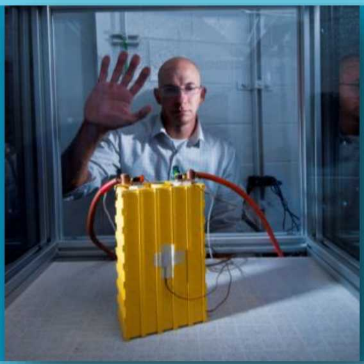
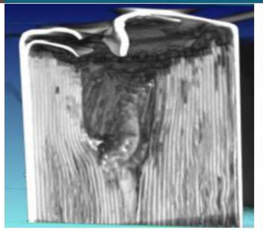
SAND2019-5904C

Mechanisms and Material Impacts of Overcharge in Lithium Ion Batteries





PRESENTED BY

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Outline

- **Introduction**
  - ✓Battery Abuse Testing Laboratory (BATLab) Capabilities
  - ✓Motivation
  - ✓Objective
- Methodology
- Results & Discussion
  - ✓NMC
  - ✓LFP
- Summary
- Acknowledgements

Capabilities and Infrastructure: Battery Abuse Testing Laboratory (BATLab)

Comprehensive abuse testing platforms for safety and reliability of cells, batteries and systems from mWh to kWh

Mechanical abuse

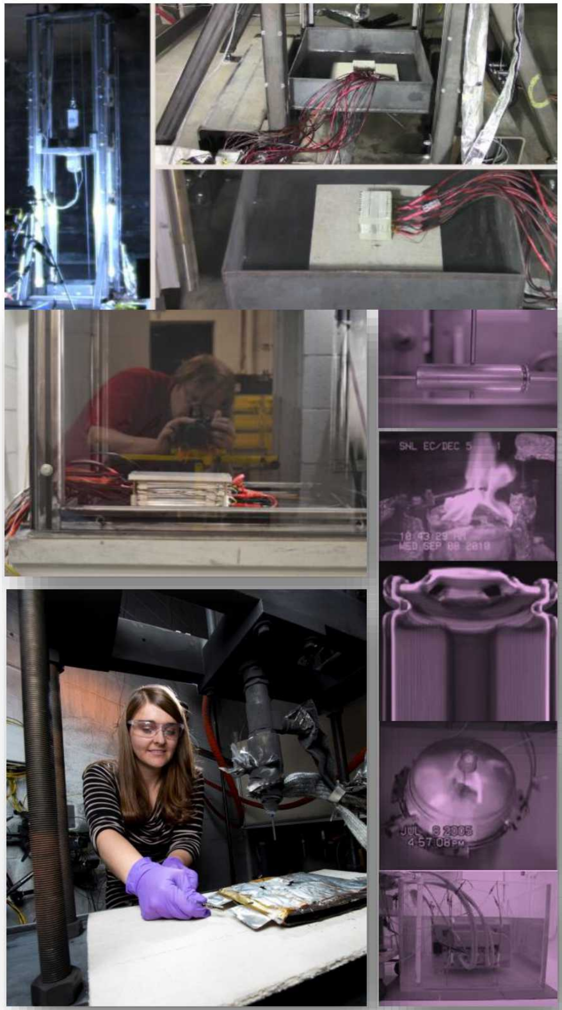
- Penetration (max. force 25 klbs, max speed 10 mm/s)
- Crush (max. force 100 klbs, max speed 2 mm/s)
- Impact (max. height 8"8', max. drop weight 700 lbs)
- Immersion

Thermal abuse

- Over temperature (250 ˚C, 5 ˚C/min)
- Flammability measurements (250 ˚C, 5 ˚C/min)
- Calorimetry (405 ˚C, 5 ˚C/min)

Electrical Abuse

- Overcharge (max. current 300 A)
- Overdischarge (max. current 300 A)
- Short Circuit (max. current 2500 A)



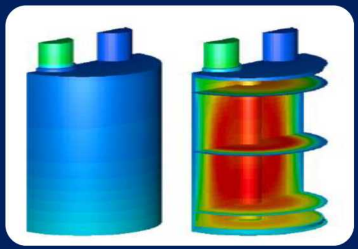
Science and Diagnostics of Battery Failure

Materials R&D

- Non-flammable electrolytes
- Electrolyte salts
- Coated active materials
- Thermally stable materials
- Battery failure post mortem materials analysis

Testing

- Diagnostics during battery failure (pictured right)
- Gas analysis
- Battery calorimetry, including during failure
- Electrical, thermal, mechanical abuse testing
- Failure propagation testing on batteries/systems
- Large scale thermal and fire testing (TTC)

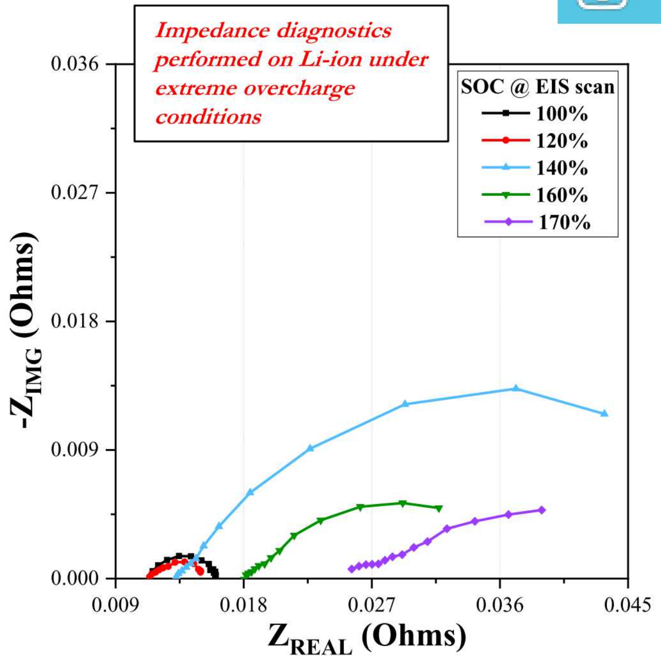


Simulations and Modeling

- Multi-scale models for understanding thermal runaway
- Validating vehicle crash and failure propagation models
- Fire Simulations to predict the size, scope, and consequences of battery fires

Procedure Development and Stakeholder Interface

- USABC Abuse Testing Manual (SAND 2005-3123)
- OE Energy Storage Safety Roadmap
- R&D programs with NHTSA/DOT to inform best practices, policies, and requirements
- Hosted International Battery Safety Workshops and Energy Storage Safety Workshop



- **Sandia is uniquely positioned to study the entire life cycle of a technology.**
- **New technologies present new risks. A high rigor environment at Sandia allows those risks to be adequately managed.**
- **Diagnostic tests can be performed under extreme failure conditions to understand the *how* and *why* of battery failure.**

How do you know if a potentially abused battery is unsafe or unstable?

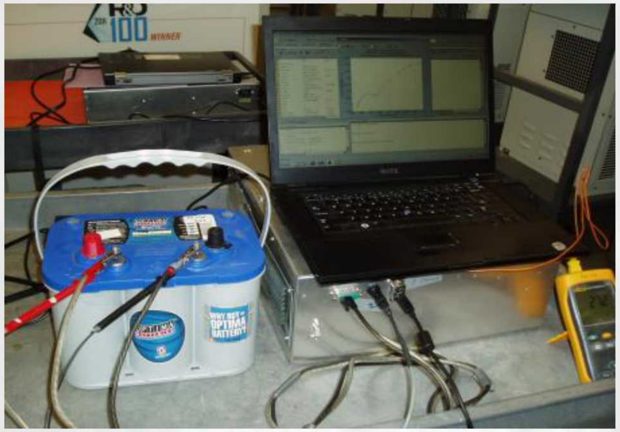
Voltage and temperature are often lagging indicators of a battery failure.

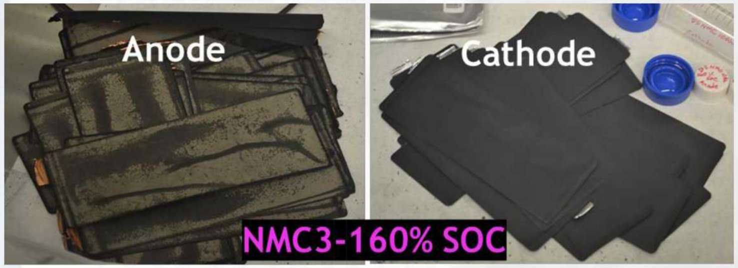
By the time a measurable trend is detected, it may be too late to arrest a catastrophic thermal runaway.

Batteries may also be unstable due to previous exposure to abusive conditions, but show little sign of problems during initial monitoring.

Objective Statements

Development and demonstration of on-board diagnostics that determine battery state of stability and trigger a battery control system response to mitigate an impending failure





Understand battery failure mechanisms during strenuous conditions to lead the design of more resilient and reliable energy storage systems that are inherently safe.

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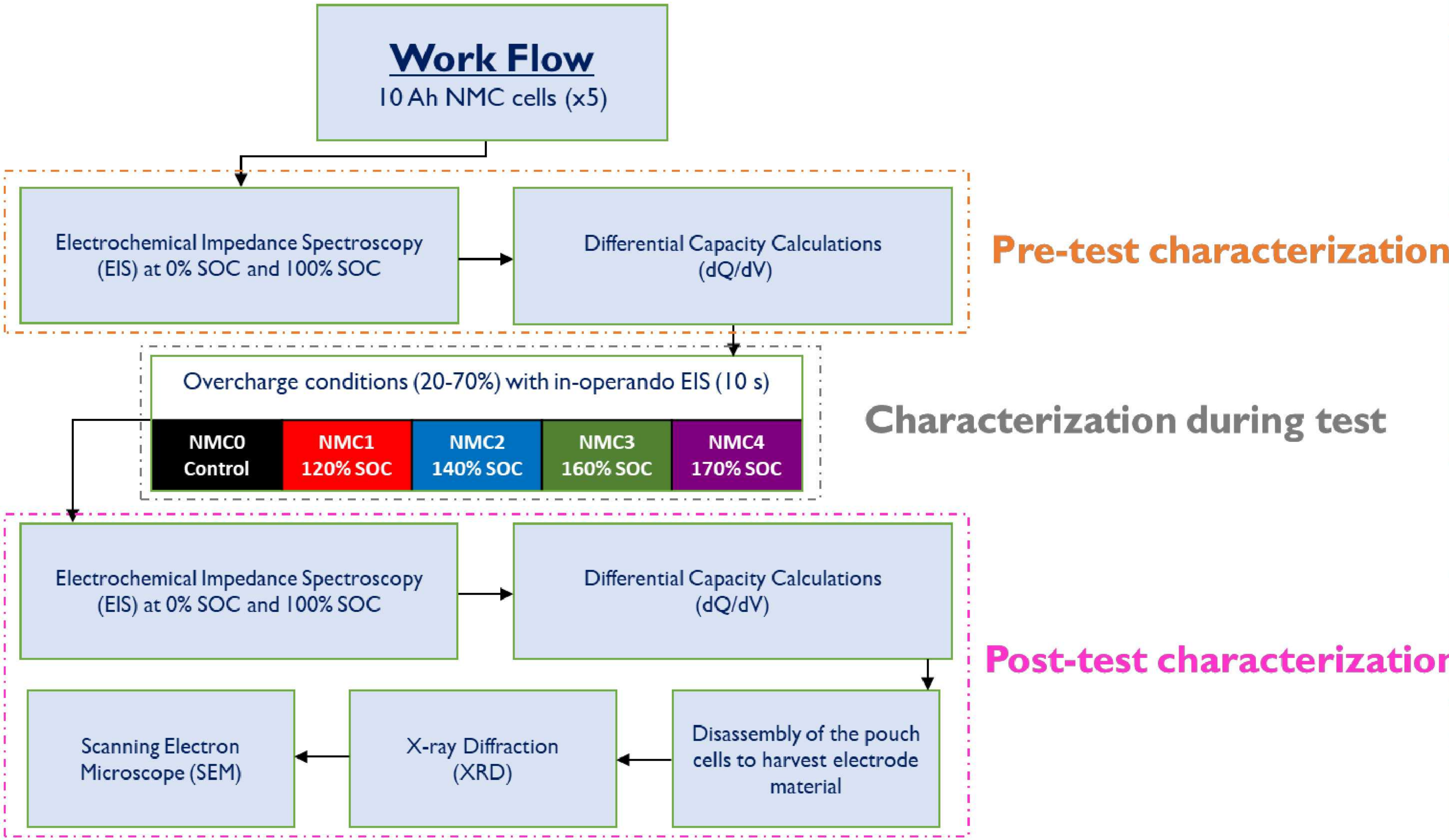
Methodology and Approach



