Sandia National Laboratories

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Electrochemical and Materials Characterization of Li-ion Cells during Long Term Cycling

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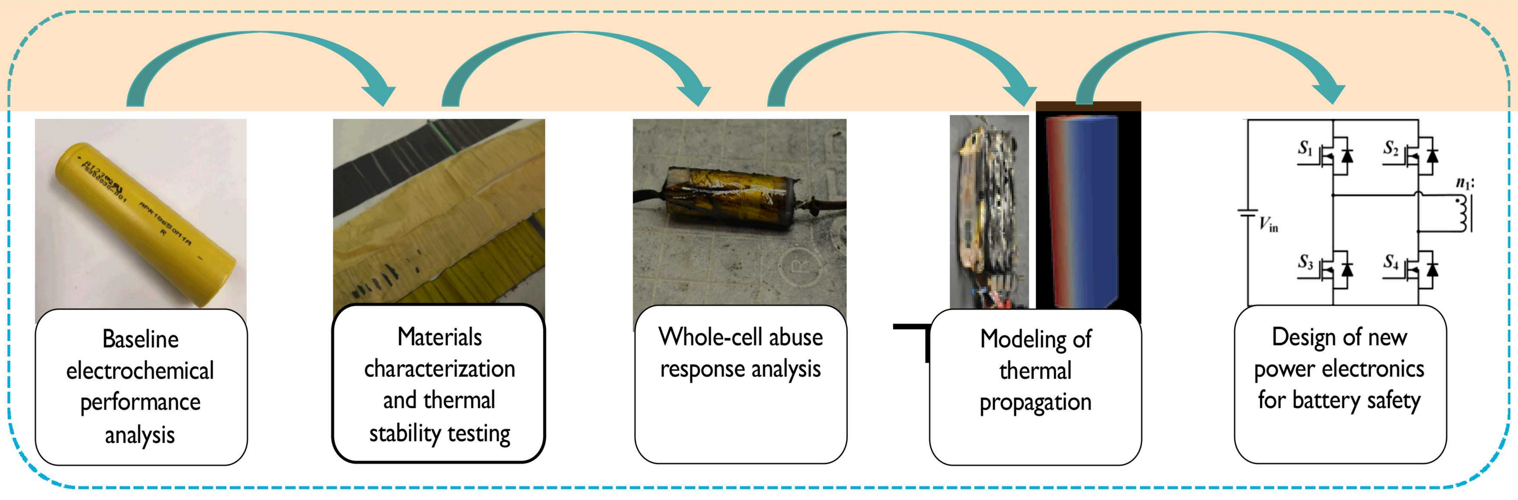
Motivations and Goals

- Characterize electrochemical and materials changes in cells through their entire life space to make a more complete picture of cell aging processes
- Link Electrochemical markers (EIS and dQ/dV tests) to trends in capacity fade
- Link Materials changes (via CT scan, XRD, SEM, DSC) to trend in capacity fade
- Correlate Materials changes to Electrochemical changes to create a better understanding of why various cell chemistries degrade differently at different conditions
- Will aid in understanding how to improve battery performance, lifespan and safety



Experimental Design and Current Status

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	20 A
Operating T	-30 to 60°C	0 to 45°C	0 to 50°C

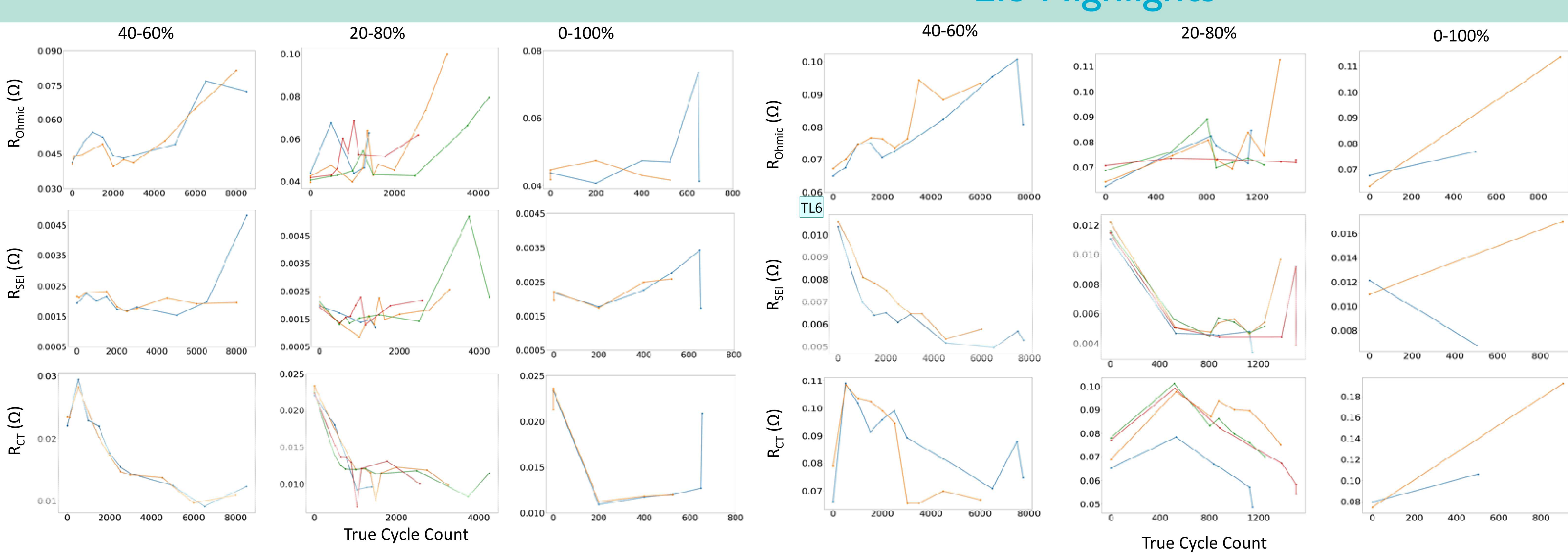
Design of experiment approach with two cells at each set of conditions, all within manufacturer specifications

