Towards Building Optimal Electrolytes for Pb-Acid Batteries Through Tunable Solvation Chemistry

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Expanding the Capability of Pb-Acid Batteries

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

Advantages: cheap materials, high discharge power, low self-discharge, recyclable, safety

Disadvantages: limited cycle life from multiple degradation processes and deep cycling

Project Rationale:

- Current lead batteries are largely designed for SLI market.
- This project will revisit battery design rules and additives used for lead acid using modern analytical tools and cycling protocols.
- Understanding the mechanisms driving utilization and cyclability could make lead acid a strong contender for stationary applications.

Integrated Multi-Institute Collaboration:

- Drawing together molecular spectroscopy (PNNL), x-ray analysis (ANL), and industrial expertise (RSR)

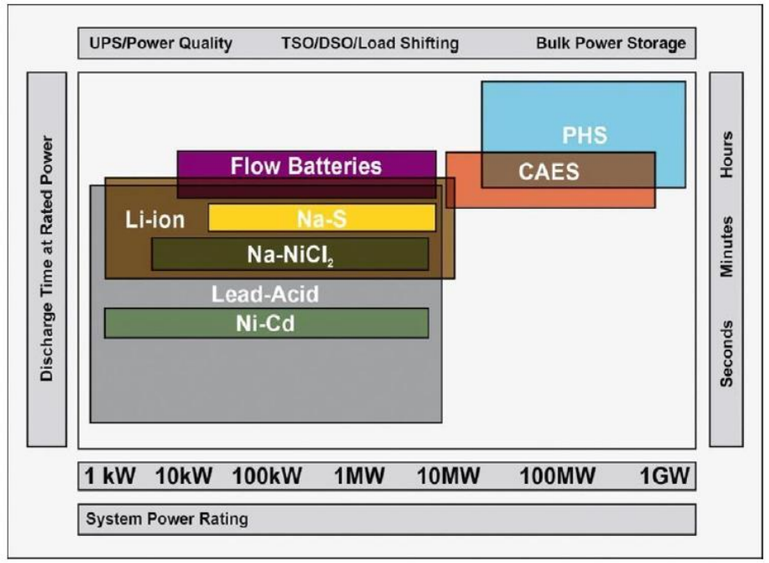
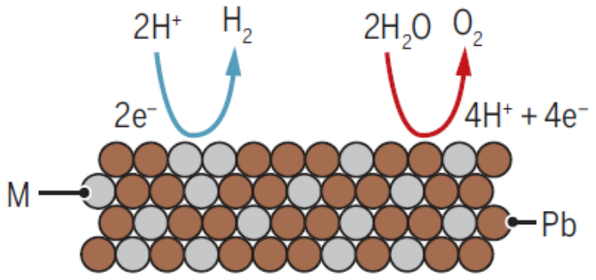


Figure Credits: May *et al., J. Energy Storage,* **15** (2018)

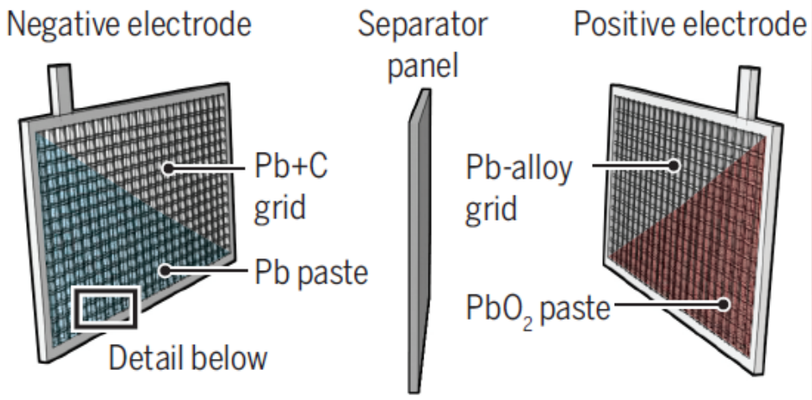
Multi-Modal Characterization Across Length Scales

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.