OC/TR – Overcharge/Thermal Ramp

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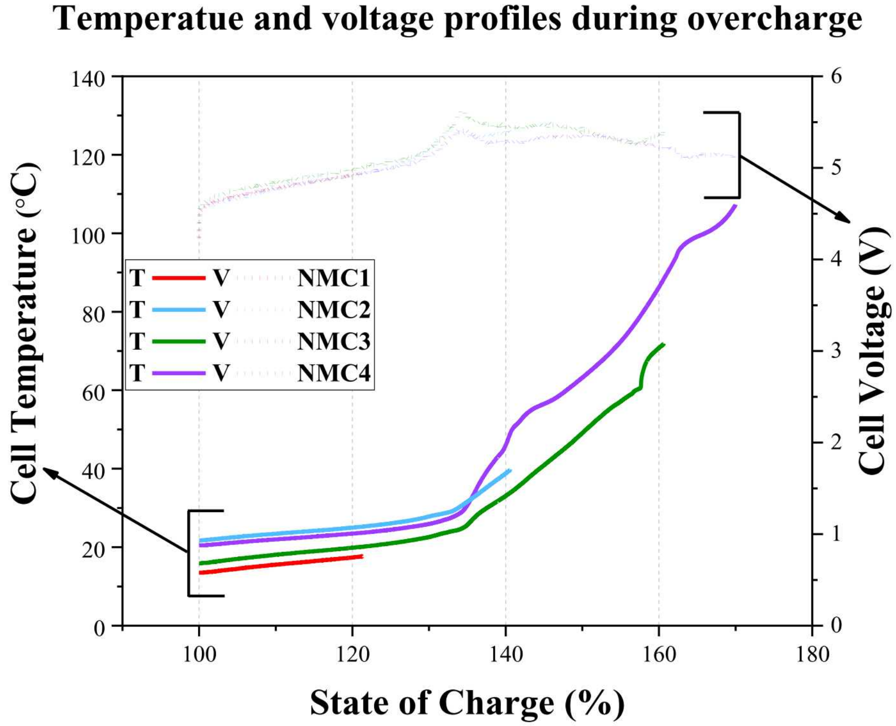
Overcharge Effects to Cell Temperature and Voltage



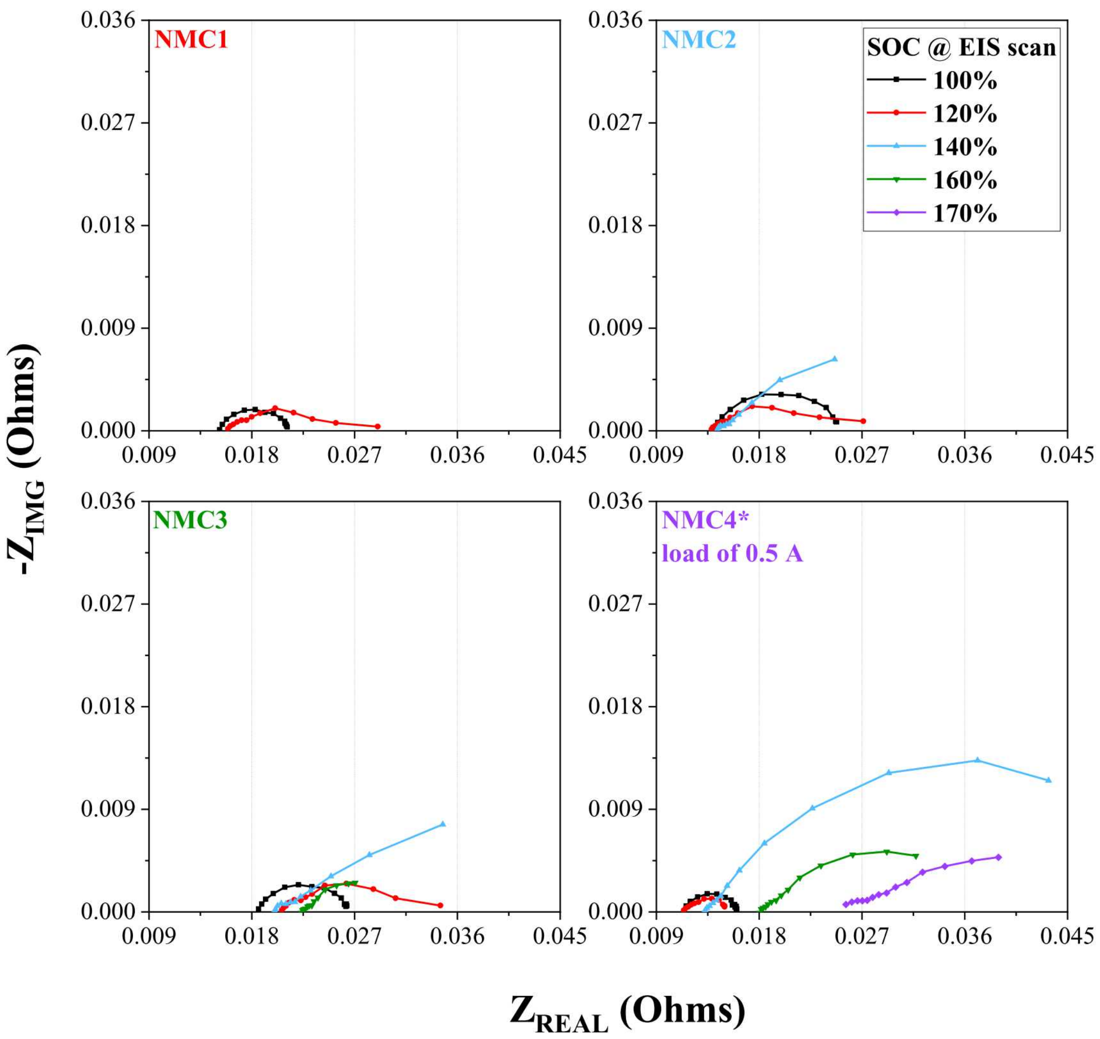
Four individual cells, NMC1, NMC2, NMC3 and NMC4, were overcharged to 120%, 140%, 160%, and 170% SOC, respectively.

Test parameters	
C-rate	1C (10 A)
Voltage limit	20 V

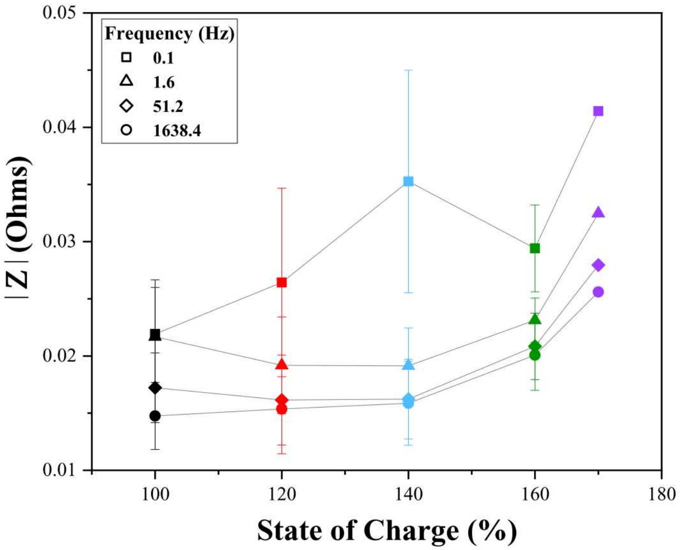
	Initial T (°C)	Max. T (°C)	ΔT (°C)
NMC1-120%	13.5	17.7	4.2
NMC2-140%	21.7	39.8	18.1
NMC3-160%	15.9	71.9	56.0
NMC4-170%	23.0	83.5	60.5

