COVALENT METROLOGY

VF | VOLTA FOUNDATION

A Metrology Toolkit for Battery Scientists

Exploring Thermo- electrochemical Aging Effects in Lithium-Ion Batteries

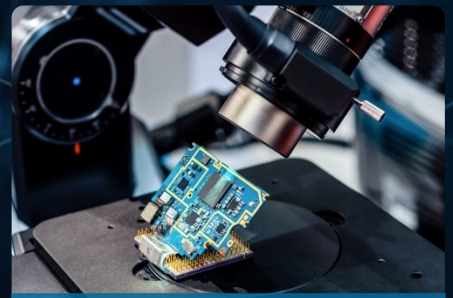
Adlai Katzenberg, PhD
Manager of Inorganic Chemistry

June 10, 2024
Volta Foundation Battery Forum



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Modern, digitally-empowered analytical services platform delivering quality data and expert analysis to accelerate advanced materials and device innovation.



Comprehensive Solutions Stack

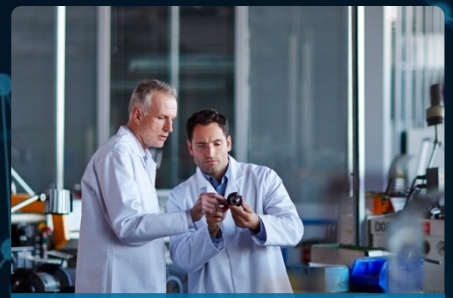
50+ Cutting-edge instruments in-house, 150+ Techniques

Analytical Services

Advanced Modeling

Method Development

Custom Consulting Solutions



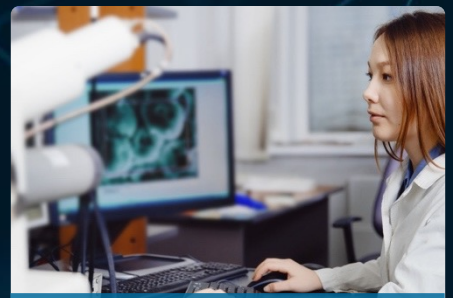
High-touch, High-Quality Services

Ionic Membership Program

Enterprise Metrology Solutions

Instant, Secure Access to Data and Reports

Expanding Toolkit in Custom Digital Platform



Flexible Business Models

LiveView™ (real-time collaboration)

Co-op and Tool-share Opportunities

Training and Certification on Instrumentation

Laboratory Audits

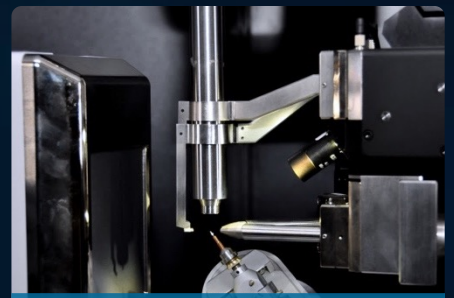
Rigaku · Anton Paar · ThermoFisher Scientific · Asylum Research · KEYENCE · J.A. Woollam · TA Instruments · PVA TePla · Teledyne CETAC Technologies · HORIBA Scientific · Digital Surf

Rich Network of Partnerships

Partner to World's Leading Instrument Manufacturers and Labs

Expanding access to Advanced Instruments and Analysis Tools

Lab Connections and Applications Learning



Who We Are, Who We Serve

50+ People, 14 PhDs

Comprehensive, Modern Analytical Capabilities

$20M +State-of-art Lab in Sunnyvale, CA

600+ Clients, 15-30 new clients / week

With support from *Qnovo*

COVALENT METROLOGY



Qnovo™

Intelligent Battery Software for BMS

BREAKTHROUGH TECHNOLOGY

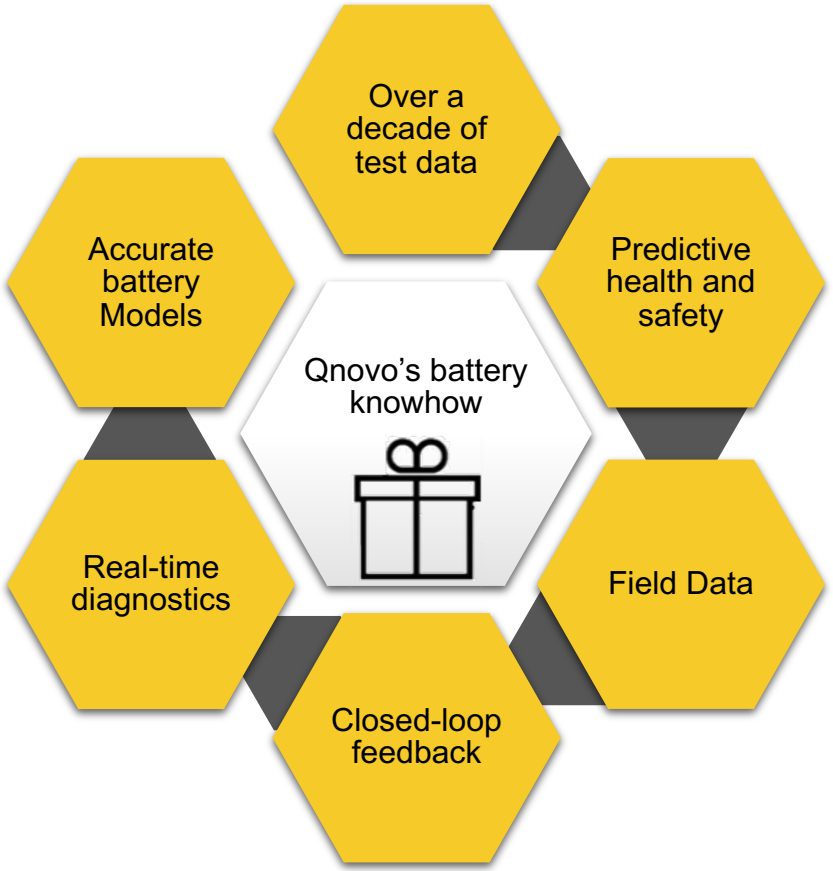
- 14 Years R&D
- 50+ Patents
- Pioneering technology in:
  - Battery intelligence &
  - Adaptive charging
- In-depth battery know-how, from materials to cell design to BMS

CUSTOMERS

Global EV Automakers
Fleet Managers
Charging Providers

SELECT INVESTORS & PARTNERS

Constellation. NXP OGCI CLIMATE INVESTMENTS OIL AND GAS CLIMATE INITIATIVE
ROCKPORT CAPITAL USVP U.S. VENTURE PARTNERS BorgWarner



Today's Challenges for All Battery Innovators

- **An intense competition** is taking place to find enabling solutions **to Electrify Everything**
- **Performance at all levels:**
  Single layer, multi-layer, cell modules in practical use
- **Scaling up:**
  Lab -> pilot -> full-scale -> mega factory
- **Balance performance in many dimensions:**
  Energy capacity I Power I Charge time I Cycle life I Power fade I Calendar life I Safety I Cost

Additional Differentiators and Challenges:

- Recyclability
- Preferred raw materials / avoidance of problematic materials
- Faster / cheaper production process
- Mechanical properties
- Ultra-thin
- 3D printing, structural batteries



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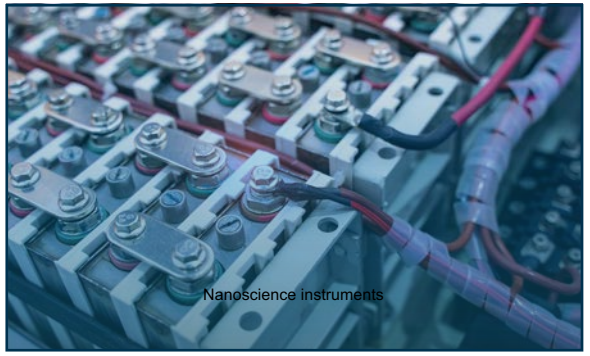
Metrology Plan

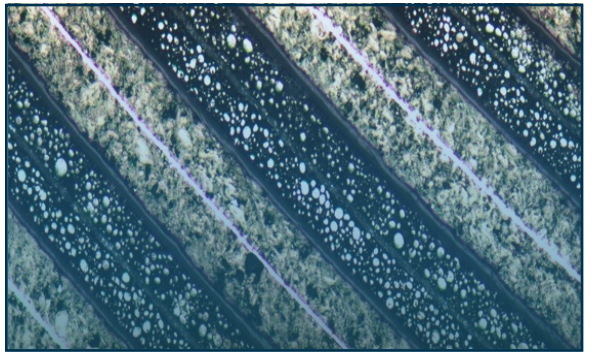
COVALENT METROLOGY

Source Relevant Cells from a Reputable Supplier → Tear-down and Characterize → Accelerate aging → Identify failure modes









Metrology Plan

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1 Battery Tear Down

- Opening of cell
- Separation and Collection of targeted components
- All done in air-free Argon Glovebox

2 Baseline Characterization

	Analysis Objectives	*Techniques*
Architecture	• Format • Casing and jellyroll integrity	• Optical inspection • 2D X-ray
Anode	• Dimensions • Morphology • Chemistry • Integrity	• Ion mill + SEM-EDS • TGA • Raman
Cathode	• Dimensions • Morphology • Chemistry • Integrity	• Ion mill + SEM-EDS • TGA
Electrolyte	• Solvent(s), Salt • Additives • Contaminants • Gas	• GCMS • Liquid NMR (1H, 13C, 19F, 31P)
Separator	• Morphology • Chemistry • Polymer ID	• Ion mill + SEM-EDS • FTIR

