Electrolyte Degradation Mechanisms in Pb Acid Batteries

April 16, 2021

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

Enabling Pb-Acid Batteries for Grid Storage

Using molecular-level investigations to help transform Pb-acid batteries into a viable grid storage technology

Project Rationale:
- Current Pb-acid batteries are largely designed for SLI market
- Revisiting battery design rules and additives using modern analytical tools and cycling protocols
- Understanding mechanisms driving utilization and cyclability to make lead acid a strong contender for stationary applications

FY20 Research:
- Fundamental studies on H_2SO_4 solution structure and dynamics as a platform for direct studies on batteries (manuscript submitted to JPC) and Pb^{2+} interactions (manuscript in preparation)

FY21 Research:
- Elucidating $PbSO_4$ nucleation processes
- Electrolyte and additives evolution during cycling process

Integrated Multi-Institute Collaboration:
- Drawing together molecular spectroscopy, microscopy and cell testing (PNNL), X-ray analysis (ANL), and industrial expertise (RSR)

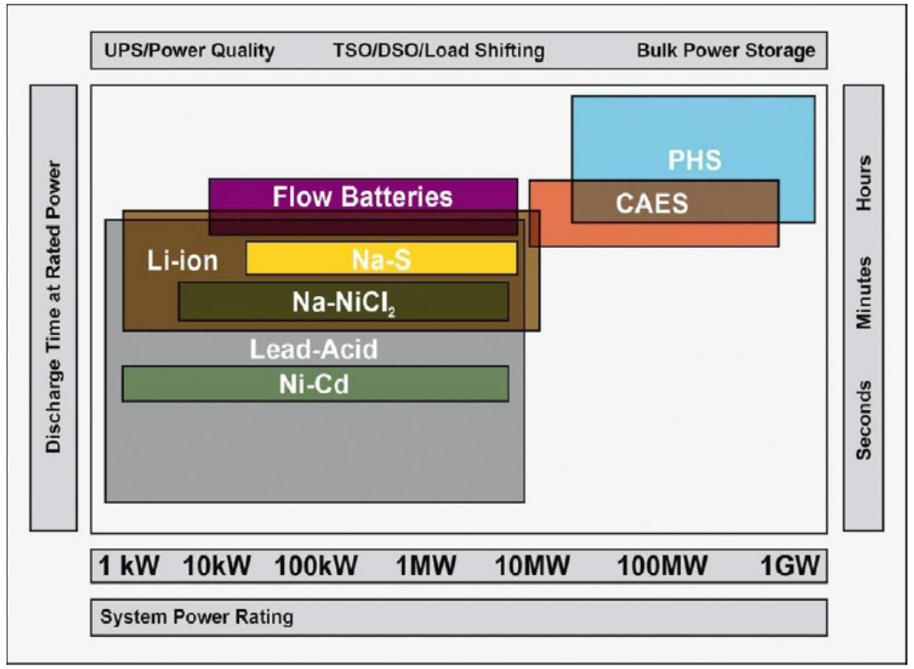
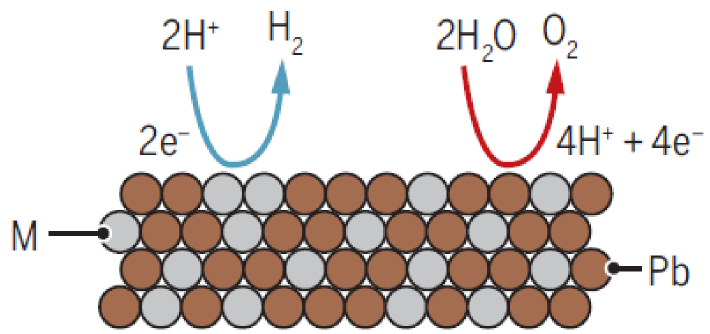


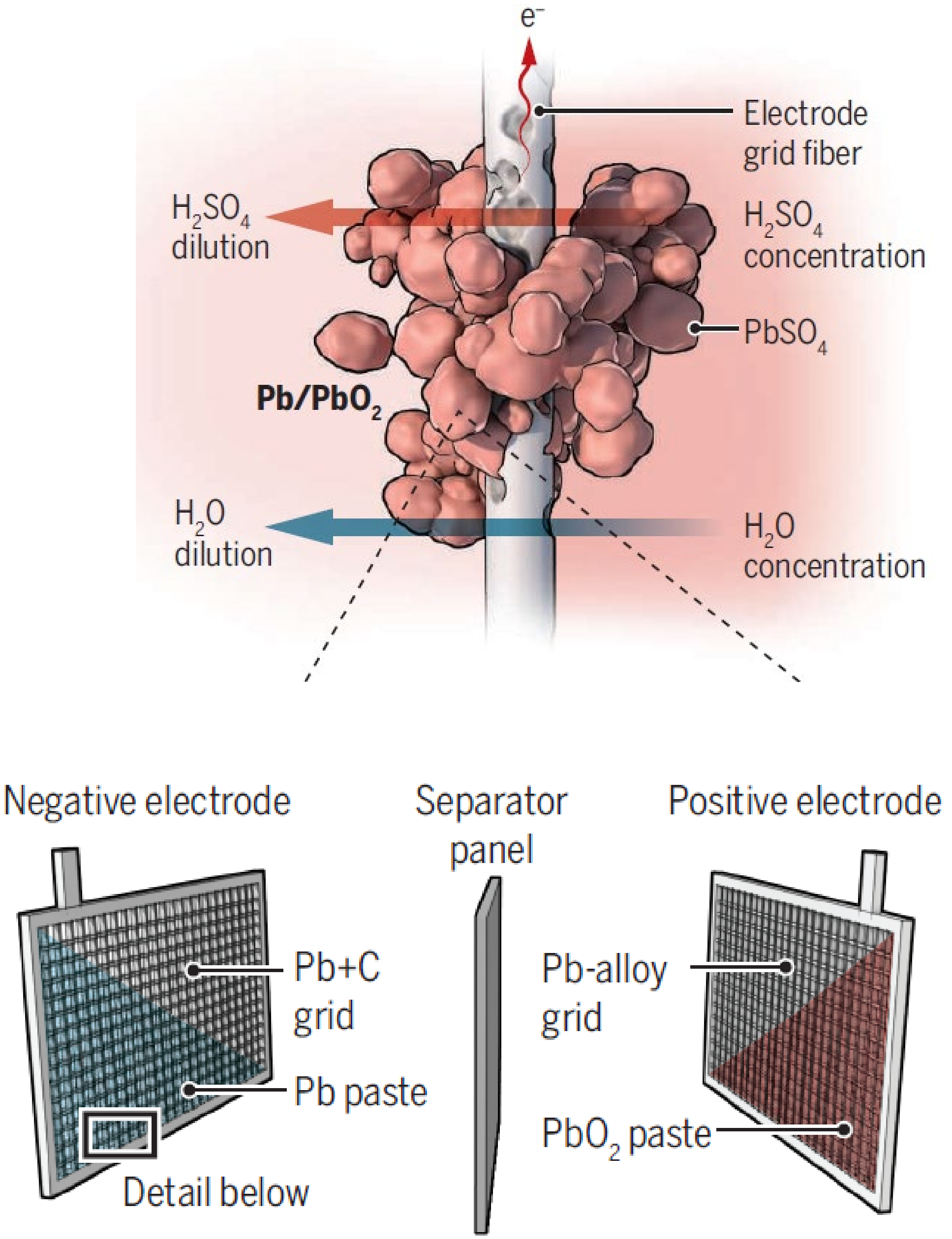
Figure Credits: May *et al.*, *J. Energy Storage*, **15** (2018)

Multi-Modal Characterization Across Length Scales

Maximizing utilization and cycle life involves processes linked over a wide range of length scales, from the molecular to the cell level

- Cell level (10^{-3} – 1 m):
  - grid design, stratification
- Particle level (10^{-9} - 10^{-5}m):
  - conductive networks, porosity
- Molecular level:
  - Pb solvation, nucleation and growth/dissolution of $PbSO_4$



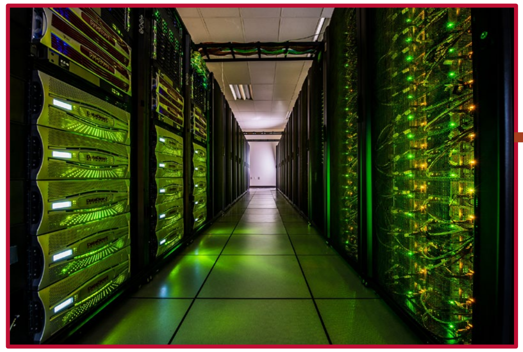


Understanding cell-level issues related to performance (charge acceptance, sulfation, grid corrosion) requires knowledge at all three length scales.

