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Path Dependence of Li-Ion Battery Degradation During Cycling to 80% Capacity

PRESENTED BY

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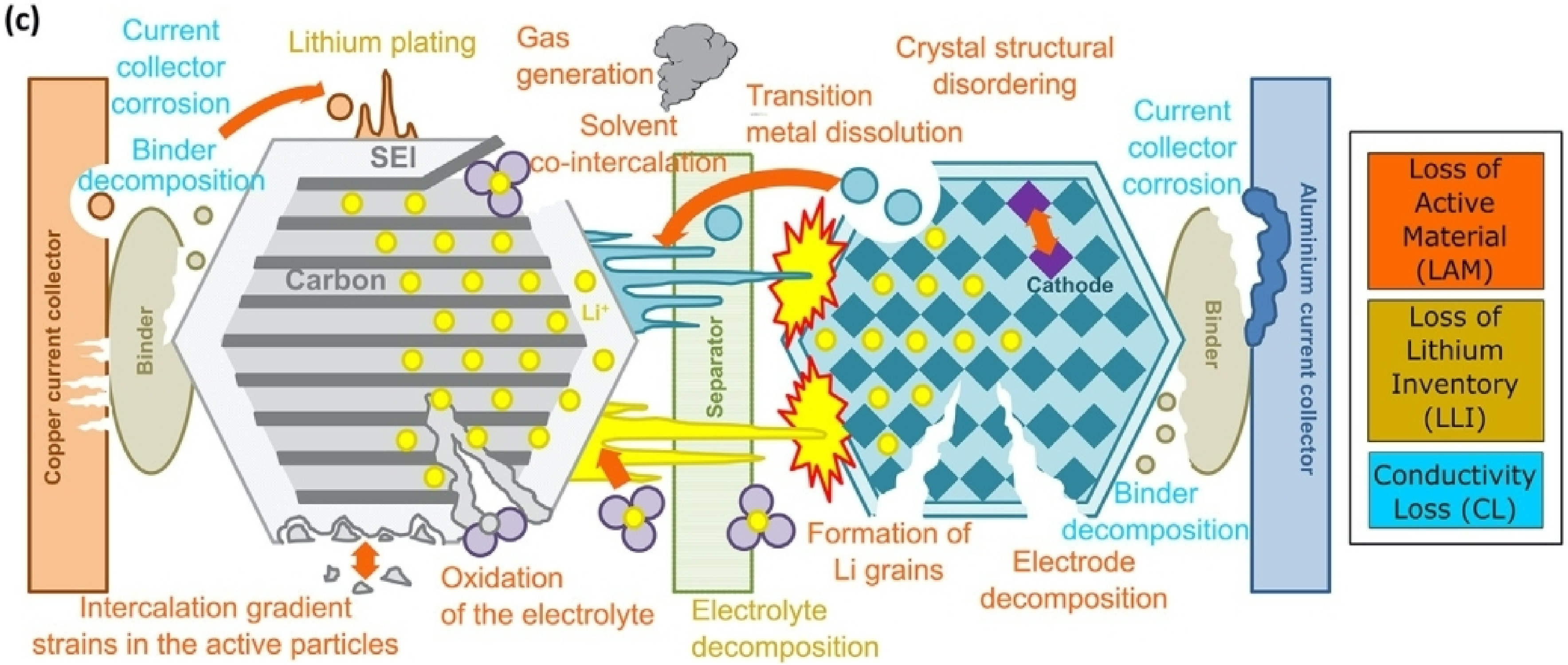
Agenda

- Introduction
  - Degradation Mechanisms
  - Study Motivation
- Experimental Approach
- Results
  - Main trends observed
  - Understanding Impact of Temperature on NMC cells
- Conclusions

Degradation in Li-ion Batteries



Pastor-Fernandez, et. al, JPS, 2017

Conductivity Loss (CL)
- Current collector corrosion
- Decomposition of binder

Loss of Lithium Inventory (LLI)
- Li-plating
- SEI layer formation

Loss of Active Material (LAM)
- Metal dissolution
- Phase change of electrode material
- Pulverization of electrode

Unknowns about Cell Degradation Prevent Optimal Use

- Manufacturer spec sheets focus on safe operating limits, not performance
- Unaddressed questions:
  - What are optimal cycling conditions for each cell chemistry?
  - How do cells behave beyond 80% initial capacity?
  - What causes rapid capacity fade in cells at different conditions?
  - How does safety change with increased cycling?

Broad Study of Li-ion Cycling to Understand Performance and Degradation

Approach

1. Cycled 18650 format cells to 80% initial capacity[1] and now, to end of life (EOL) of 40% initial capacity
2. Electrochemical characterization during cycling
3. Materials characterization on selected cells at 80% capacity and EOL

[1]Preger et al. "Degradation of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions" *J. Electrochem. Soc.,* **2020***, 167,* 120532.