3 Cell Abuse

4 Targeted Post-Mortem Analysis

Cell Overview, Specs, and Initial Metrics

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LG INR21700 M50LT

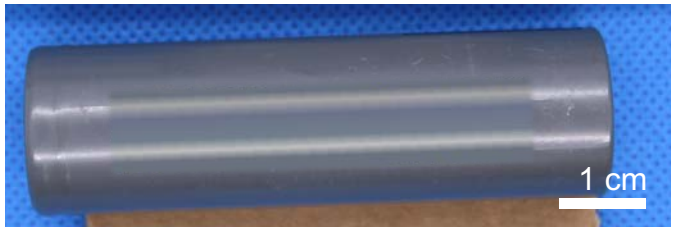
- Lithium-ion
- NMC cathode
- Graphite/Si Anode

Standard Charge		
Constant Current	0.3	C
Constant Voltage	4.2	V
End Condition	50	mA
Charging time	4	hr

Standard Discharge		
Constant Current	0.2	C
End Voltage	2.5	V

Nominal Specs		
Capacity	4.8	Ah
Voltage	3.69	V
Max Charge Voltage	4.2	V
Max Charge Current (0-25 °C)	0.3	C
Min Discharge Voltage	2.5	V
Max Discharge Current (0-25 °C)	0.5	C
Initial DC Impedance	17 - 29	mOhm
Cycle Life (% initial energy at 1000 cycles)	> 80	%



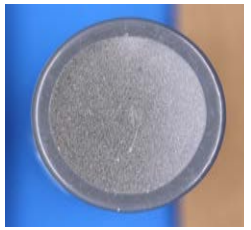


[+] terminal (Cathode)





[-] terminal (Anode)



Chen *et al. J. Electrochem. Soc.* 2020 **167** 080534

Teardown and Characterization Plan

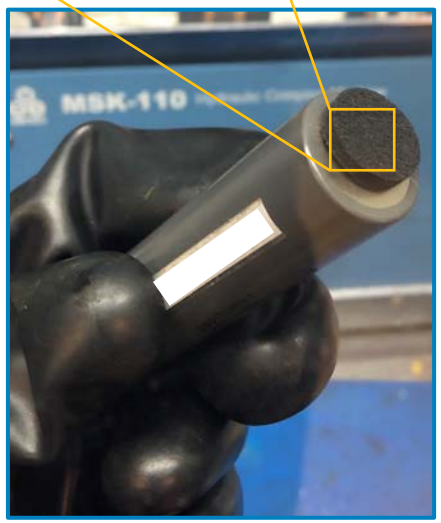
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Discharge to 0 SOC → Pierce casing, sample gas → Remove end cap, collect electrolyte → Extract Jelly Roll → Separate and clean components



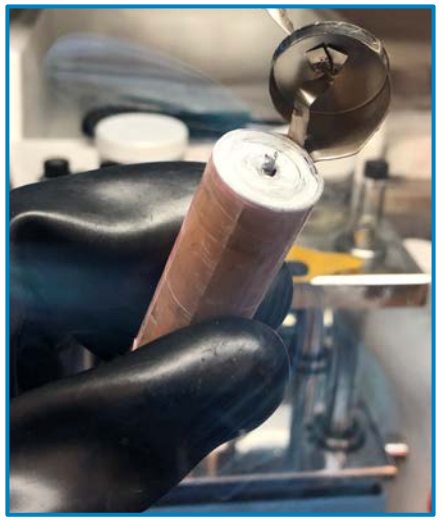


Sample via gas-tight syringe, to GC-TOF-MS



Centrifuge, collect liquids, GCMS+NMR





Separator



Cathode

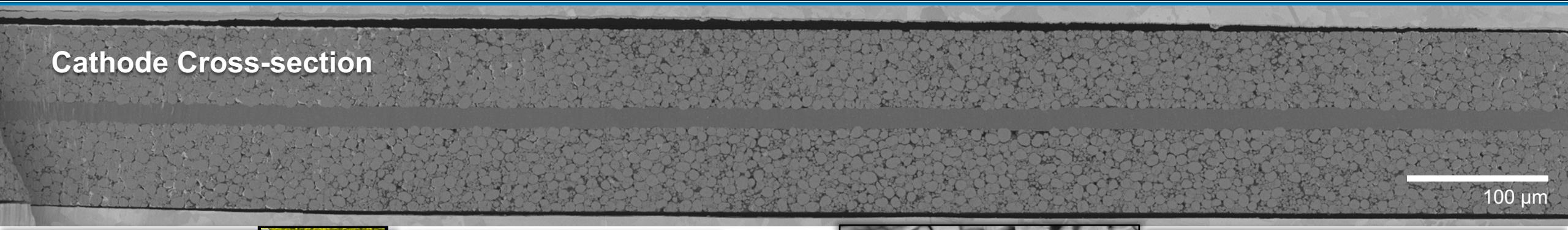


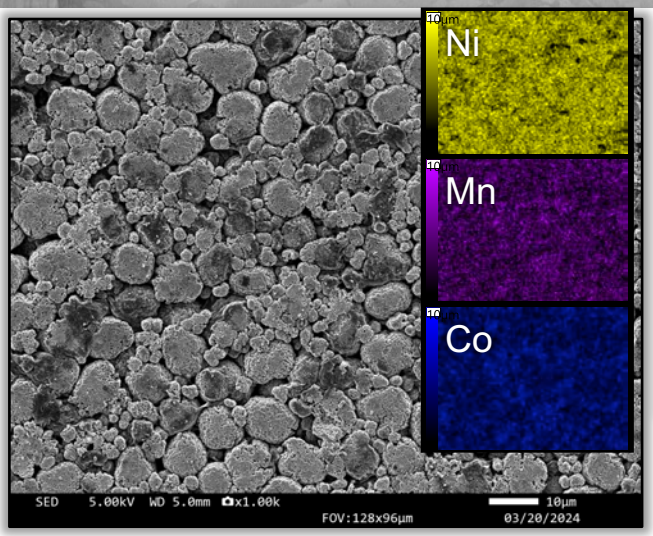
Anode



Baseline Characterization - Cathode

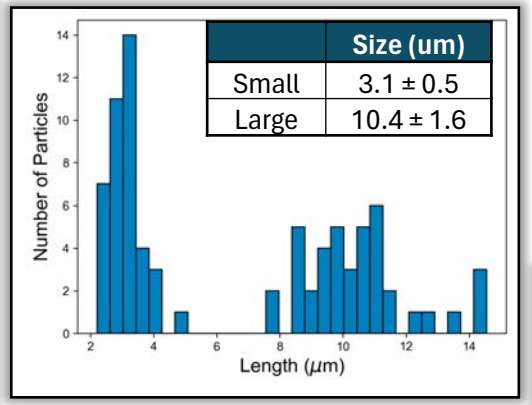
Cathode Cross-section





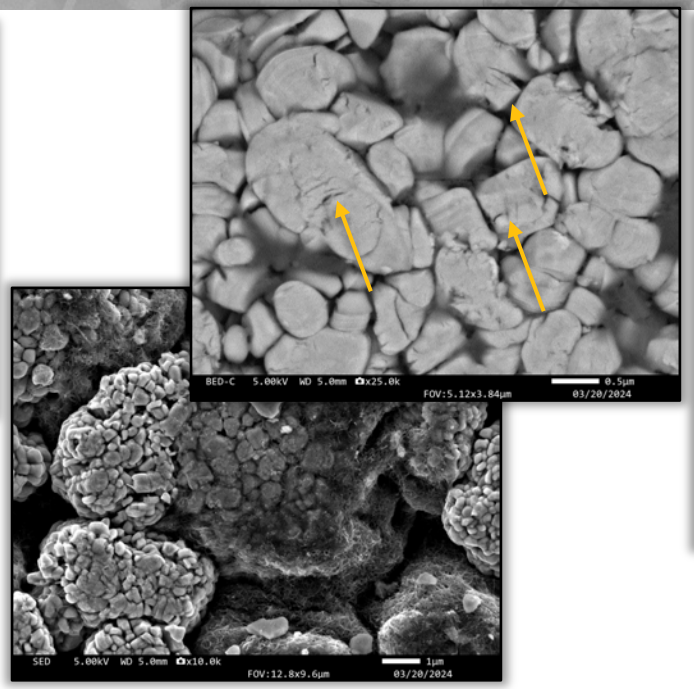
Component	Thickness (µm)
Foil	15.01 ± 0.67
Coating	57.08 ± 1.99

- Nominally NMC-811.
- Coating well adhered to foil
- Trace Nb detected by LA-LI-TOF-MS

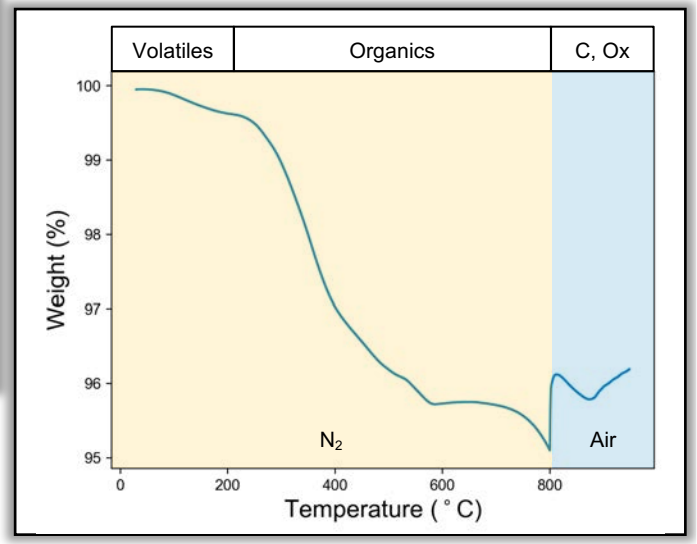


	Size (um)
Small	3.1 ± 0.5
Large	10.4 ± 1.6

Element	Mass%	Atom%
Mn	**2.9**	**1.5**
Co	**5.2**	**2.5**
Ni	**54.1**	**25.9**
C	7.2	16.9
O	29.9	52.6
P	0.1	0.1
S	0.2	0.2
Al	0.3	0.3