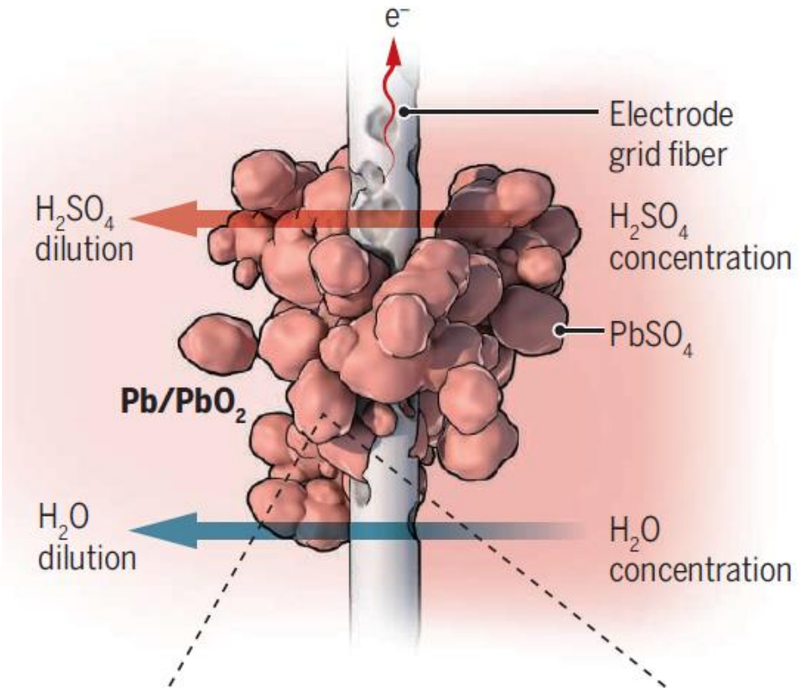


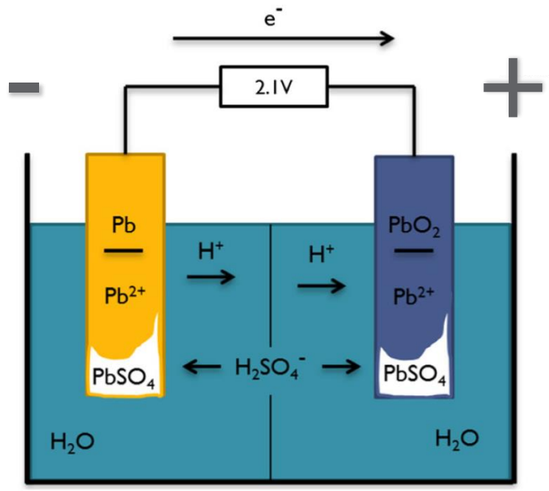
Figure adapted from: Papa Lopes *et al.*, *Science*, **360** (2020)

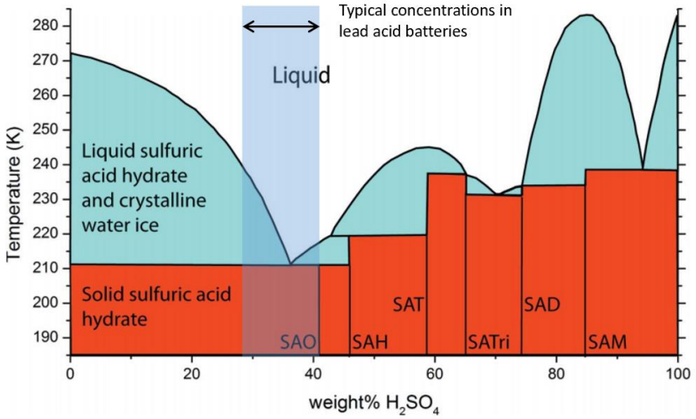
Molecular-Level View of the Electrolyte

The electrolyte performs a central role in Pb-acid performance: charge transport and the electrochemical reaction itself

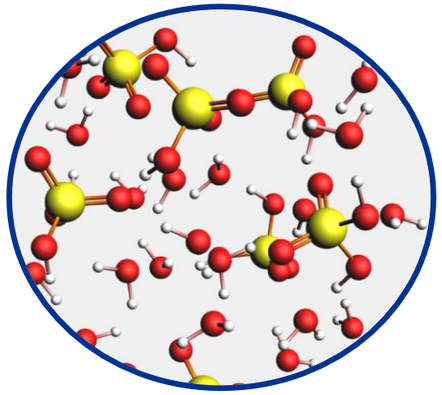
- SO_4^{2-} availability and lignins: critical for high discharge rates
- Pb^{2+} solubility: critical for high charge rates

Understanding the structure of the acid and its interactions with Pb^{2+} ions and additives, such as lignosulfonates, is a crucial first step for understanding nucleation/dissolution during charge/discharge.

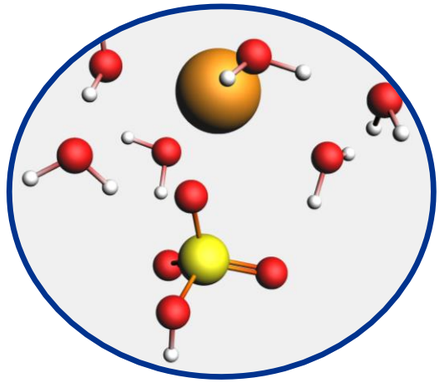




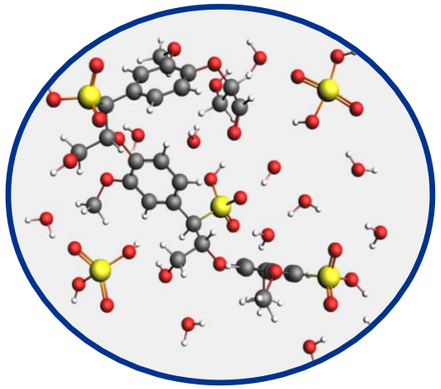
Sulfuric acid solution forms a deep eutectic, which is why Pb-acid batteries can operate at low temperatures (adapted from J. Appl. Cryst. 45, 2012)



H_2SO_4 (aq)



$PbSO_4$ (aq)



Lignosulfonate (aq)

Schematic Figure Credit: Huang *et al.*, *Int. J. Energy Res.*, **40** (2016)

Integrated, Multi-Modal Techniques

Contending with the complicated molecular-scale processes which drive performance

- PDF, EXAFS
- DFT Shift Calculation
- ^{17}O, ^{33}S NMR Linewidth, Shift
- ^{17}O NMR T_1, ^{1}H PFG Diffusivity
- Viscometry
- ICP-MS
- *In situ* Raman Spectroscopy