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Battery	LFP* (A123)	NCA (Panasonic)	NMC (LG Chem)
Capacity	1.1 Ah	3.2 Ah	3.0 Ah
Voltage	3.3 V	3.6 V	3.6 V
Max Discharge Current	30 A	6 A	20A
Operating T	-30 to 60^{o}C	0 to 45^{o}C	0 to 50^{o}C

*LFP cells have not reached 80% and will not be discussed here

LFP NCA NMC

Cycling Conditions and Procedure

- At least 2 cells cycled at each condition
- Capacity check done at beginning and end of each round of cycling
- Electrochemical Impedance Spectroscopy (EIS) done after every 3% decrease in capacity
- Cycling done by Arbin Battery cyclers

Cycling Conditions

DOD, Temperature, Discharge Rate*			
40-60%, 25°C, 0.5C	0-100%, 15°C, 1C	0-100%, 15°C, 2C	40-60%, 25°C, 3C
20-80%, 25°C, 0.5C	0-100%, 25°C, 1C	0-100%, 25°C, 2C	20-80%, 25°C, 3C
0-100%, 25°C, 0.5C	0-100%, 35°C, 1C	0-100%, 35°C, 2C	0-100%, 25°C, 3C

*0.5C charge rate for all

Characterization Work Flow

During Cycling

Electrochemical Impedance Spectroscopy (EIS)

Every 3% Decline in Capacity

Incremental Capacity Analysis (ICA)

Every Round of Cycling

Prior to Disassembly

X-Ray Computed Tomography (XCT)

0 and 100% SOC (1 full cycle at 25°C)

Cell Disassembly

At 0% SOC

Post Mortem

X-Ray Diffraction (XRD)

Powder Scrapped from Current Collector (CC)

Scanning Electron Microscopy (SEM)

Material on CC Characterize in Ar

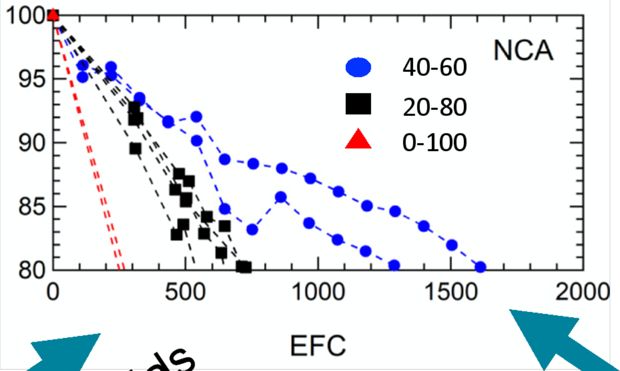
Energy Dispersive Spectroscopy (EDS)

Mapping and Semi -Quantitative

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP)

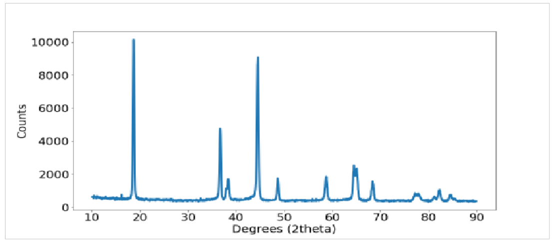
Correlating Materials and Electrochemical Changes to Understand Variations in Capacity Fade

Capacity Fade



Materials Characterization

X-Ray Diffraction (XRD)

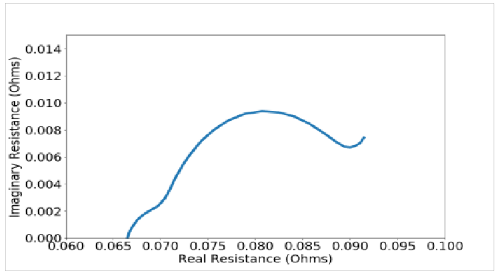


Understand trends in materials degradation

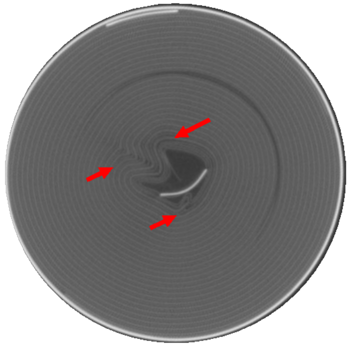
Understand trends in electrochemical changes

Electrochemical Characterization

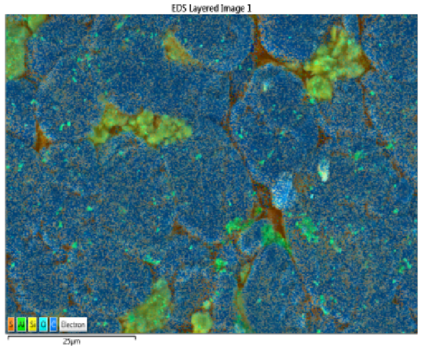
Electrochemical Impedance Spectroscopy (EIS)



X-ray Computed Tomography (XCT)

