Application of inelastic neutron scattering to understand lignosulfonate stability and lead battery failure mechanisms

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Outline

- Borregaard: The *Integrated* Biorefinery
- Why Neutrons?
- Initial Neutron Scattering Results
- Preliminary Interpretation
- More Neutron Scattering Results
- Summary, Acknowledgements, & Path Forwards

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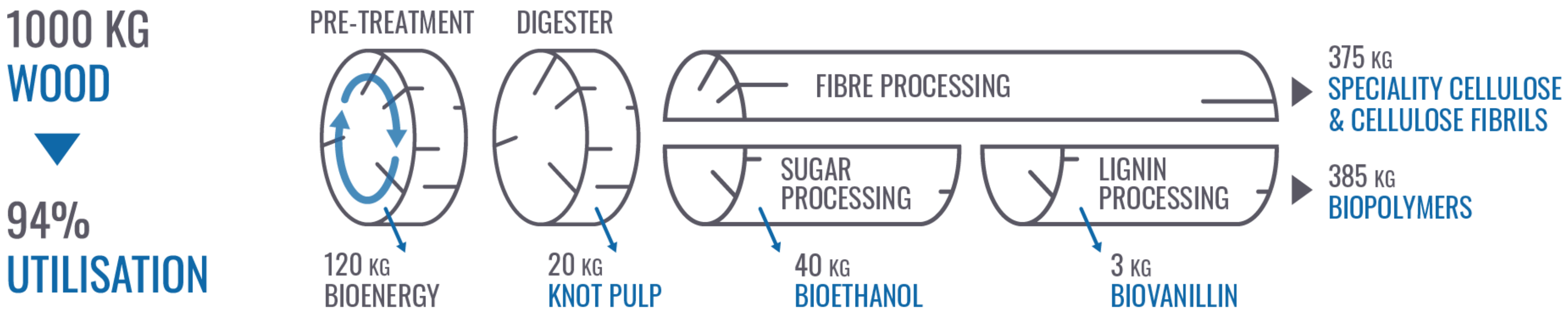
Borregaard: The World's Most Advanced Biorefinery



BIOPOLYMERS
Concrete additives
Animal feed
Agrochemicals
Batteries
Briquetting
Soil conditioning

BIOVANILLIN
Food
Perfumes
Pharmaceuticals

SPECIALITY CELLULOSE
Construction materials
Filters
Inks and coatings
Casings
Food
Pharma
Personal care
Textiles

CELLULOSE FIBRILS
Adhesives
Coatings
Agricultural chemicals
Personal care
Home care
Construction

BIOETHANOL
Biofuel
Disinfectants
Pharmaceutical industry
Home care
Personal care
Paint/varnish
Car care

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Borregaard by the Numbers

EMPLOYEES

1150

PRODUCTION

- Biopolymers
- Speciality cellulose
- Bioethanol
- Biovanillin
- Cellulose fibrils
- Fine chemicals

800 PRODUCTS

RAW MATERIAL

1 MILLION

m³ Norway Spruce
375,000 tonnes lignin raw material

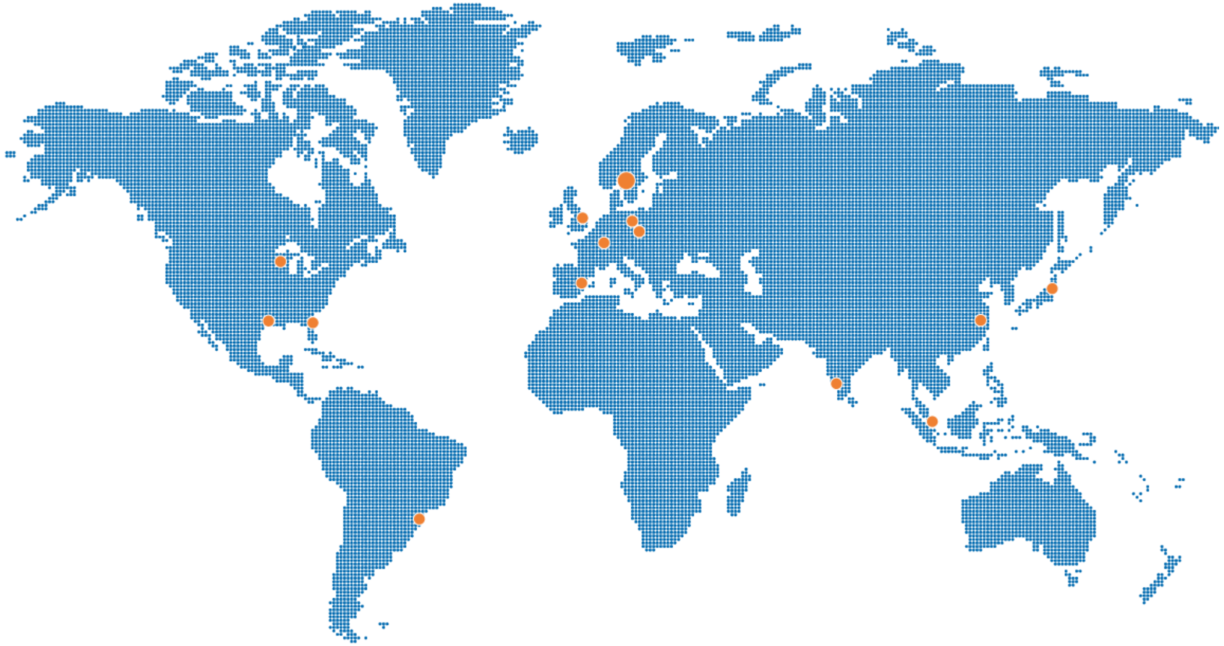
BORREGAARD IN THE WORLD

Business in	Sales to	Sales outside Norway
13 countries	**100** countries	**97** percent

FINANCIAL FIGURES

Turnover	Result EBITDA	Investment
7.6 billion NOK	**1.9** billion NOK	**861** million NOK

A Global Company with International Manufacturing Operations



- Six manufacturing sites on two continents
- Over 125 years in pulp & paper
- Over 100 years of experience with lignosulfonates

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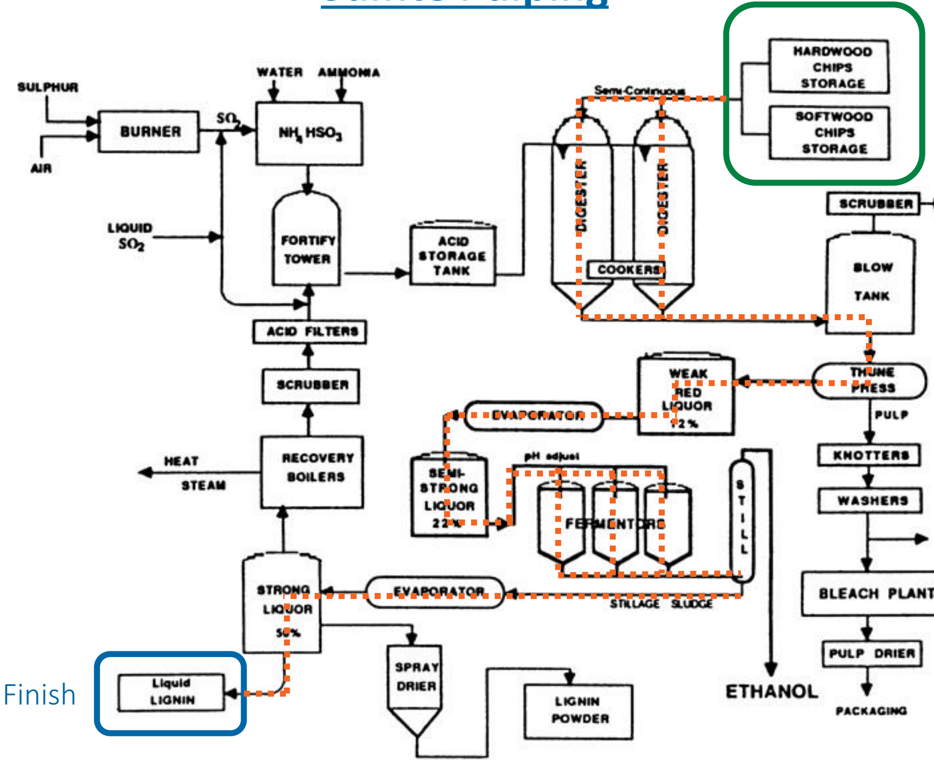
Sulfite Pulping

Start



Finish

Appl. Biochem. Biotechnol. **1993**, *39-40*. 667-85.