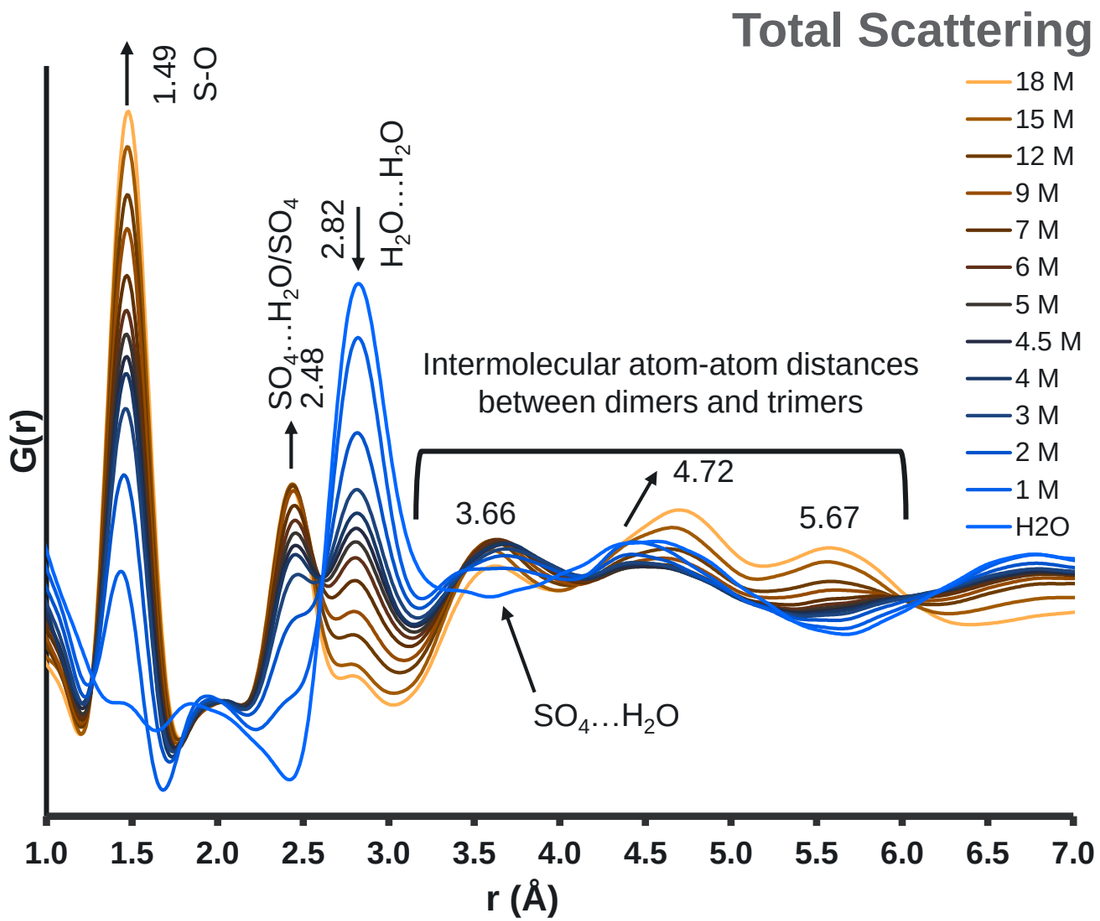
Solution Structure and Interactions

Transport and Dynamics

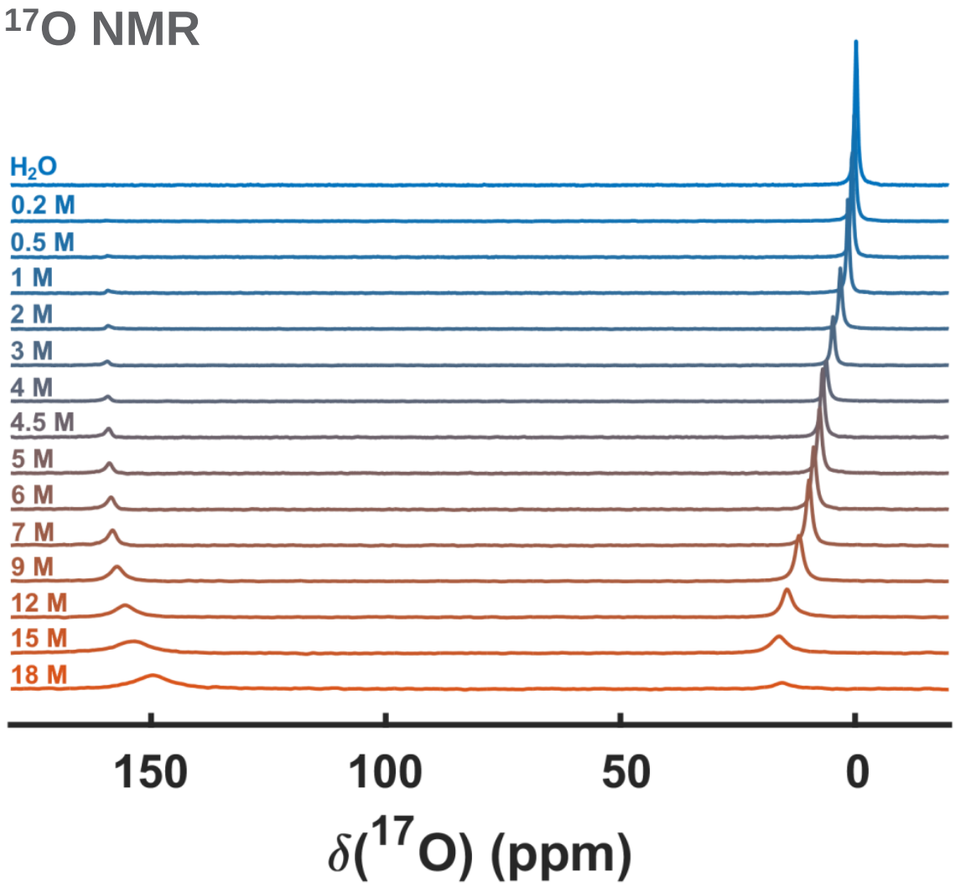
Degradation Monitoring

Molecular-Scale Results on Aqueous H_2SO_4

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



