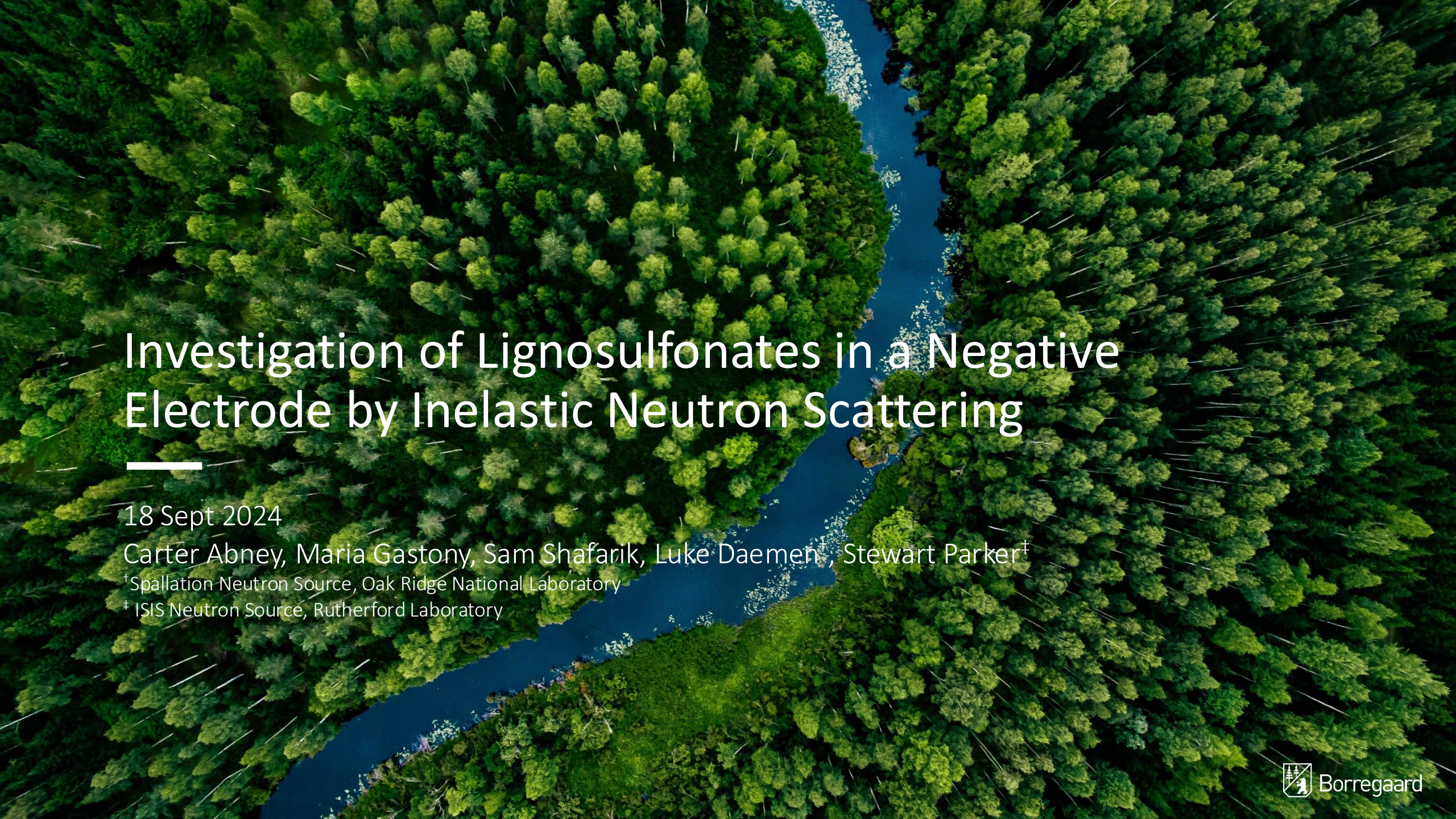

# Investigation of Lignosulfonates in a Negative Electrode by Inelastic Neutron Scattering

18 Sept 2024

Carter Abney, Maria Gastony, Sam Shafarik, Luke Daemen[†], Stewart Parker[‡]

[†]Spallation Neutron Source, Oak Ridge National Laboratory

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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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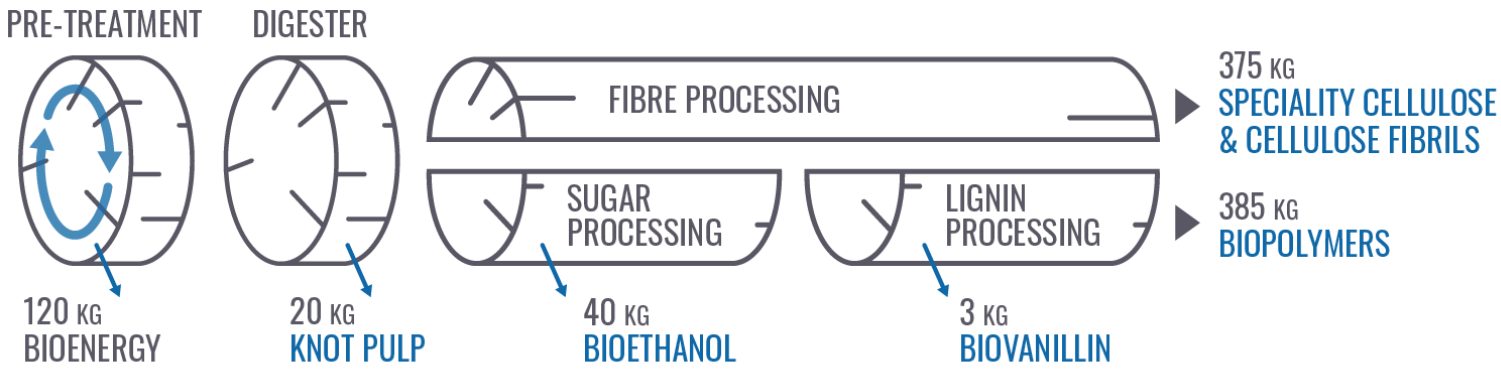
# Borregaard: The World's Most Advanced Biorefinery

1000 KG
WOOD

94%
UTILISATION




**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

1070

## PRODUCTION

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

800 PRODUCTS

## RAW MATERIAL

1 MILLION

$m^3$ Norway Spruce
375.000 tonnes lignin raw material

## BORREGAARD IN THE WORLD


| Business in | Sales to | Sales outside Norway |
|---|---|---|
| 13 countries | 100 countries | 95 percent |

## FINANCIAL FIGURES

| Turnover | Result EBITDA | Investment |
|---|---|---|
| 5.8 billion NOK | 1.4 billion NOK | 700 million NOK |