Figure adapted from: Papa Lopes *et al.*, *Science*, **360** (2020)

Integrated, Multi-Modal Techniques

Contending with the complicated molecular-scale processes which drive performance



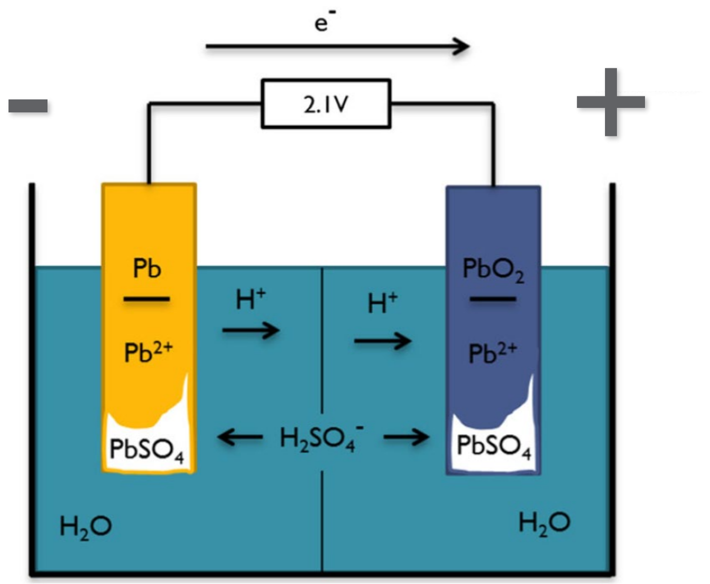
Solution Structure and Interactions
- PDF, EXAFS
- DFT Shift Calculation
- ^{17}O, ^{33}S NMR Linewidth, Shift

Transport and Dynamics
- ^{17}O NMR T_1, ^{1}H PFG Diffusivity
- Viscometry

Degradation Monitoring
- ICP-MS
- *In situ* Raman Spectroscopy

How does SO_4 control Pb-acid performance

Big picture: how much H_2SO_4, HSO_4^-, and SO_4^{2-} present at any point? (as a function of temperature, concentration, charge state etc.).



(1) $H_2O + H_2SO_4 \leftrightarrow HSO_4^- + H_3O^+$ (always happens IF there is enough H_2O present. 12 M is the crossover for this)
(2) $H_2O + HSO_4^- \leftrightarrow SO_4^{2-} + H_3O^+$ (less likely, strongly temperature dependent)

Subsequent questions:

1. How 'big' is the sulfate anion, i.e. how big is its hydration shell?
2. How do hydrated sulfate anions interact?
3. How does this connect the depressed freezing point = deep eutectic?
4. Ultimately, how does this affect the solvation of Pb^{2+} and other cations?

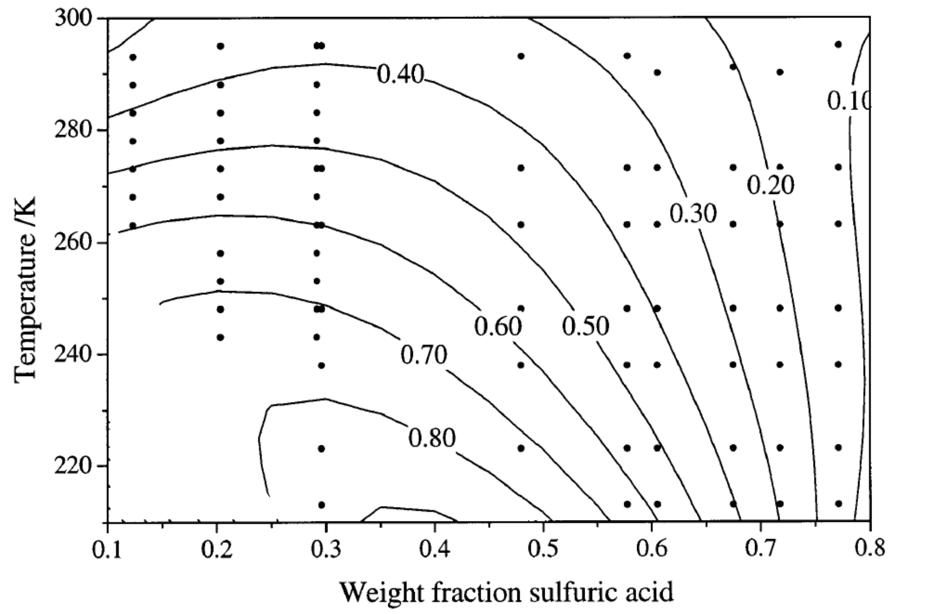
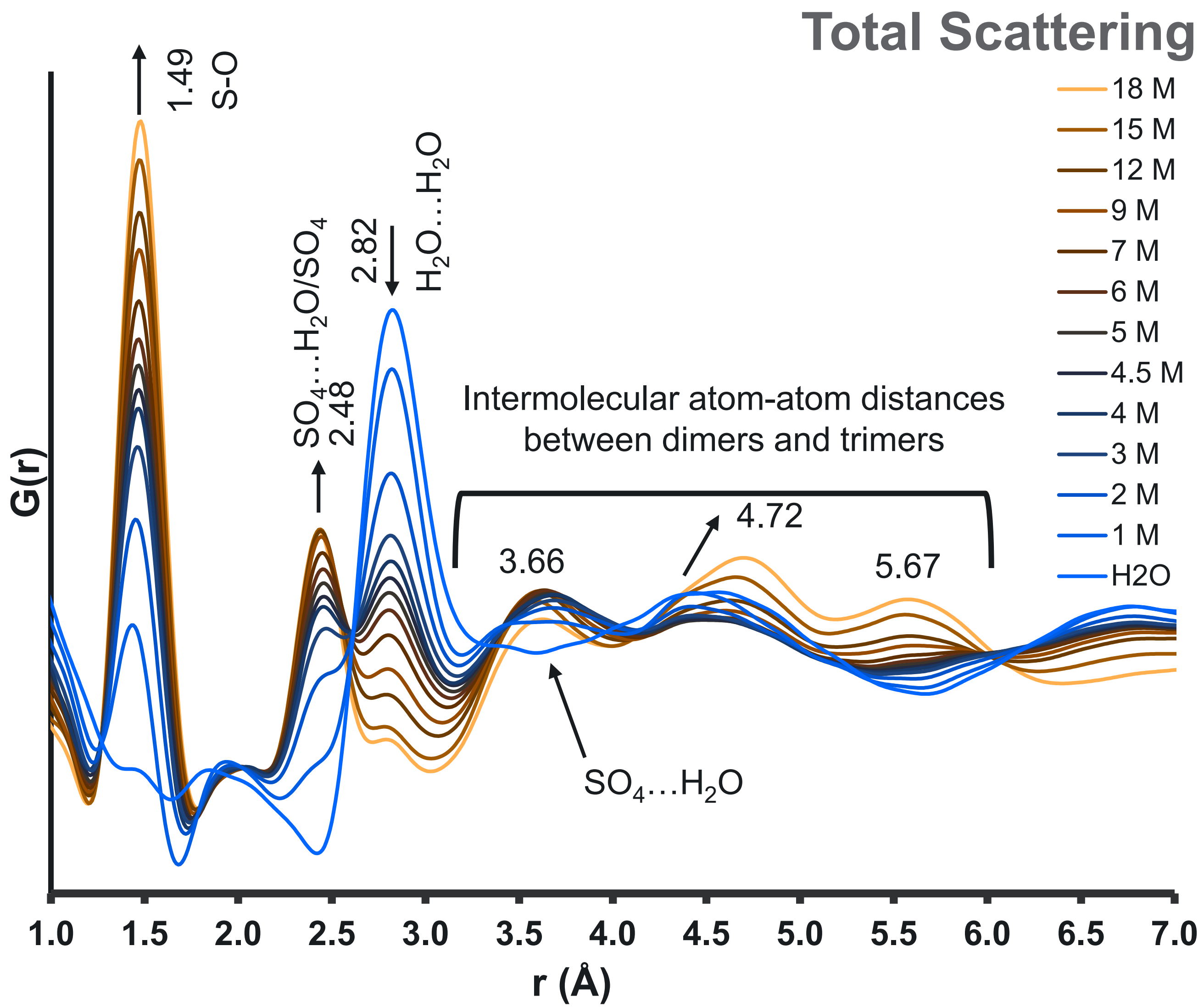