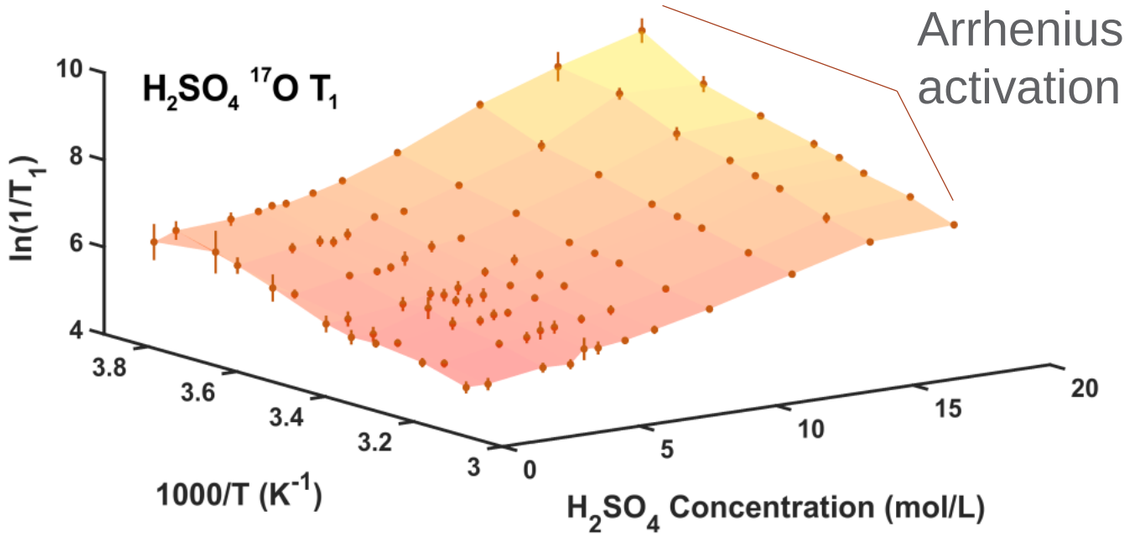
Pair distribution function analysis (PDF): Increase in longer range structure with increase in concentration



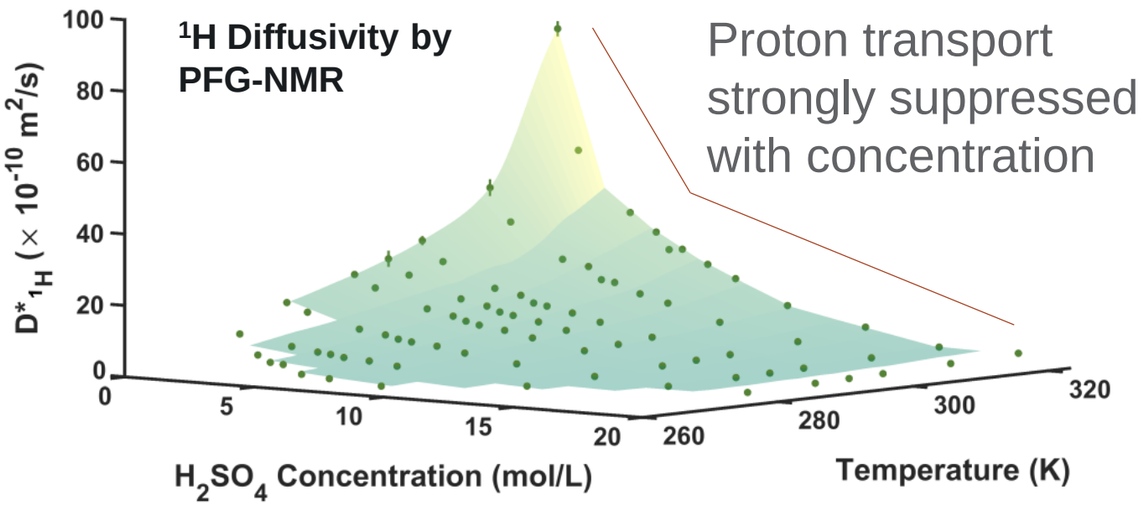
^{17}O NMR: H_2O Increasingly bound to sulfate species with increasing concentration