In-operando EIS

Nyquist plots of the EIS collected during overcharge with an active load of 10 A



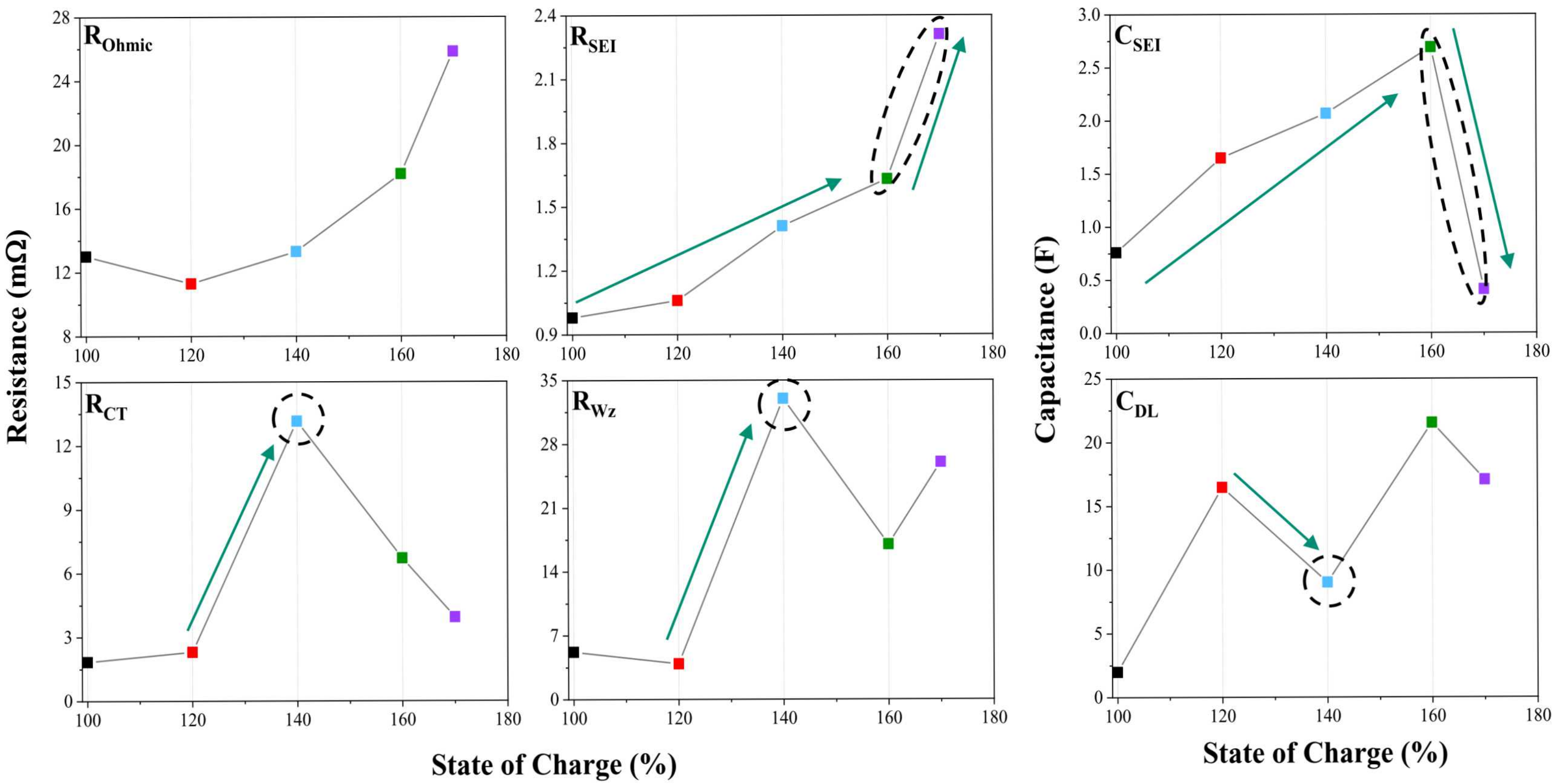
Impedance magnitude at 4 critical frequencies

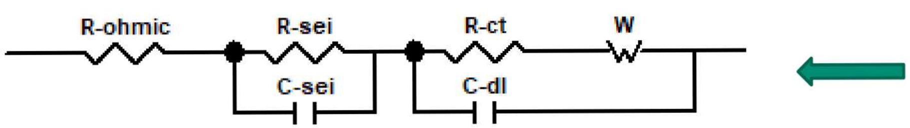


$$|Z| = \sqrt{Z_{REAL}^2 + Z_{IMG}^2}$$

- The R_{ohmic} increased for higher states of charge above 120% SOC. This change is associated with conductivity loss within the cell components.

NMC4 - 170% SOC: In-operando EIS

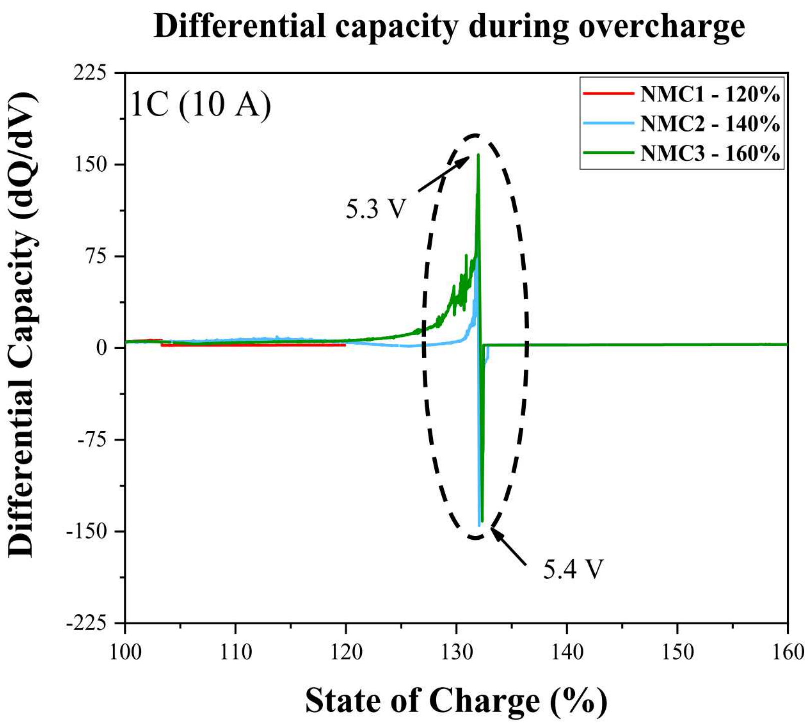


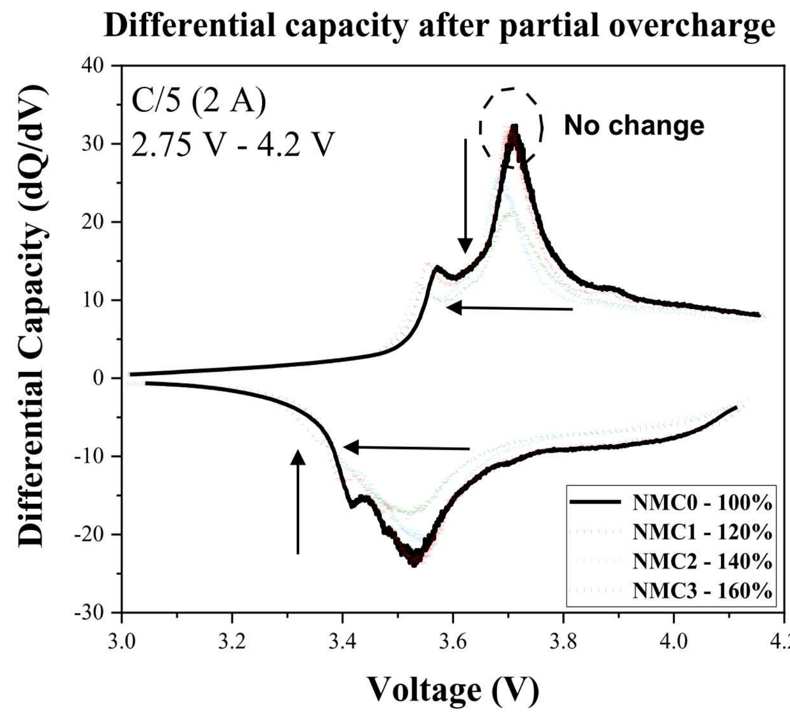


Equivalent Circuit

- The R_{SEI} slightly increased after each level of overcharge as well as the C_{SEI}, which could indicate a growth in the SEI layer.
- The R_{CT} significantly increased after 140% SOC and subsequently decreased for high SOC's.

Differential Capacity (dQ/dV)

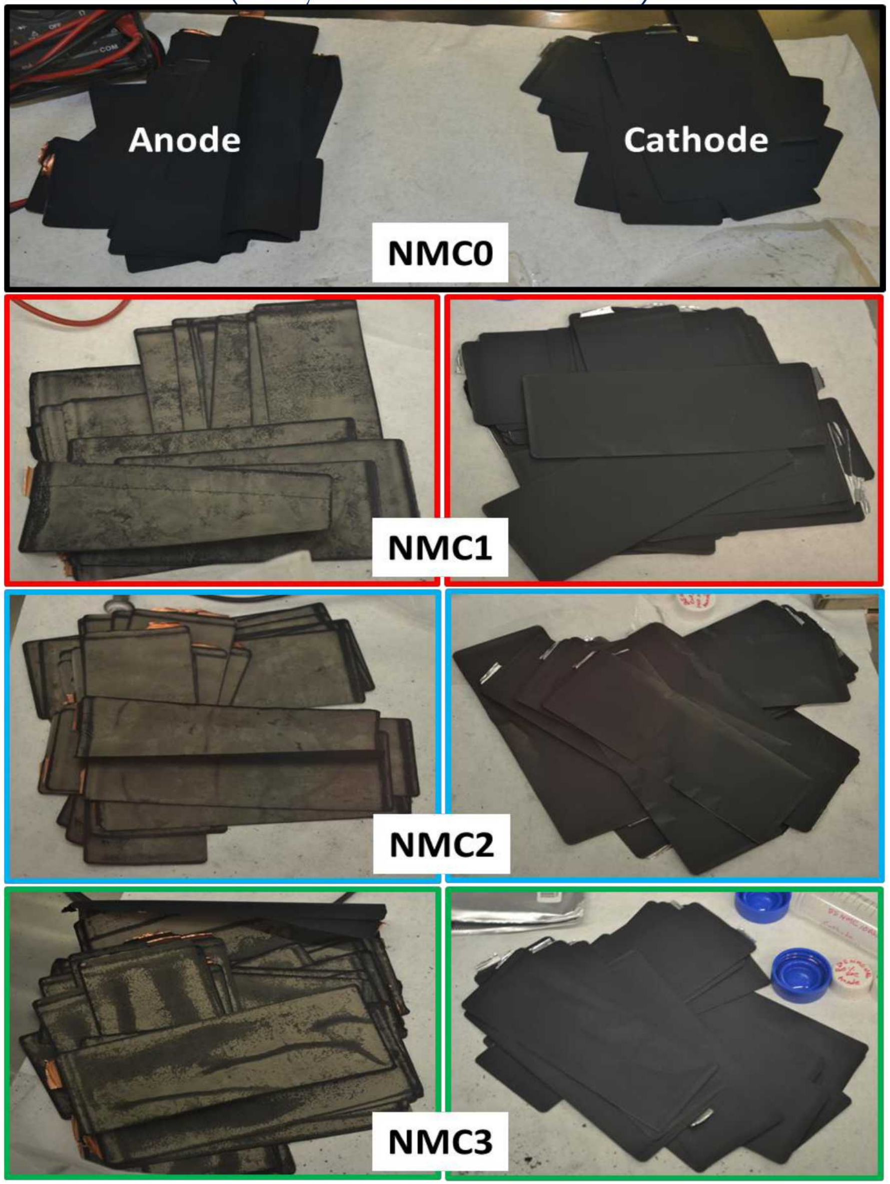




- The differential capacity for NMC1 (120% SOC) exhibited no change in the redox processes of the cell.
- NMC2 (140% SOC) and NMC3 (160% SOC) presented a decreased dQ/dV, characteristic of loss of active material.
- The dQ/dV calculated during the OC procedure identified a redox reaction between 130-135% SOC.

Disassembly Images

The electrodes were harvested at 0% SOC after the overcharge procedure was completed (fully lithiated cathode).