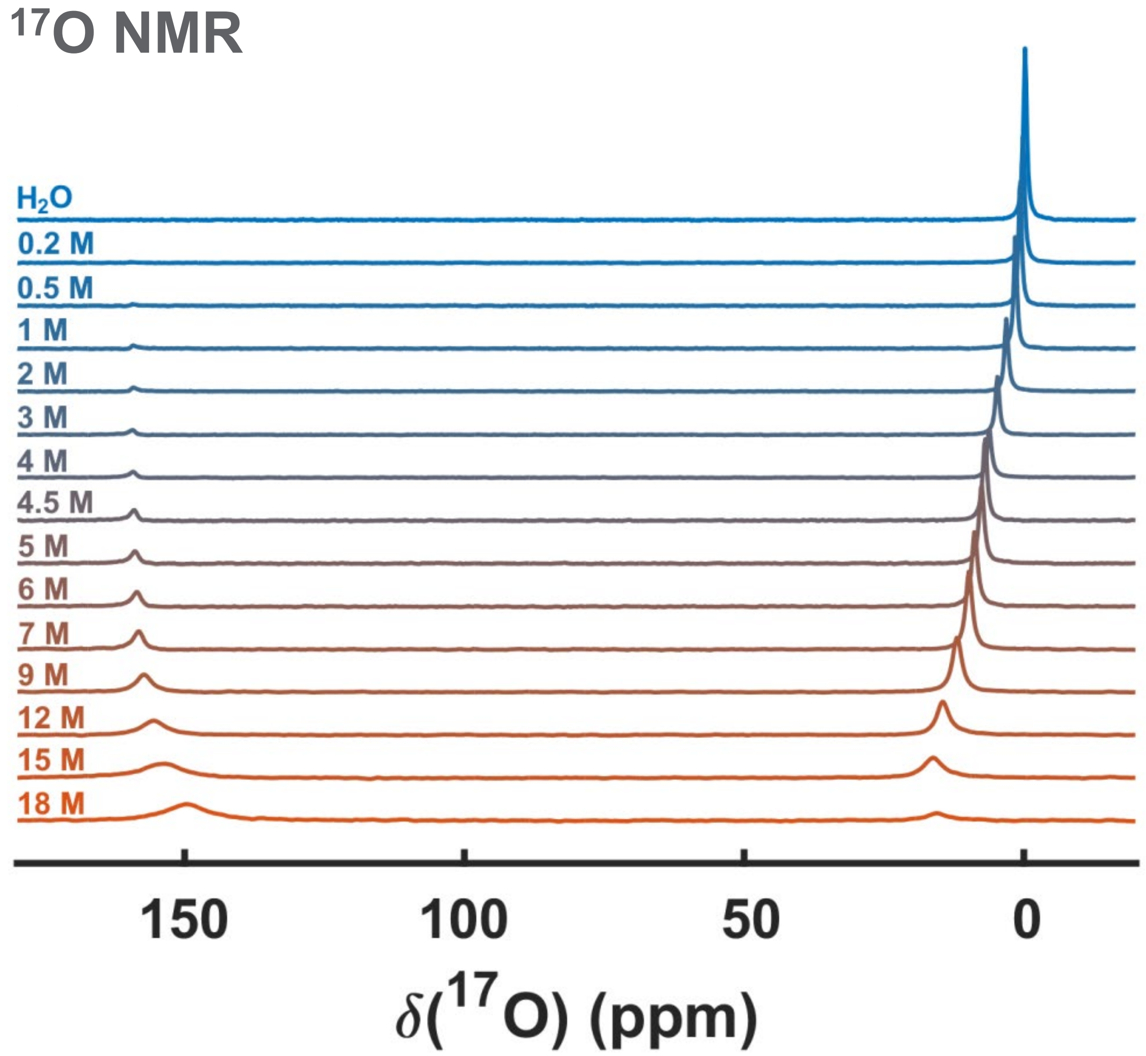
Figure 10. Contour plot of the calculated degree of dissociation in all the relevant (*w*, *T*) space. (●) (*w*, *T*) with experimental data from this work.

Molecular-Scale view of Aqueous H_2SO_4

Influence of concentration on solution structure probed by total scattering and NMR for the first model system: aqueous sulfuric acid



Pair distribution function analysis (PDF): Increase in longer range structure with increase in concentration



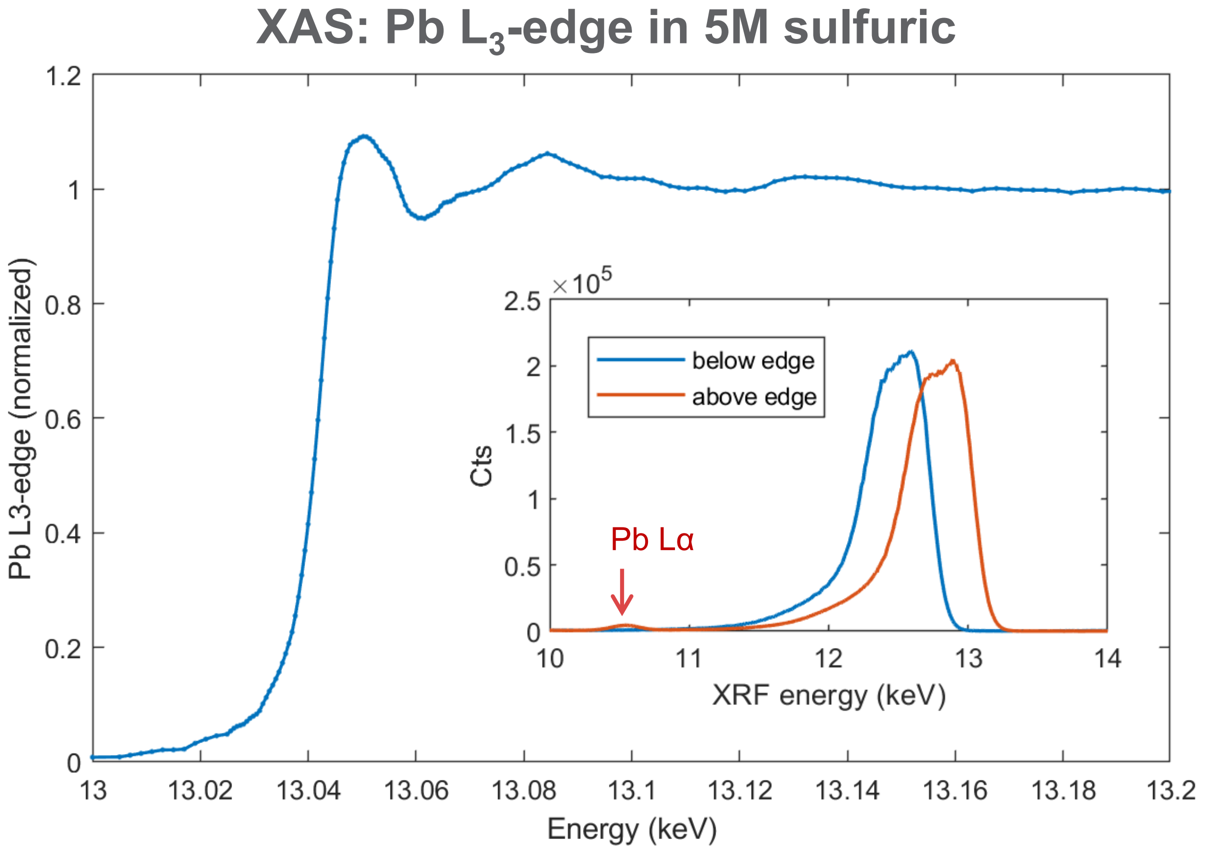
^{17}O NMR: H_2O Increasingly bound to sulfate species with increasing concentration