Dynamics and Transport of Aqueous H_2SO_4

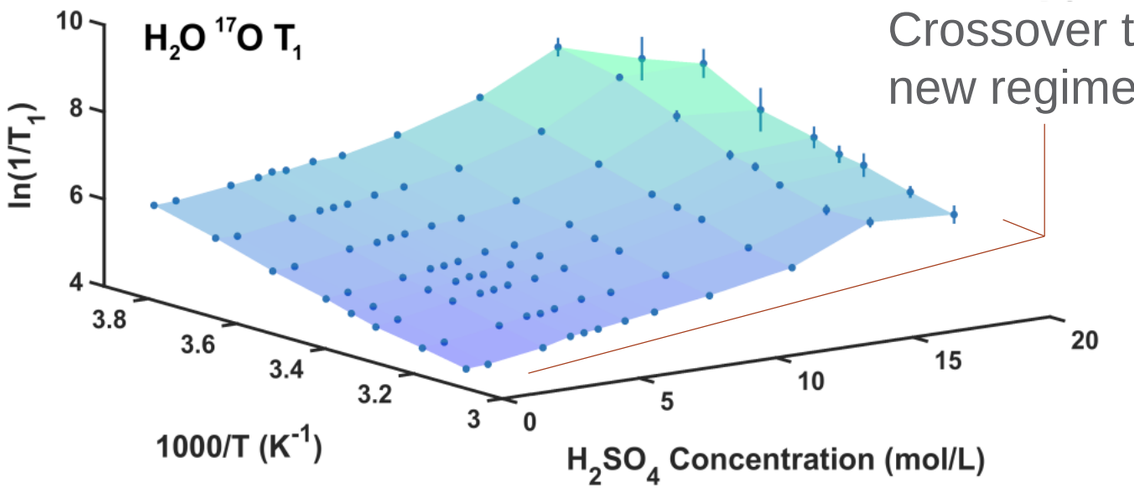
Comprehensively determining how the molecular-scale motion is influenced by concentration and temperature in the sulfuric acid model system