Downstream Processing

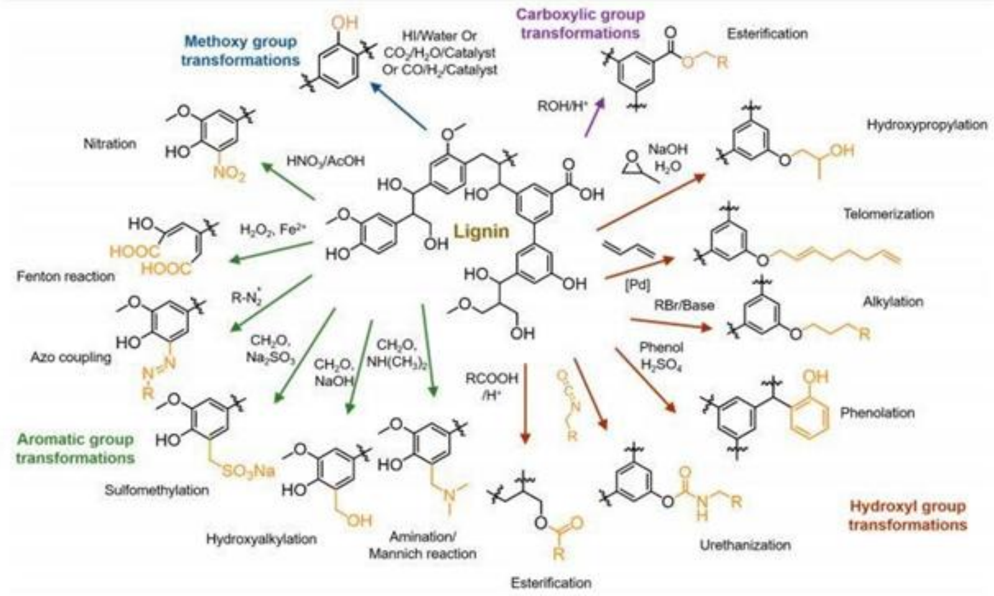
Sugar Conversion

Purification

Fractionation

Ion Exchange

Chemical Modification & Blending



J. Appl. Biotechnol. Bioeng. **2020**, *7*. 100-105.

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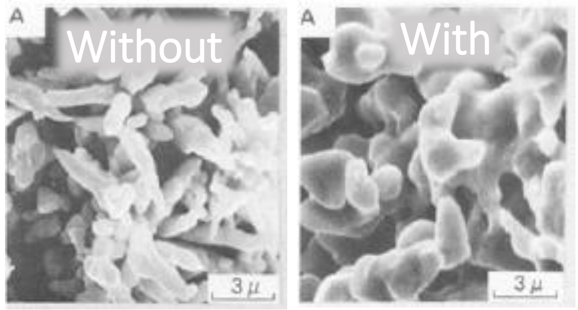
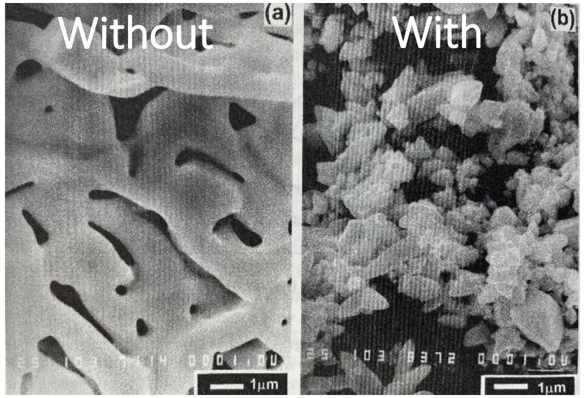
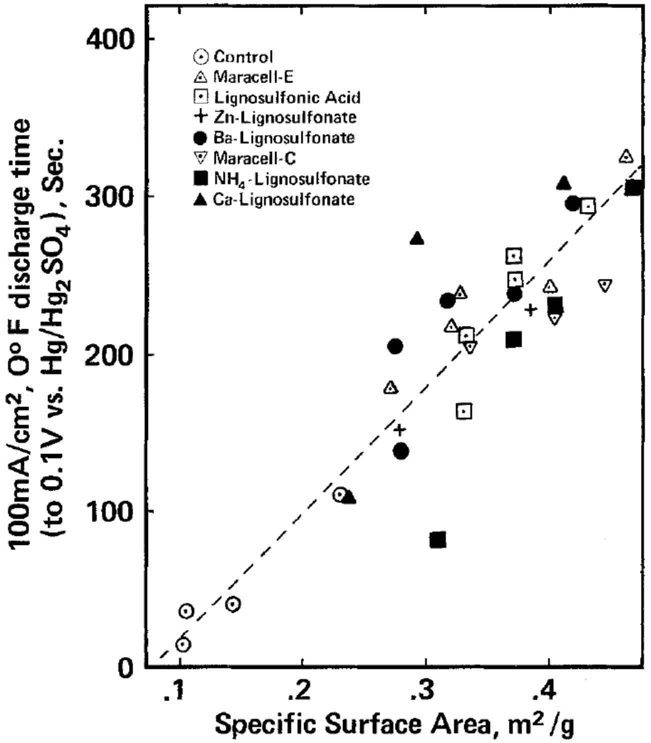
The Critical Role and Effect of Lignosulfonates as Organic Expanders

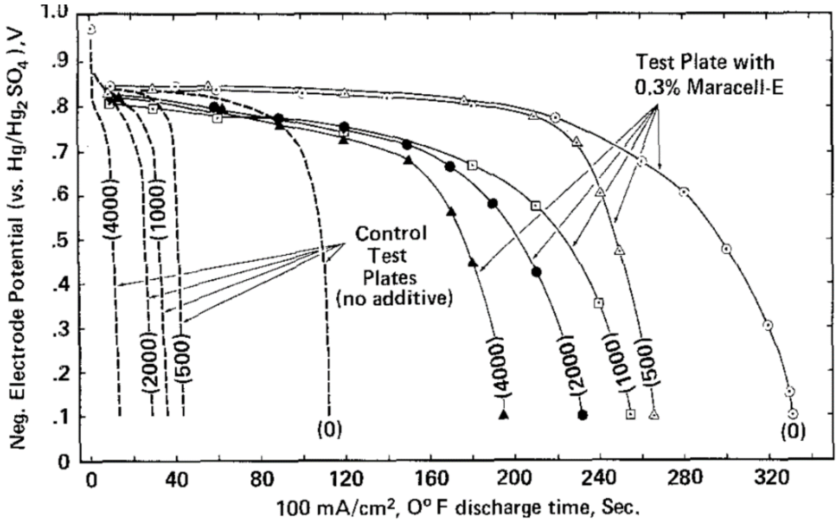


Mahato, *J. Elec. Chem. Soc.* 1977



D. Pavlov, *J. Appl. Electrochem* 1985





Expanders:

- Increase electrode external surface area
- Accelerate ion transport to improve discharge performance
- Prevent formation of $PbSO_4$ passivation layer and increase cycle life