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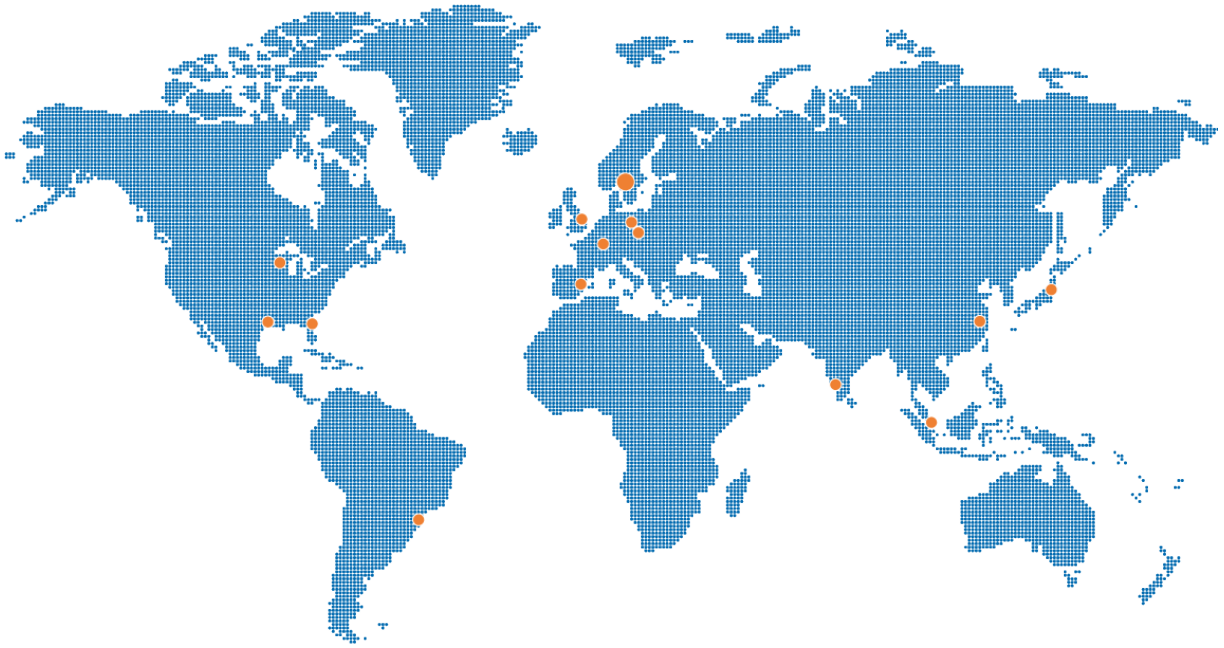
# A Global Company with International Manufacturing Operations




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



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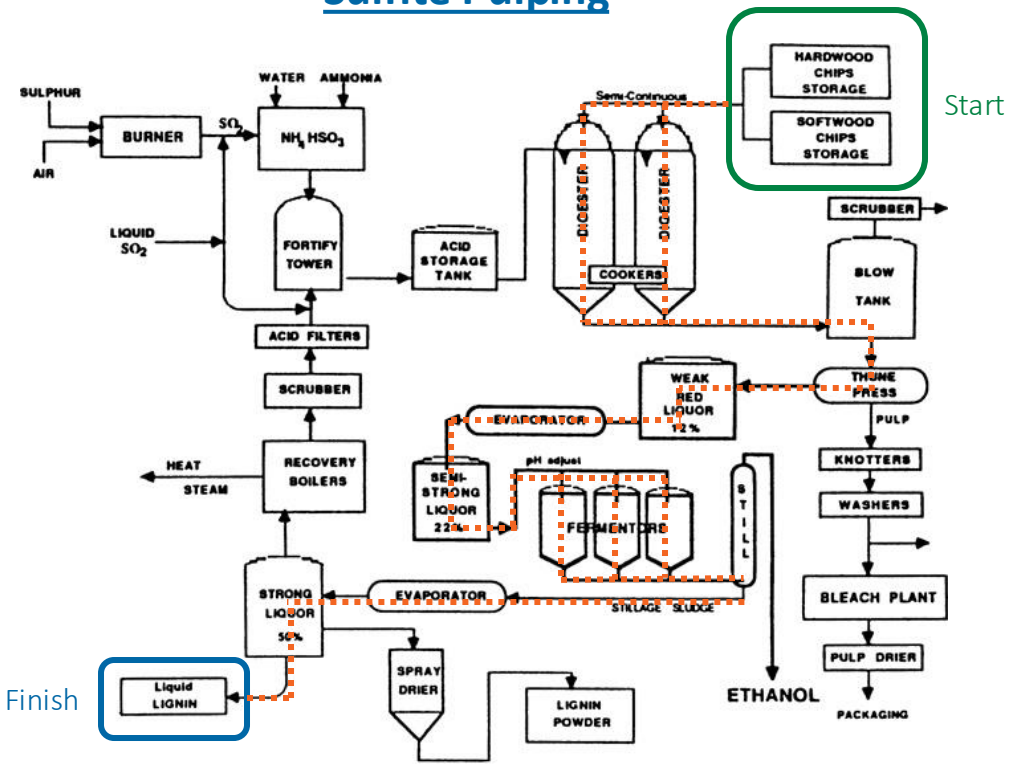
# Borregaard: The World's Most *Integrated* Biorefinery

## Sulfite Pulping

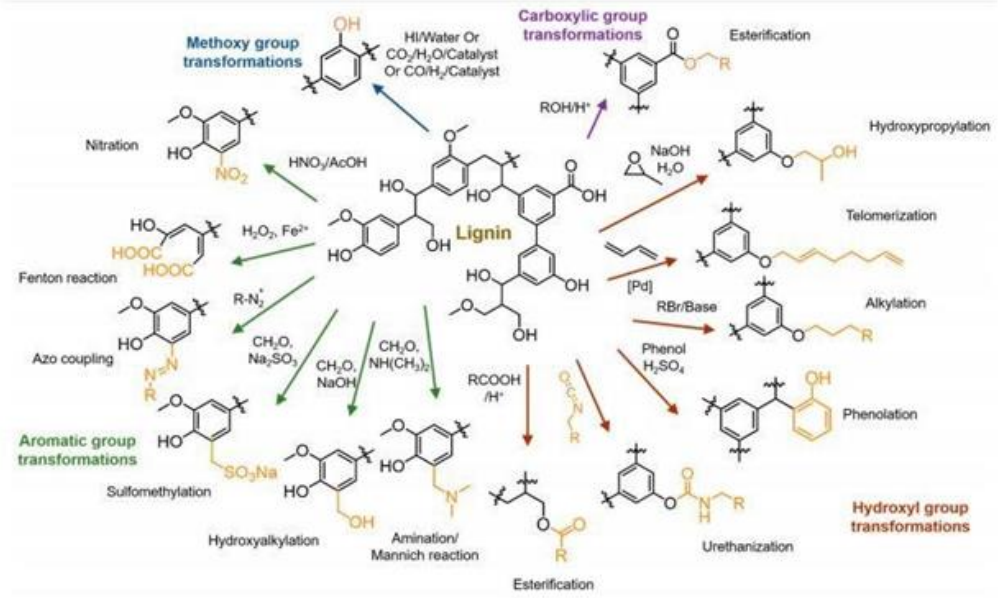



*Appl. Biochem. Biotechnol.* **1993**, *39-40*. 667-85.