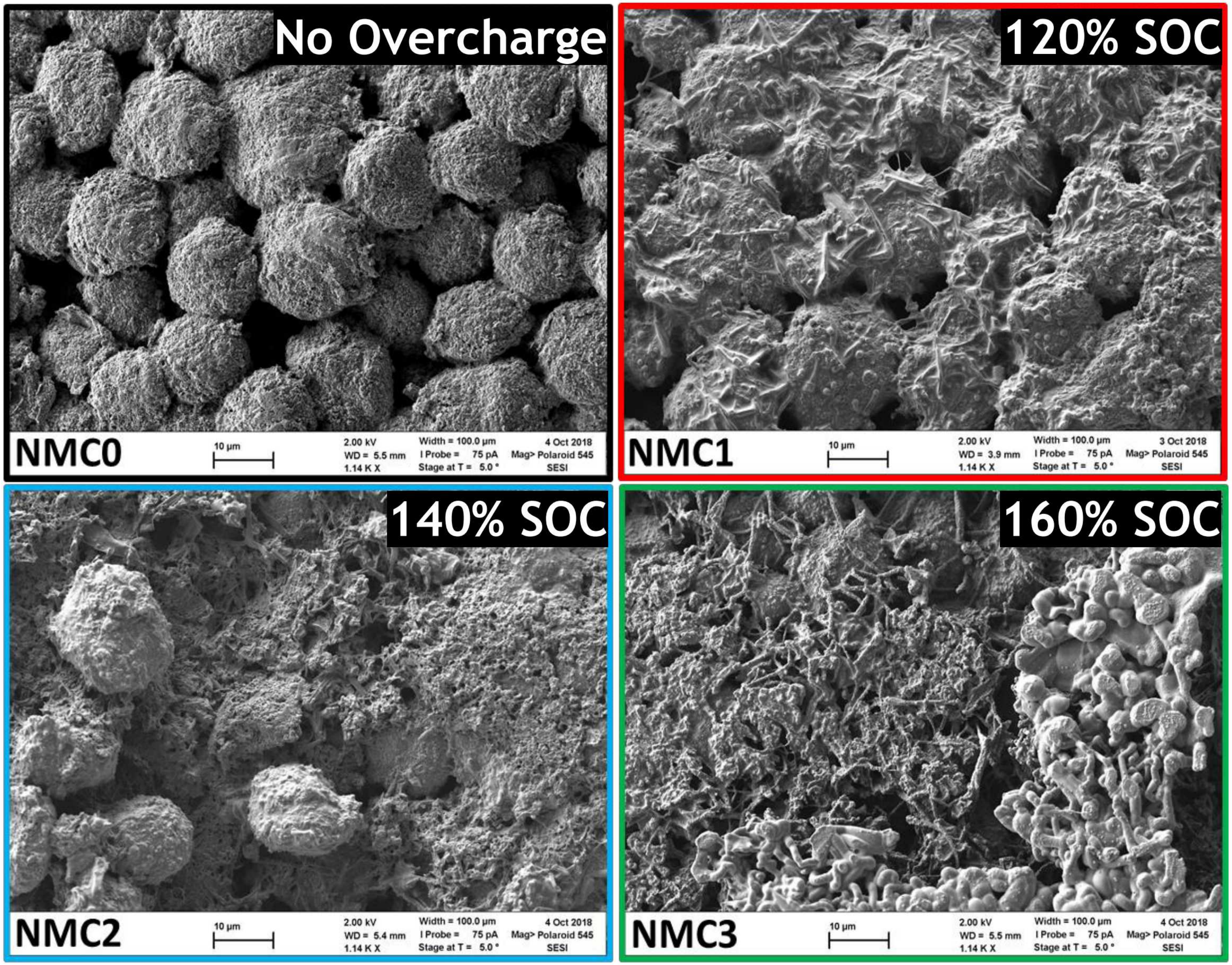
No Overcharge

120% SOC

140% SOC

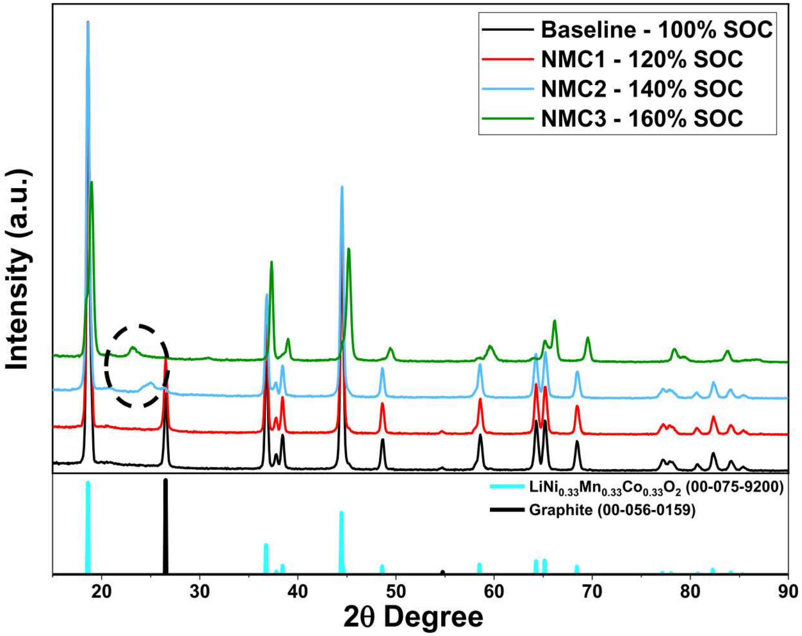
160% SOC

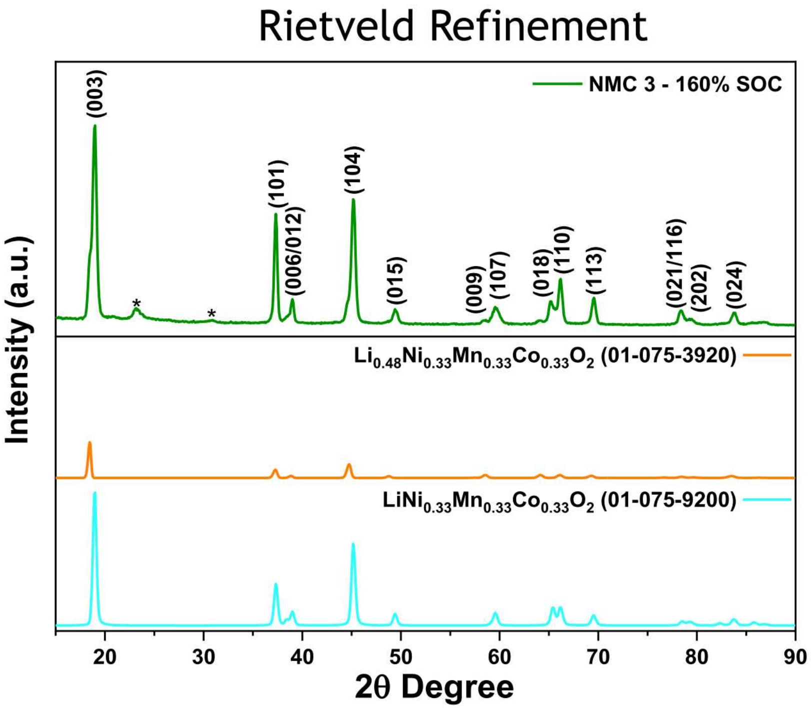
Microstructural Changes: Anode



SEM – Amy Allen and Barry Ritchey (2555)

X-ray Diffraction (XRD): Cathode

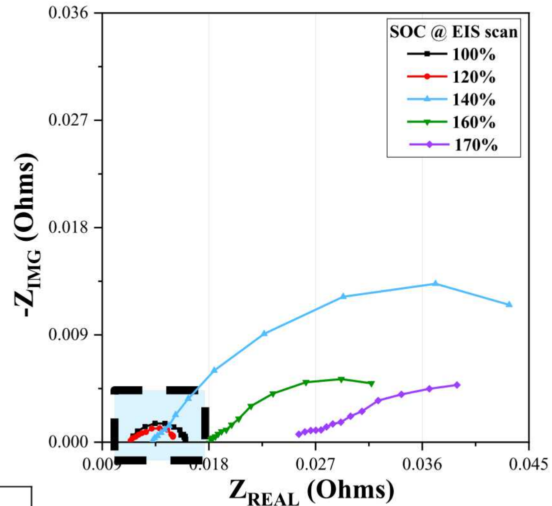




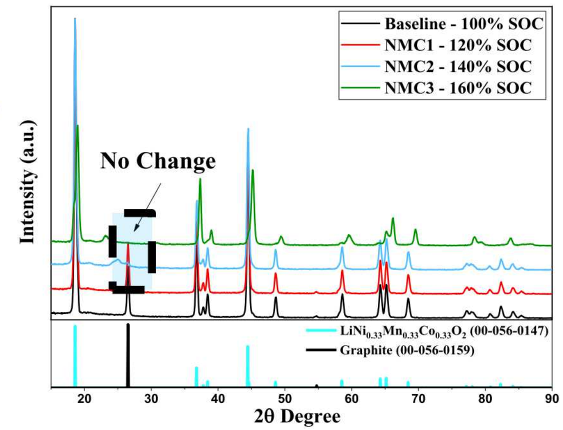
- XRD diffractograms of the positive electrode revealed changes for SOC's >140%.
- NMC3 diffraction peaks were shifted to higher degree values, indicating a general shrinkage of the lattice.
- Rietveld refinement for NMC3 based on lithiated vs. delithiated NMC presented a combination of phases with 86% lithiated NMC and 14% delithiated NMC, suggesting a decomposition of the cathode and loss of lithium inventory.

Conclusion: NMC Overcharge

Electrochemical Impedance Spectroscopy during overcharge procedure

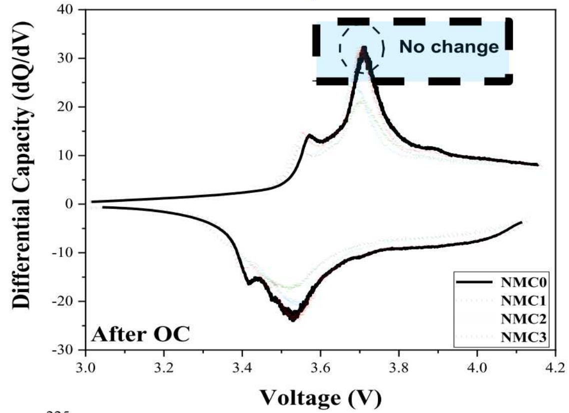


X-ray Diffraction (Cathode)