- Homogeneous distribution of Ni/Mn/Co
- Bimodal particle size distribution
- Moderate cracking and thin fibers visible at high magnification

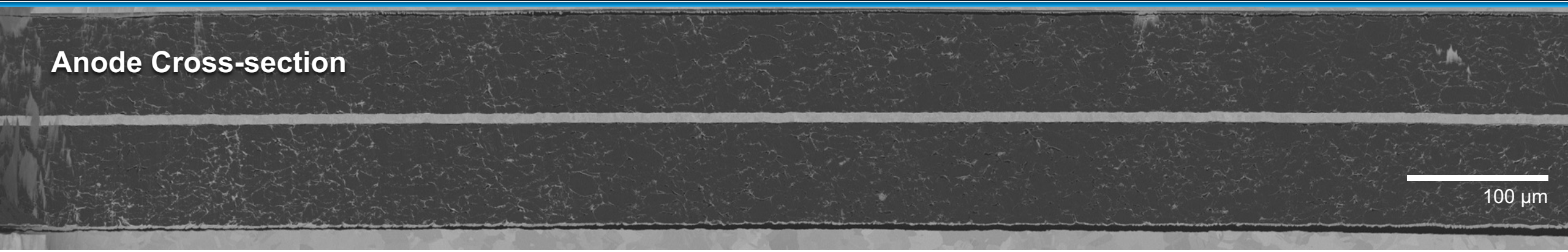


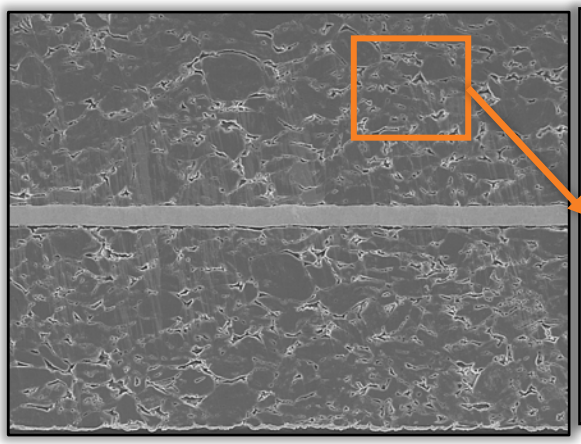
Component	Volatiles	Organics	Oxidation	Residue
Mass %	0.4	3.9	1.01	96.4

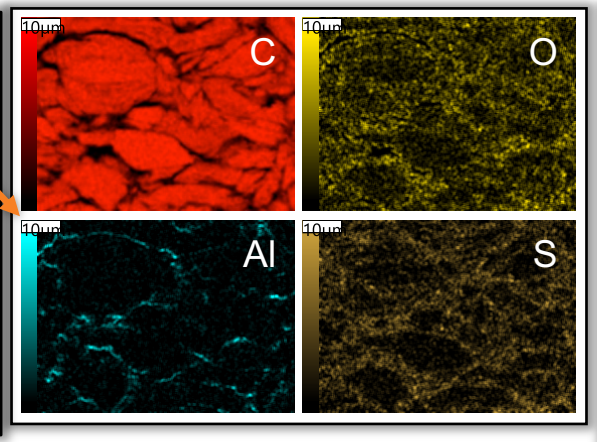
Baseline Characterization - Anode

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Anode Cross-section



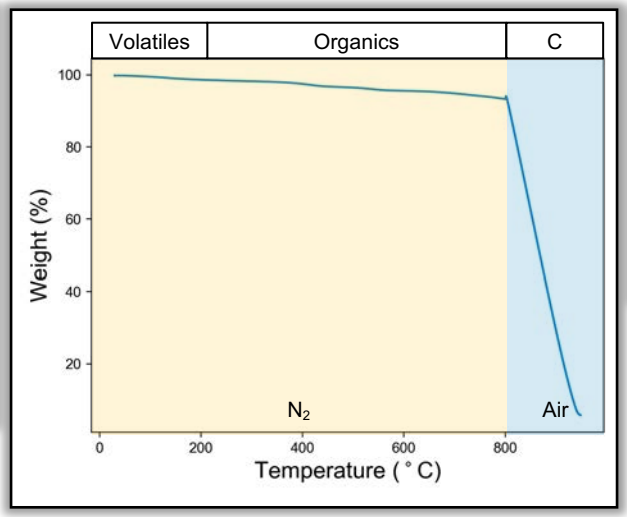




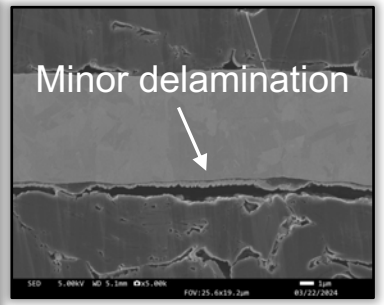
Component	Thickness (µm)
Foil	8.38 ± 0.15
Coating	78.34 ± 1.42

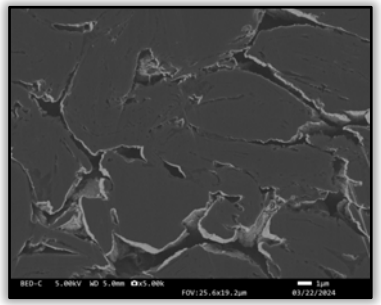
- No Si detected by SEM-EDS, Raman, or XPS
- Trace Al localized to particle surfaces

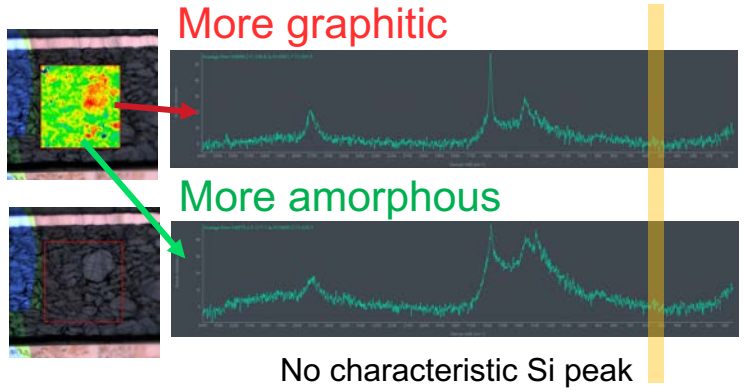
Element	Mass%	Atom%
C	**85.4**	**89.9**
O	10.6	8.4
F	1.4	0.9
Al	0.3	0.2
S	0.8	0.3
Cu	1.5	0.3