## Downstream Processing

*Sugar Conversion* *Purification* *Fractionation* *Ion Exchange*

*Chemical Modification & Blending*




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



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# Borregaard Battery Center of Excellence in Rothschild, WI USA

Internal Studies performed on 2V Cells

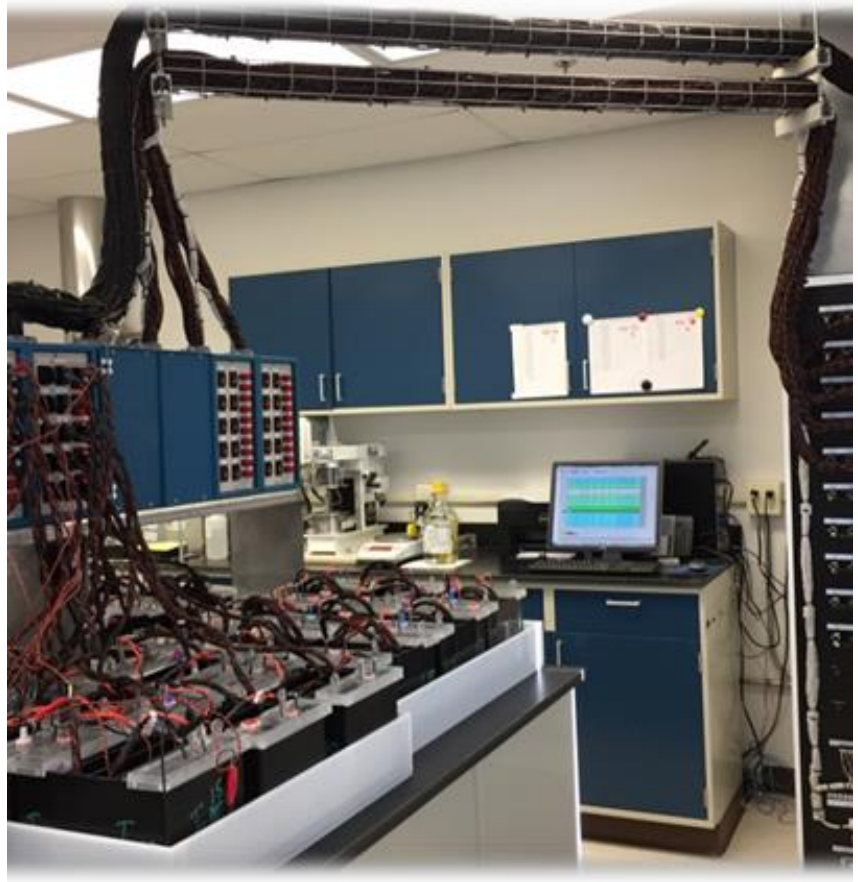
- Nominal C20 Capacity of 9.5 Ah
- SLI Design, Group 55 grid (14 cm x 10.5 cm)
- 3 plate 2V cell; 2 positives, 1 negative
- Polyethylene separator

Battery Testing

- Dedicated lead and lithium labs
- Maccor 4100 testing units (144 channels)
- Cells tested per SAE J537, ILNAS 50342-6 §7.3 “DCA” and “17.5% DoD” life test

Additional R&D equipment

- Anton Paar Rheometer
- Agilent HPLC
- Perkin Elmer ICP
- Bruker XRF
- Jeol NeoScope SEM
- Anton Paar DLS / ζ-potential
- CMC & THINKY planetary mills
- StatEase statistical software
- Support from Sarpsborg R&D
- MoU with UW-SP





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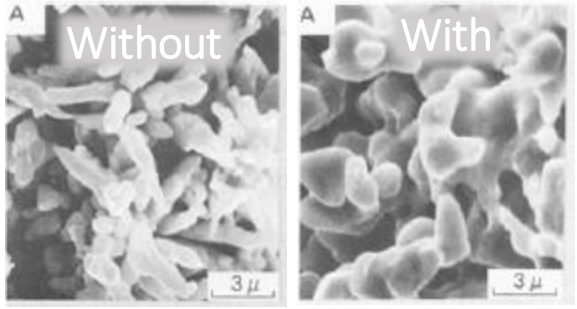
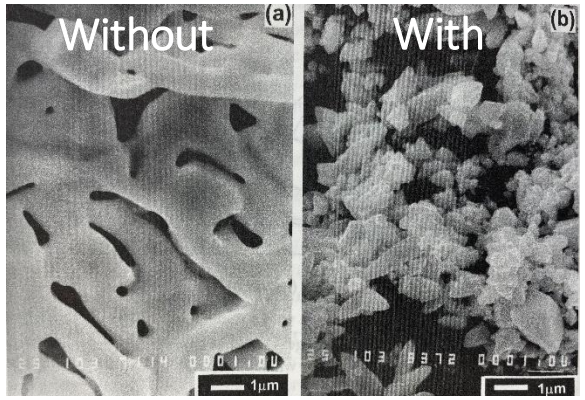
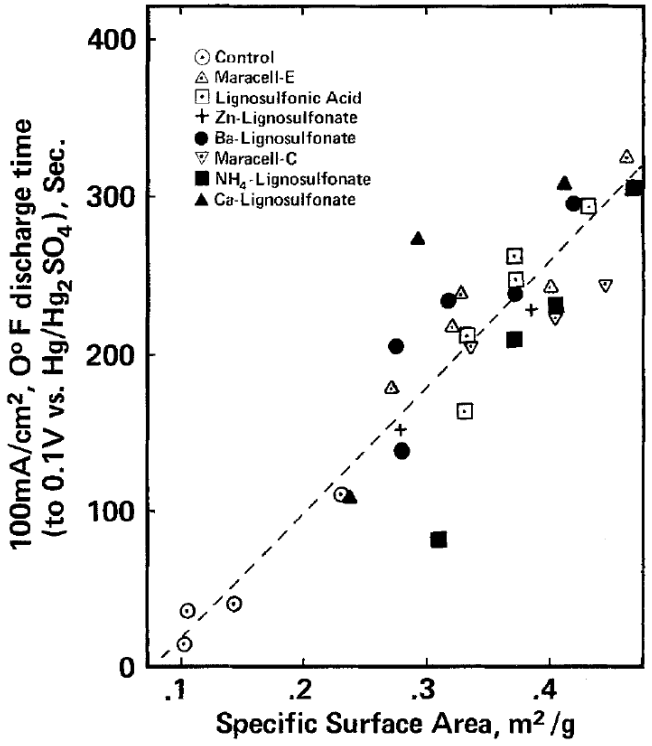
# The Critical Role and Effect of Lignosulfonates as Organic Expanders