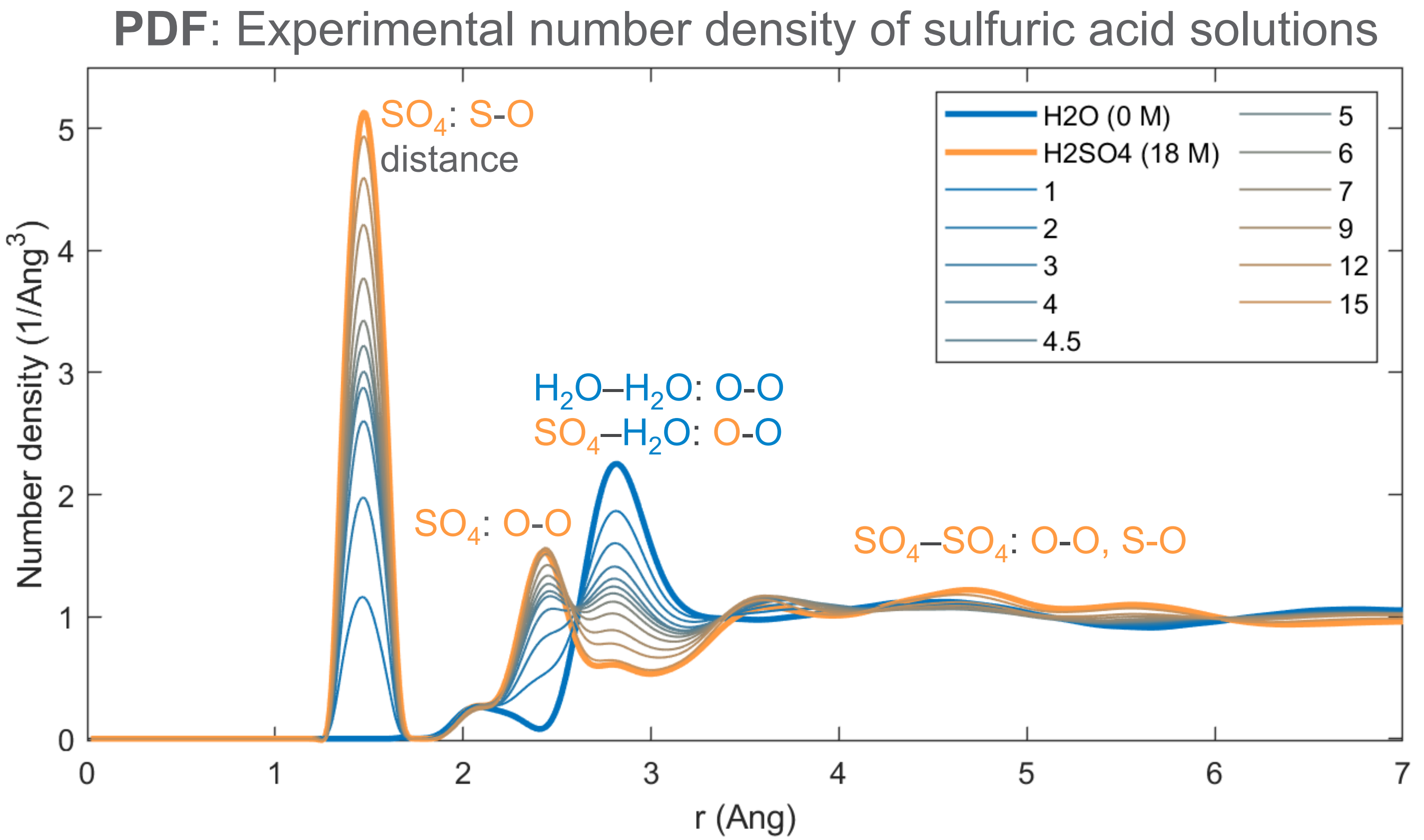
Solvation structure of sulfuric acid

X-ray scattering and spectroscopy from liquid species: direct comparison to MD simulations at PNNL to understand solvation, nucleation, and growth.

Total x-ray scattering (right) used to measure and analyze the overall number density in sulfuric acid.

- Currently analyzing data as a function of concentration and temperature.
- X-ray diffraction from the acid also used to measure local changes in acid concentration in battery electrodes.





X-ray absorption spectroscopy used to study the local solvation structure of Pb-ions in solution.

- Recent measurements using state of the art fluorescence detectors make it possible to analyze < 1 ppm solutions. Early results indicate Pb coordinated by water and sulfate anions at high acid concentration.

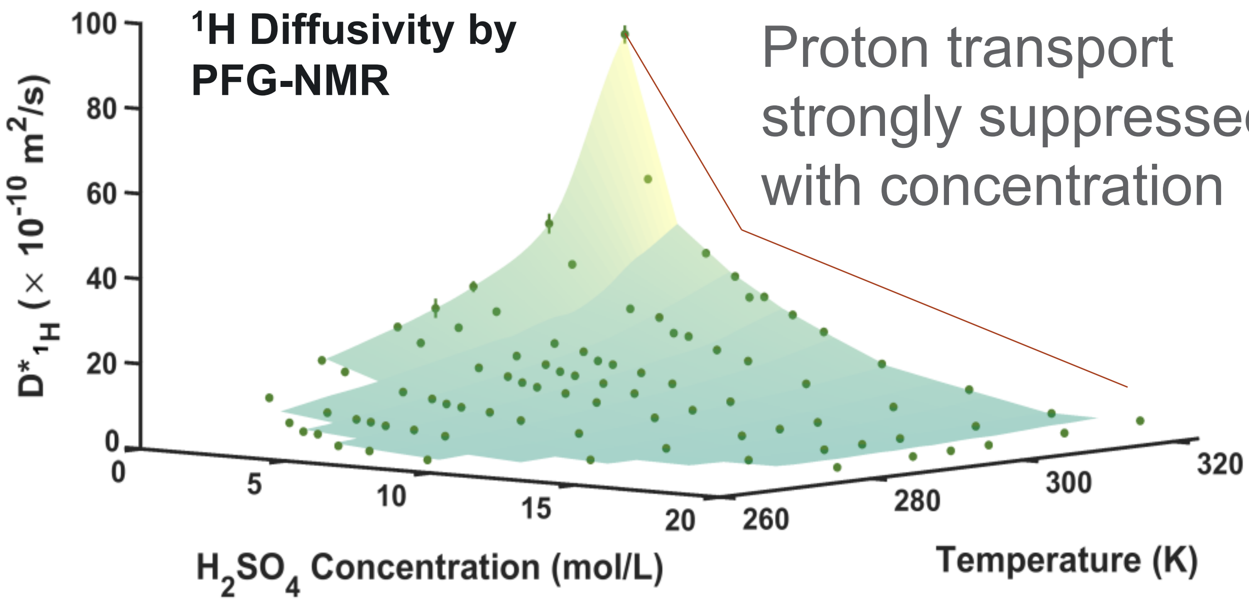
Dynamics and Transport of Aqueous H_2SO_4

Comprehensively determining how the molecular-scale motion is influenced by concentration and temperature in the sulfuric acid model system