Component	Volatiles	Organics	Oxidation	Residue
Mass %	1.8	4.9	87.6	5.7





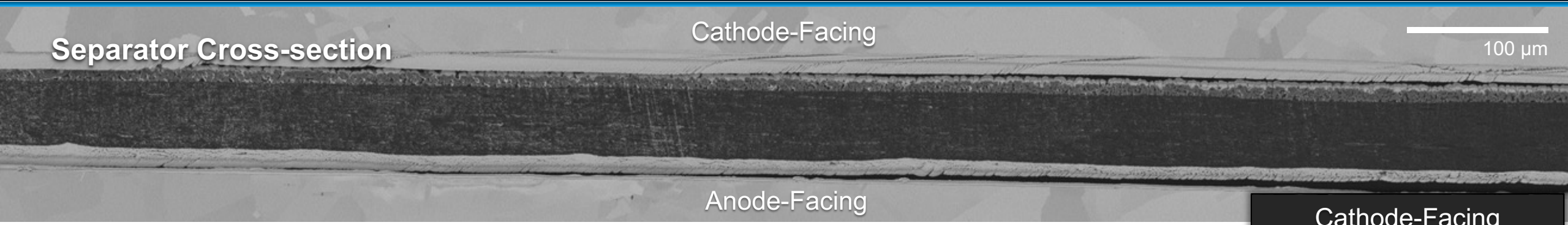


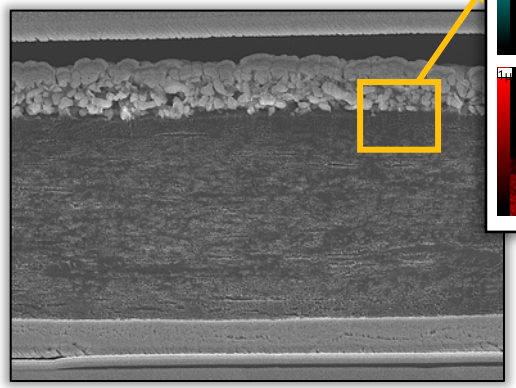
No characteristic Si peak

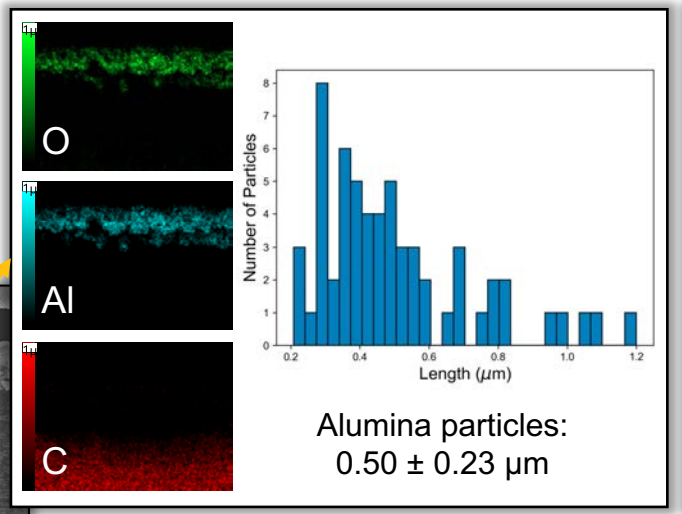
Baseline Characterization - Separator

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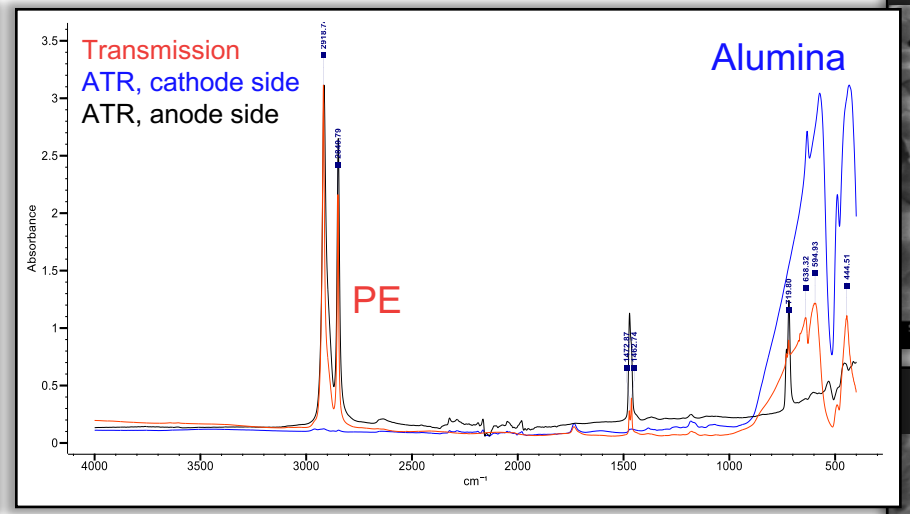
Separator Cross-section

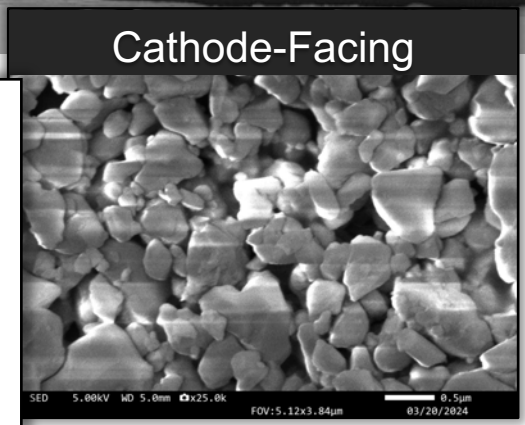


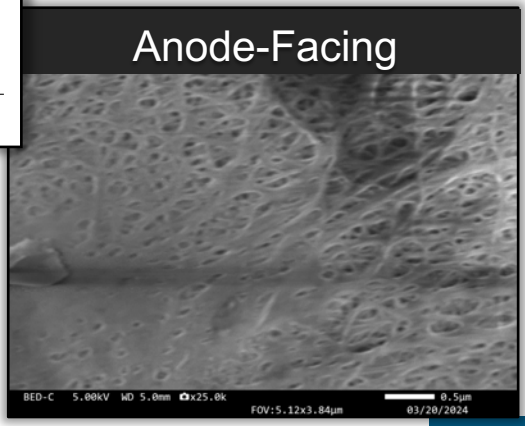




Alumina particles:
0.50 ± 0.23 µm







Component	Thickness (µm)
Polymer	10.16±0.41
Alumina	1.76±0.15

Element	Mass%	Atom%
C	60.1	75.0
O	17.6	16.4
Al	10.5	5.8

- Base material is polyethylene
- Alumina coating with binder on anode side

Baseline Characterization – Electrolyte

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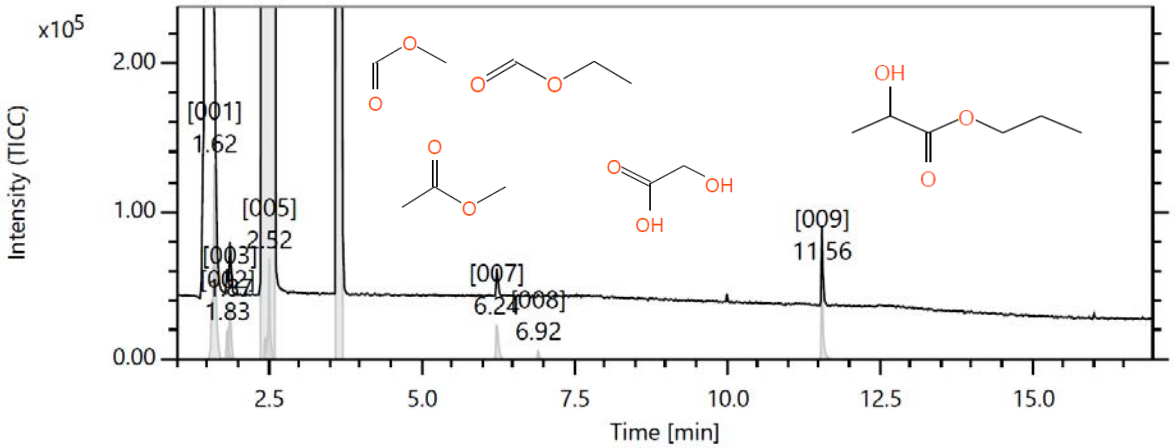
Liquid – collected via centrifugation

$^{1}H/^{31}C/^{19}F/^{31}P$ - NMR

Compound	Chemical Shift	Mass Ratio
Dimethyl carbonate	3.69	68.8
Ethyl methyl carbonate	4.09-4.13	4.9
Ethylene carbonate	4.48	25.4
Methyl formate	4.29	0.9

GCMS

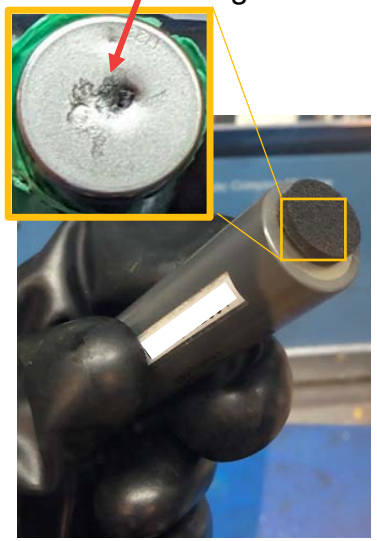
ID	Area [%]	Library Name	Formula
001	0.53	Methyl formate	C2 H4 O2
002	0.06	Ethyl formate	C3 H6 O2
003	0.10	Methyl acetate	C3 H6 O2
005	0.19	Hydroxyacetic acid	C2 H4 O3
008	0.01	Propyl 2-hydroxypropanoate	C6 H12 O3



- 7:3 DMC:EC
- $LiPF_6$ is the only P/F-containing species detected
- No $LiPF_6$ breakdown products
- No FEC/VC additives

Gas – collected via sampling septum

Small puncture in cell casing



Formula	Mass	Relative Intensity [%]	Intensity
C H4	16.03097	2.90%	14928.76
H2 O	18.01078	0.62%	3178.2
H F	20.00659	0.04%	201.62
C O	27.99465	0.52%	2654.99
N2	28.0056	69.85%	359216.8
C2 H6	30.04665	0.25%	1302.17
O2	31.98927	17.16%	88230.51
Ar	39.96173	N/A	407399.3
C O2	43.98941	0.48%	2487.17
C3 H8	44.06306	0.05%	271.38
C2 H6 O	46.04247	0.05%	278.93
C2 H4 O2	60.02199	0.06%	307.45
O F3 P	103.9634	8.01%	41193.9

As-received cell shows clear signs of solvent and salt decomposition

- C1-C3 hydrocarbons
- $CO + CO_2$
- HF, PF_3O
- Electrolyte fragments

Metrology Plan

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1 ~~Battery Tear Down~~

2 ~~Baseline Characterization~~

3 Cell Abuse

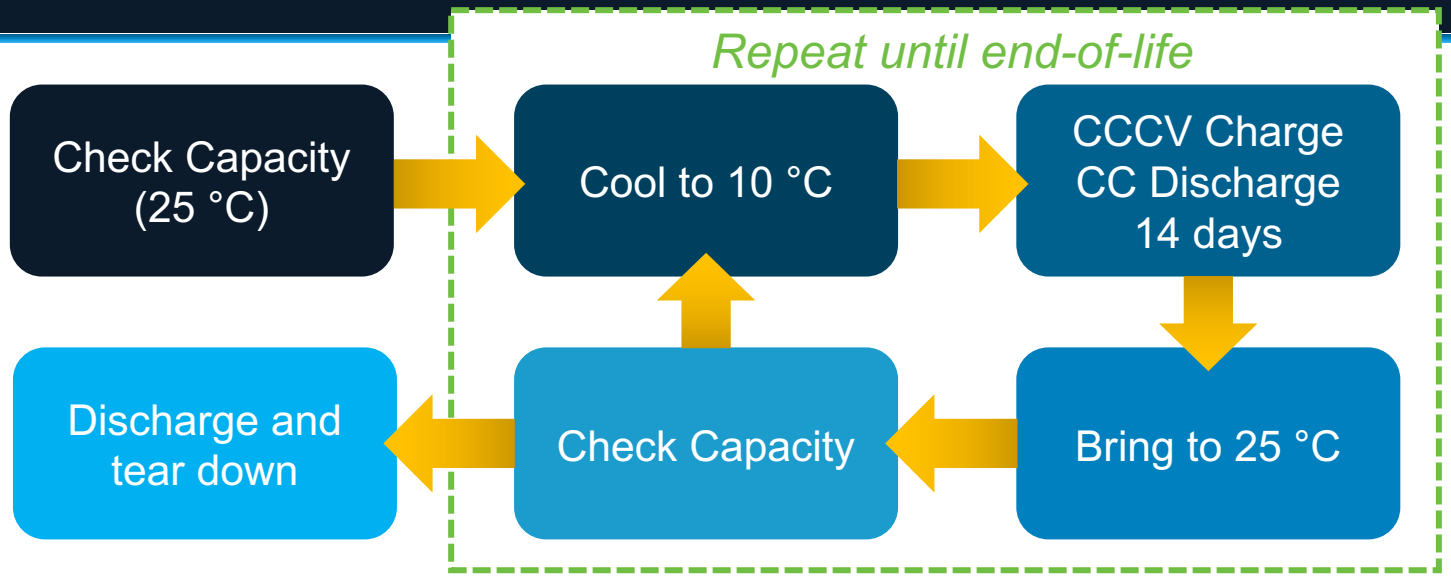
Accelerated Anode Aging

- High current, low temperature
- Track capacity retention, ESR
- Tear-down at end-of-life