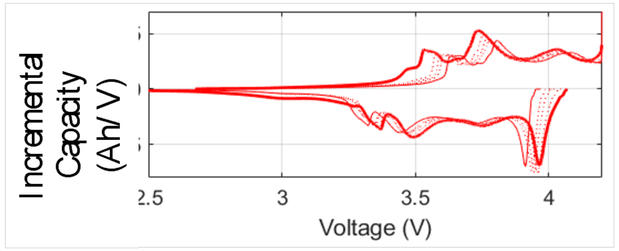


SEM and EDX



Link trends to understand degradation mechanisms

Incremental Capacity Analysis (ICA)



Topline Conclusion: Loss of Lithium Inventory in Cells Dominates Capacity Fade During Cycling to 80% Capacity

- Trends in capacity fade data correlate well with electrochemical and materials degradation trends
- LLI generally dominates degradation to 80% capacity
  - Mechanism of LLI changes for NMC cells but not NCA cells
- LAM was significant in the most rapid decay conditions

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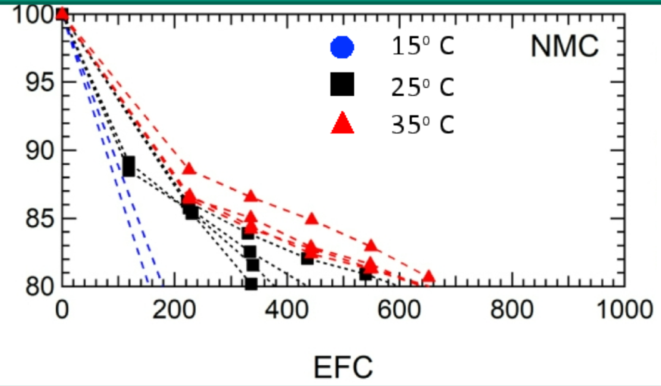
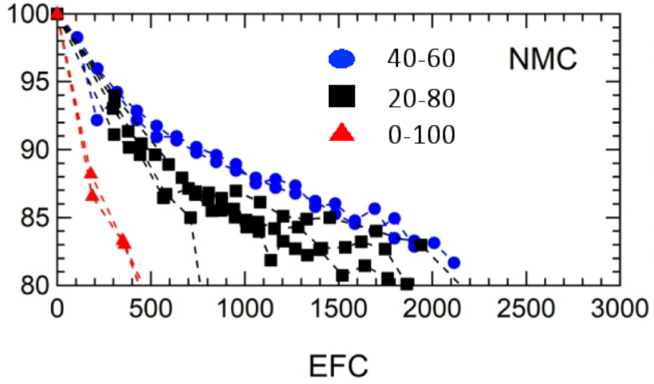
Will illustrate these trends by looking at NMC cells cycled at different temperatures

Trends in NMC Cycling

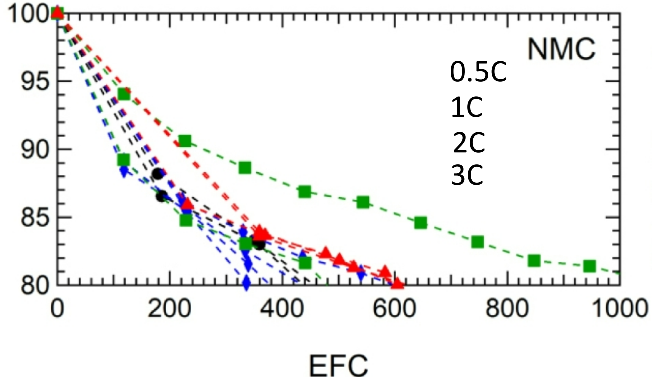
- NMC Cells show increased loss of capacity at lower temperatures