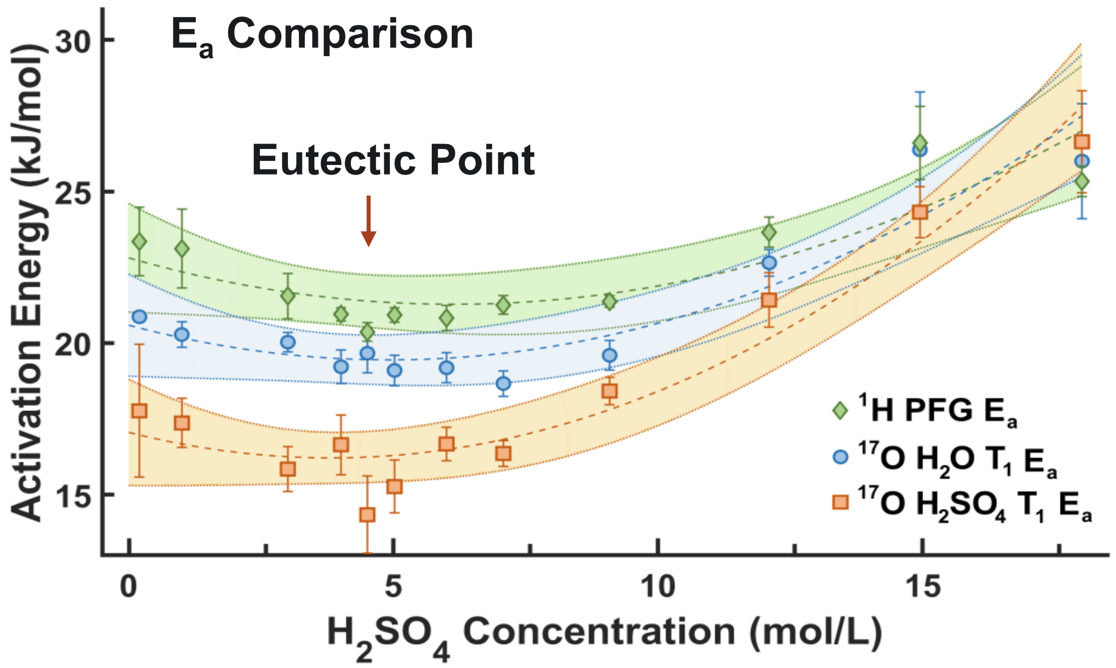
Multinuclear NMR (^{1}H, ^{17}O and ^{33}S) study conducted over a wide concentration (0 – 18 M) and temperature (-10 – 50 °C) range.

^{1}H PFG NMR analyzing proton self-diffusivity revealed differing dynamical regimes above and below the concentration of deep eutectic point.

Strongly correlated dynamics of the water and sulfate species in the high-concentration regime influences the mass transport in sulfuric acids.



Proton transport strongly suppressed with concentration

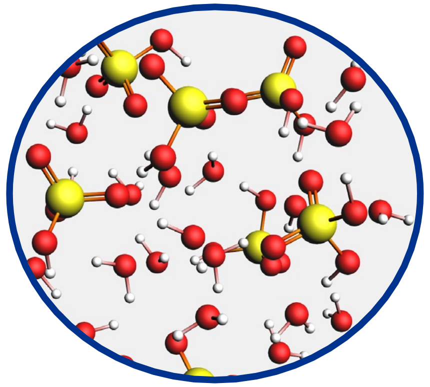


Electrolyte Degradation – Integrated Analytics

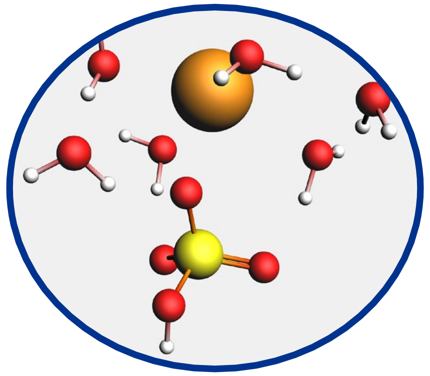
Two-pronged approach, examining fundamental Pb-ion/lignosulfonate interactions and degradation mechanisms of commercial cells

Probing the Role of Lignosulfonate

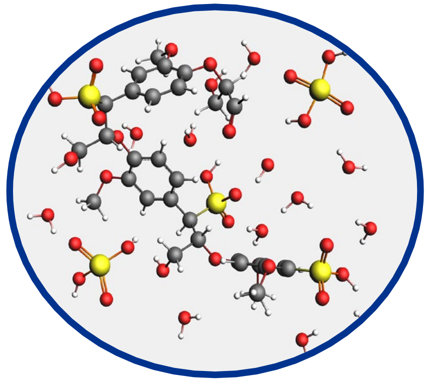
- SO_4^{2-} availability and lignins: critical for high discharge rates
- Pb^{2+} solubility: critical for high charge rates



H_2SO_4 (aq)



$PbSO_4$ (aq)

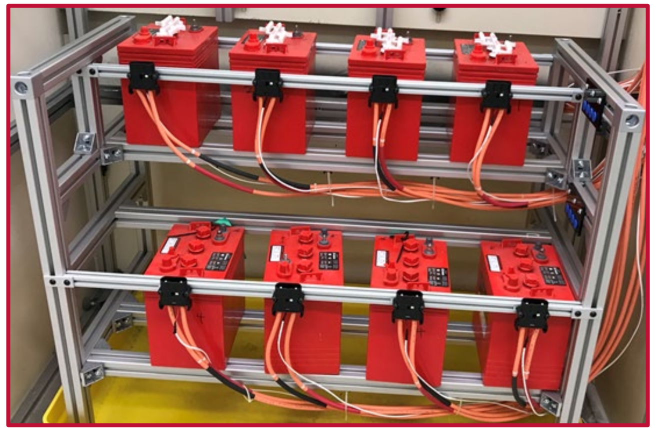


Lignosulfonate (aq)

Understanding nucleation/dissolution during cycling and preventing sulfation

Full-Cell Performance Prediction

- Deep cycling without full recharge leads to sulfation (can produce active material cracking)
- Fast cycling: stratification of electrolyte



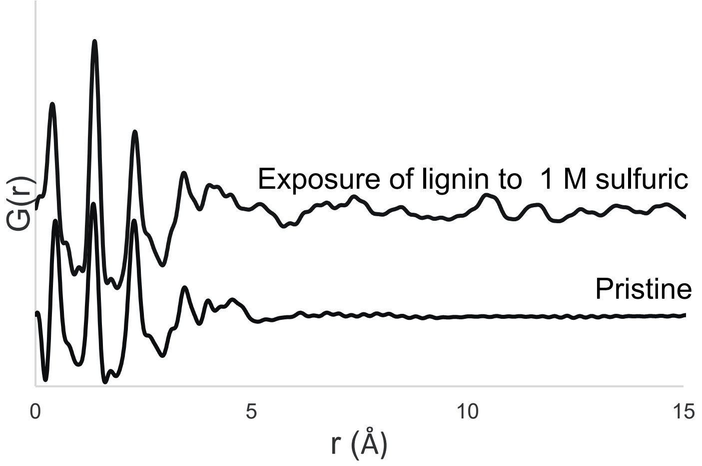
In-depth characterization of extracted electrolyte and post-mortem plate analysis: degradation mechanisms and correlation to performance

Probing the Role of Lignosulfonate

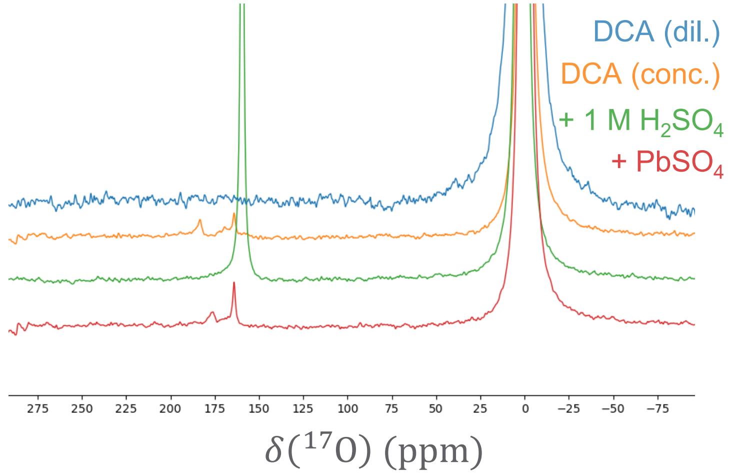
Lignosulfonates (LS) are an essential modifier for achieving high discharge rates, and will be a major focus of upcoming investigation