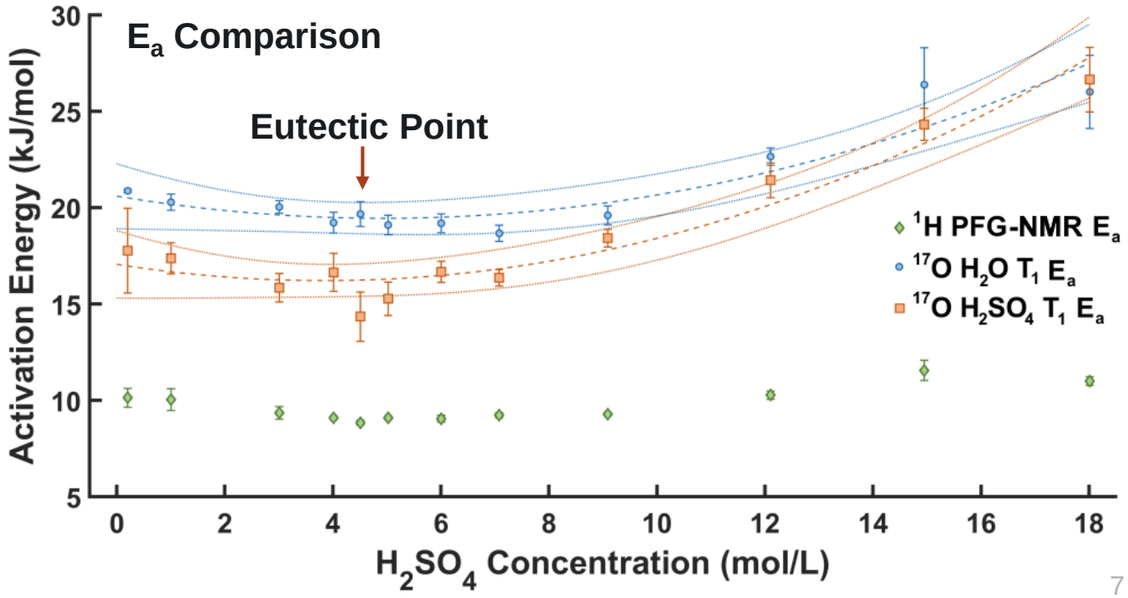
Arrhenius activation



Proton transport strongly suppressed with concentration



Crossover to new regime

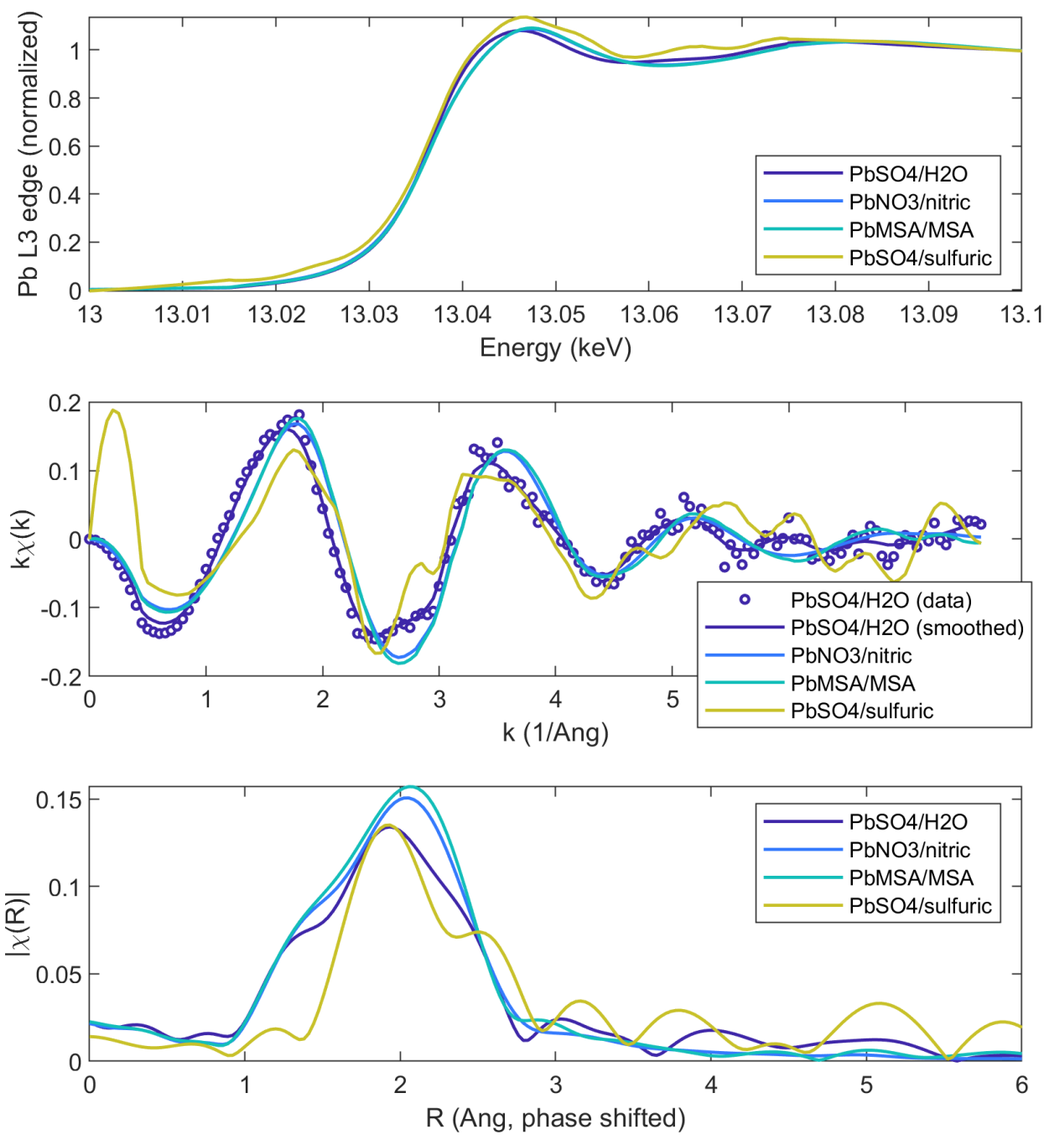


Refer to Poster #196.

Pb^{2+} Ion Pairing – Role of Solvation Chemistry

Examining how the solvation structure of the acid system is impacted by Pb^{2+} ions

- Preliminary x-ray absorption fine structure (XAFS) measurements on Pb shown, right.
  - Low concentrations (1-10 ppm) are challenging, even at a synchrotron.
- Near-edge and extended fine structure show longer ranged structure for Pb in 1.3 M sulfuric acid, suggesting weak nucleation of $PbSO_4$ in solution.
  - Also studying by differential PDF.
- Future measurements will incorporate new methods for eliminating lifetime broadening (HERFD-XANES) and upgrades to fluorescence detector (7-element Ge SDD), and will also study effect of lignins.

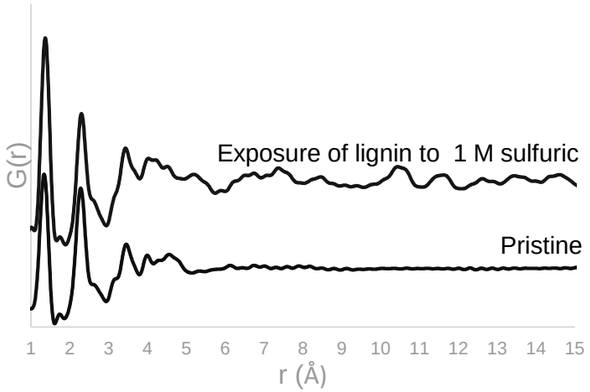


Probing the Role of Lignosulfonate

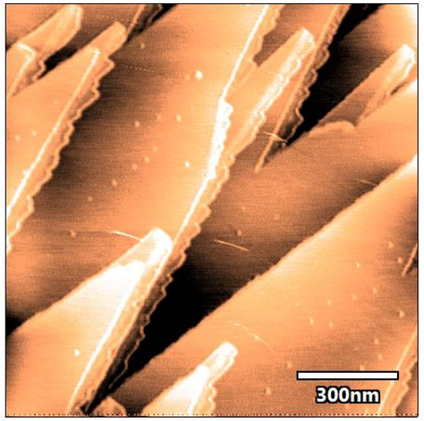
Lignosulfonates are an essential modifier for achieving high discharge rates, and will be a major focus of upcoming investigation

- We will analyze the effect of lignosulfonates on $PbSO_4$ growth in the electrolyte and at electrode surfaces

- Using PXRD and PDF, track lignin stability and structural changes when exposed to sulfuric acid.
- ICP and PDF will quantify Pb uptake and identify the Pb environment with lignins



- Using ^{17}O NMR, sidechain signatures will be identified, and the influence on T_1 in various H_2SO_4 concentrations will be quantified



AFM of $BaSO_4$ 001 in solution

- Atomic force microscopy in solution will be used to study the adsorption of lignins and the resulting $PbSO_4$ products.
- GISAXS and scanning probe methods will be used to evaluate the morphology of $PbSO_4$ on Pb and $BaSO_4$ surfaces

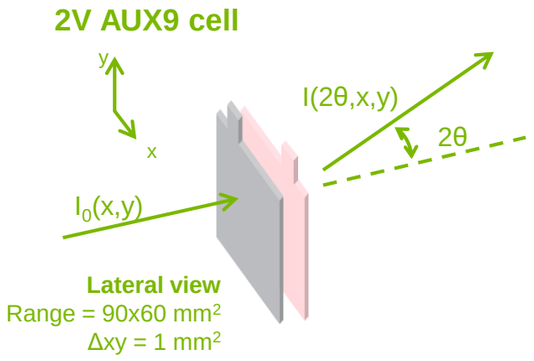
- Viscometry will benchmark lignosulfonate uptake in extracted samples