Cycling conditions for all cells

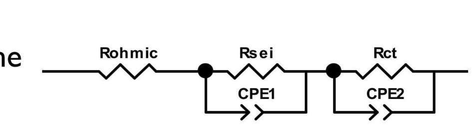
DOD, Temperature, Discharge Rate*			
40-60%, 25°C, 0.5C	0-100%, 15°C, 1C	0-100%, 15°C, 2C	40-60%, 25°C, 3C
20-80%, 25°C, 0.5C	0-100%, 25°C, 1C	0-100%, 25°C, 2C	20-80%, 25°C, 3C
0-100%, 25°C, 0.5C	0-100%, 35°C, 1C	0-100%, 35°C, 2C	0-100%, 25°C, 3C

- Commercial NMC and NCA cells were previously cycled to 80% capacity by Preger et al.
- Selected cells were pulled to undergo post mortem characterization:
    - Xray CT Scan (completed)
    - XRD (In progress)
    - SEM/EDX
    - DSC
- Initial EIS (analysis completed) and dQ/dV (analysis in progress) data is being analyzed
- Remaining cells are being cycled to end of life and materials and electrochemical characterization of them will be conducted at that point

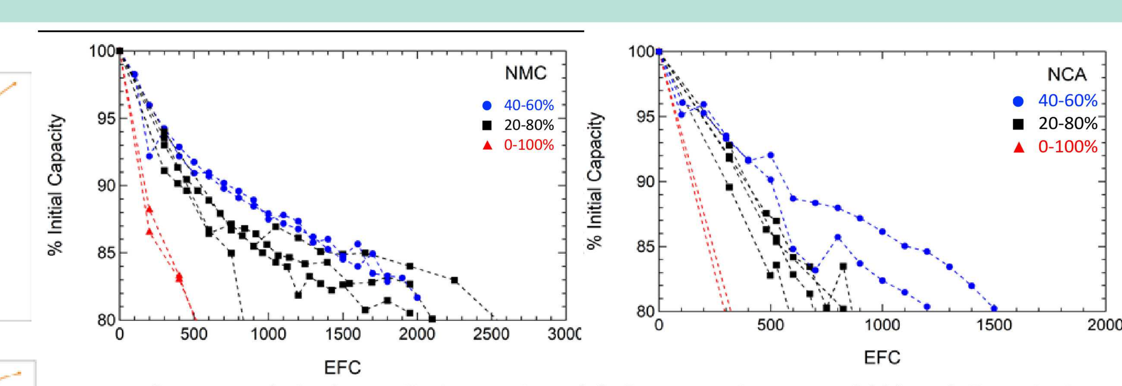
EIS Highlights



Fitted R values from EIS spectrums taken during cycling to 80% initial capacity of NMC cells (left) and NCA cells (right) cycled at different SOC ranges listed at the top if the figure. EIS was taken at 0% SOC at 25C, at 50mV amplitude and a range of .1Hz to 1MHz using a Solatron potentiostat. Fitting was done using Zview and the adapted Randles circuit shown to the right.