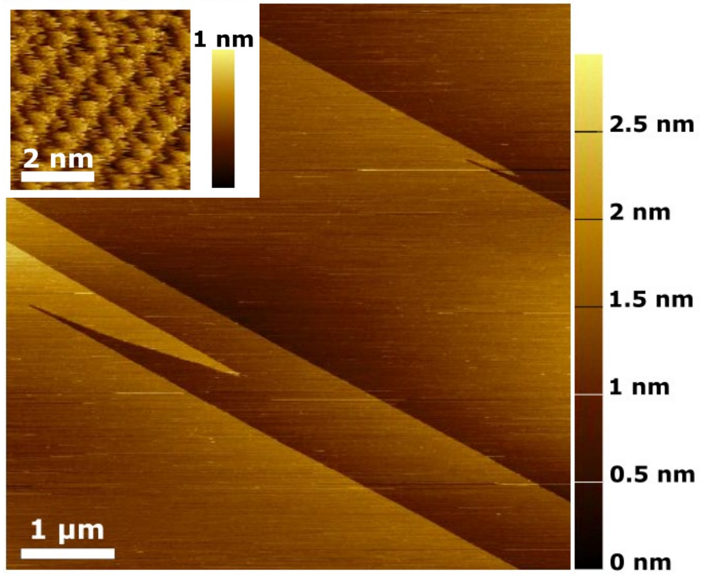
- We will analyze the effect of commercial and designed LS (Prof. X. Zhang at UW) on $PbSO_4$ growth in the electrolyte and at electrode surfaces

- **PXRD and PDF:** tracking lignin stability and structural changes with acid exposure
- **ICP and PDF:** quantifying Pb uptake and identifying the Pb/LS environment



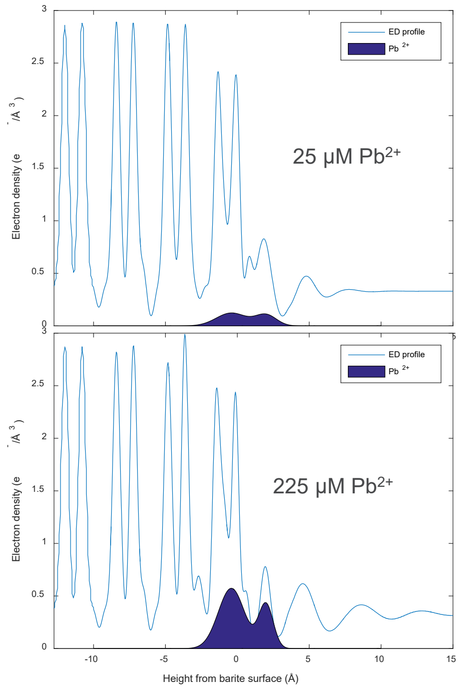
- **^{17}O NMR:** sidechain signatures, dynamical influence of Pb^{2+} binding
- **^{207}Pb MAS-NMR**: examining Pb^{2+} uptake in LS precipitate





Liquid-cell AFM

- **AFM:** studying lignin sorption and $PbSO_4$ growth in solution
- ***In situ* Raman and XPS:** quantifying LS functional moieties with model compounds



- **X-ray surface diffraction and resonant scattering:** interfacial structure of $PbSO_4$ (001) surface and role of LS
- **GISAXS:** resulting $PbSO_4$ morphology

Example of analysis from surface x-ray scattering and resonant scattering of Pb incorporation on $BaSO_4$ (001)

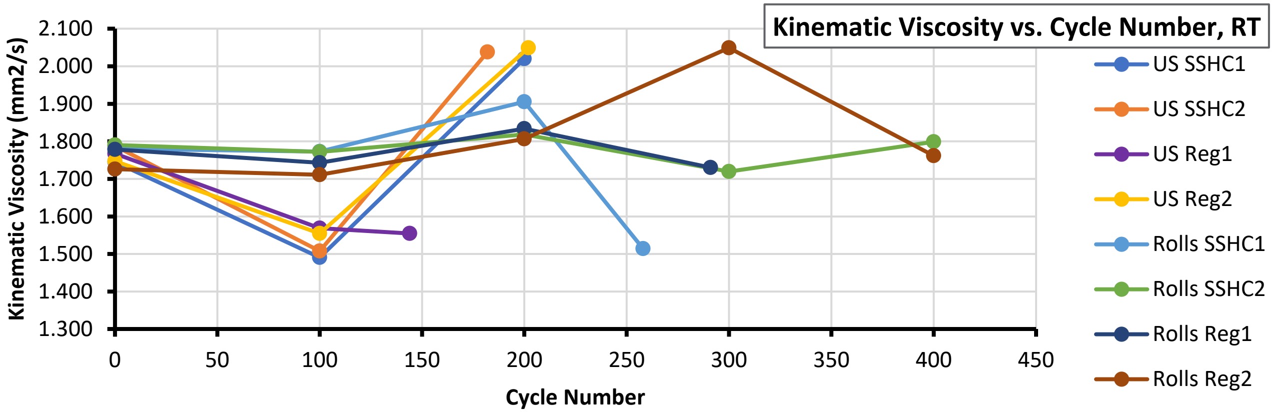
Predicting Performance From Molecular Insights

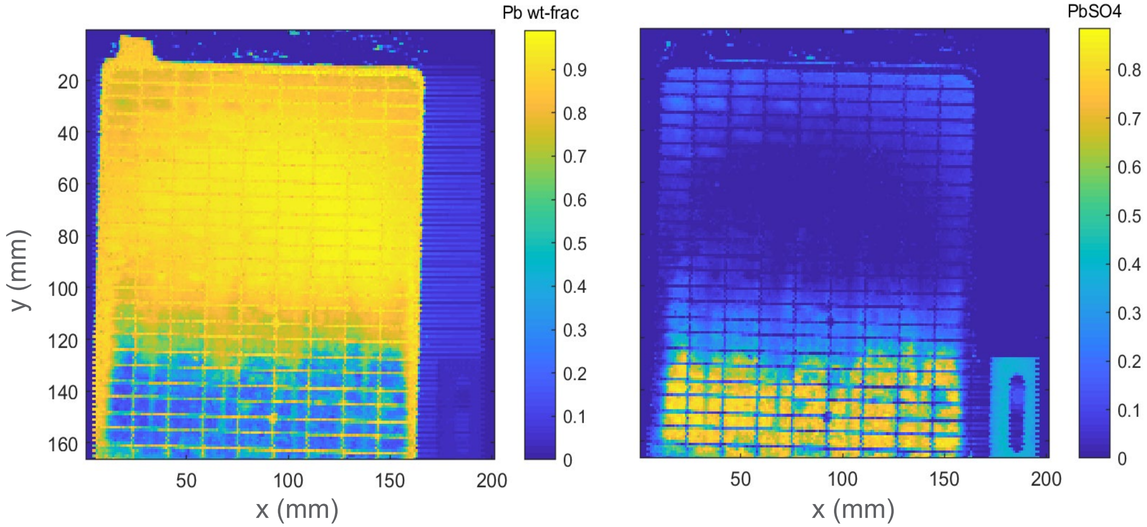
Progressing to real-world electrolytes from the molecular scale will generate new insights about cell-level performance and tunable solvation

- We will analyze periodically-extracted electrolyte samples from commercial cells which are cycled aggressively, and perform post-mortem characterization of the electrode plates

- **Viscometry and multinuclear NMR:** identifying degradation products in the electrolyte and tracking solvation dynamics evolution with cycling

- **ICP:** trace speciation of electrode grid breakdown products





Teardown of PNNL-cycled battery at Argonne and resulting diffraction maps from negative plate.