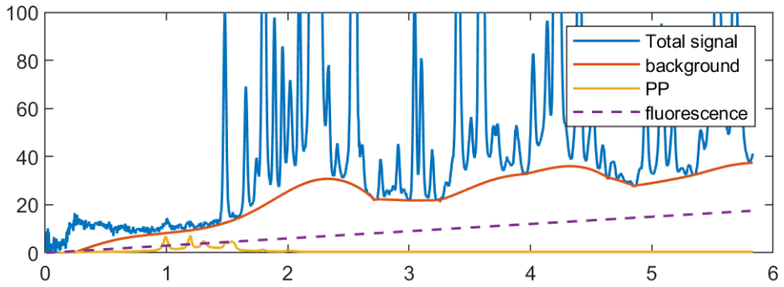
- *In situ* Raman of model lignosulfonate solutions will support ^{17}O spectral identification and fingerprinting for extracted samples

In Situ XRD Reveals Local Electrolyte Evolution

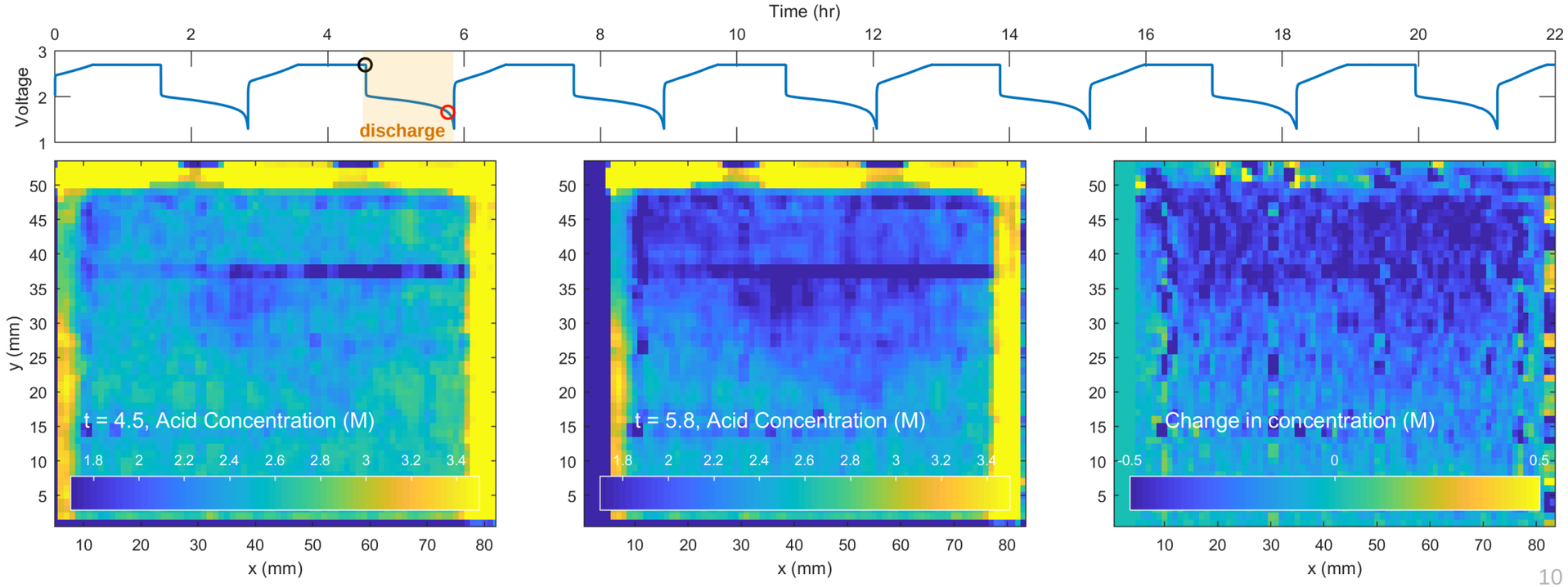
Imaging local concentration changes in the electrolyte of a flooded cell during cycling can link evolution to long-term performance

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.