D. Pavlov, *Lead-Acid Batteries Science & Technology,* 2011

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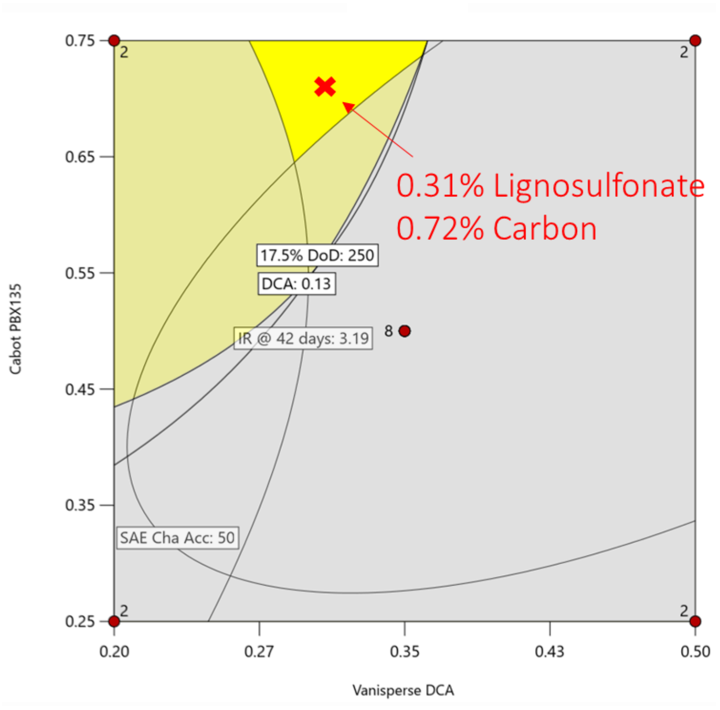
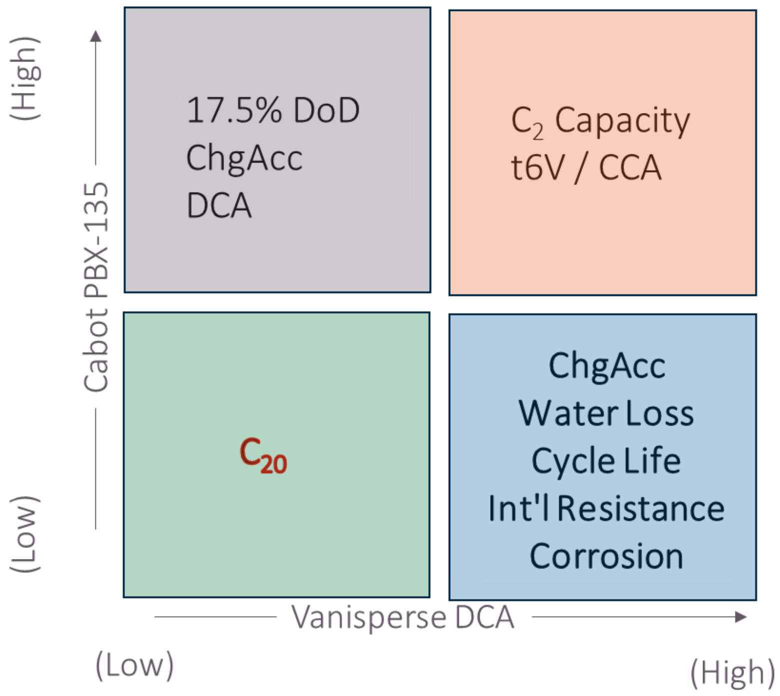
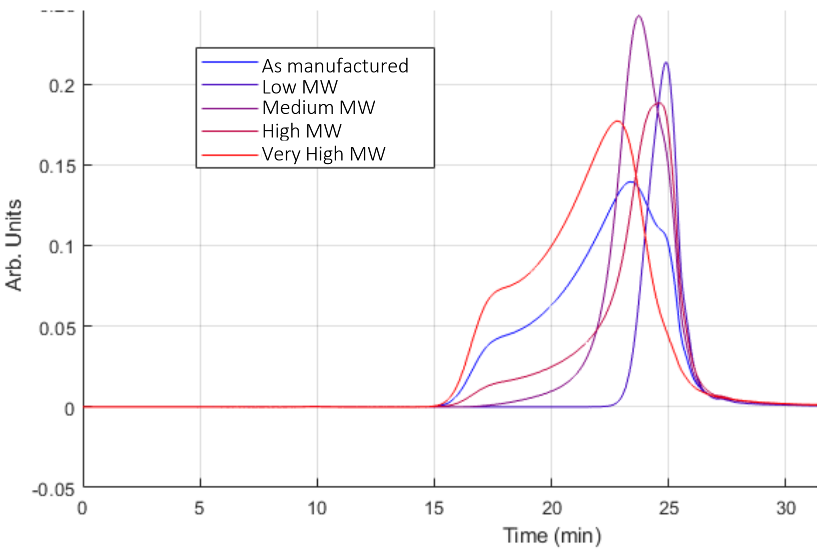
Lignosulfonates Deliver More than Just Cold-Crank

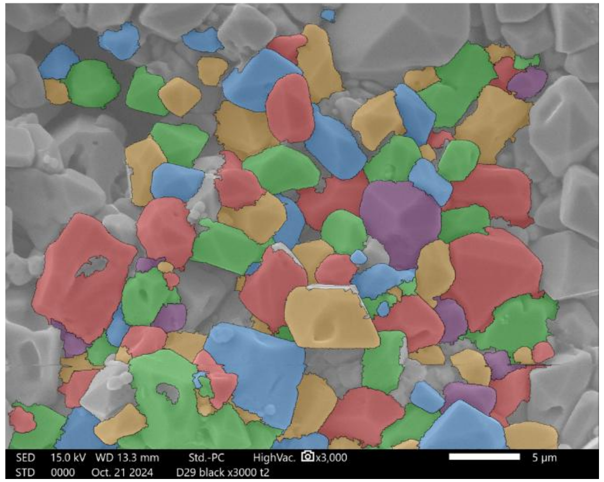
- Response-surface methodology varying lignosulfonate and carbon dosage
- Pre-competitive research funded by the CBI
- 12V Flooded batteries prepared by East Penn
- Tested by JBI (independent 3rd party)