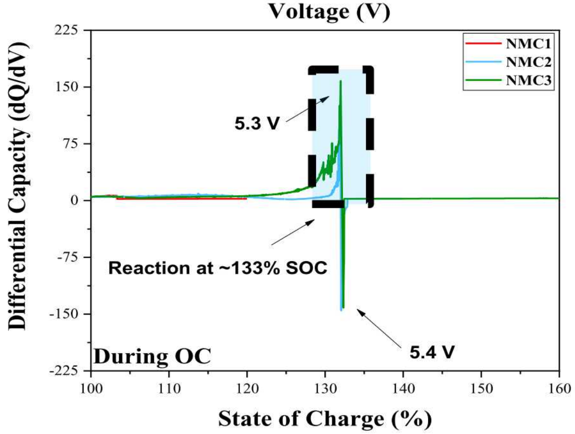


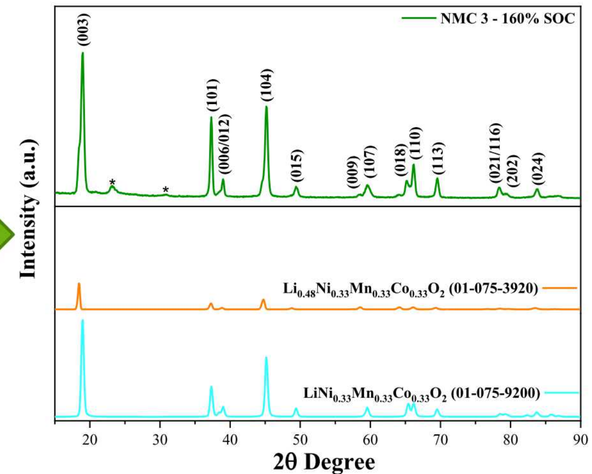
Rietveld Refinement for 160% SOC

Phase	% (+/- 5%)
Lithiated NMC	86
Delithiated NMC	14



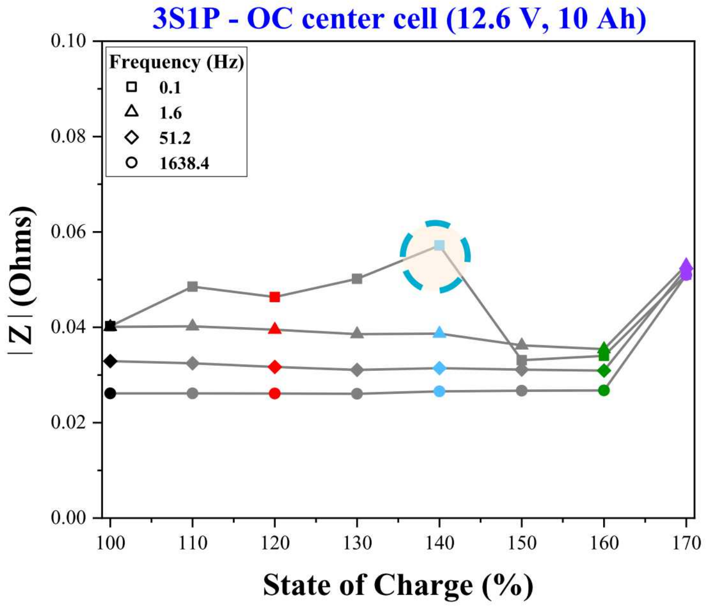
Differential capacity of the cell after and during overcharge



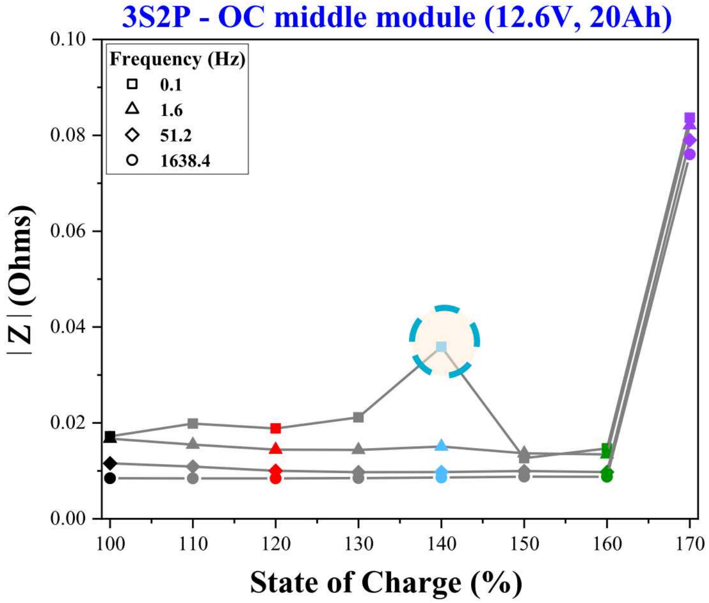


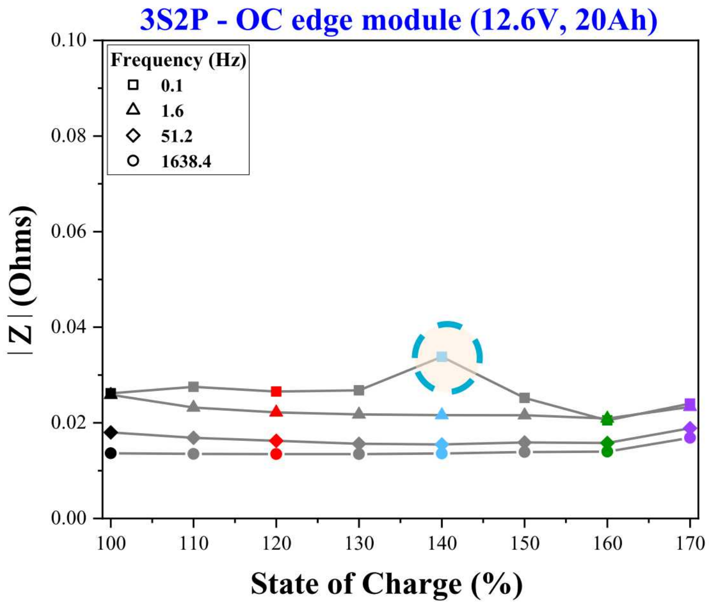
Harvested from NMC3 – 160%SOC

Is the marker identified for single cells applicable for battery packs?

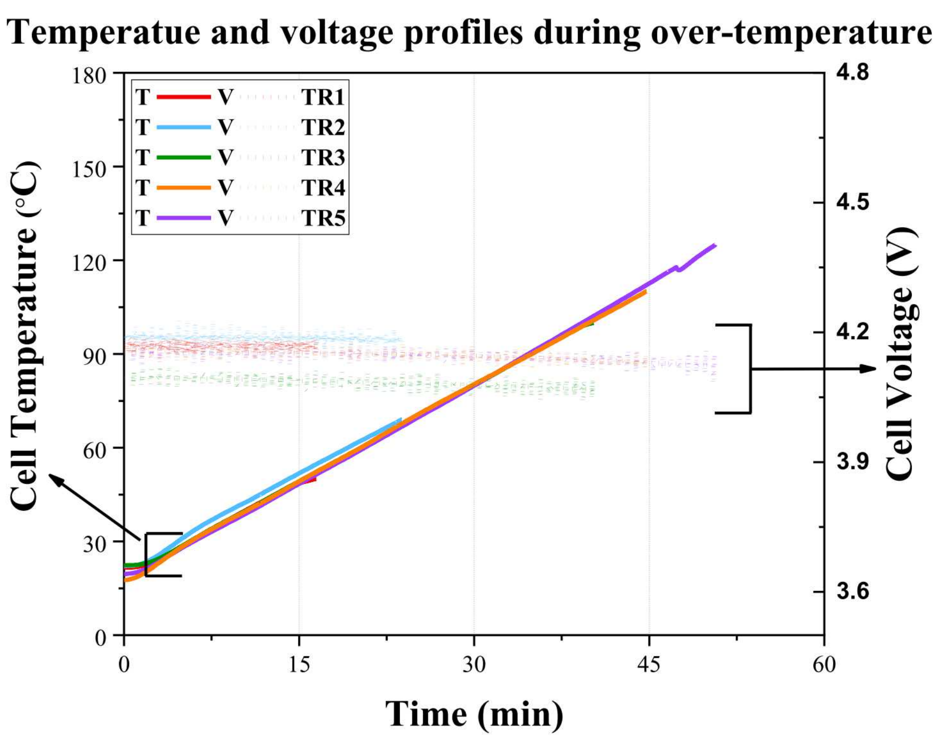


- Distinct shift ONLY observed at lower frequencies.
- Low frequency impedance measurements will be necessary when using this technique on complex pack formats.





Over-temperature Effects to Cell Temperature and Voltage

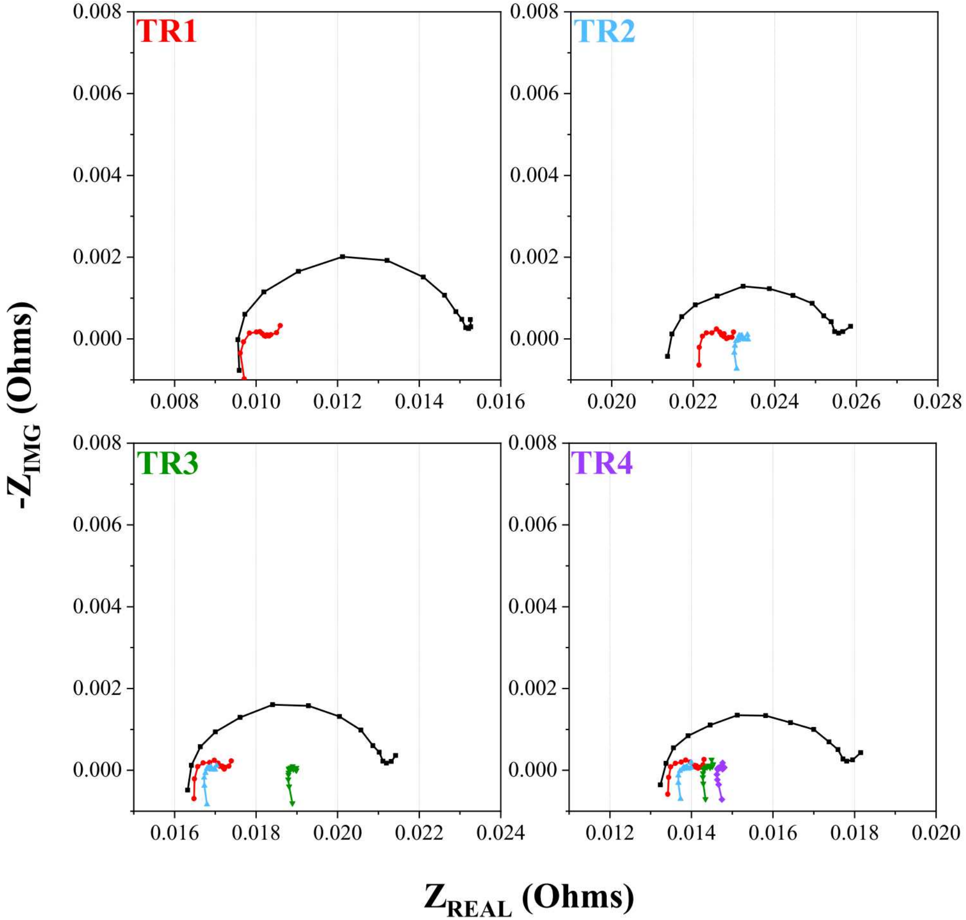


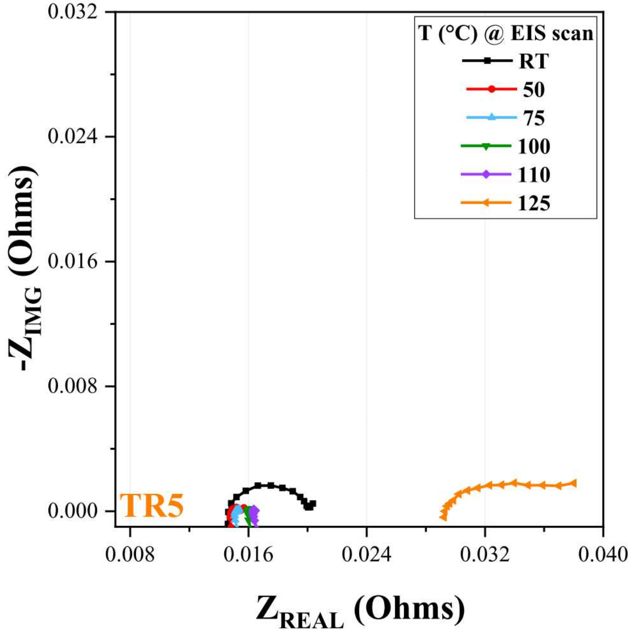
Five individual cells, TR1, TR2, TR3, TR4 and TR5 were heated to 50 °C, 75 °C, 100 °C, 110 °C and 125 °C, respectively.