4 Targeted Post-Mortem Analysis

	Likely Failure Modes	*Techniques*
Anode	• Li Plating • Cracking • Delamination • Changes in SEI	• Ion mill + SEM-EDS • XPS • **LALI-TOF-MS**
Electrolyte	• Decomposition • Gas formation – reduction and oxidation products	• **GC-TOF-MS** • Liquid NMR
Architecture	• Casing rupture • Thermal runaway • Jellyroll deformation	• Optical inspection • 2D X-ray

Low Temperature Abuse Testing – Anode Degradation





- 64 Maccor channels
- 5 incubators
- 2 potentiostats with EIS
  - Gamry Interface 4000e
  - Autolab PGSTAT 302N

25 °C

Standard Charge (CCCV)		
Constant Current	0.3	C
Constant Voltage	4.2	V
End Condition	0.1	C
Charging time	4	hr

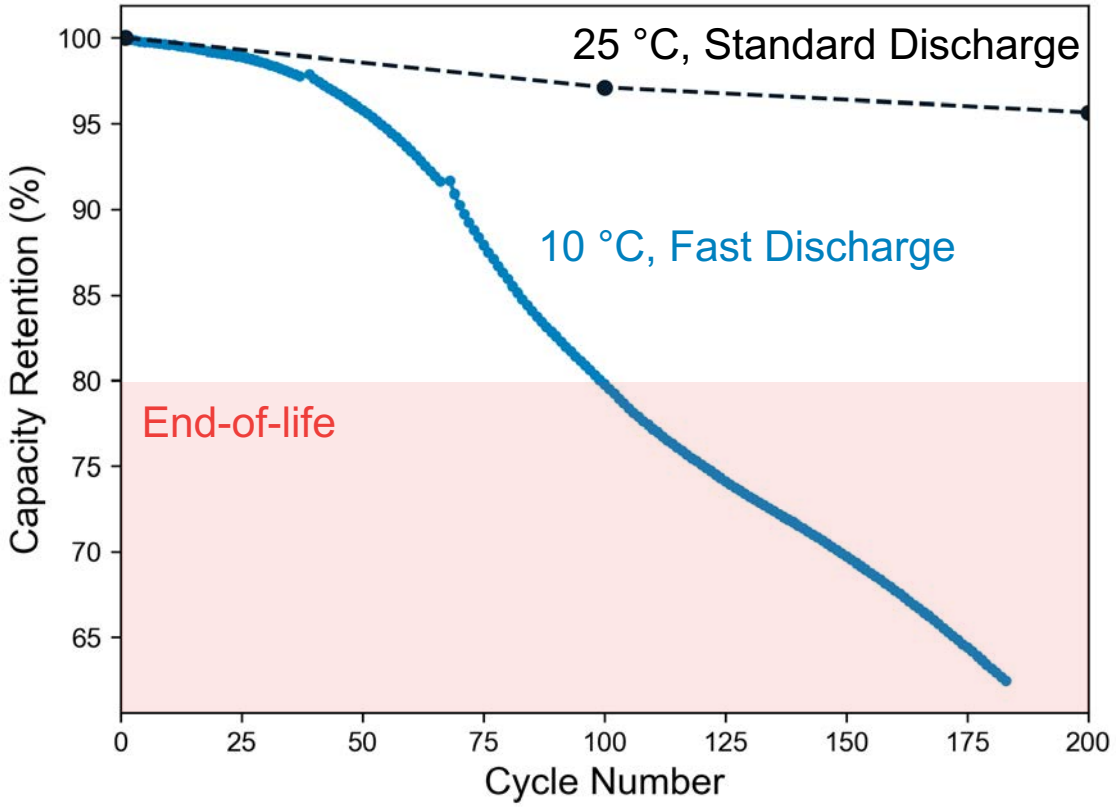
Standard Discharge (CC)		
Constant Current	0.2	C
End Voltage	2.5	V

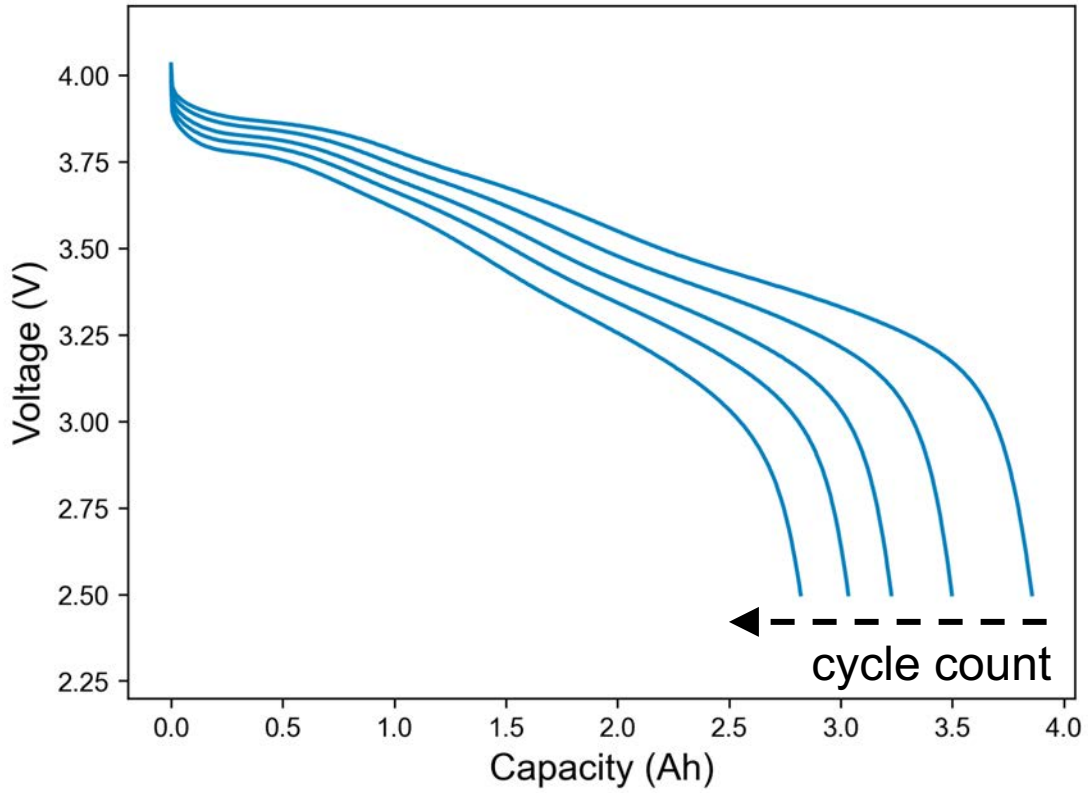
10 °C

Abuse Charge (CCCV)		
Constant Current	0.7	C
Constant Voltage	4.2	V
End Condition	0.05	C
Charging time	N/A	