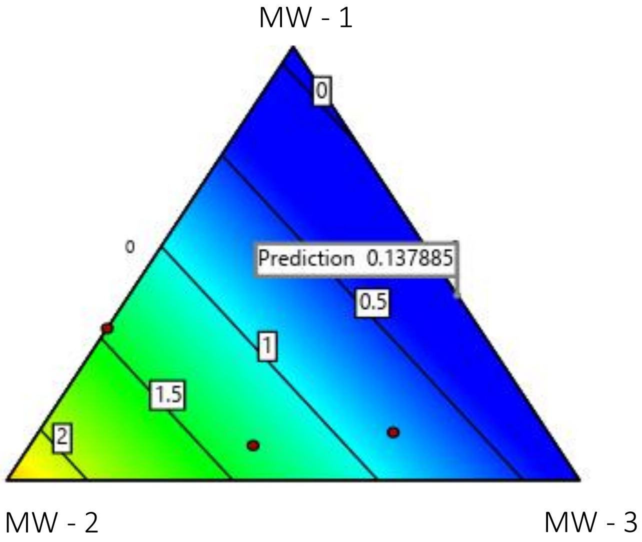


Exploring the Relationship of MW on Performance

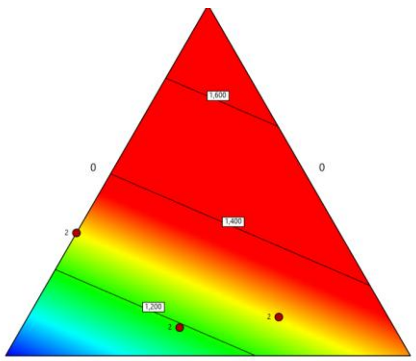




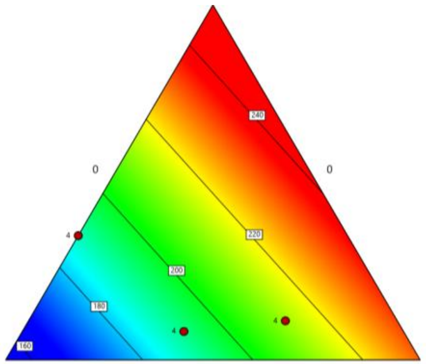
Particle Size



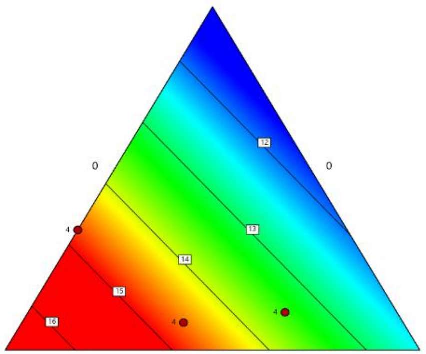
Life at 17.5% DoD



Cold-Crank

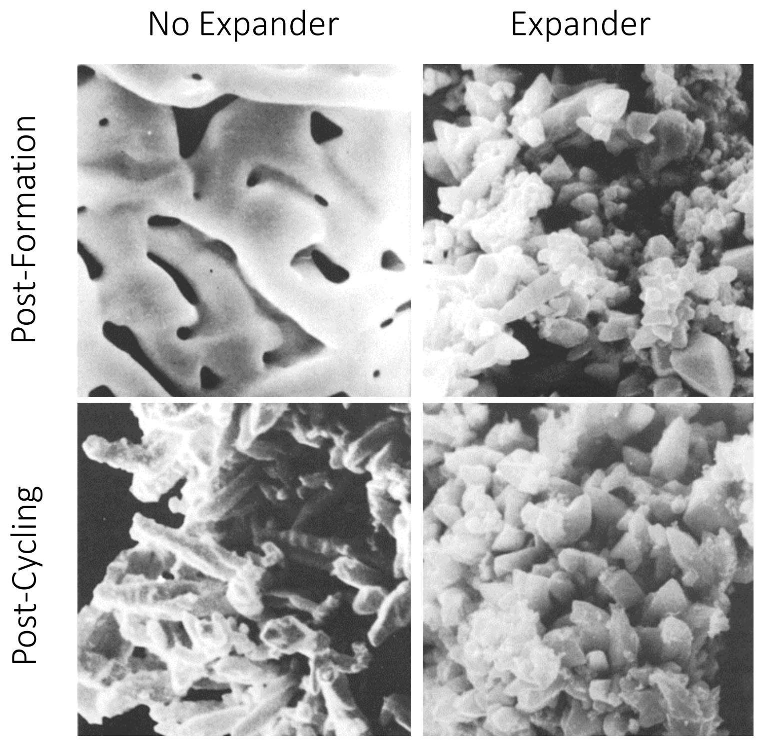


Charge Acceptance



- Fractionation used to separate different MW
- Unable to achieve perfect separations
- Fits of MW used with StatEase to account for different MW contributions

Is Lignosulfonate Decomposition Responsible for Battery Failure?



J. Appl. Electrochem **1985,** *15*, 39-52

"As lignosulfonate disintegrates slowly during battery operation and hence, the negative plates lose capacity…" (pg 312)

"When the battery is cycled at 60 C and is of the VRLA type, expanders containing lignin and its derivatives disintegrate…" (pg 325)

"So the capacity performance of the negative plates depends on the nature of expander(s) used and on its (their) stability…" (pg 496)

"So it can be concluded that expanders contribute to building the energetic structure of NAM [sic]… The stability of the energetic structure on cycling will depend on the stability of the expander used." (pg 498)

D. Pavlov, *Lead-Acid Batteries Science & Technology,* 2011

"the strong oxidizing atmosphere… under the internal oxygen cycle will degrade the organic… <u>there is little quantitative evidence of such degradation</u>…" (pg 143)

D.A.J. Rand et al, *Valve-Regulated Lead-Acid Batteries,* 2004

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Neutron Scattering is Uniquely Capable for such Systems

Spallation Neutron Source, Oak Ridge Nat'l Lab

Neutrons interact with the nucleus of atoms, whereas x-rays interact with the electron cloud

- X-rays scatter strongly off heavy elements
- Neutrons scatter off atoms in a way that is independent of their Z-number
- Carbon, hydrogen, and light elements are strong neutron scatterers, while lead is not
- Scattering for H is *at least* 20× that of any other atom – spectra dominated by hydrogenic motion

This makes neutrons sensitive to organic species, even if present at low concentrations in systems that are predominantly heavy elements

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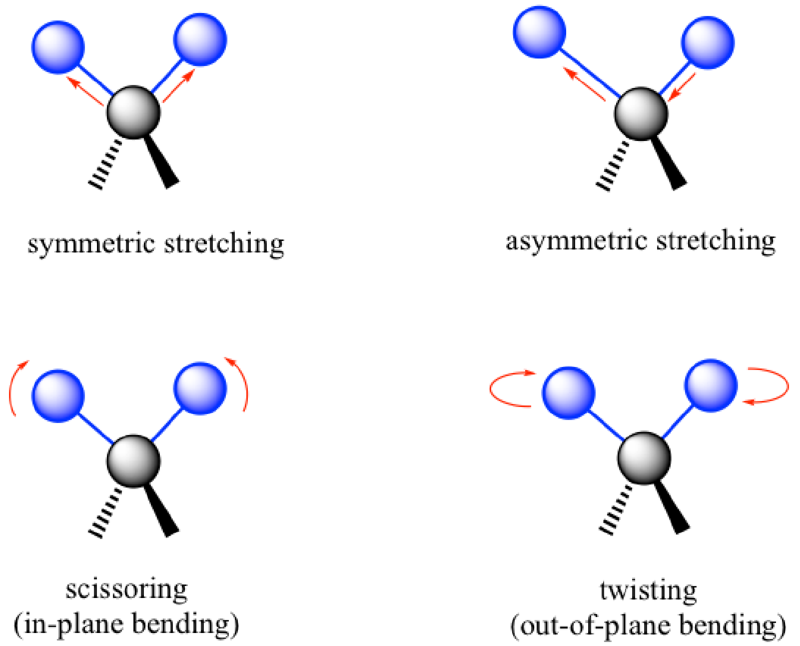
INS is Vibrational Spectroscopy, but with Neutrons

Vibrational spectroscopy provides information about molecular structure and intermolecular interactions

- Molecules absorb at frequencies characteristic of their structure
- Common examples are IR (dipole) and Raman (polarizability)

INS uses neutrons rather than photons for vibrational spectroscopy

- Neutrons have mass, so an inelastic scattering event transfers both energy and momentum
- Absence of selection rules due to momentum transfer
- Opportunity for exploiting differences in isotopic sensitivity



Appl. Spec. **2011**, 1325 - 1341

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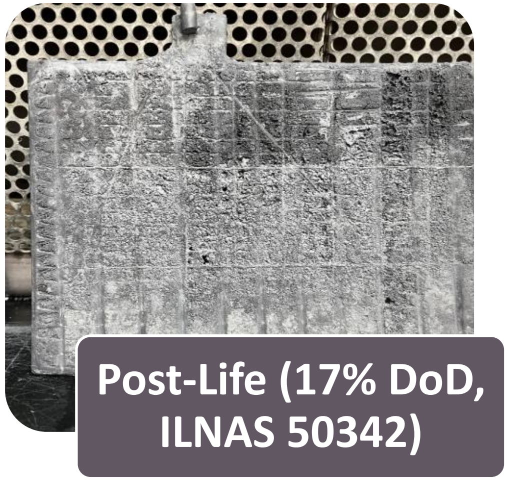
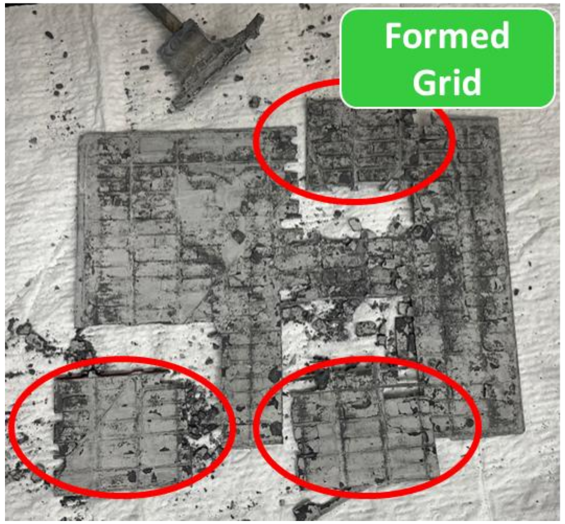
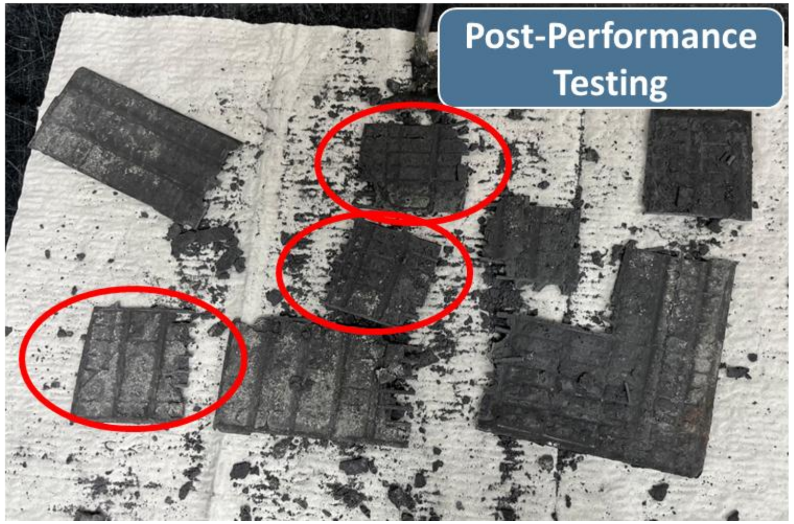
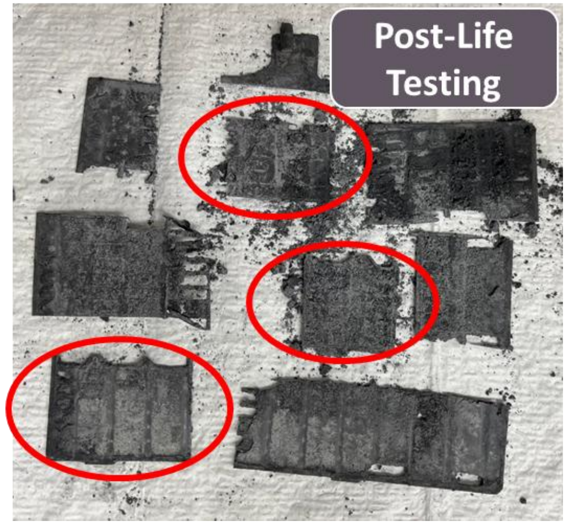
Grids Were Harvested for Analysis During 2V Cell Testing