Test parameters	
Heating rate	2 °C/min

	Initial T (°C)	Max. T (°C)	ΔT (°C)
TR1 - 50 °C	21.6	50	28.4
TR2 - 75 °C	22.1	75	52.9
TR3 - 100 °C	22.4	100	77.6
TR4 - 110 °C	17.6	110	92.4
TR5 - 125 °C	19.5	125	105.5

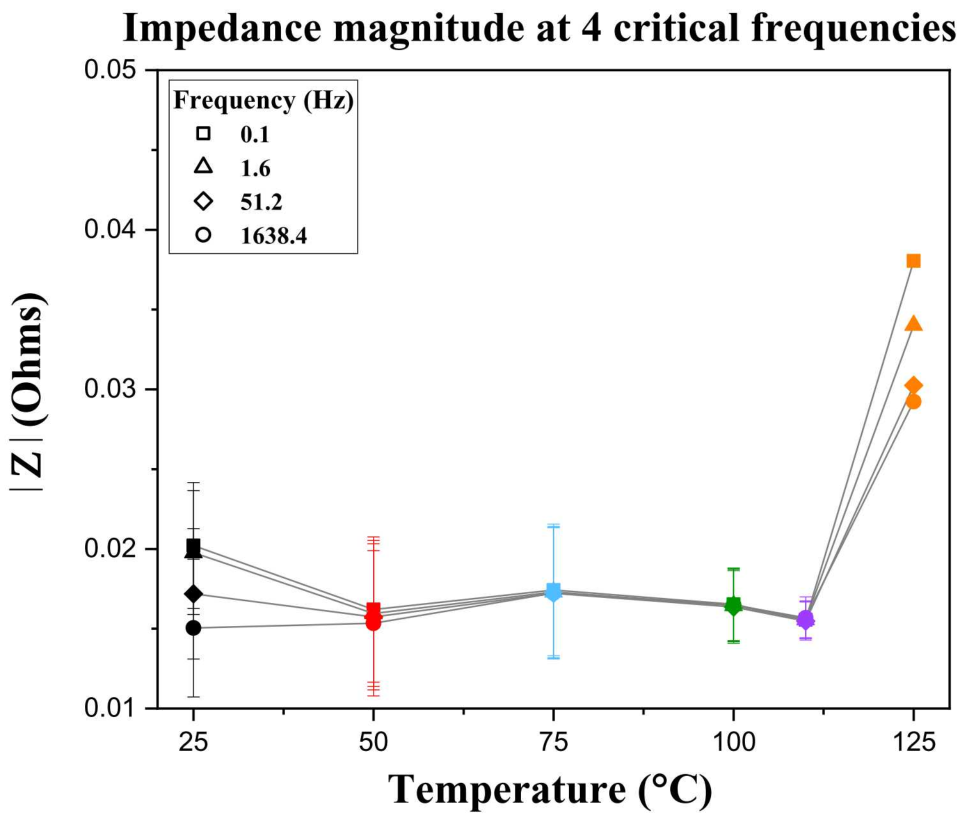
In-operando EIS





- Minor changes observed up to 100 ˚C, while significant changes began to develop in the EIS curves above that point.
- The technique is most effective at detecting temperatures that approach dangerous levels, and would likely not provide a signal at more moderate temperatures.

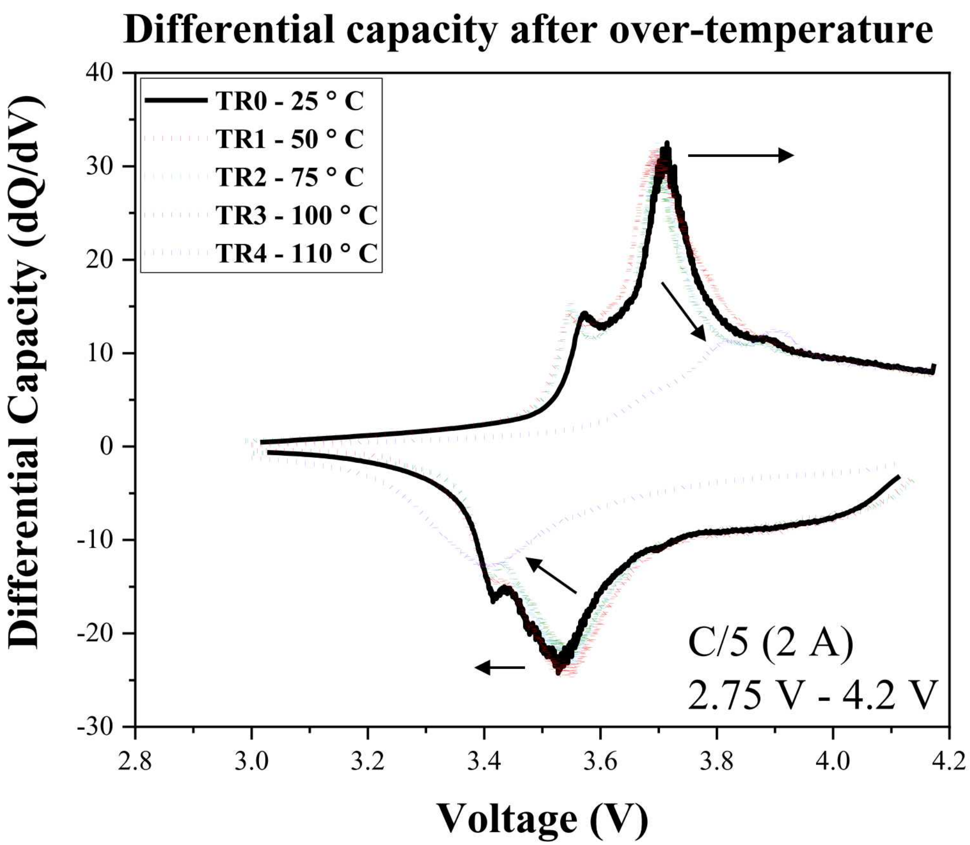
TR5-125°C : Magnitude of the complex impedance



$$|Z| = \sqrt{Z_{REAL}^2 + Z_{IMG}^2}$$

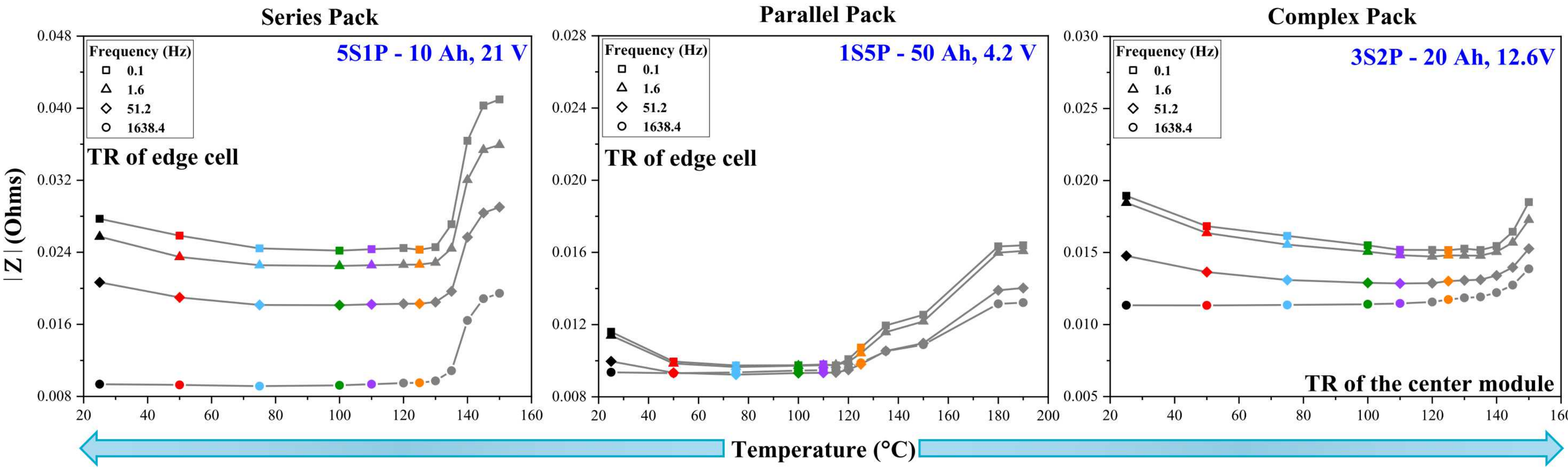
- To better understand the changes after 100°C, we analyzed the magnitude as a function of T.
- The data showed significant increments in resistance after ~110°C for all frequencies.

Differential Capacity (dQ/dV)



- Minor changes observed until above 100 ˚C, where we begin to see signs of significant damage to the battery.
- TR5 (125 ˚C) was significantly damage by the over-temperature procedure to the point of not being operational.

Identified marker applicable to battery packs in series, parallel or complex configuration?