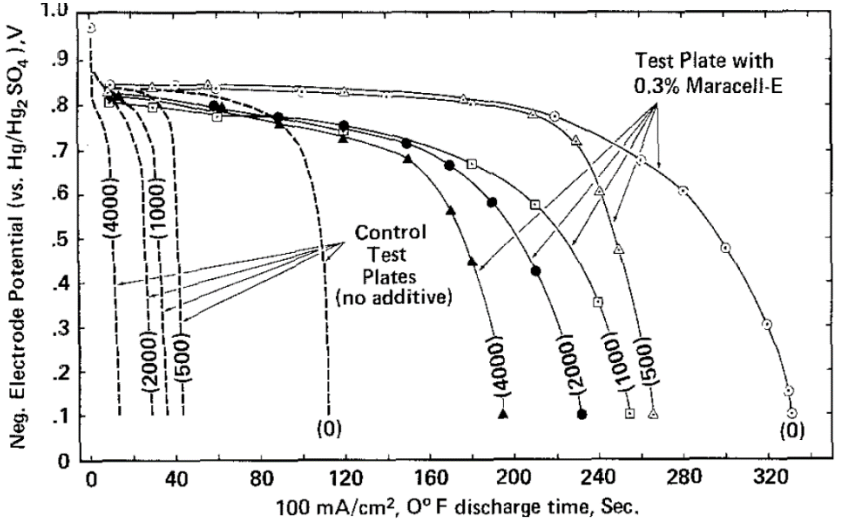



Mahato, *J. Elec. Chem. Soc.* 1977




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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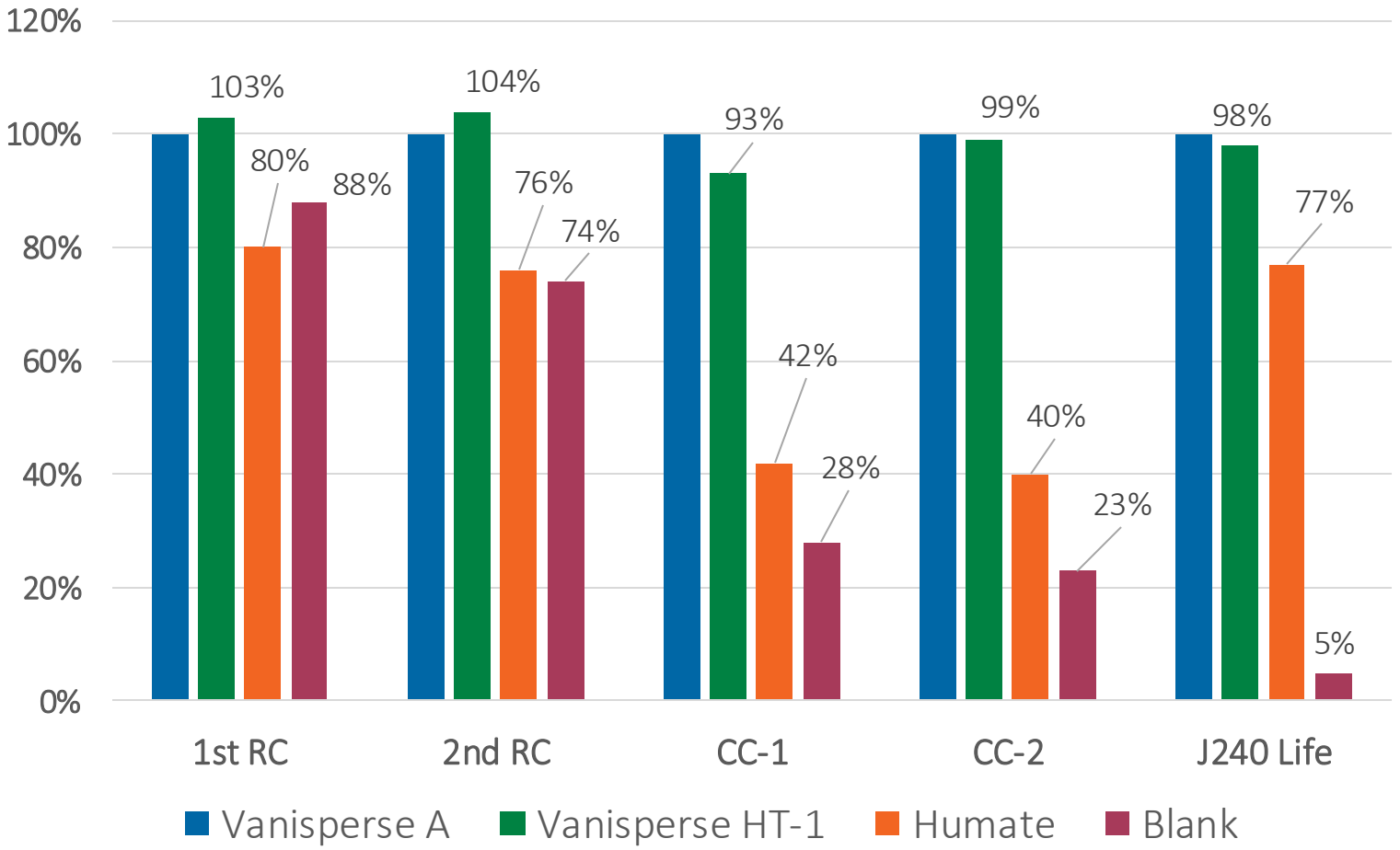
# Vanisperse Improves Capacity, Cold-Crank, and Battery Life

- Group 24 SLI Batteries
  - 640 A cold-crank
  - 105 min @ 25A res. capacity
- 0.6 wt% $BaSO_4$, 0.1 wt% Carbon, 0.3 wt% Expander
- Batteries formed as per manufacturer specification
- Tested by JBI Corp, Genoa OH, USA (Independent 3rd party testing lab)



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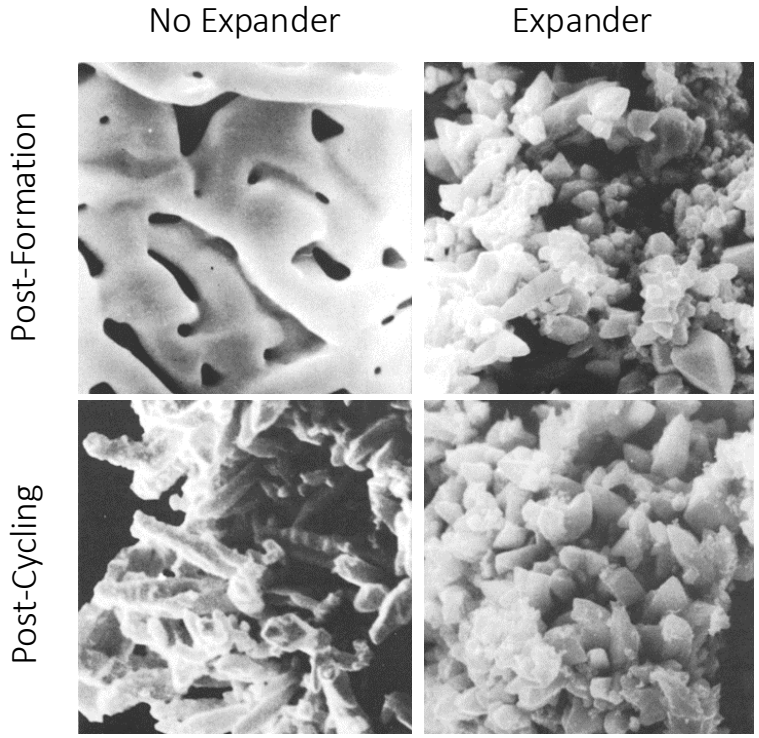
# Is Lignosulfonate Decomposition Responsible for Battery Failure?