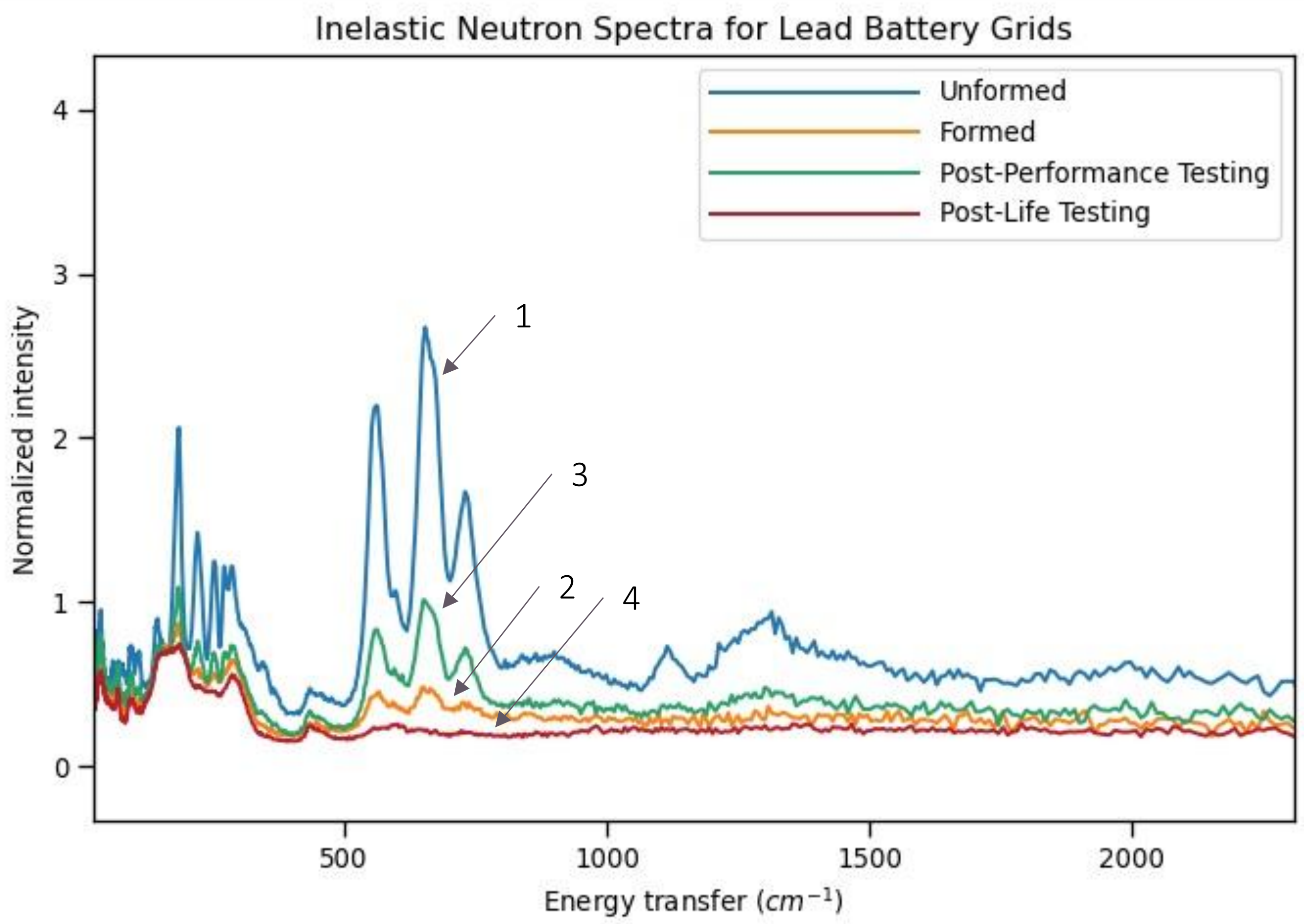




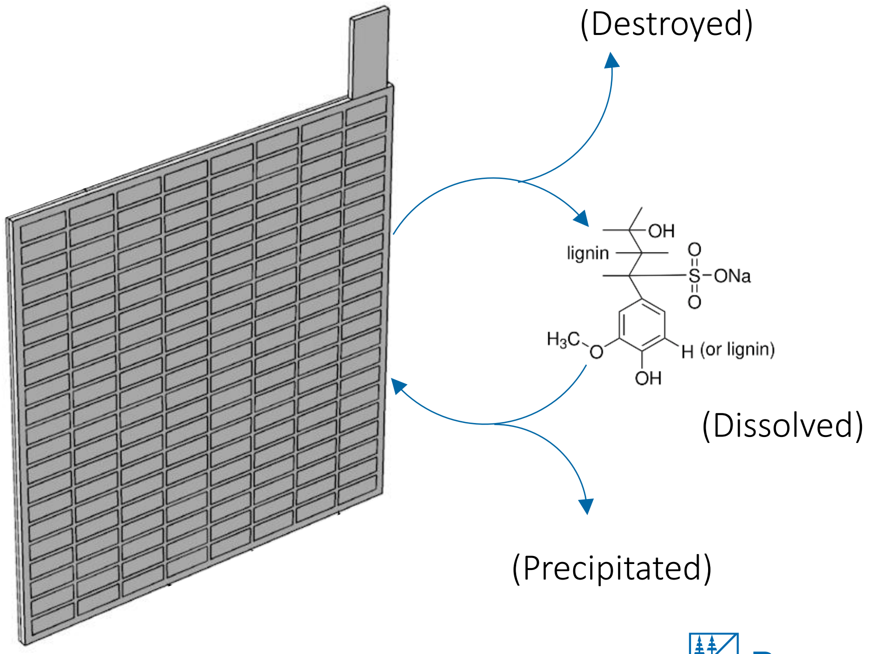




First Ever Spectroscopic Data of Lignosulfonates in a Lead Battery Electrode!