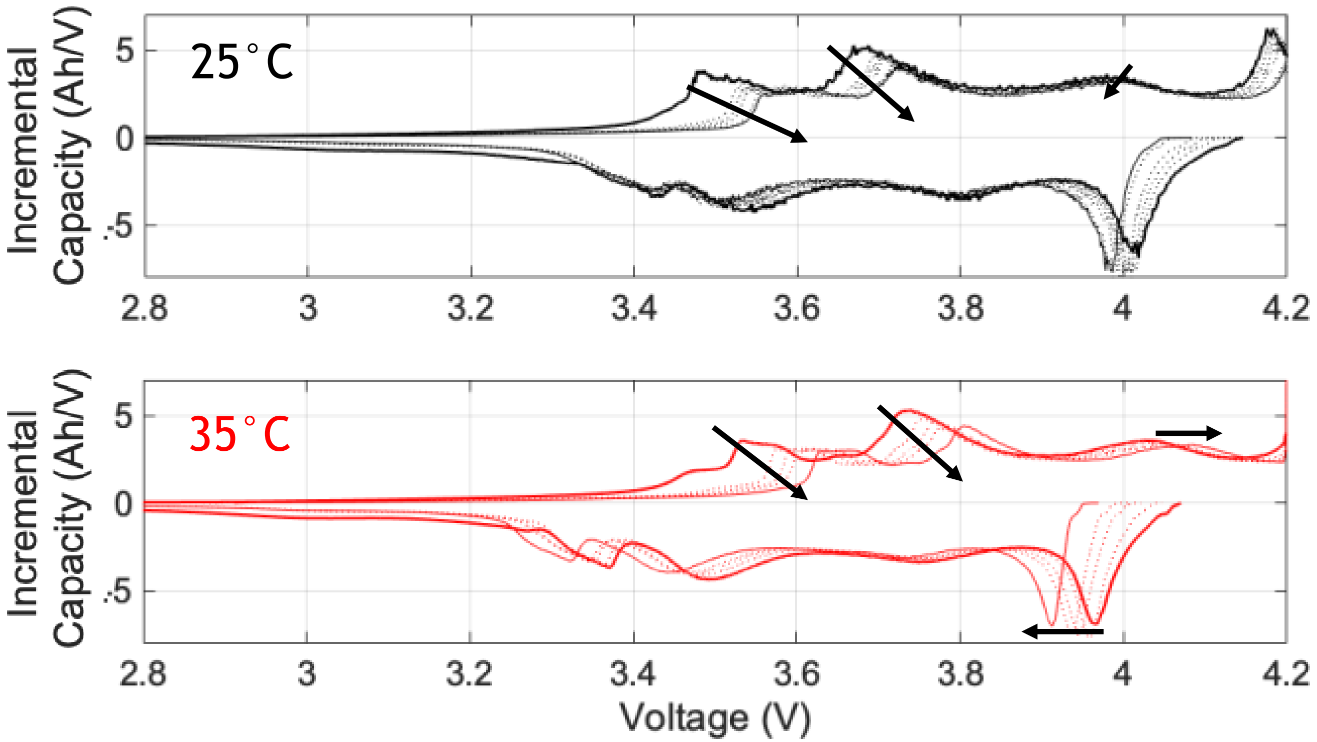
- Increased SOC range increased capacity fade

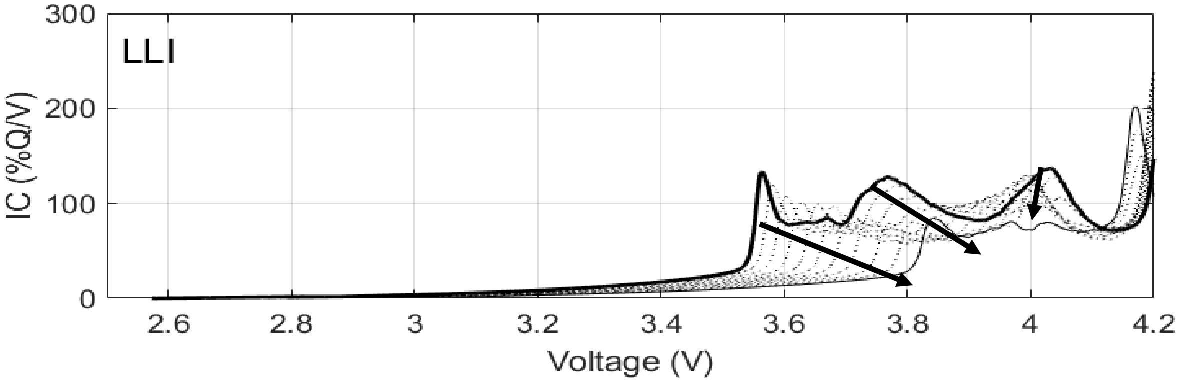


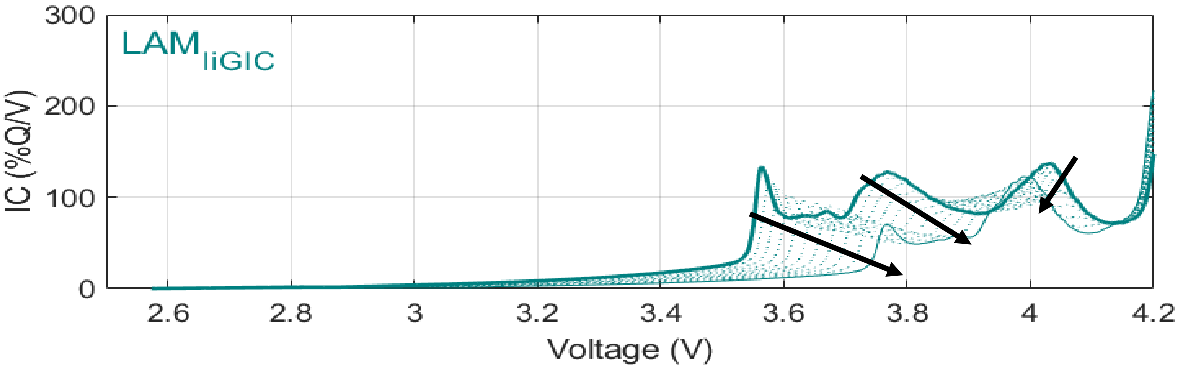
- No strong correlation is observed for varied discharge rate
- Cells were not disassembled for this condition