- **High-energy diffraction mapping:** post-mortem electrode plate characterization and spatial heterogeneity of degradation processes

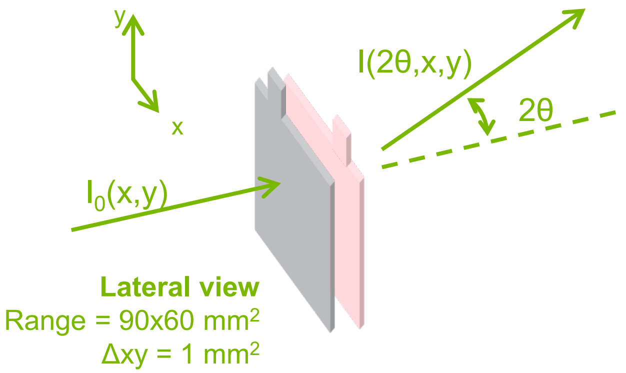
- Analyzing local electrolyte concentration and variation in sulfate size and morphology
- Select regions will be sent back to PNNL and studied with ^{207}Pb MAS-NMR

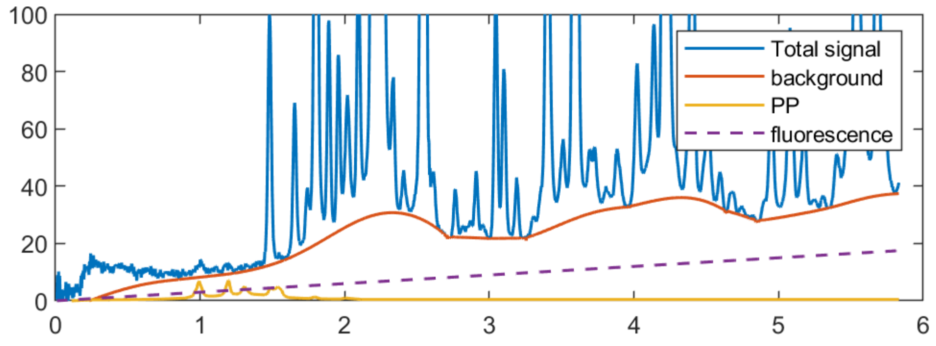
In Situ XRD Reveals Local Electrolyte Evolution

Imaging local concentration changes in the electrolyte of a flooded cell during cycling can link evolution to long-term performance

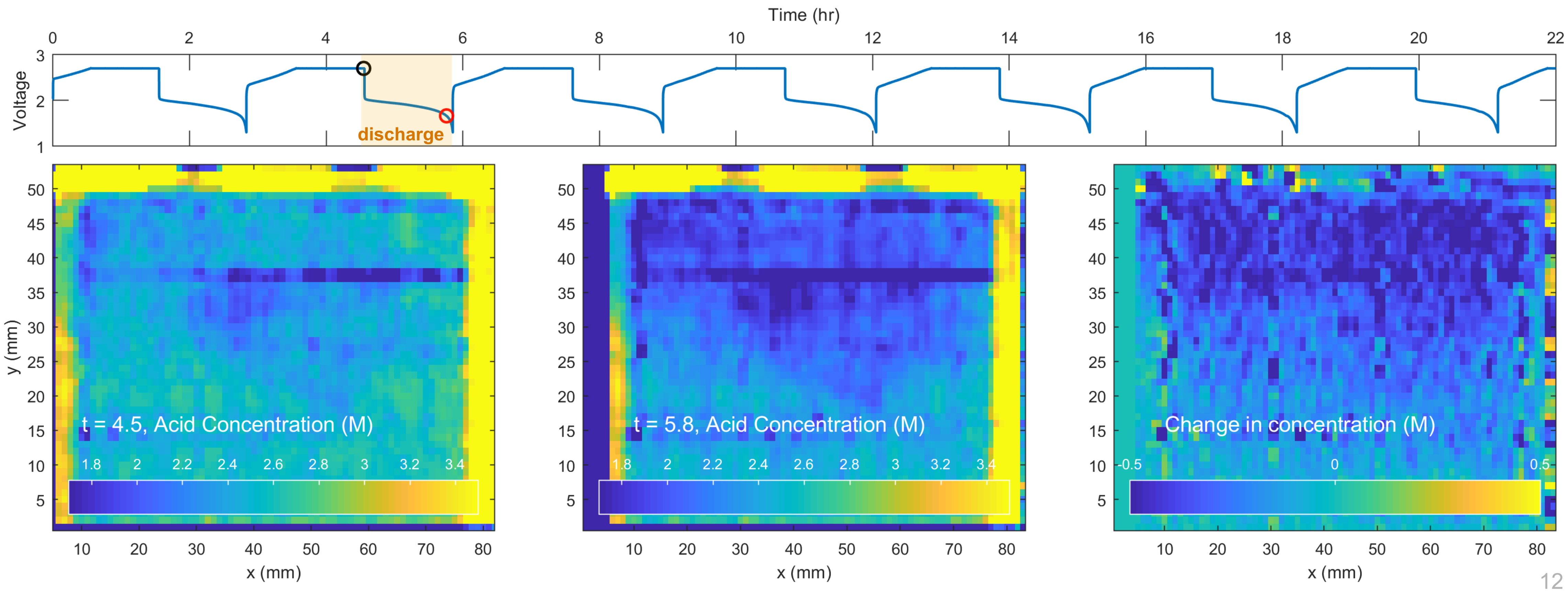
Using the results from this project, we are able to connect the background signal in previous XRD data with components from HSO_4 and H_2O, providing spatial maps of electrolyte concentration.

2V AUX9 cell





Example of acid concentration maps measured during **discharge**: concentration reduction correlates with change in $PbSO_4$ discharge product (not shown)