- Samples were harvested from the same region of the battery grids
- Features between 500 – 800 cm^{-1} suggest the lignosulfonate content in the grid changes during cycling



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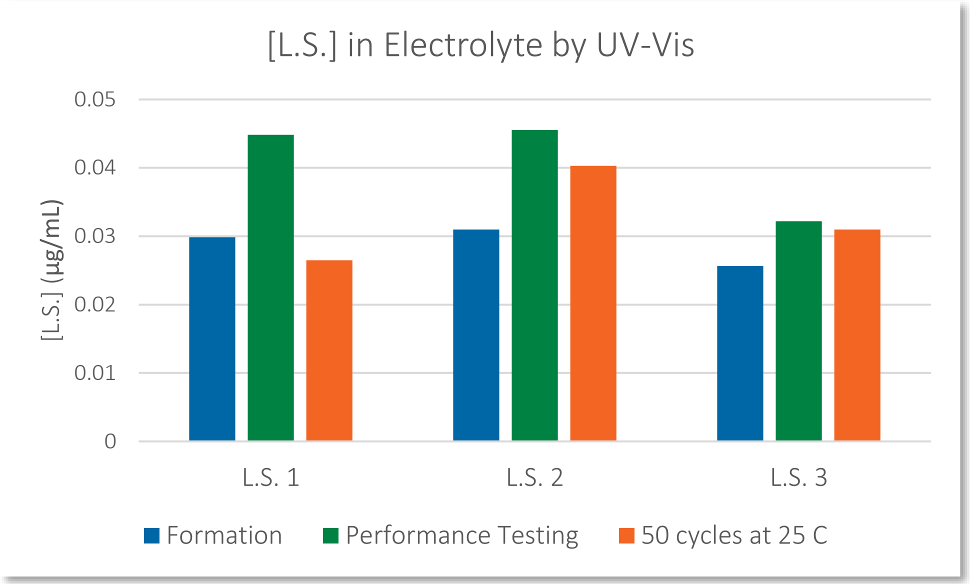
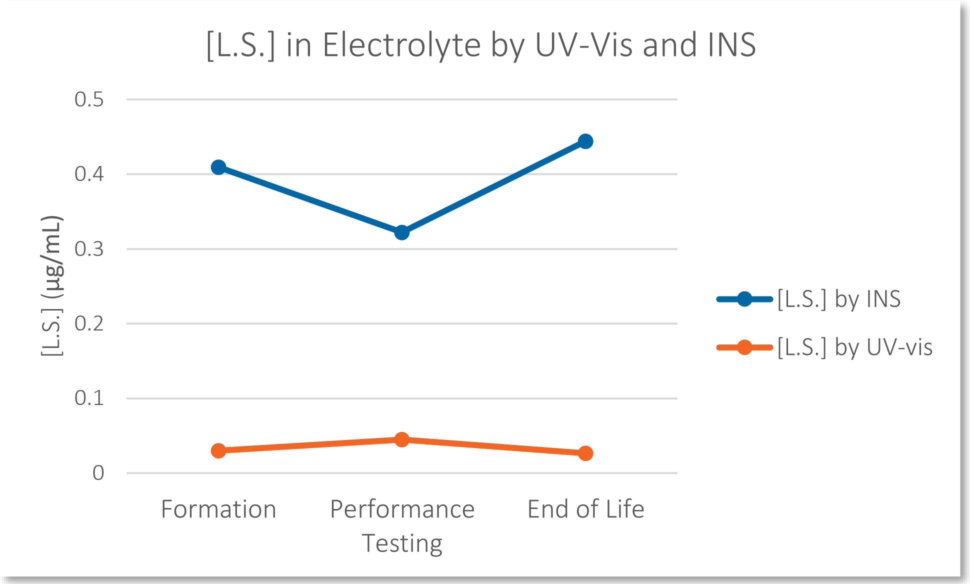
UV-Vis Enables Quantification of Lignosulfonates in the Electrolyte





- Behavior of different lignosulfonates explored in 2V cells
- UV-vis analysis performed on electrolyte during cycling
- INS signal for cured electrode used to estimate the expected amount of lignosulfonate in the electrolyte

金科力 JINKELI

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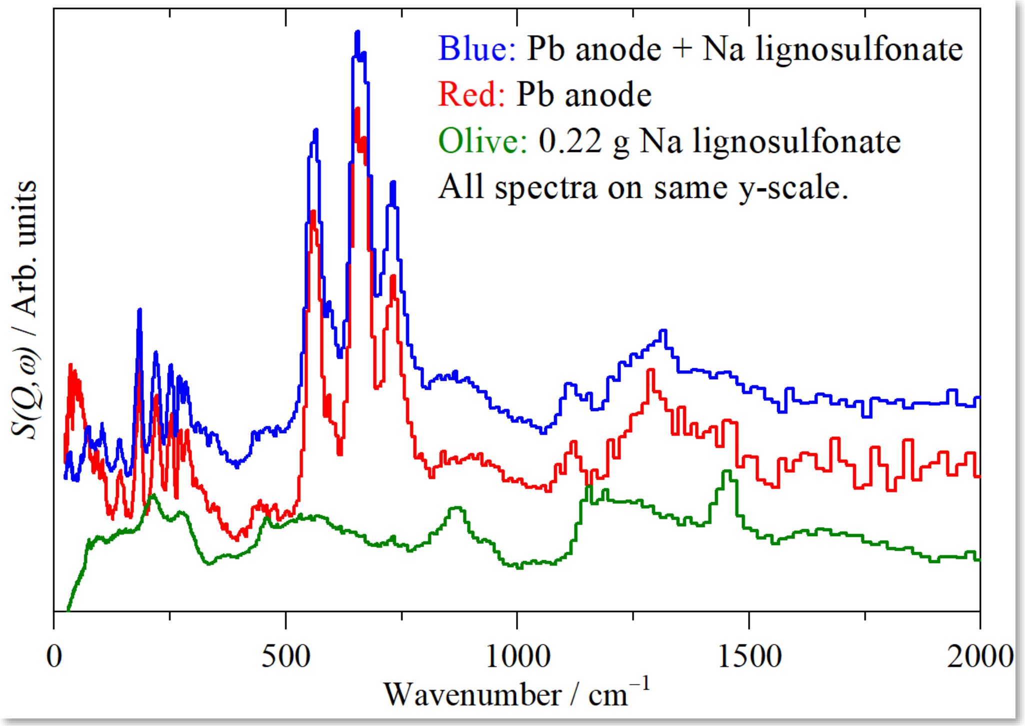
Additional Control Samples Measured in the UK

ISIS Neutron & Muon Source, Rutherford Appleton Labs, UK



TOSCA – Inelastic Neutron Spectrometer

- Same technique as VISION
- 10% of the flux, so 10× the time

Simple control experiment:

- Cured electrode without lignosulfonate
- Cured electrode with 4x normal dosage of lignosulfonate