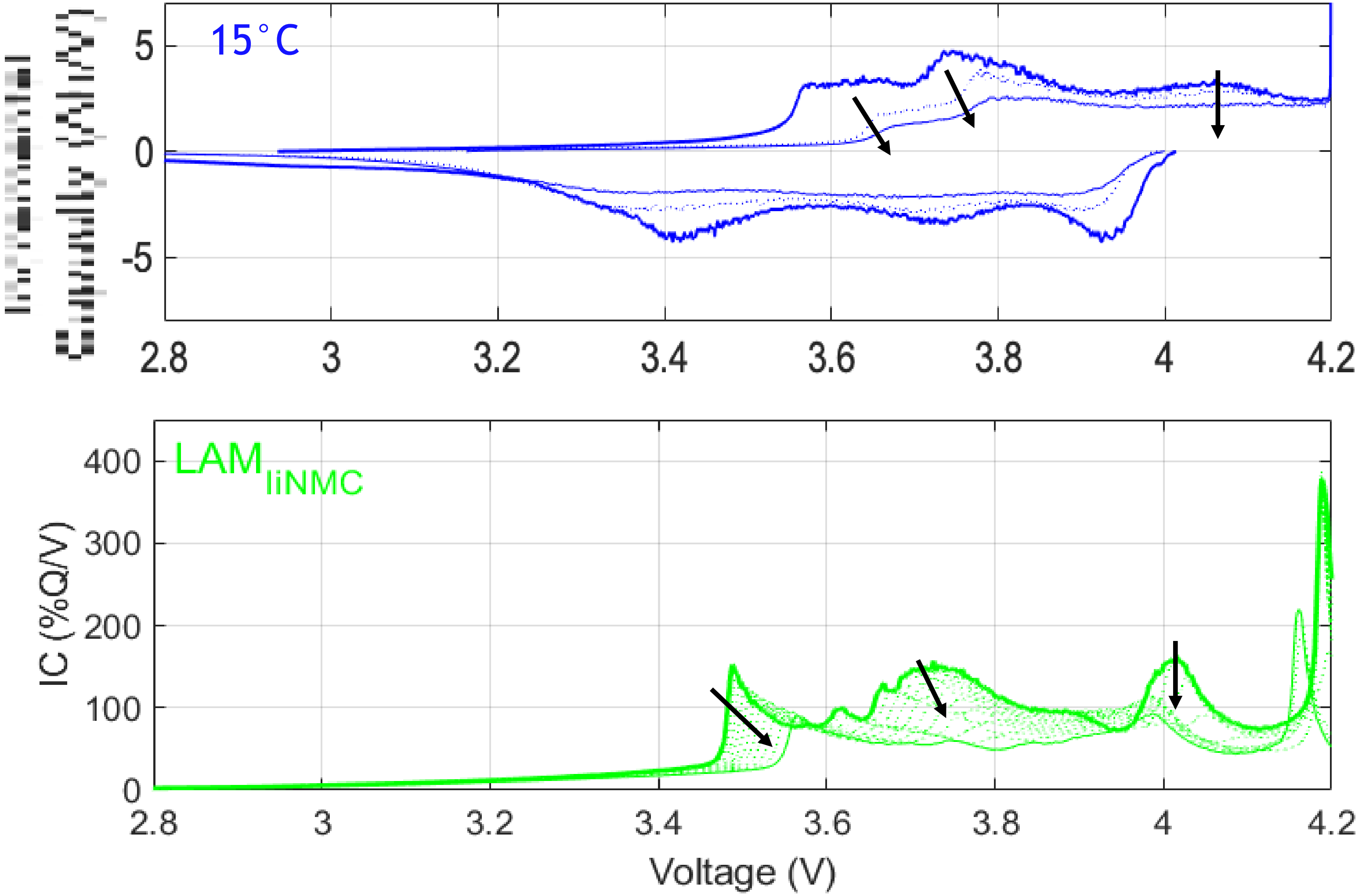
ICA of NNMC Shows LLI Dominates Degradation at Higher Temperatures.