- *Series Pack:* Signals of cell damage detected at high temperatures (120 ˚C and above).
- *Parallel Pack:* Increases in the scalar impedance were identified at temperatures above 120 ˚C. However, the parallel packs did further limit the detection capabilities.
- *Complex Pack:* At this level of complexity, we begin to see the signal becoming washed out as the resistances detected within the entire pack begin to counteract any behaviors observed due to cell failure

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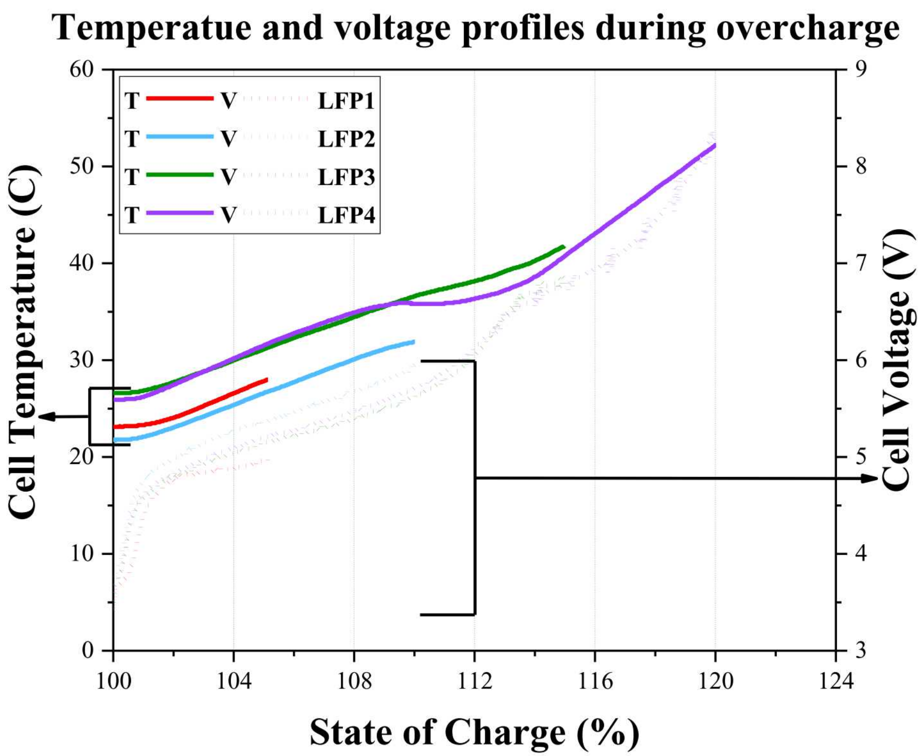
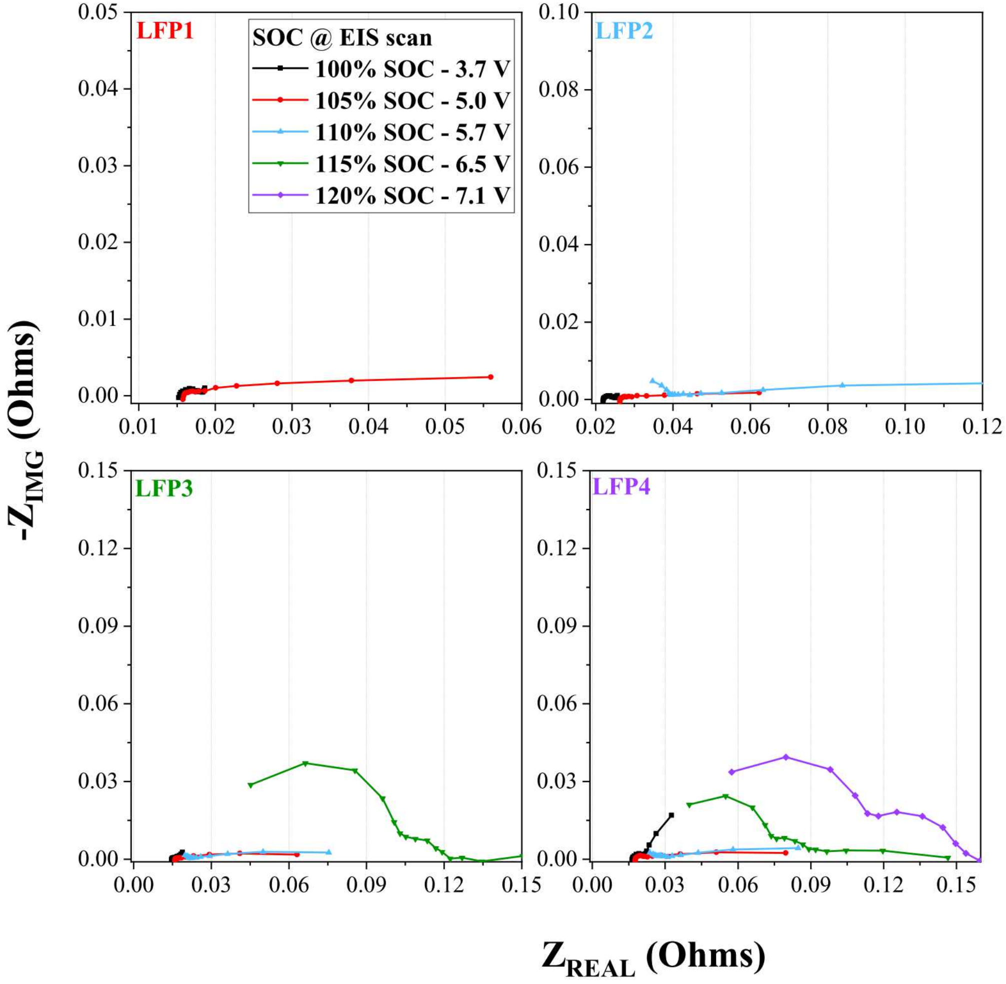


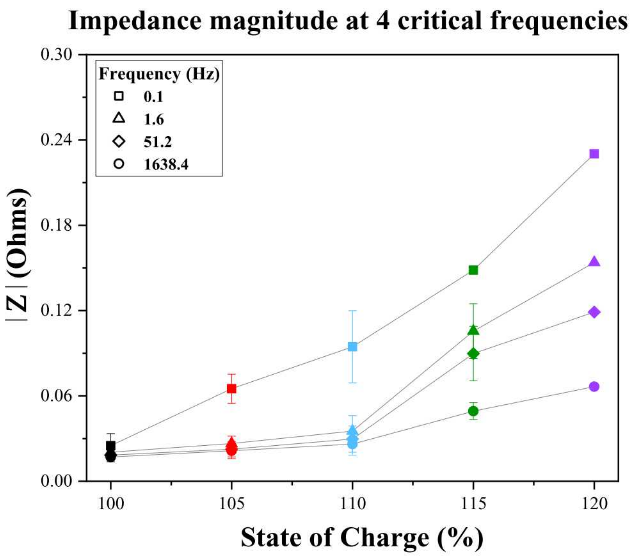
Four individual cells, LFP1, LFP2, LFP3, and LFP4, were overcharged to 105%, 110%, 115%, and 120% SOC, respectively.

Test parameters	
C-rate	1C (10 A)
Voltage limit	20 V

	Initial T (°C)	Max. T (°C)	ΔT (°C)
LFP1 – 105%	23.1	28.0	4.9
LFP2 – 110%	21.8	31.9	10.1
LFP3 – 115%	26.6	41.8	15.2
LFP4 – 120%	25.9	52.2	26.3

In-operando EIS

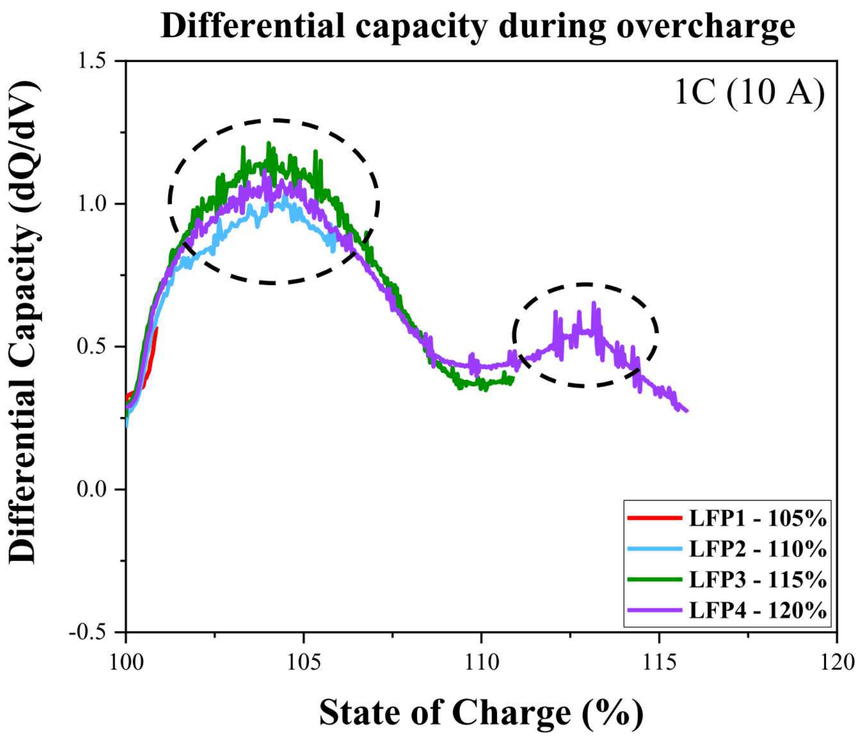


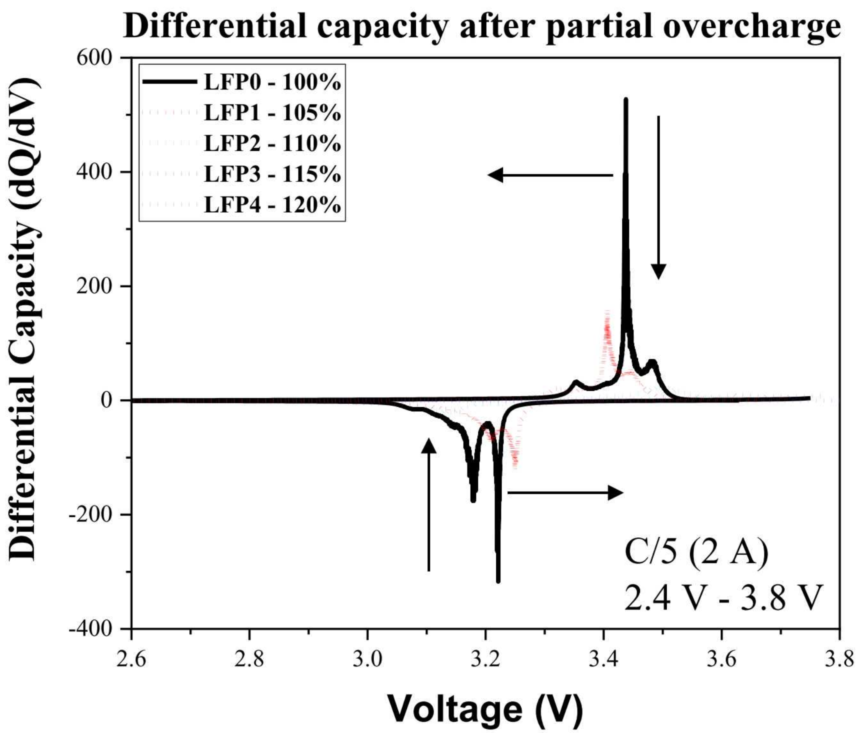


$$|Z| = \sqrt{Z_{REAL}^2 + Z_{IMG}^2}$$

- The complex impedance results during in-operando testing of a single LFP cell showed smaller initial changes up to 105% SOC, but more significant changes above that point.