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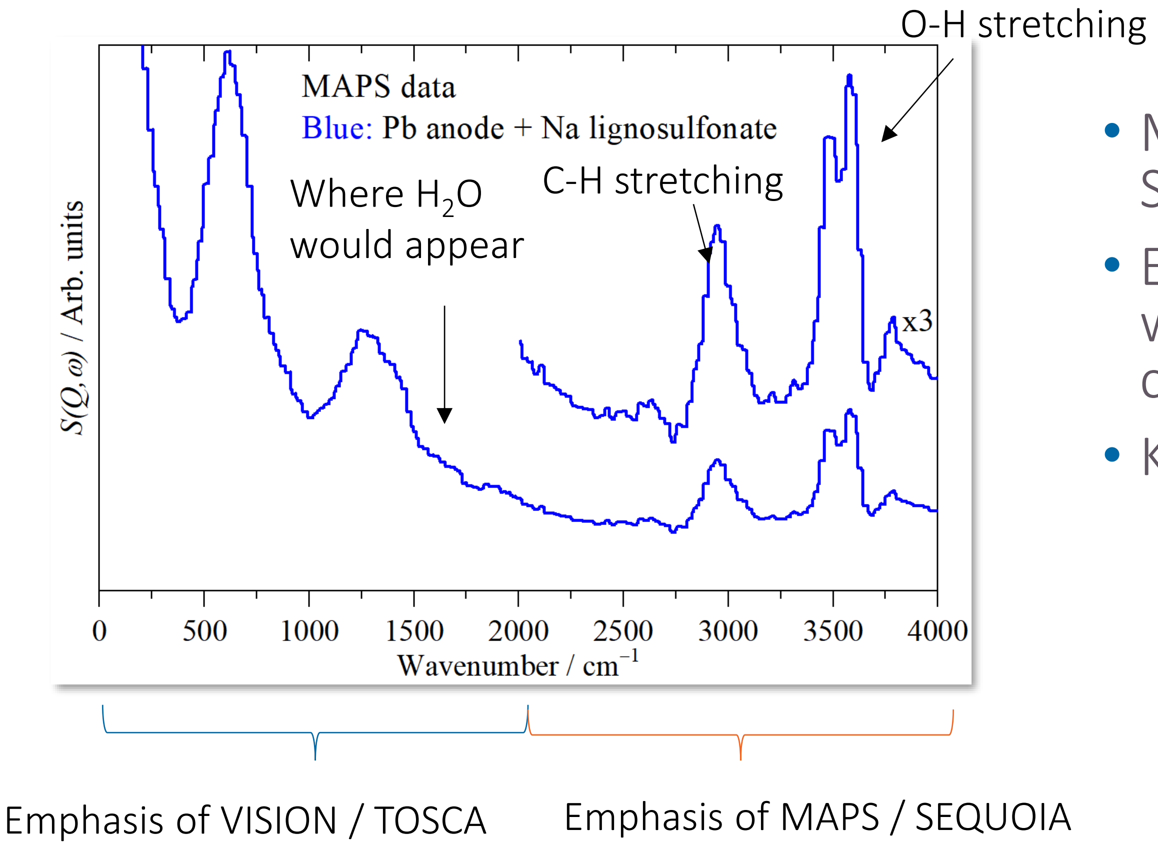
Direct Geometry INS Results Reveal Promising Features



- MAPS – A direct geometry Inelastic Neutron Spectrometer
- Enables meaningful data collection at higher wavenumbers, at the expense of set-up complexity
- Key features indicative of lignosulfonate:
  - C-H stretching around 3000 cm^{-1}
  - Feature at 3500 cm^{-1} denotes –OH in two environments, suggesting H-bonding
  - Absence of H_2O frequency at 1500 cm^{-1}

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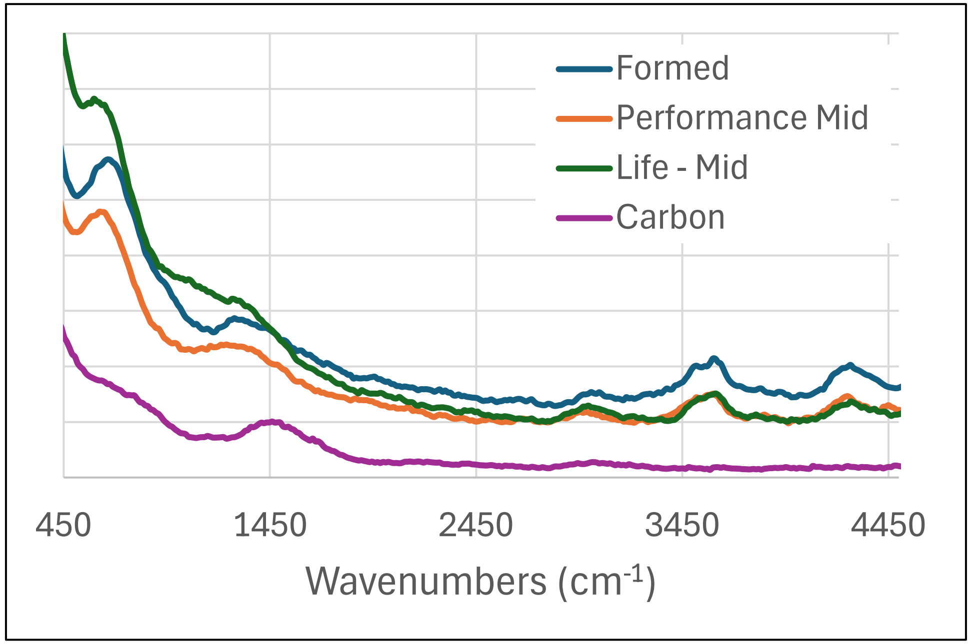
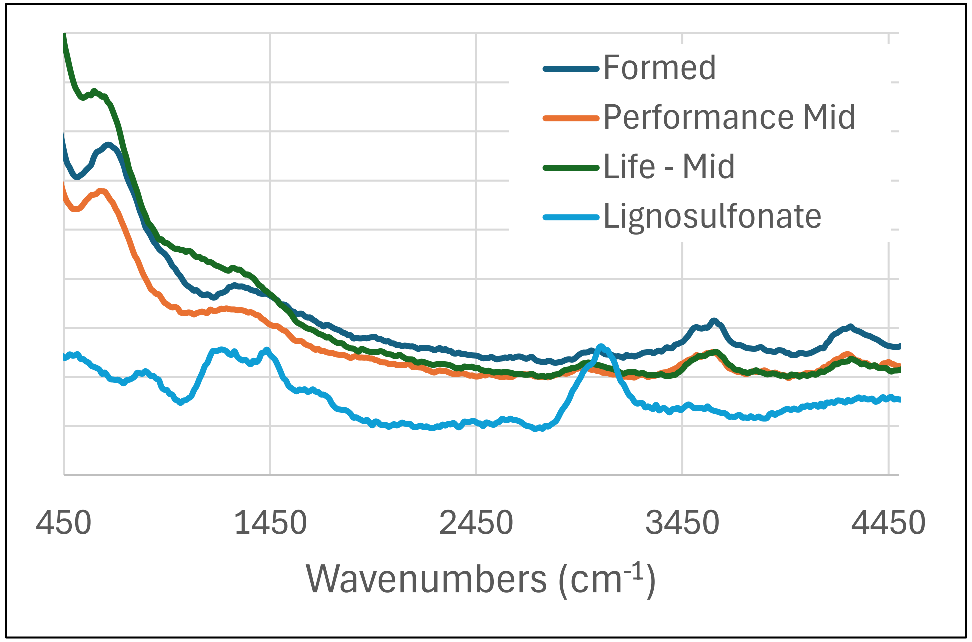
Confirmation of the Lignosulfonate C-H Peak





- Carbon and lignosulfonates measured separately as controls
- 1 g Carbon measured in control spectrum exceeds the total amount added to the full battery paste
  - 30x more concentrated than in the experimental data
- Lignosulfonate is scaled down by 95% to achieve comparable intensity

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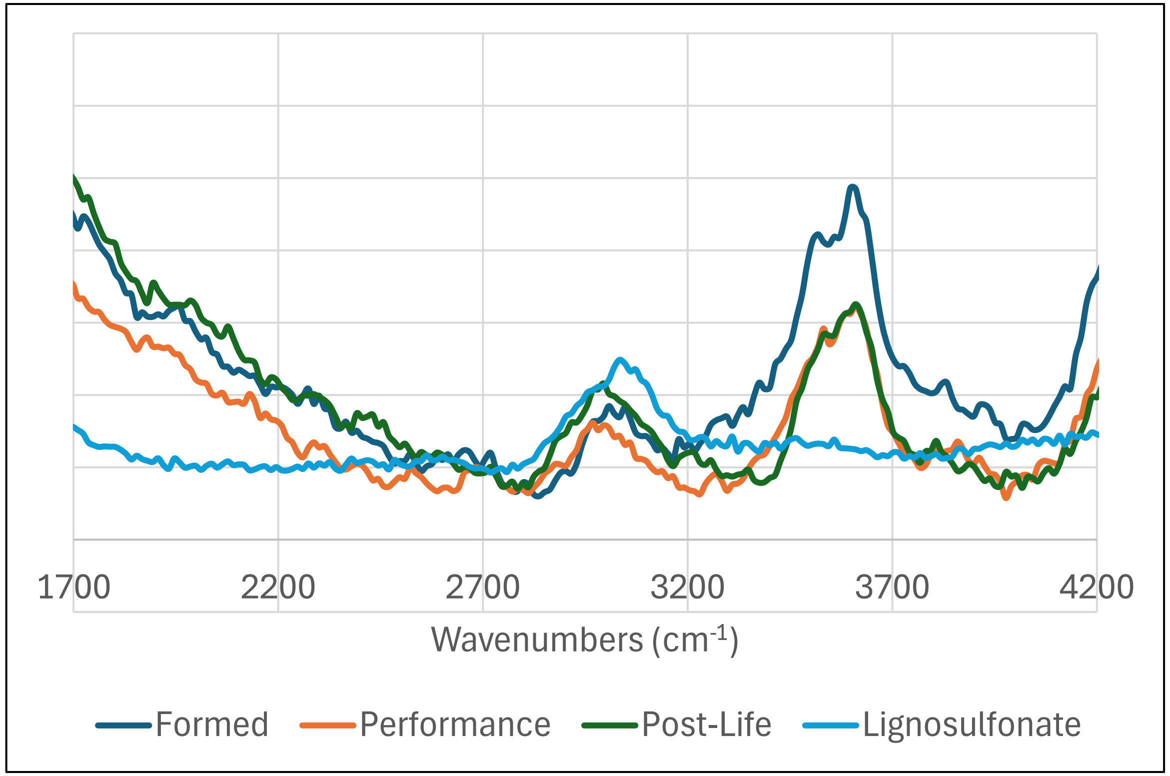
Spectroscopic Mass is Consistent with Paste Recipe