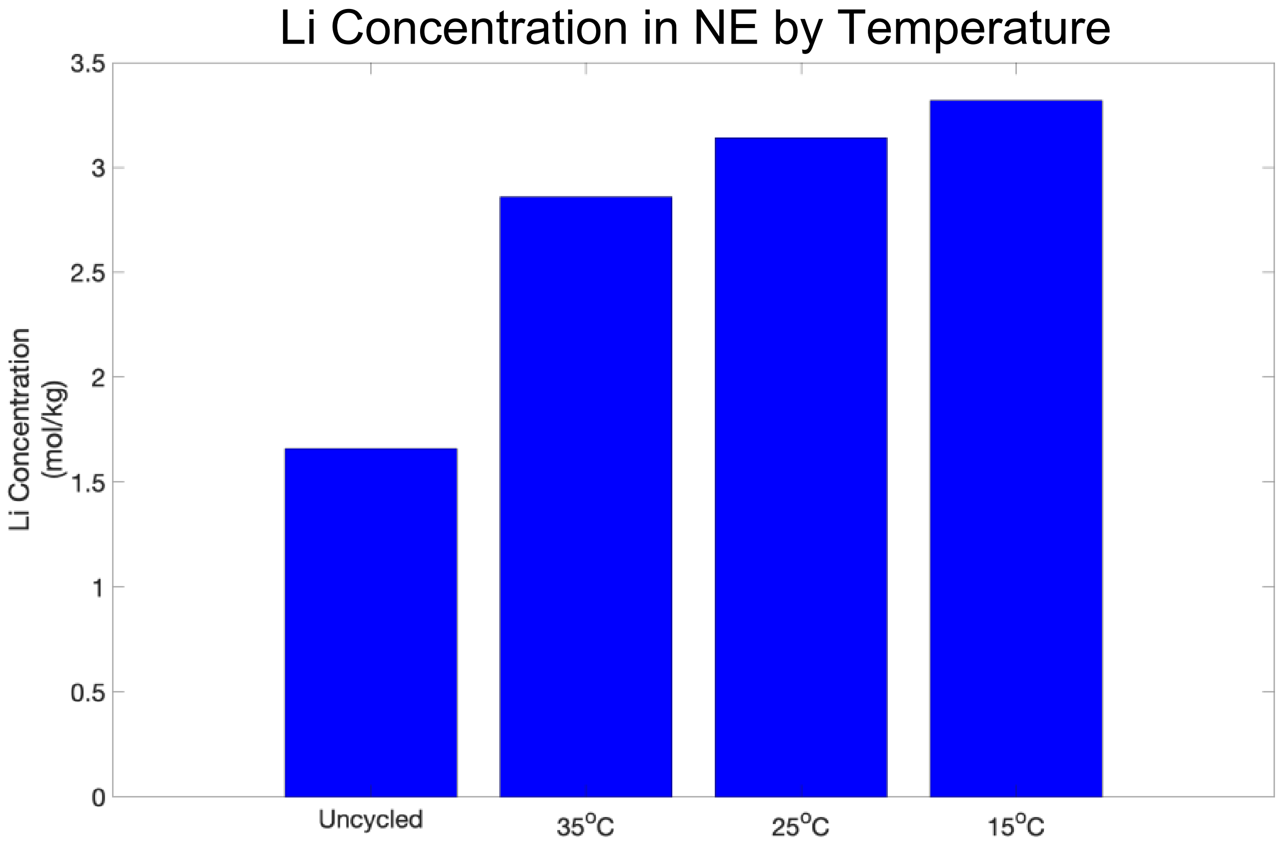


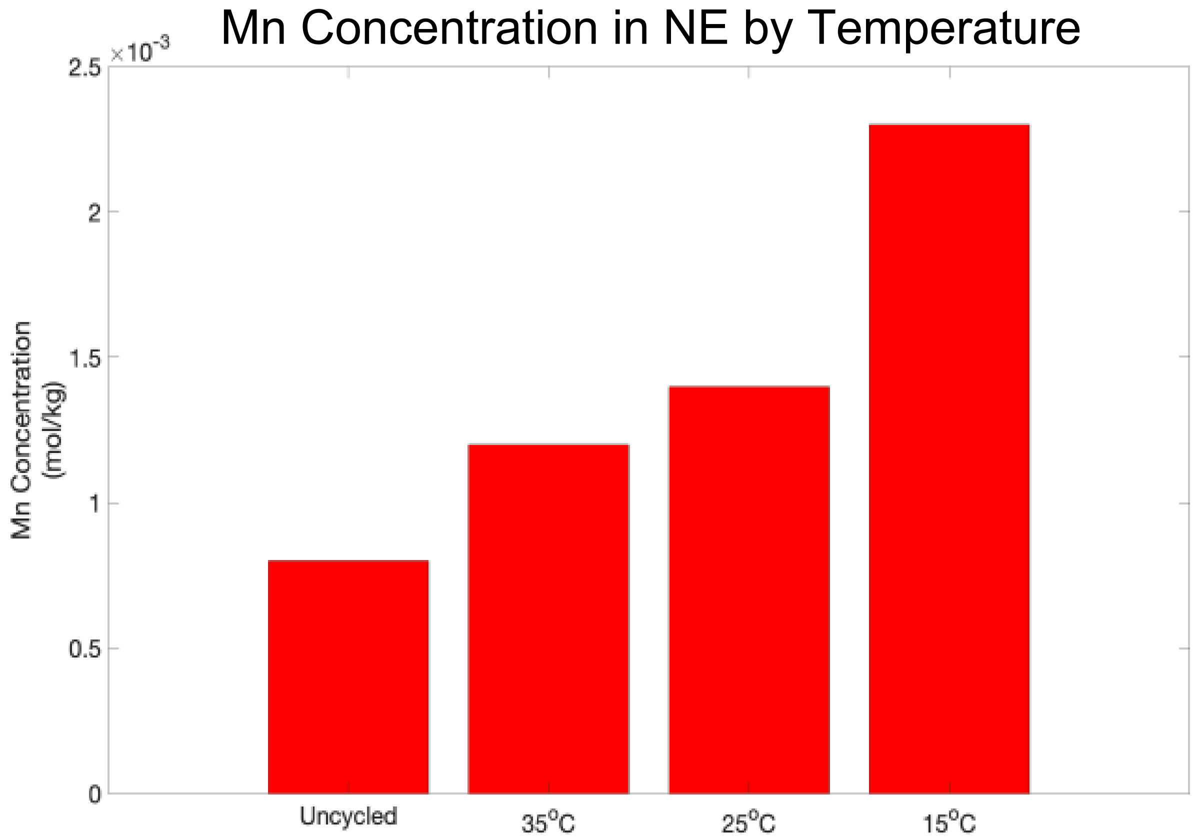


ICA of NMC Cells at 15C Shows that LLI and LAM at the PE likely Occur



ICP of NMC NEs Show LLI and LAMpe Increase at Lower Temperatures



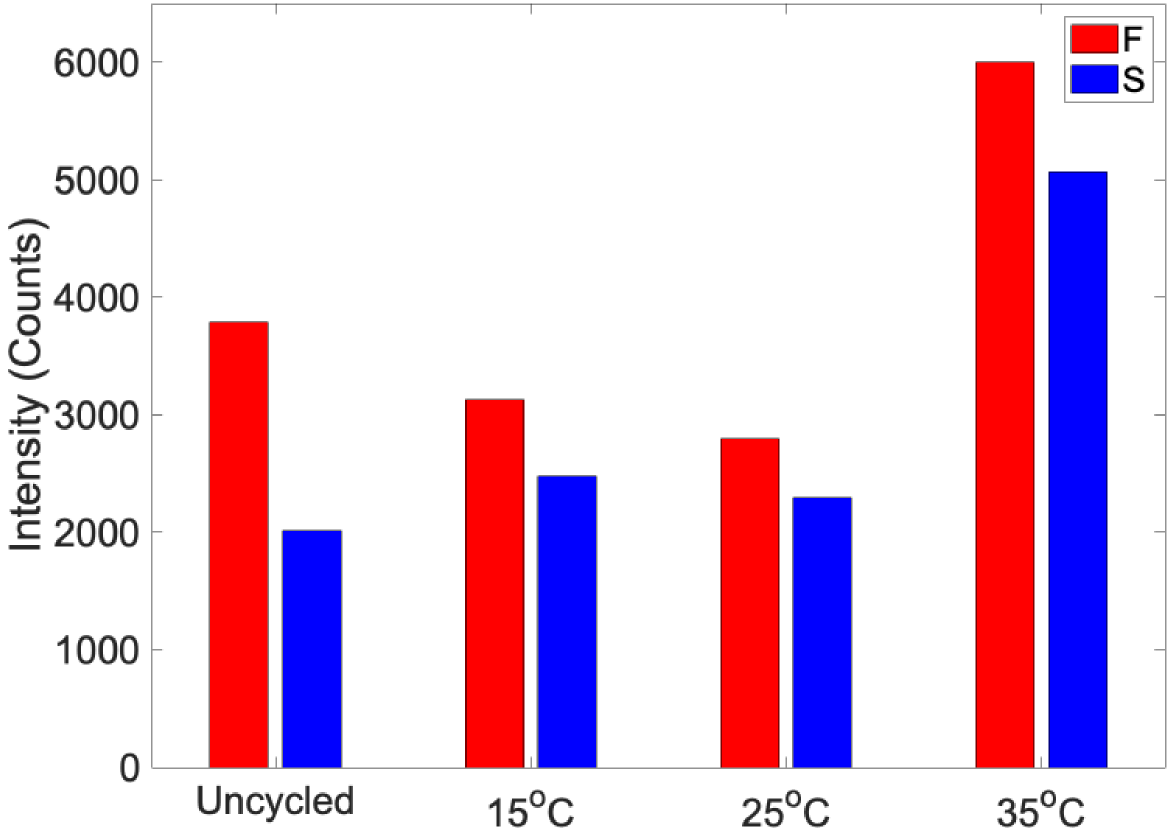


- Li stranded in the NE increases with decreasing temperature
- 15°C cell Li content is double that of the uncycled cell

- Mn diffusion to the NE increases consistently as temperature decreases
  - Mn in the NE more than double from uncycled to 15°C
- 15°C cell is only cell analyzed to observe Co diffusion to NE