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



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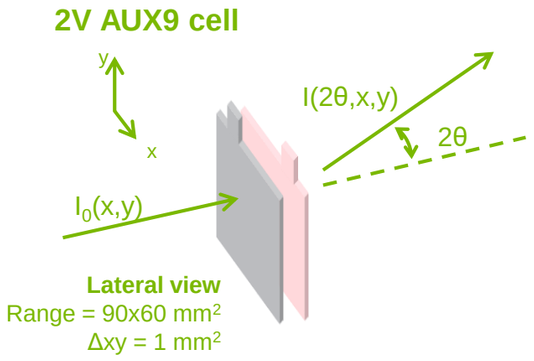
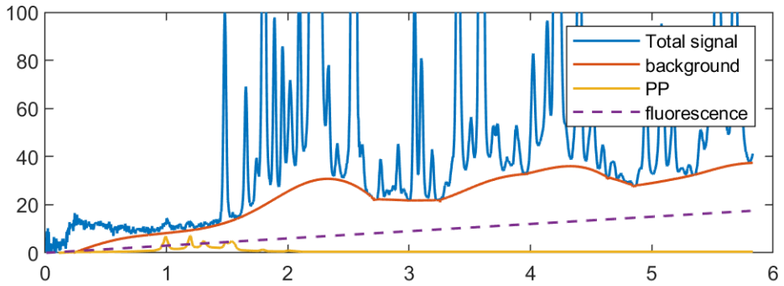
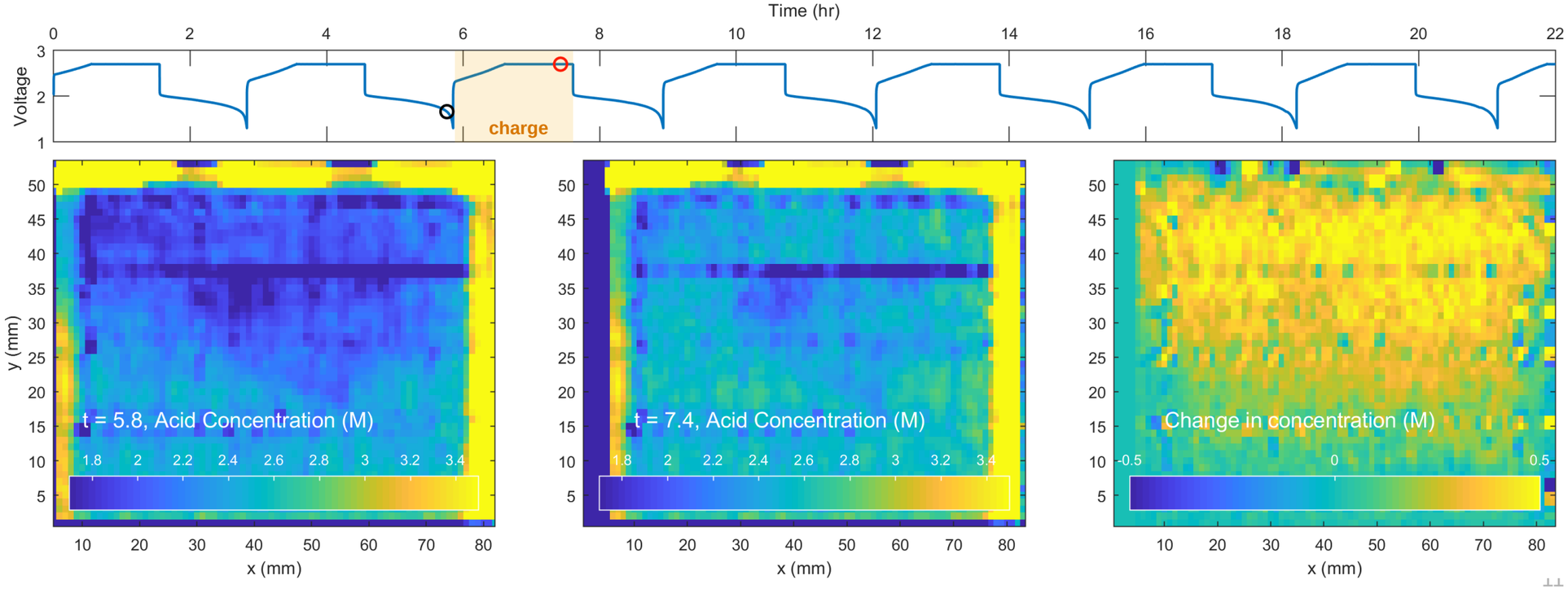




Example of acid concentration maps measured during **charge**: concentration increase correlates with active region in plates near the top.



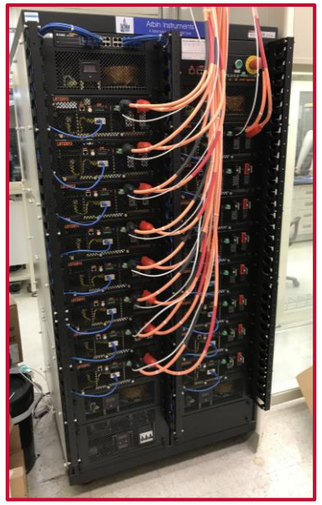
Predicting Performance From Molecular Insights

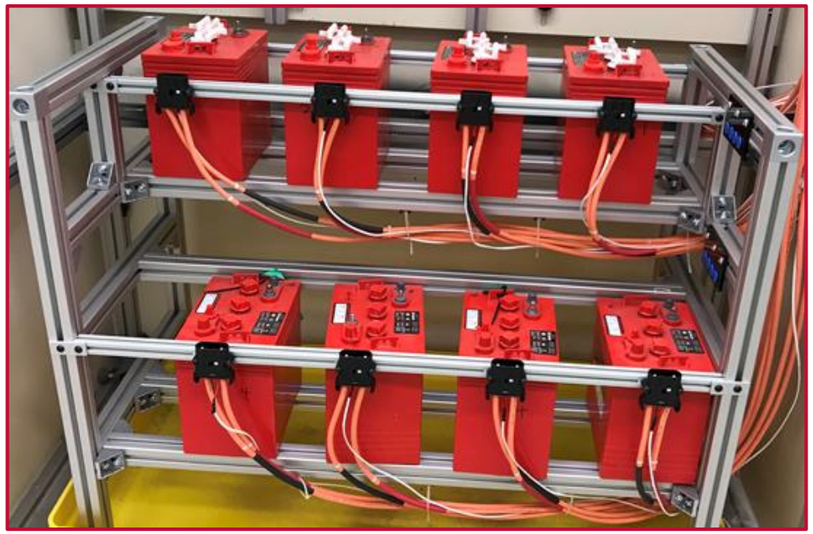
Progressing to real-world electrolytes from the molecular scale will generate new insights about cell-level performance and tunable solvation

Medium- and high-stress tests underway for commercial Pb-acid cells, with periodic electrolyte extraction

Correlated with benchmarks about solution structure, dynamics, and transport in the model systems

Insights from this comparison will inform further studies on potential additives for performance enhancement





Further information:
Poster #125
Poster #196

Thank you

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