*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… there is little quantitative evidence of such degradation…" (pg 143)*

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



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# We Need to Analyze the Lignosulfonate *within* a Lead Battery

This.  Is.  Hard.

# 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

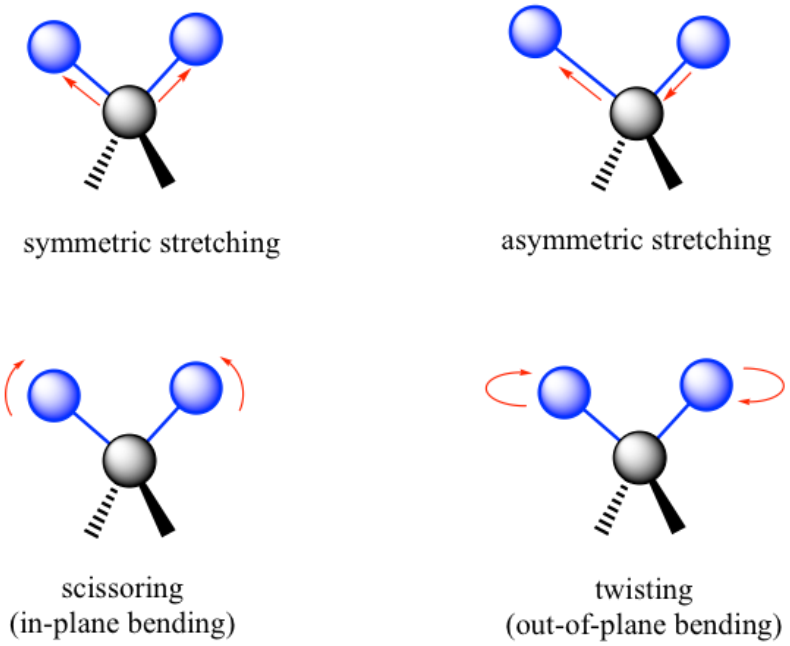
# INS is Vibrational Spectroscopy, but with Neutrons

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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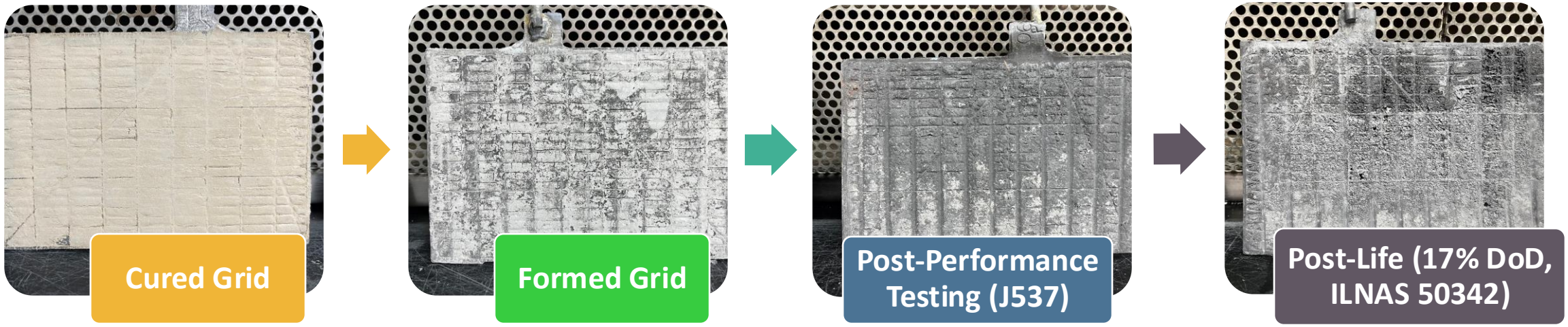
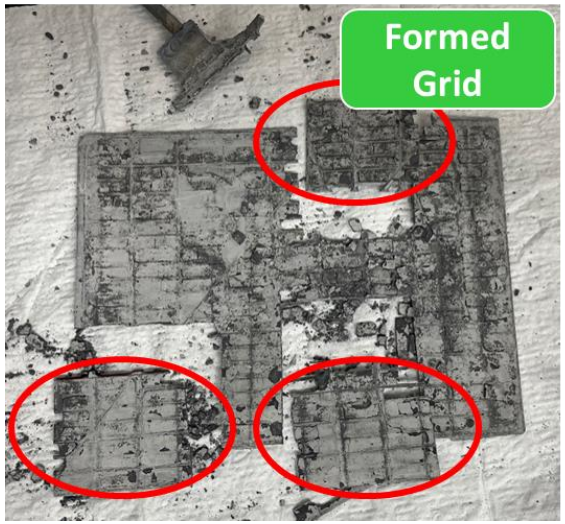
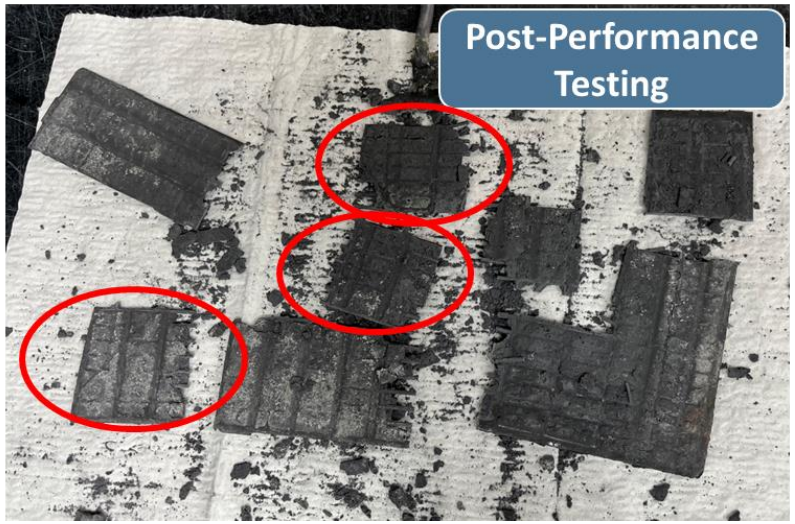
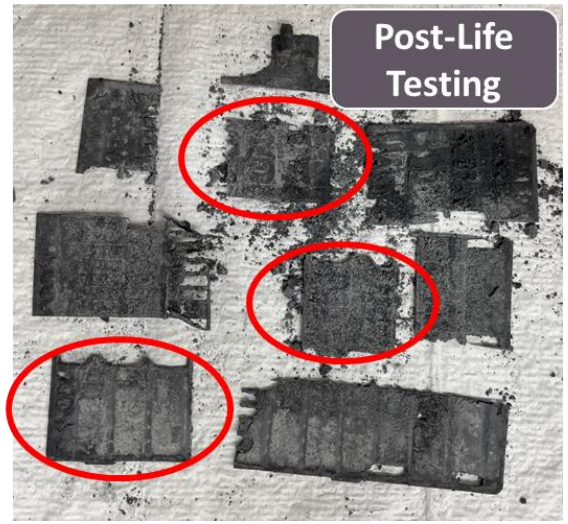
# Grids Were Harvested for Analysis During 2V Cell Testing