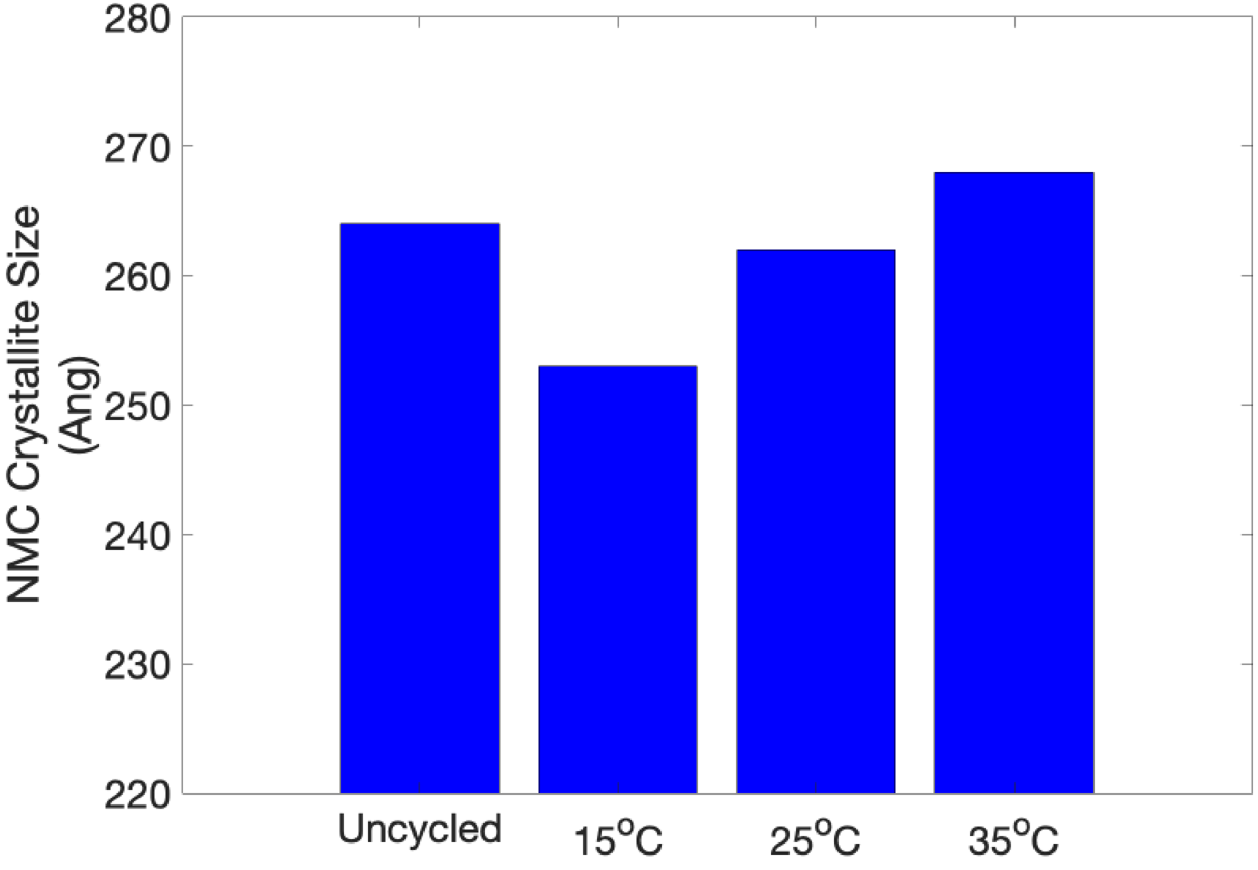
Semi-quantitative EDS Analysis shows SEI Formation is Unlikely below 35°C

- Florine and sulfur are elements generally associated with SEI layer formation
- For the 15 and 25°C cells we see that F and S decrease relative to the uncycled cell
- F and S only increase at 35°C suggesting that this is the only condition with significant SEI formation
- May indicate that at lower temperatures Li-plating is occurring
- Suggesting that the mechanism of LLI is temperature dependent as has been observed by Walmann et al previously



NMC PE Crystallite Size Decreases at Lower Temperatures

- At lower temperatures NMC crystallite size decreases
  - 15°C cell showing a 11Ang decrease
- At 35°C the crystallite size actually increases by 4Ang
- Suggesting that the NMC material is very sensitive to temperature
  - Lower temperatures will increase the amount of LAMpe
  - Higher temperatures may heal LAMpe that occured



NMC Degradation is Dominated by LLI and LAMpe at Lower Temperatures

	CL	LLI	LAM
EIS	All Cells	All Cells	N/A
ICA	35 ^{o}C Cell	All Cells	15 ^{o}C Cell
XRD	N/A	Increases with Decreased Temp	15 ^{o}C Cell PE
SEM	N/A	All Cells	15 ^{o}C Cell PE
EDS	N/A	All Cells	N/A
ICP-OES	N/A	Increases with Decreased Temp	Increases with Decreased Temp
XCT	Increases with Decreased Temp	N/A	N/A

Materials and Electrochemical Changes can be Correlated to Understand Degradation Mechanisms

Conclusions

- Capacity fade correlates well with electrochemical and materials analysis
- LLI is the dominant degradation mode to 80% capacity
  - In NMC cells LLI mechanisms is Li-plating at low temperatures and moves to SEI formation at high temperatures
- Rapid capacity fade appears to be combination of LLI and LAM

Next steps

- Complete cycling study down to end of life
- Repeat characterization work
- Abuse testing of aged cells

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