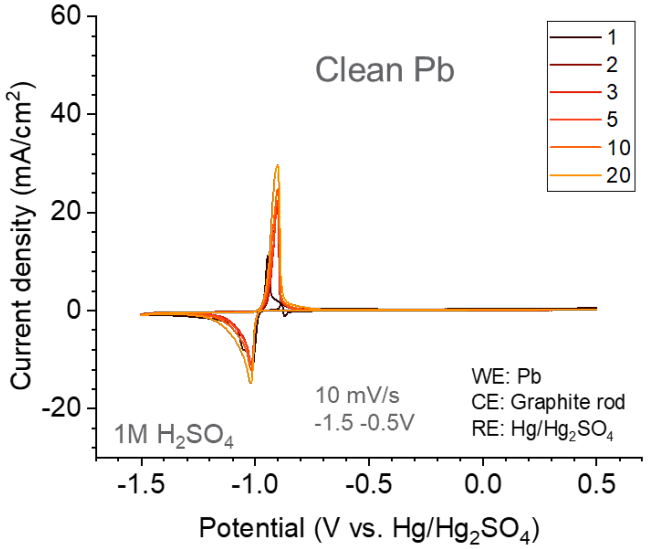

With barite

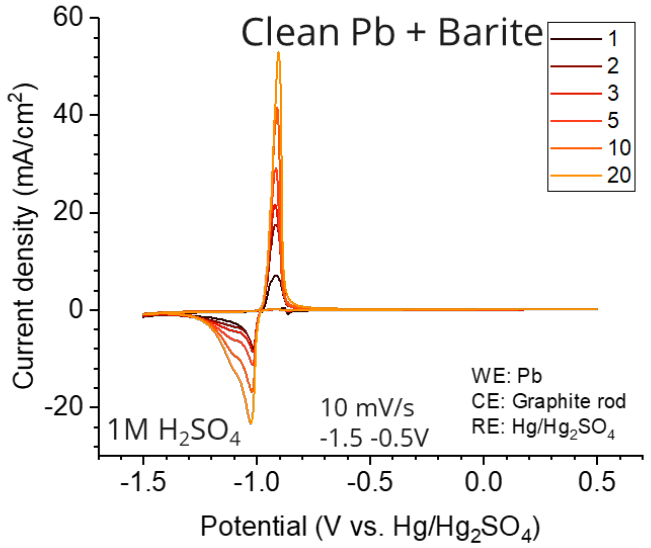


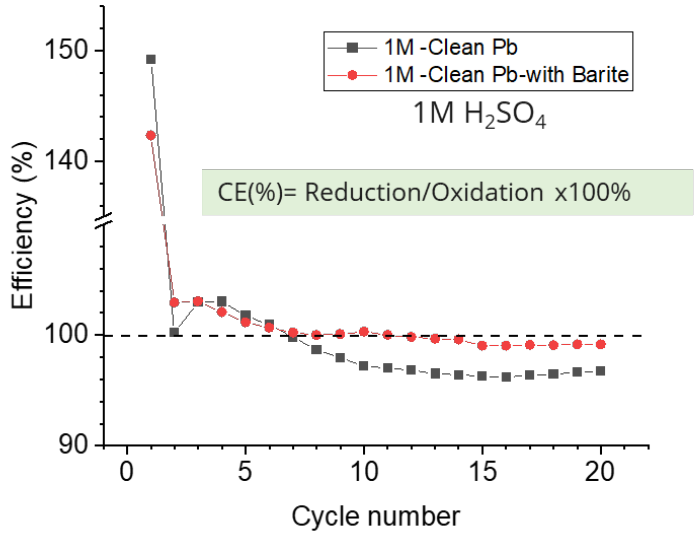

At reduced state ($PbSO_4 \rightarrow Pb$)

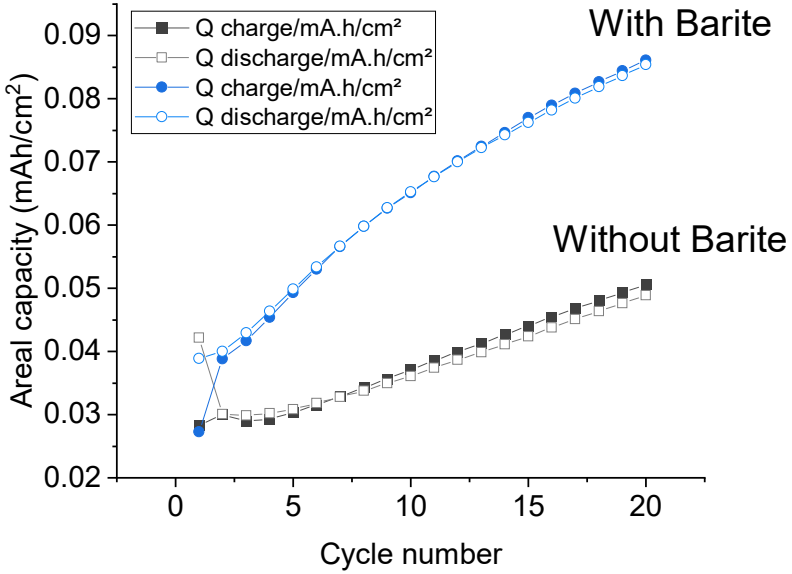
Dense $PbSO_4$ surface limits the ion transport ⇨ irreversible conversion $PbSO_4 \rightarrow Pb$

# The Barite Additive Increases Lead Activation with Number of Cycles




- The barite – contained electrode delivered higher Coulombic efficiency, suggesting higher reversible Pb-$PbSO_4$ conversion
- The barite additive increases the lead activation with cycle number

# Conclusions & Impact

- We demonstrated the role of lignin in reducing hard sulfation
  - Particle size and size distribution
  - Hydrogen ion transport
  - Reducing chemical passivation
- Small molecule such as 1-heptane sulfonate binds too strongly to the surface
- Lignin + Barite composition work together
  - Smaller size and non dense packing of $PbSO_4$
  - Reduced loss in lead inventory
  - Dissolution mechanism favors bulk over surface
- **Impact** – Better understanding of expander's role allows design of synthetic expanders with less batch-to-batch variability and improved cycling life

# Future Direction/Next Steps

- Study the effect of organic molecules in affecting the crystallization of $PbSO_4$
  - Nucleation and growth studies (in situ AFM and optical microscopy)
  - Atomic scale composition mapping (Atom probe tomography)
  - Chemistry of adsorption to $PbSO_4$ (DNP-NMR)
- Understand the role of lignin in formation of porous $PbSO_4$
  - Evolution of porosity (X-ray CT)
  - Diffusion of protons within $PbSO_4$ layers (NMR on cycled lead negative electrode top, middle, and bottom)
  - Partitioning of lignin in different concentrations of $H_2SO_4$ (density segregation of lignin, time-resolved, slice-selective NMR)
- Decouple the effect of barite and lignin (in-situ tools)
- Test small ligands to mimic electrochemical and morphological features similar to lignin, based on its structure, and optimum bonding with Pb metal (DFT calculations, electrochemical cycling, impedance, and DRT studies)

# Acknowledgements


- *This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.*
- *OE-30 team at PNNL and ANL*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