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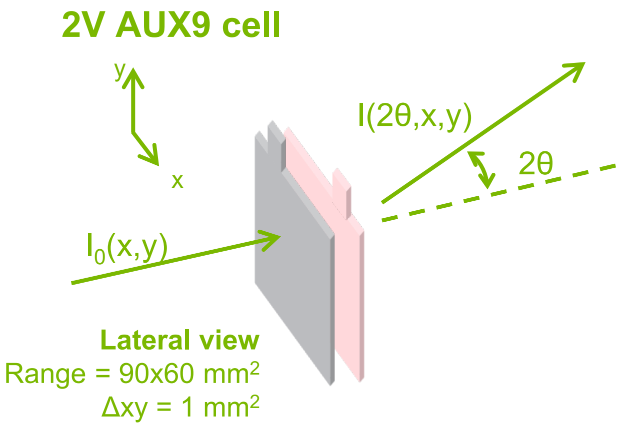
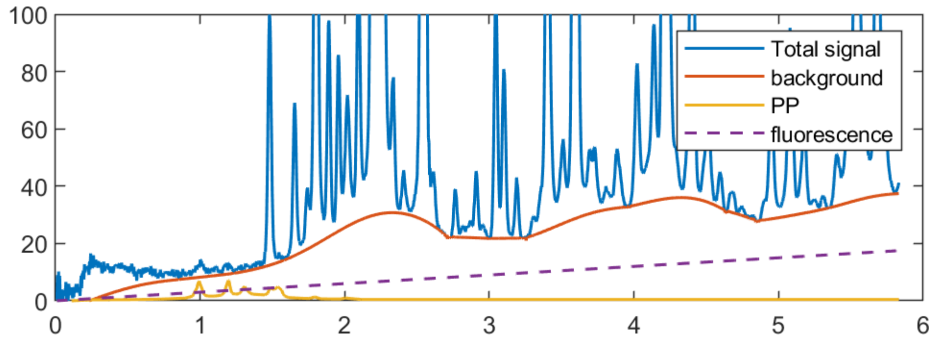
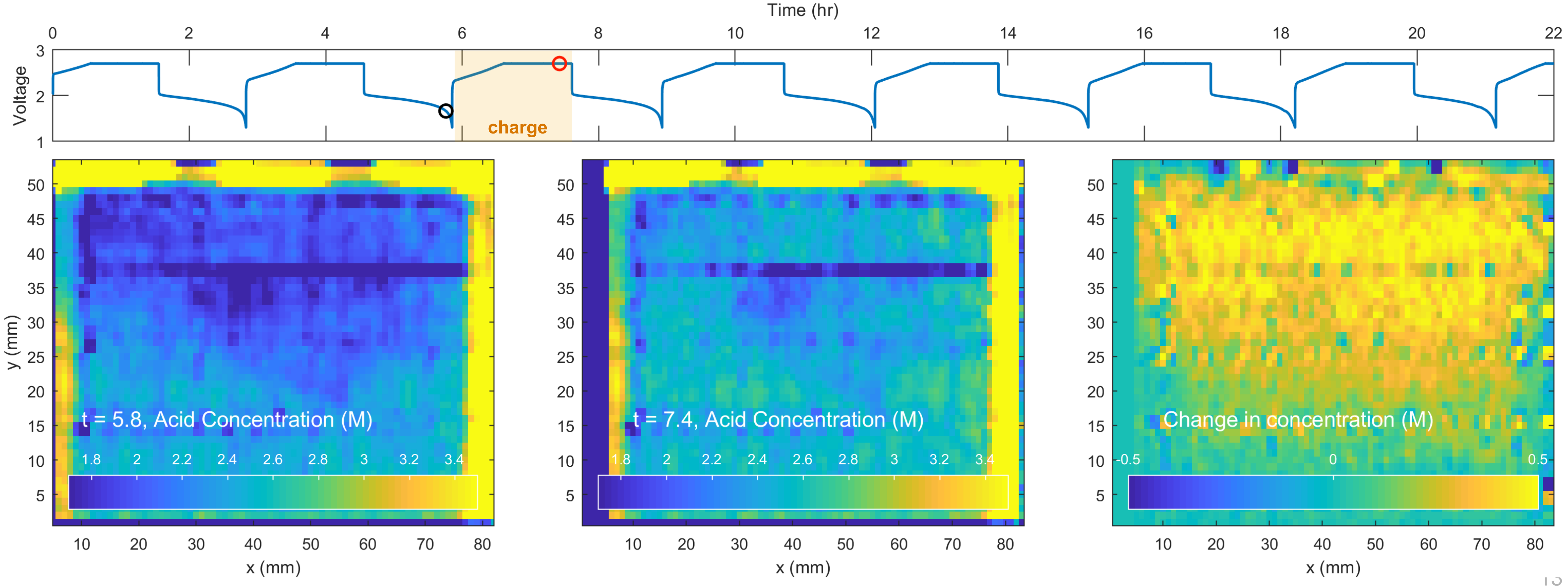




Example of acid concentration maps measured during **charge**: concentration increase correlates with active region in plates near the top.

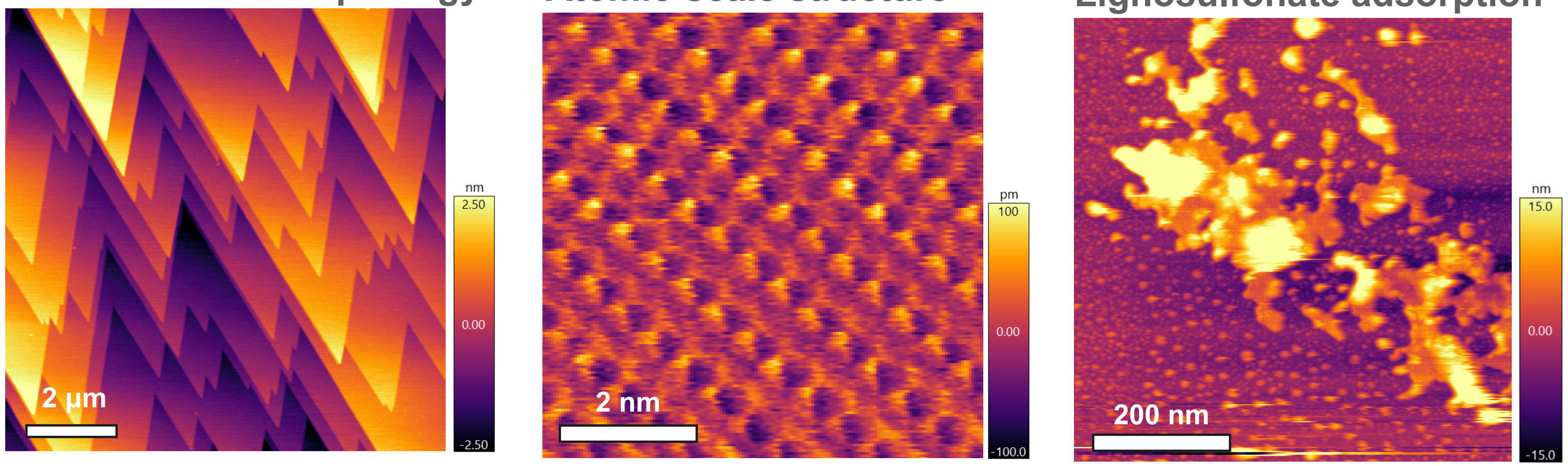


Lead Sulfate Nucleation Pathways

In-situ imaging to reveal $PbSO_4$ nucleation mechanisms on barite and lignosulfonate-modified barite surfaces.

Cypher VRS
Video-rate in-situ atomic force microscopy

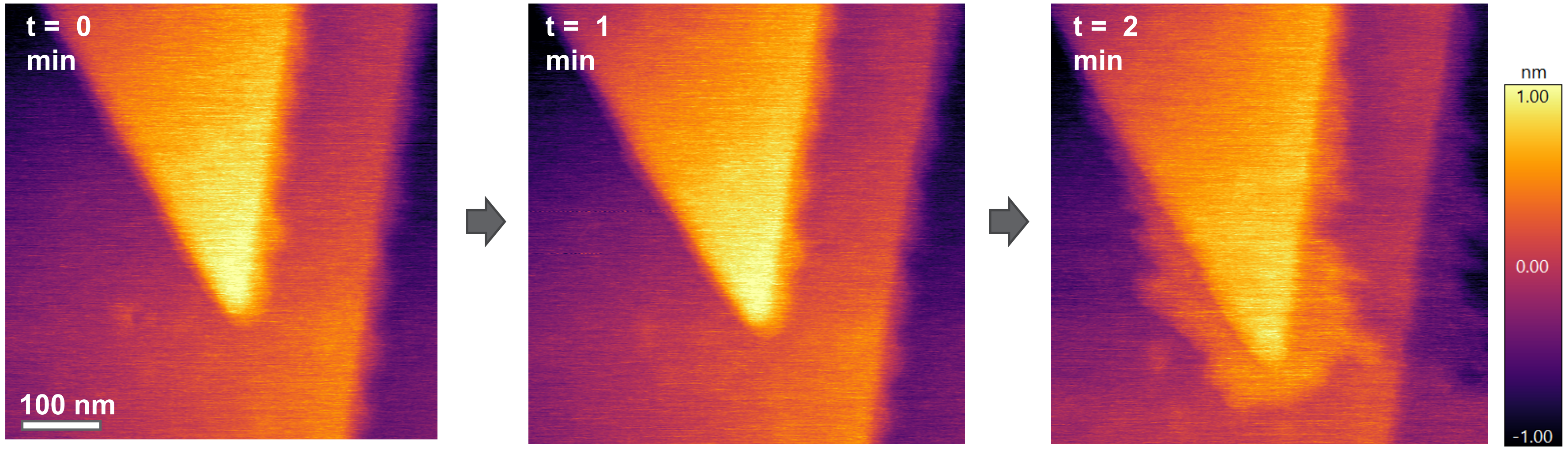
Barite Surface Morphology | **Atomic-scale structure** | **Lignosulfonate adsorption**



How does battery chemistry impact the $PbSO_4$ nucleation pathway and resulting microstructure?

- Lead-sulfate saturation
- Sulfuric acid concentration
- Lignosulfonate modification.

High-speed imaging of $PbSO_4$ film growth on barite



Thank you

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity through the Energy Storage program under contract No. 57558. PNNL is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.