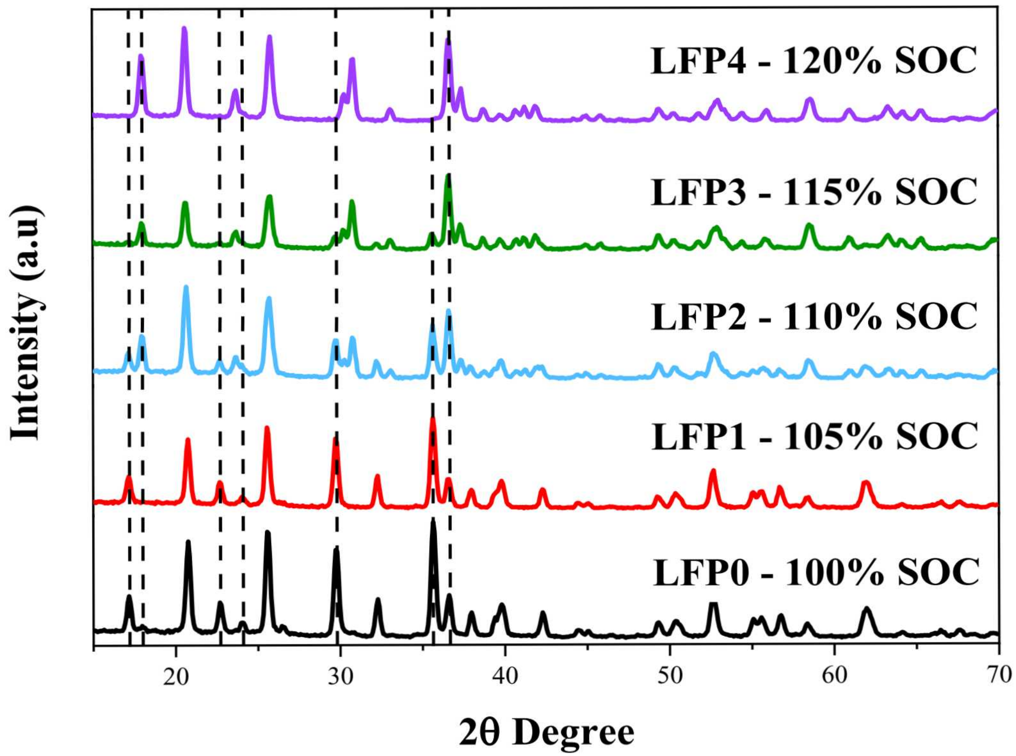
Differential Capacity (dQ/dV)





- The differential capacity calculated during the overcharge procedure showed a reaction at ~104% SOC and ~113% SOC.
- The calculations post-overcharge demonstrated significant performance decay for all the levels of SOC studied.

X-ray Diffraction (XRD): Cathode

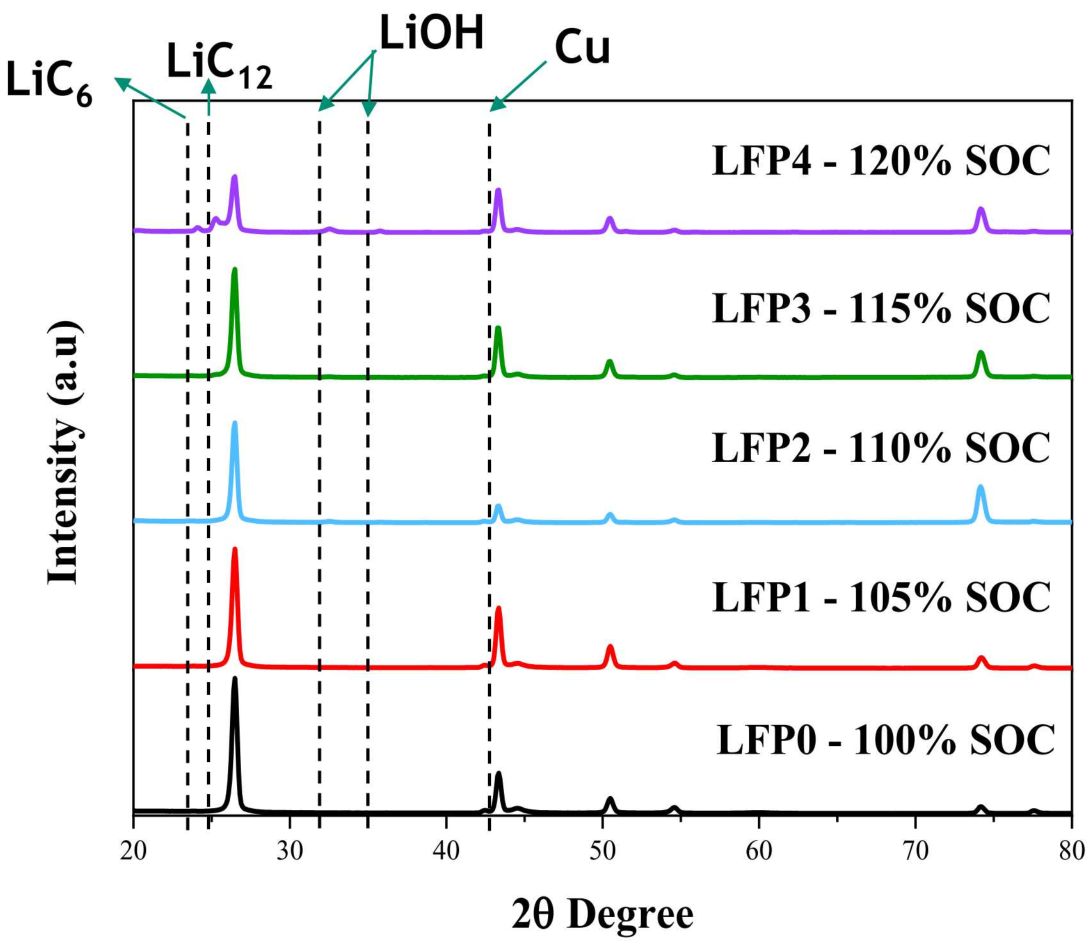


Electrodes were harvested when the cell was at ~0%SOC (fully lithiated).

SOC (%)	$LiFePO_4$ phase (%)	$FePO_4$ phase (%)
100%	100	0
105%	100	0
110%	43	57
115%	17	83
120%	0	100

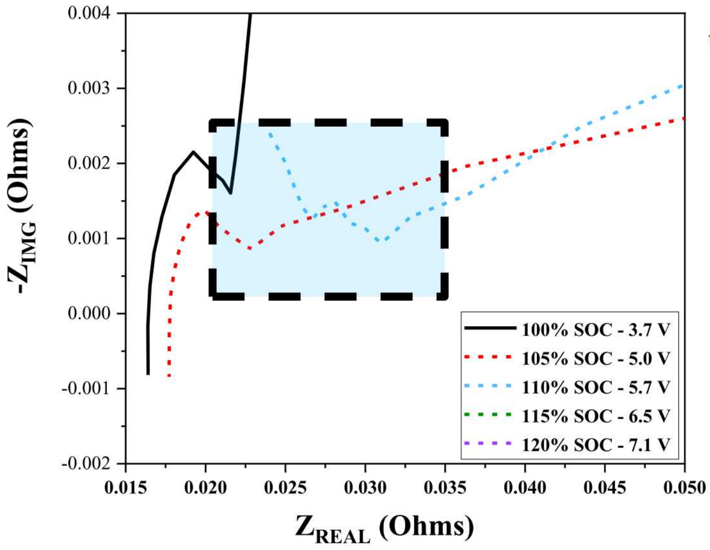
X-ray Diffraction (XRD): Anode

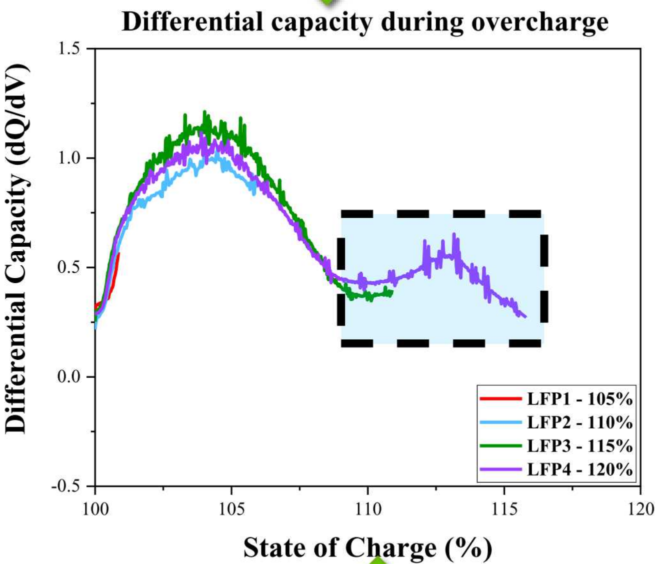
Electrodes were harvested when the cell was at ~0%SOC (fully delithiathed).



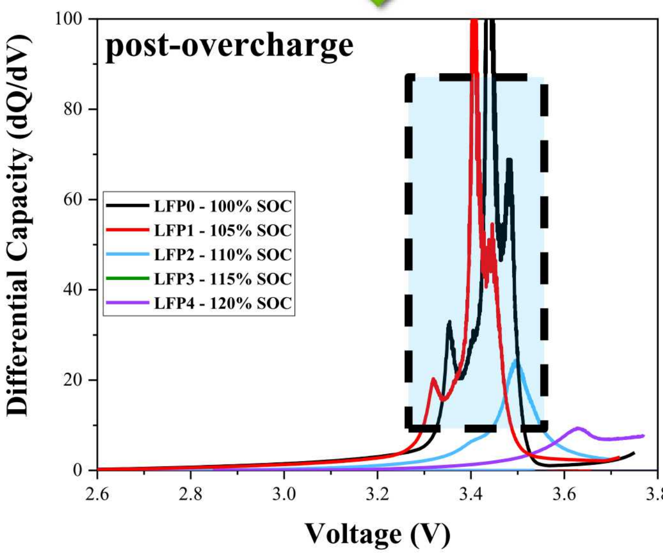
- The diffractograms for 100%-115% SOC presented peaks corresponding to graphite and copper.
- The diffraction peaks for 120% SOC displayed multiple elements, including Cu, LiOH, graphite, LiC_{12} and LiC_6.

Conclusion: LFP Overcharge





SOC (%)	$LiFePO_4$ phase (%)	$FePO_4$ phase (%)
100	100	0
105	**100**	**0**
110	**43**	**57**
115	17	83
120	0	100



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Summary

- Overcharge procedures were applied to 10 Ah NMC and 10 Ah LFP single cells.
- The electrochemical and structural characterization indicated a clear marker for the NMC cells at 140% SOC and for the LFP cells at 110% SOC.
- EIS, dQ/dV and XRD results suggest that NMC cells could stand a mild OC (20%) and still be operational with minimal risk of thermal runaway while LFP cells are not tolerant to small levels of OC. LFP cells displayed significant degradation with only 3-4% overcharge.
- In the near future, we will investigate if the markers identified for these cells are consistent across manufacturers and/or capacities.

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- John Hewson
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- Armando Fresquez
- Yuliya Preyer
- Ivanov Sergei

INL

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- Tanvir Tanim
- Jon Christophersen

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