Abuse Discharge (CC)		
Constant Current	0.7	C
End Voltage	2.5	V

Rapid Decay in Cell Capacity Under Abuse Conditions

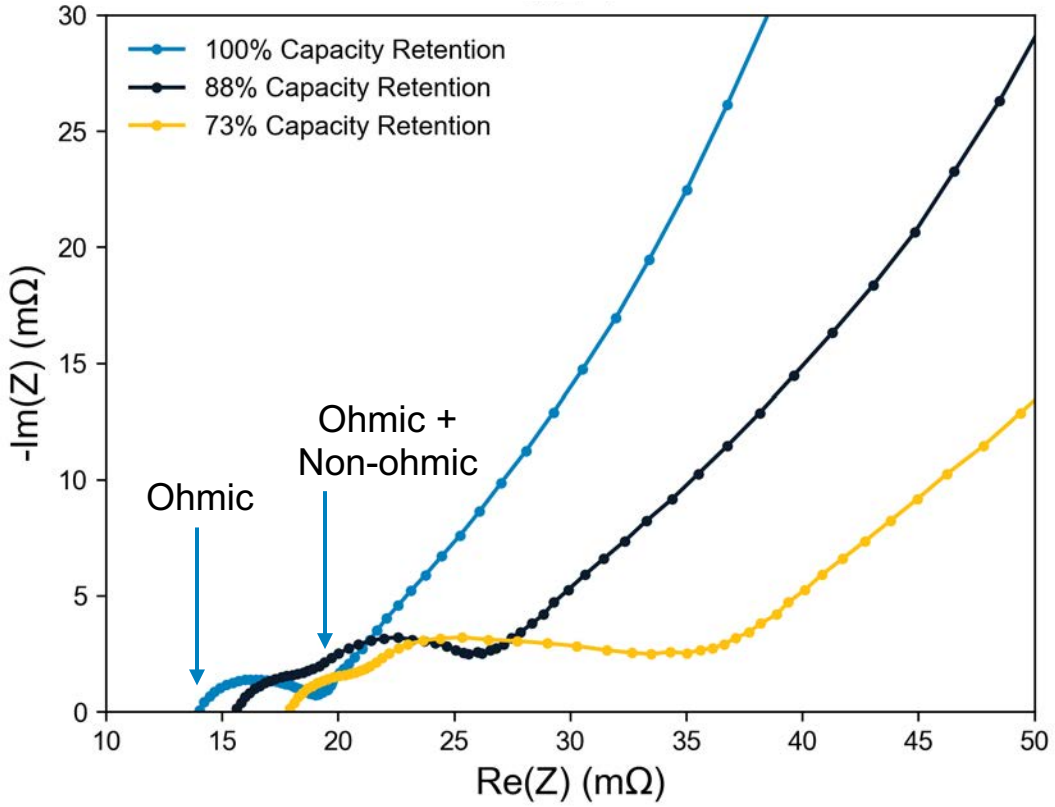


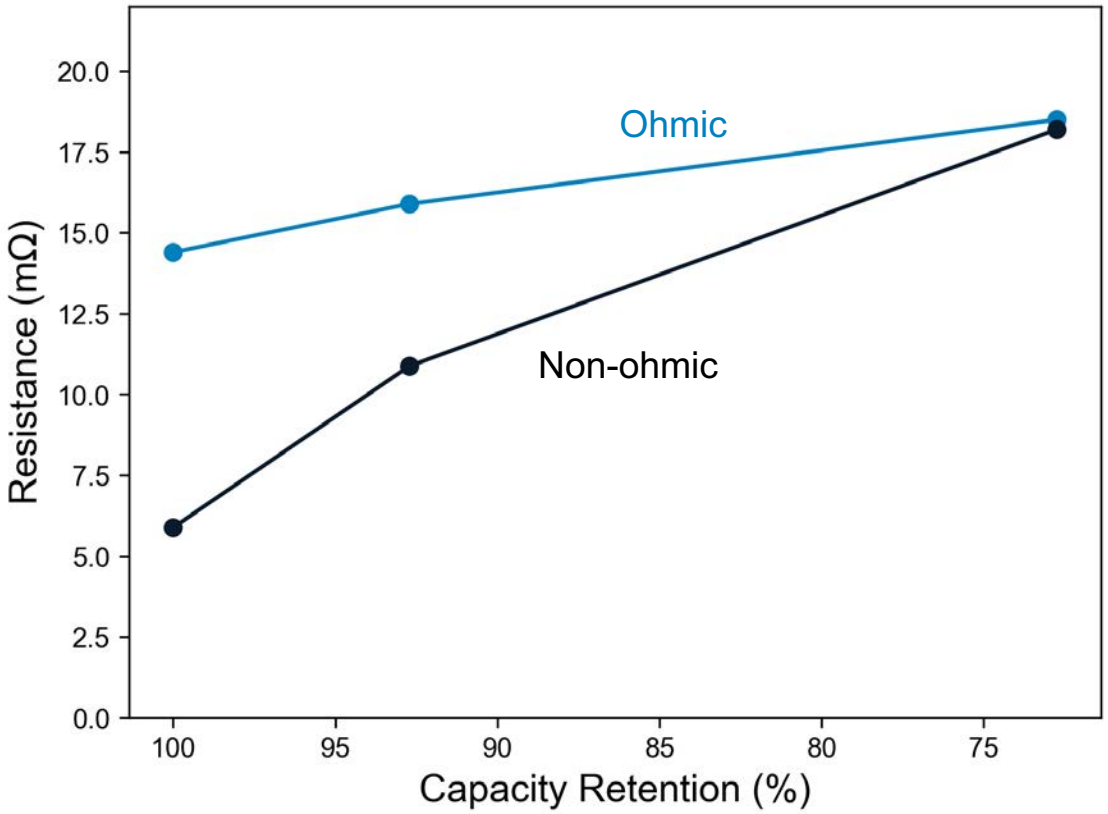


End-of-life reached in ~100 cycles – 10X faster than rated. Why?

Aging-Driven Changes in Cell Resistance

EIS at room temperature, 100% SOC: 1 MHz to 1 mHz, I_{rms} = 100 mA





Capacity loss correlates to significant increases in ESR and non-ohmic resistances

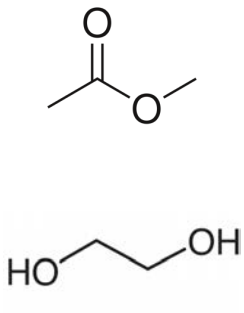
Points to Li loss, electrolyte decomposition, SEI thickening, etc

Electrolyte Decomposition Clear In Gas Phase

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- Significant reduction in collected electrolyte volume
  - As-received: > 1 mL
  - End-of-life: < 50 uL
- Only minor changes in liquid-phase composition

Compound	Relative Mass [%], As-Received	Relative Mass [%], End-of-Life
Ethylene Carbonate	25.4	22.7
Dimethyl Carbonate	68.8	70.2
Ethyl Methyl Carbonate	4.9	5.7
Methyl Formate	0.9	1.0
Methyl Acetate	Not Detected	0.1
Ethylene Glycol	Not Detected	0.3



Gas Phase – TOF-MS

Formula	Mass	Relative Intensity [%], As-Received	Relative Intensity [%], End-of-Life
C H4	16.03097	2.90%	78.68%
H2 O	18.01078	0.62%	Not Detected
H F	20.00659	0.04%	0.19%
C O	27.99465	0.52%	1.65%
N2	28.0056	69.85%	0.29%
C2 H6	30.04665	0.25%	7.72%
O2	31.98927	17.16%	0.10%
Ar	39.96173	N/A	N/A
C O2	43.98941	0.48%	5.36%
C3 H8	44.06306	0.05%	1.22%
C2 H6 O	46.04247	0.05%	0.78%
C2 H4 O2	60.02199	0.06%	Not Detected
O F3 P	103.9634	8.01%	4.01%

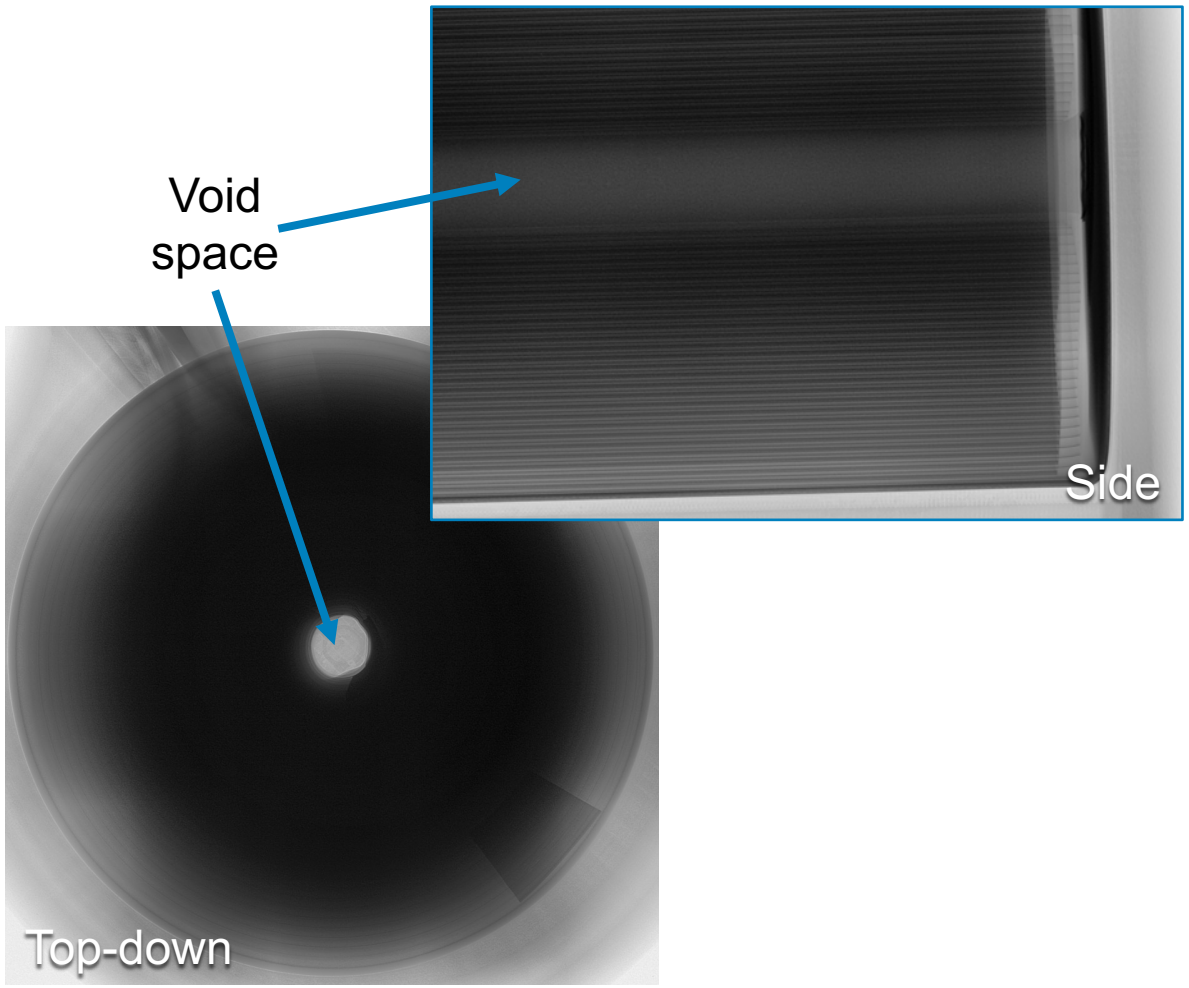
End-of-Life:

- Hydrocarbons dominate gas composition
- N_2, O_2, H_2O gone
- CO, CO_2 increased

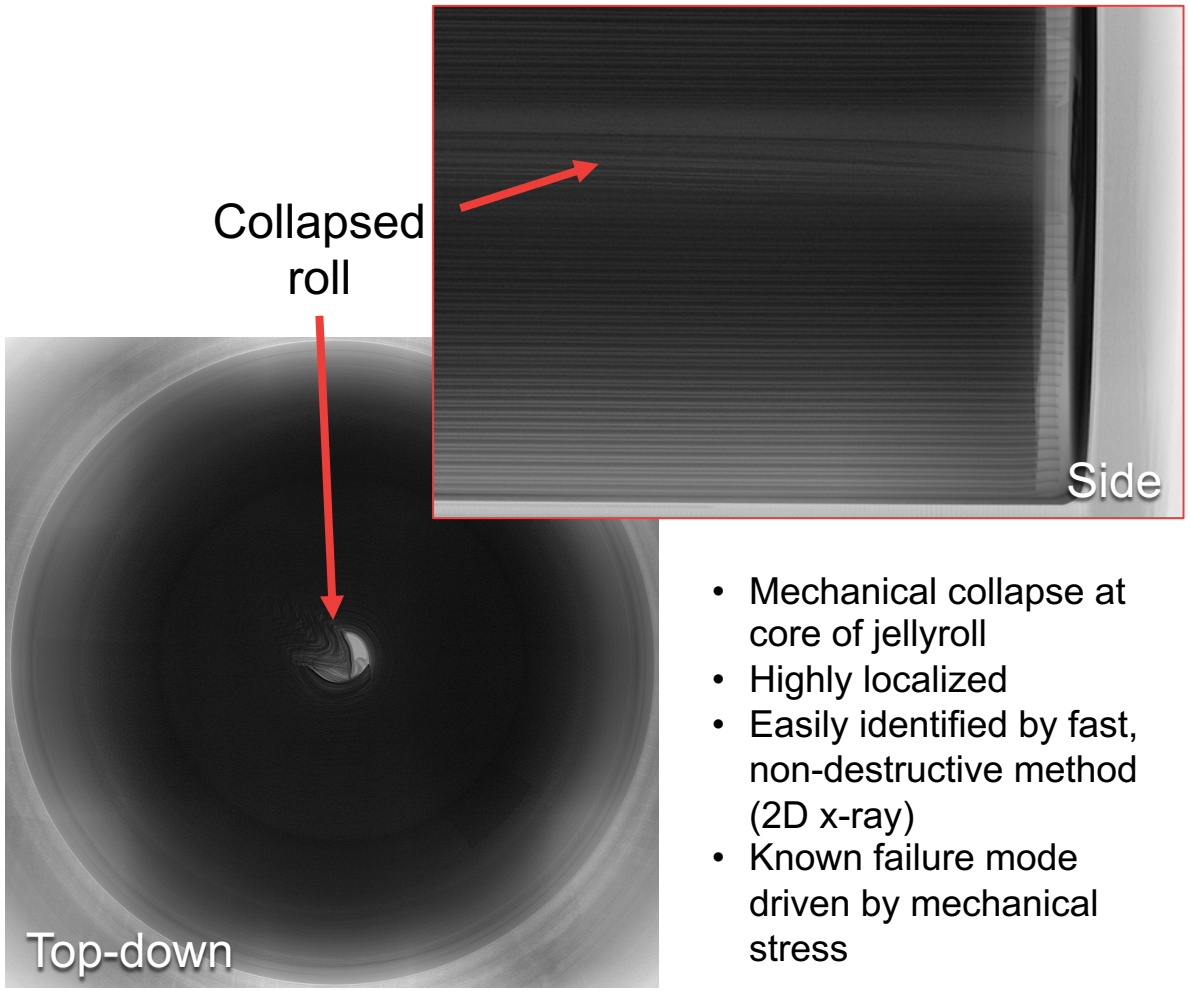
2D X-ray Reveals Jellyroll Collapse

COVALENT METROLOGY

As-Received



End-of-Life



- Mechanical collapse at core of jellyroll
- Highly localized
- Easily identified by fast, non-destructive method (2D x-ray)
- Known failure mode driven by mechanical stress

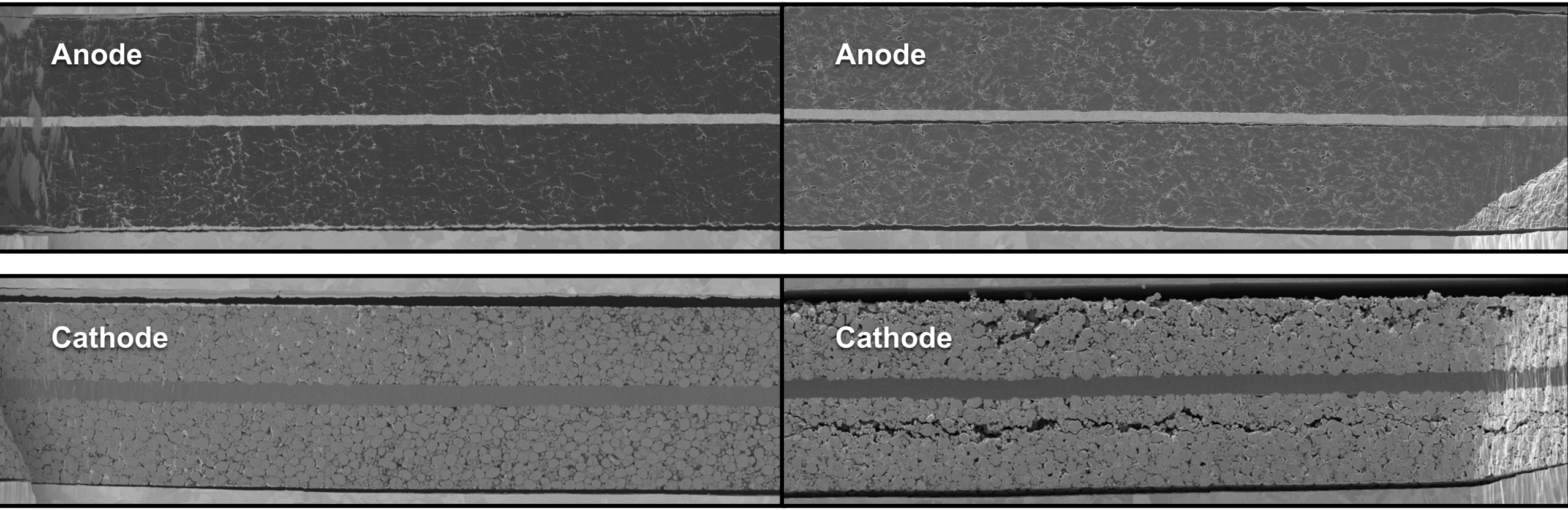
Carter et al, *Journal of Power Sources*, **437**, 2019, 226820
Chen et al, *Energies*, 2022, *15*, 8244

Mechanical Failure in Both Electrodes

COVALENT METROLOGY

As-Received

End-of-Life



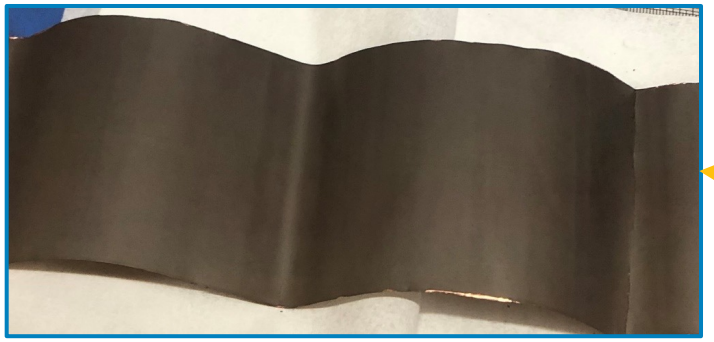
- Significant cracking (cathode) and delamination (anode)
- What chemical changes are observed?