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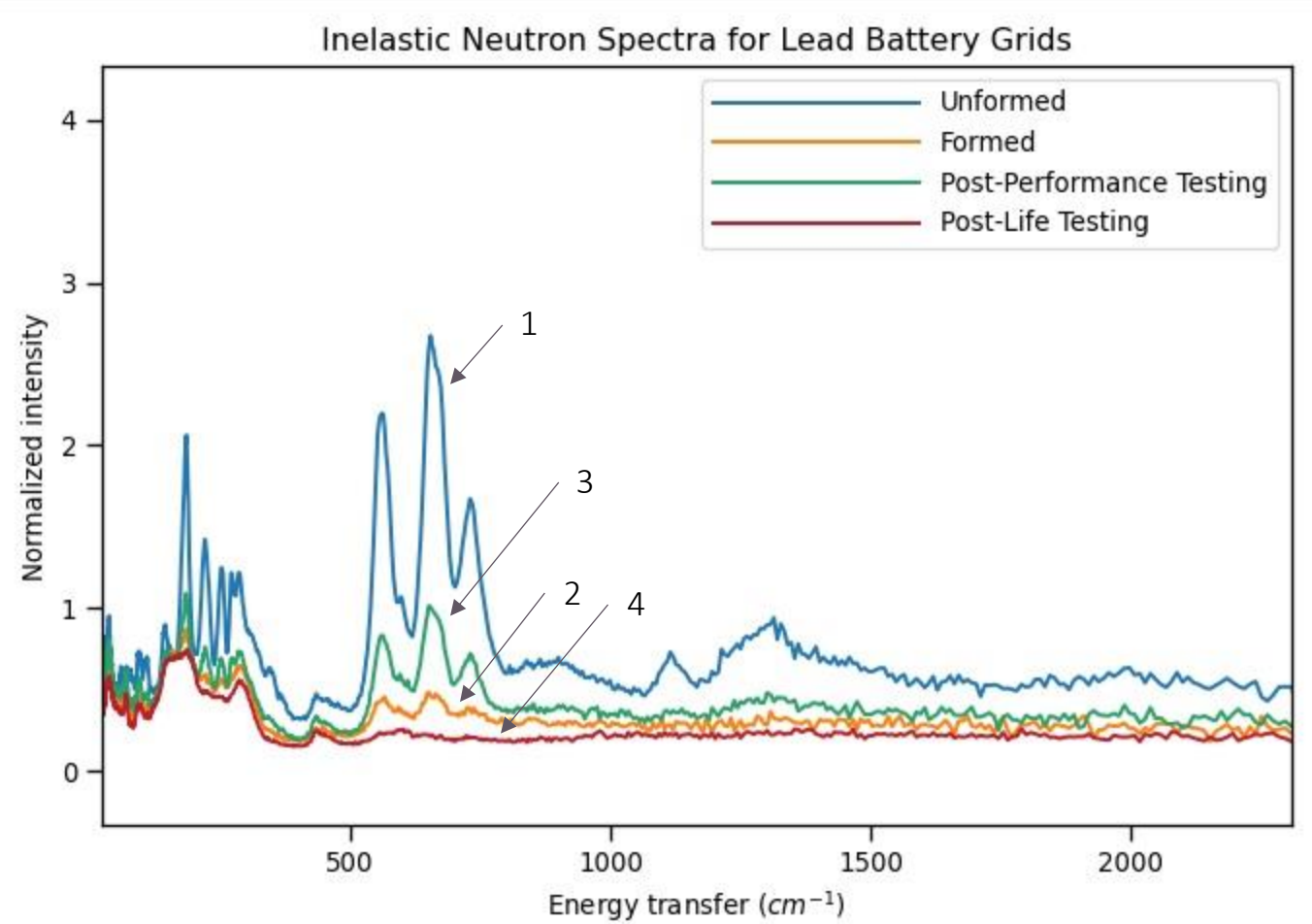
# First Ever Spectroscopic Data of Lignosulfonates in a Lead Battery Electrode!




- 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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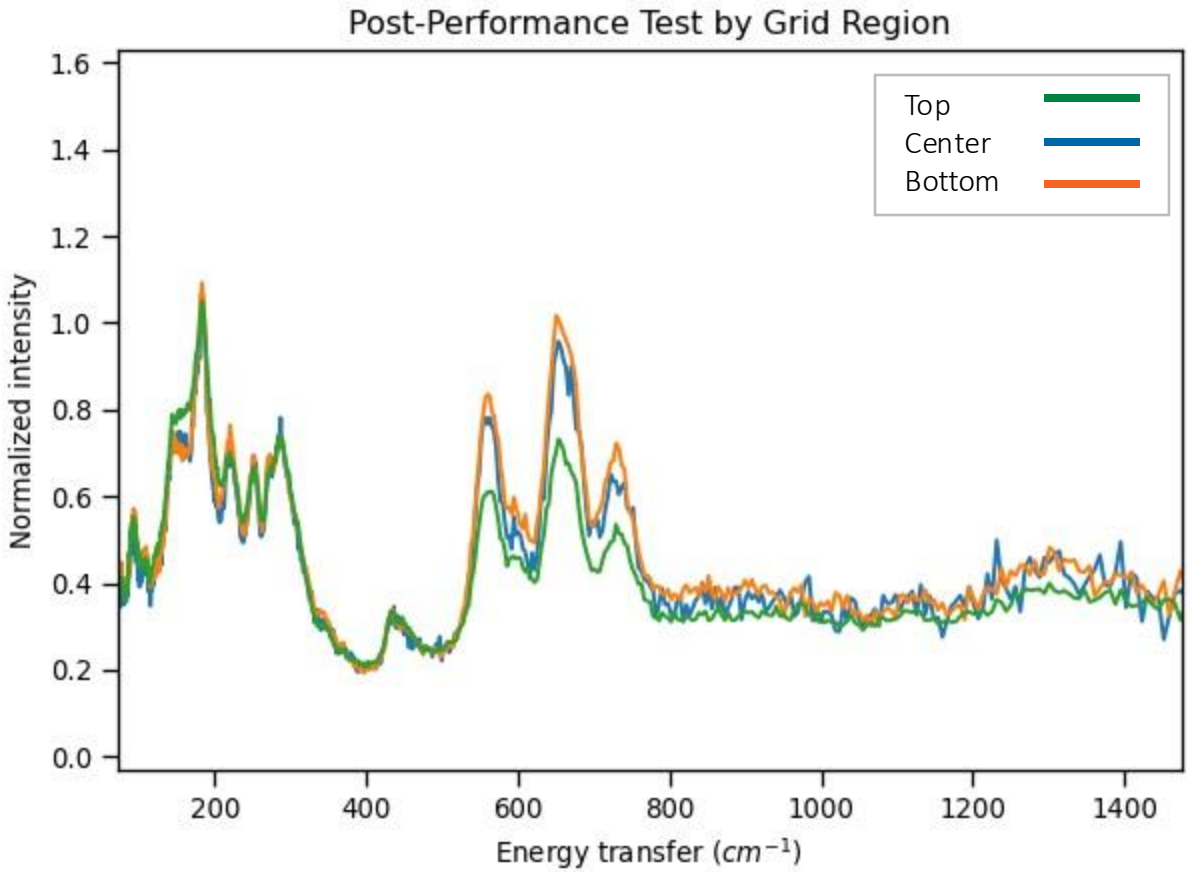
# Preliminary Results Suggest Differences Based on Location