- Lignosulfonate peak intensity was scaled to minimize the residual between experimental peaks
- Lignosulfonate quantity measured in the experimental sample is consistent with the quantity added during electrode preparation
    - The quantity calculated from the sample mass of the control and scaling: **55 mg**
    - The quantity in experimental sample calculated from the paste recipe: **52 mg**
- Data collected on samples harvested from different grid positions were also comparable



This result implies formation does not significantly degrade or destroy the lignosulfonate!

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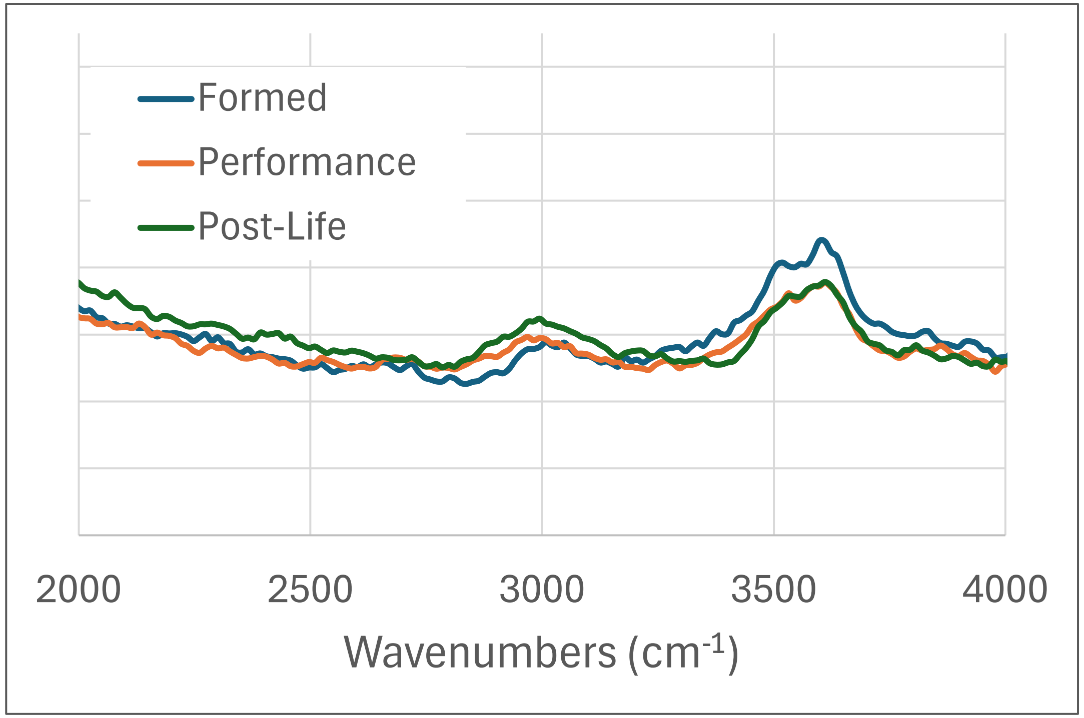
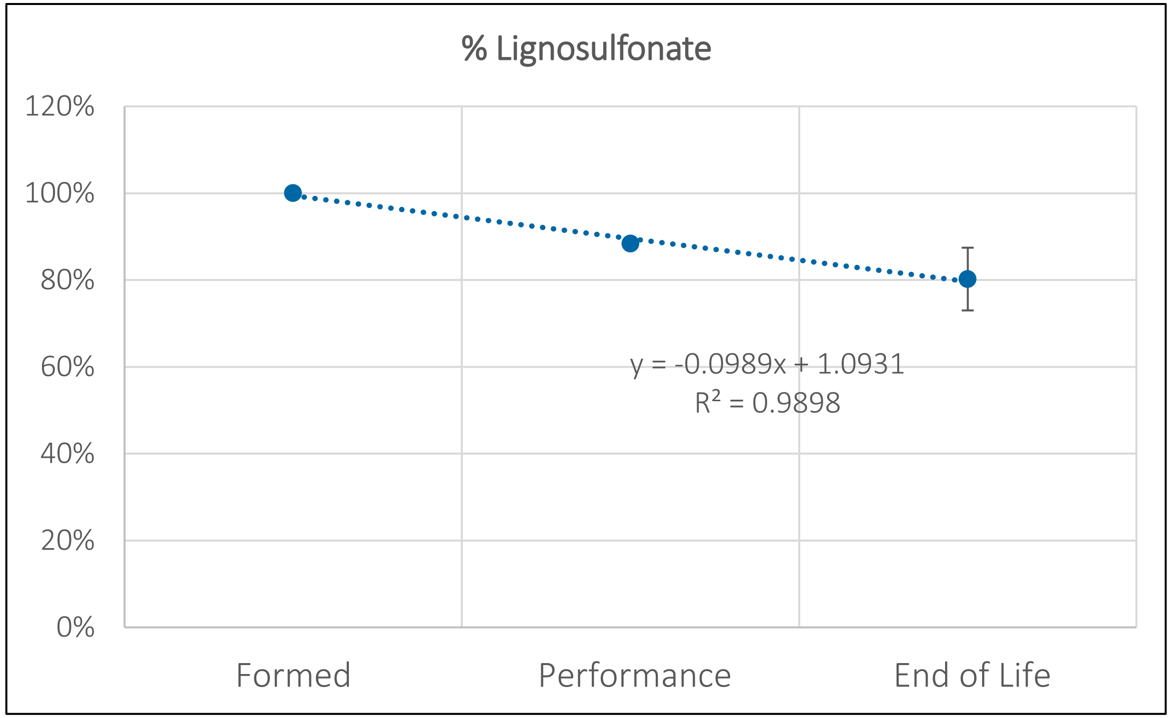
C-H Peak Intensities Change Minimally





This result suggests lignosulfonate destruction may not be the sole cause of negative sulfation

- Further work is needed to investigate the electrode / electrolyte interface

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Summary & Next Steps

Summary:

- Neutron scattering can detect lignosulfonate in a lead battery electrode
- The peak intensity for the electrode is appropriate for the dose of lignosulfonate added to the paste
- Peak intensity does not appear to vary significantly between stages of battery life or positions on the electrode
- UV-vis does indicate a small quantity of lignosulfonate does dissolve

Conclusions:

- Lignosulfonates do not appreciably degrade during formation
- Bulk lignosulfonate degradation did not cause battery failure

Next Steps:

- Corroborate these findings using lignosulfonate with greater acid solubility
- Apply technique to study lignosulfonates at elevated temperatures and under PSoC cycling conditions
- Evaluate the role of interfacial lignosulfonate in battery performance through CV and Neutron Reflectometry

Acknowledgements

A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. The beam time was allocated to VISION on proposal number IPTS-30432.

We gratefully acknowledge the Science and Technology Facilities Council (STFC) for access to neutron beamtime at ISIS, and also for the provision of sample preparation, MAPS, and TOSCA facilities.