2D X-ray Reveals Jellyroll Collapse

COVALENT METROLOGY

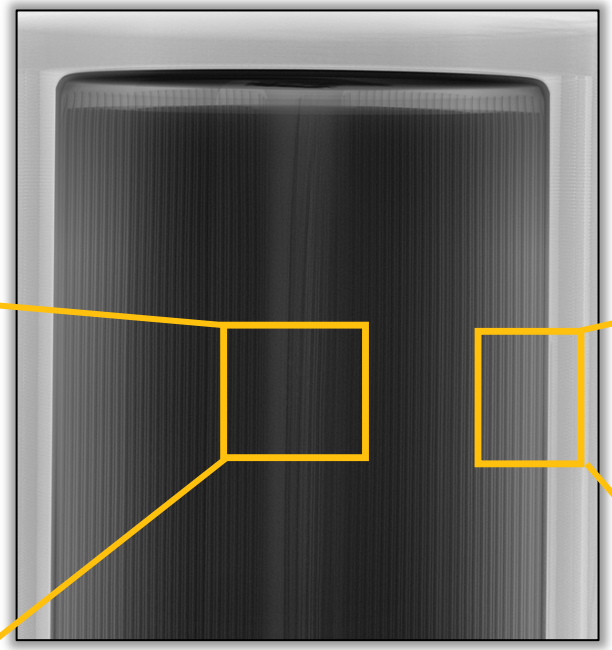
Anode - Core

As-Received



End-of-life



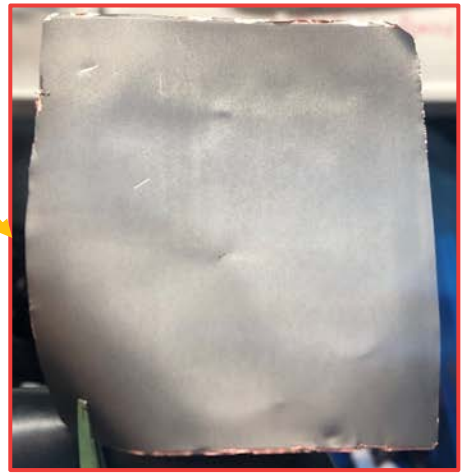


Anode - Peripheral

As-Received

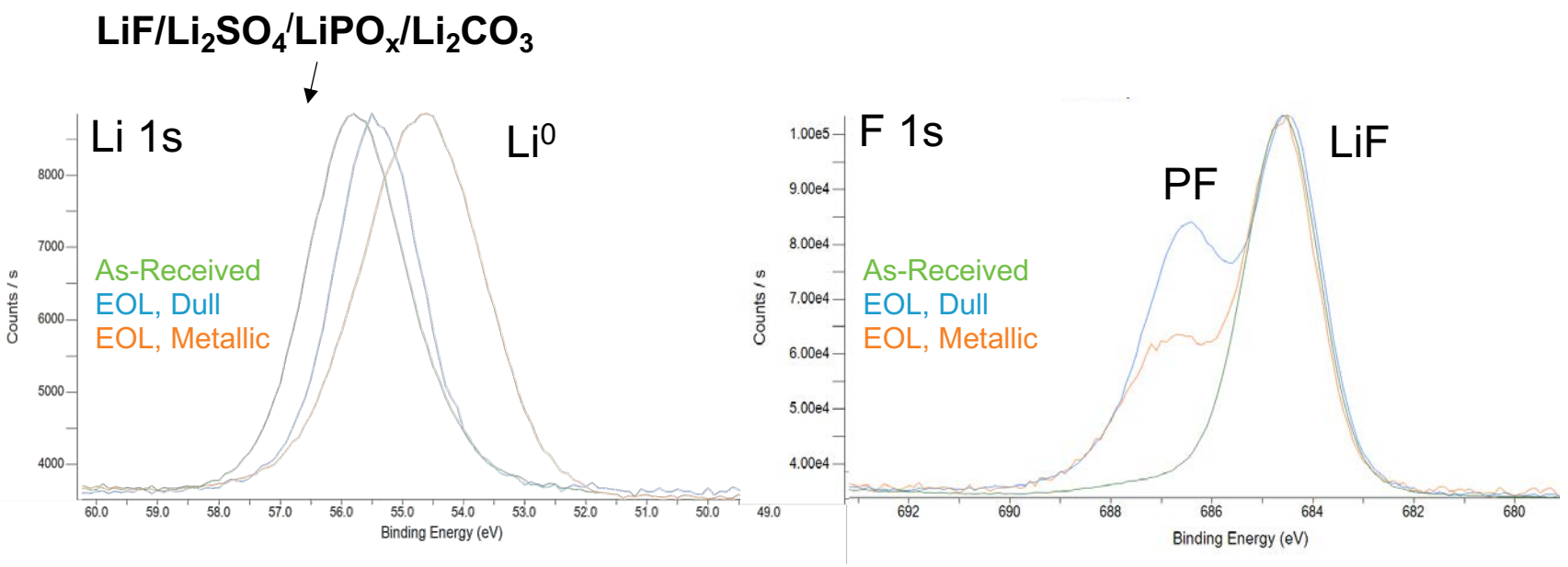


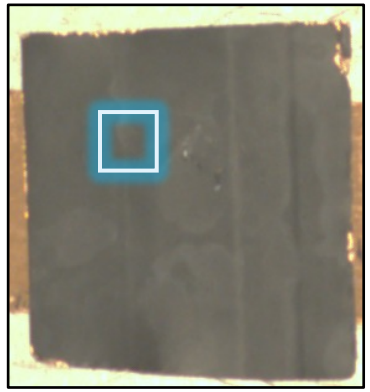
End-of-life

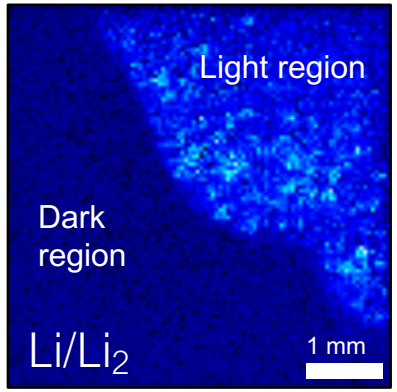


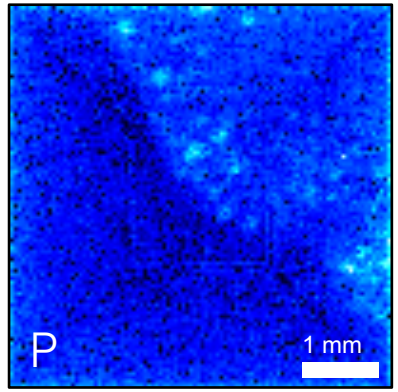
- Discoloration, including metallic deposits
- Significant anode delamination
- Localized to the **anode core**

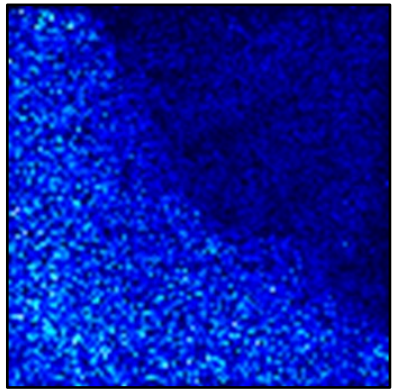
Changes in Anode Surface Chemistry











Anode Surface

- Metallic lithium at core of EOL anode
- Complex mix of lithiated species with a clear shift to lower oxidation state upon aging
- Li- and PF- surface enrichment with aging
- No significant changes in cathode surface chemistry



Massbox
(LALI-TOF-MS)

Case Study Conclusions

COVALENT METROLOGY

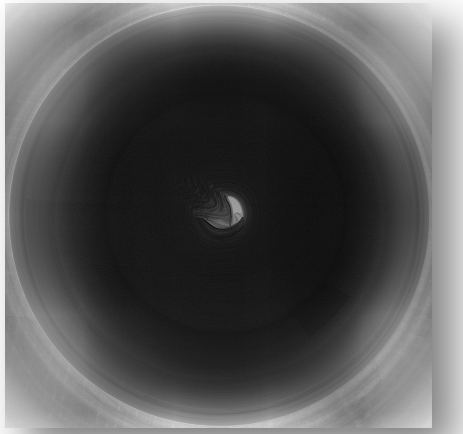
- Baseline characterization of LG INR21700 M50LT cells
- Cell performance degraded rapidly under reduced-temperature CCCV cycling

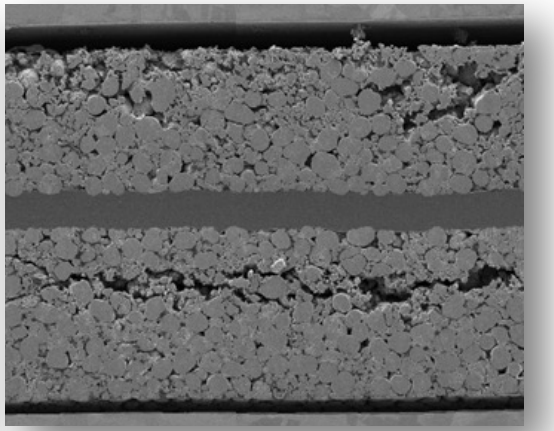
Increase in cell resistance

Mechanical failure – bulk and microscale

Decomposition of electrolyte species

Changes in anode surface chemistry





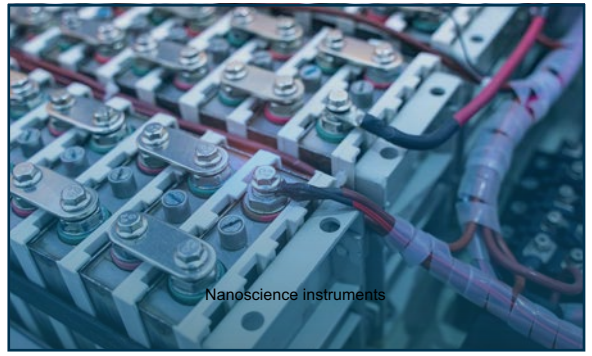
Metrology Plan

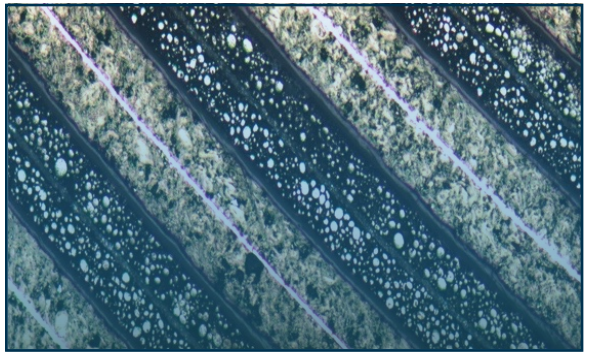
COVALENT METROLOGY

Source Relevant Cells from a Reputable Supplier → Tear-down and Characterize → Accelerate aging → Identify failure modes









COVALENT METROLOGY

Thank you.

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Q & A Session