- Samples harvested from different locations
- $PbSO_4$ is clearly seen visually, but *not detected* by INS
- Significant differences observed between Center and Top regions, attributed to the lignosulfonate differences

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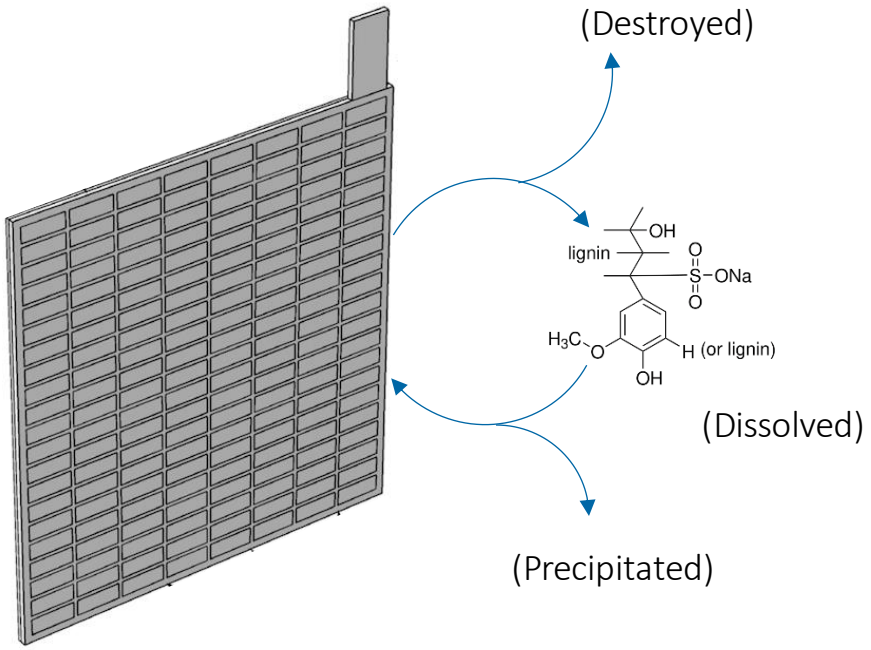
# Preliminary Results Prompt Rethinking of Lignosulfonate “Loss”




- Lignosulfonates are desorbed from the plate during formation and dissolved in the electrolyte
- They re-adsorb during battery cycling
- By some mechanism they are “lost” from the plate, driving end-of-life
  - Accelerated by cycling at PSoC
  - Destruction, Long-term dissolution, Precipitation
- Locating where the lignosulfonate “goes” will inform how to increase PSoC life



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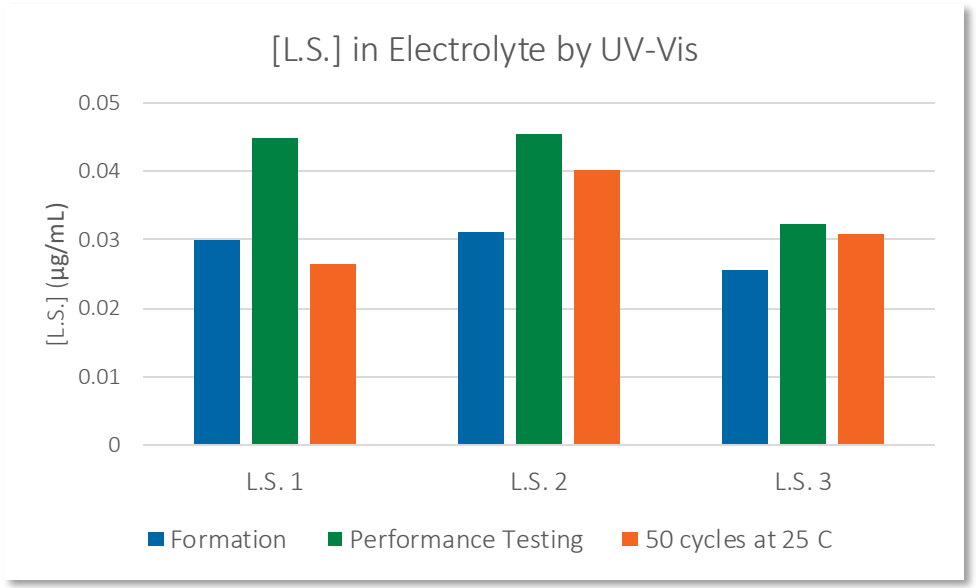
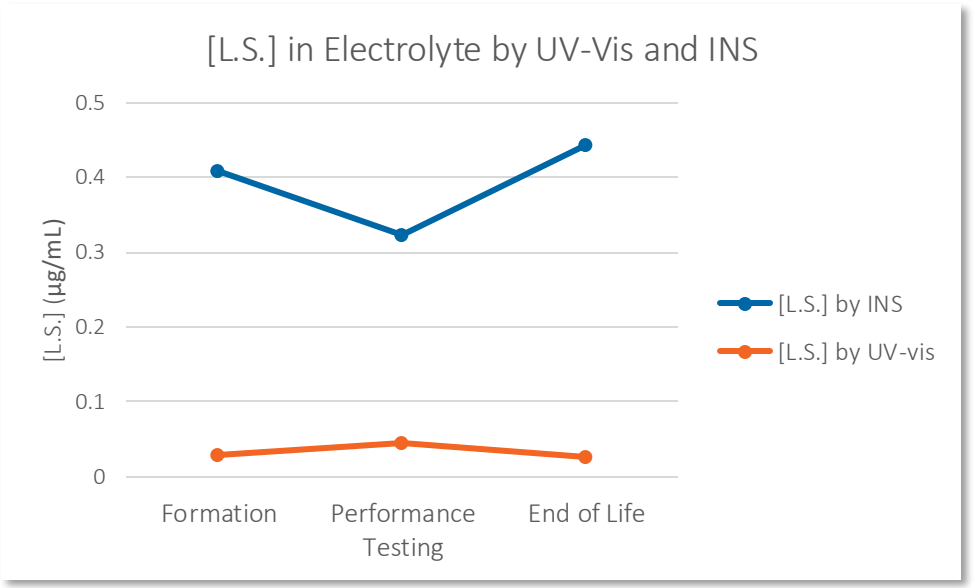
# UV-Vis Enables Quantification of Lignosulfonates in the Electrolyte




- 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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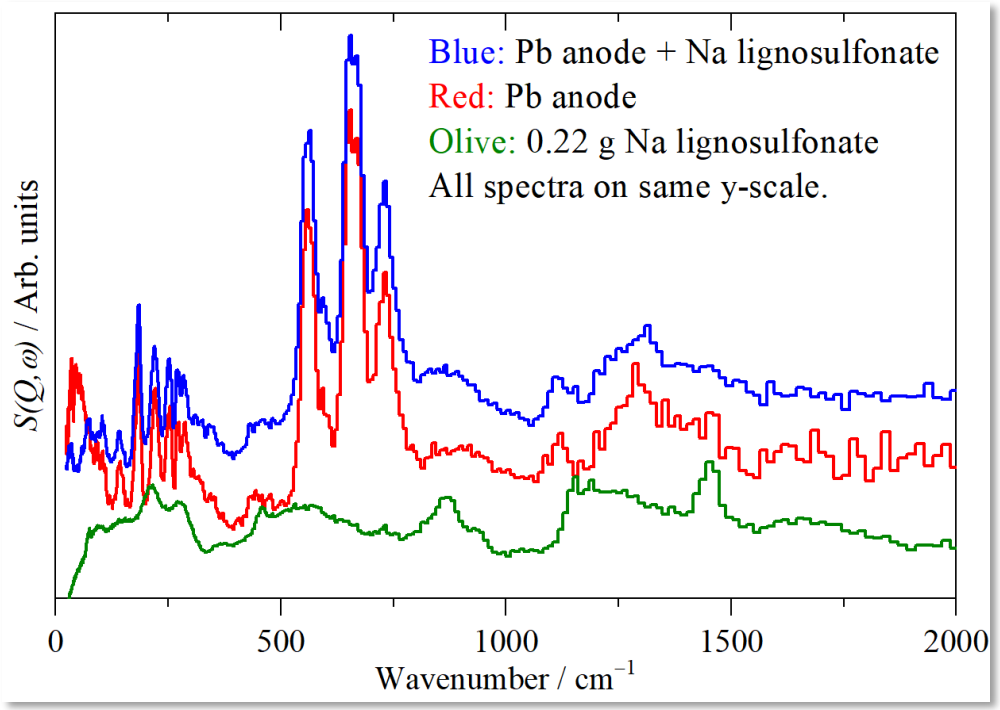
# Clarity Obtained from Control Samples Analyzed by INS

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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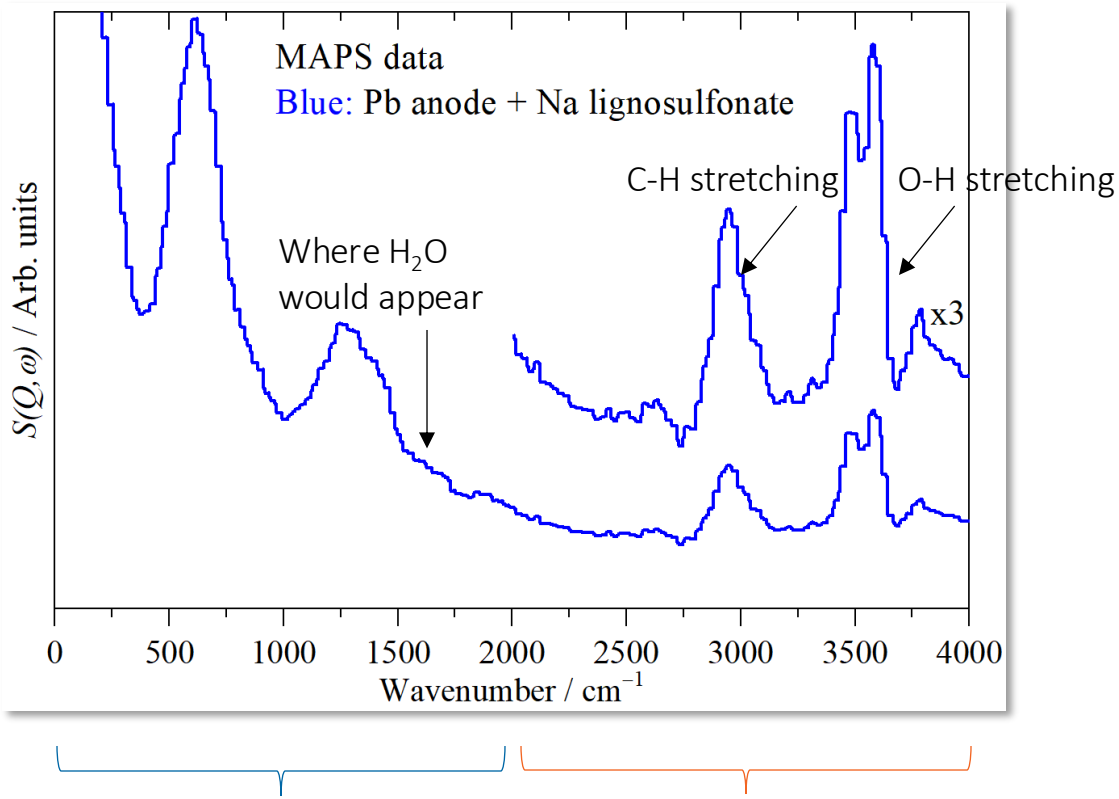
# Direct Geometry INS Delivers Spectra Consistent with Lignosulfonates




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 $cm^{-1}$

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



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# Summary & Conclusions

Inelastic Neutron Scattering has been used for the first time to investigate lignosulfonate persistence in lead batteries

- Preliminary data collected on an indirect geometry beamline (VISION, TOSCA) prompted an exciting, but unsupported hypothesis that the battery electrolyte could be a reservoir for the lignosulfonate
- UV-vis enables a convenient means for quantifying lignosulfonate concentrations in electrolytes
- Spectra collected on a direct geometry beamline (MAPS) display characteristic features of lignosulfonates
- A proposal has been submitted to MAPS to continue the proof-of-principle investigation

Neutron Scattering affords an exciting opportunity for expander R&D and developing new lignosulfonates for lead battery applications

*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-30432.1.*

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