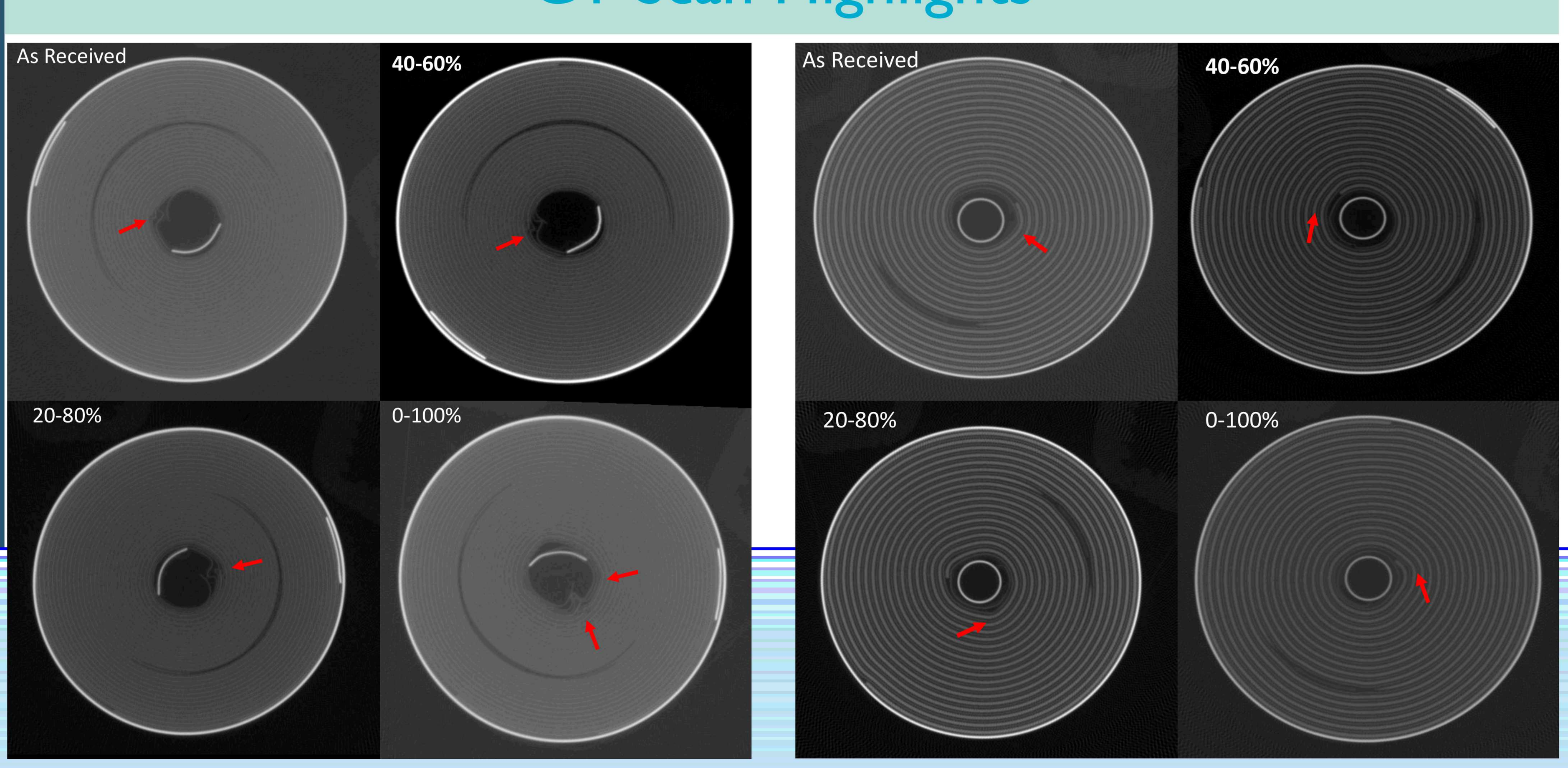
Equivalent Circuit used to fit EIS spectrums



Capacity fade for cells by cycling SOC range down to 80% in full cycled equivalent

- Both NCA and NMC cells generally saw Rohmic increase with cycled SOC range
- Rsei generally increased with increased cycled SOC range in NMC cells and decreased during cycling for NCA cells
- Rct generally decreased both NCA and NMC cells, though at higher SOC ranges for NCA cells it did increase.
- Cells that display most rapid capacity fade also have increasing trends in at least two R values

CT Scan Highlights



Mid-section CT Scan of NMC (Left) and NCA (Right) cells at 0% SOC (by voltage) as received and cycled to 80% capacity in listed SOC range at 0.5C and at 25C

- In NMC cells higher SOC ranges showed more and larger delamination points of jelly roll near center
- For NMC cells roll becomes more elliptical at the center compared to the as received
- In NCA cells higher SOC ranges showed more deformation of the jelly roll than as received, with large "dents" in the roll and generally becoming more elliptical
- NCA cells did not appear to show delamination of the roll as seen in NMC cells

Conclusions and Next Steps

- Increased rate of capacity fade is correlated with increasing Rohmic and either Rsei or Rct suggesting that multiple degradation modes interact to cause the most rapid degradation of cells
- Increased SOC range appears to increase degradation from deformation of the internal structure of the cell, likely from the larger expansion and contraction of anode and cathode at the higher SOC ranges
- Suggest that Rohmic trend seen in EIS data is correlated to IR losses that result from deformation of the jelly roll structure
- Future work will focus on correlating chemical and materials changes (XRD, SEM/EDX, DSC) to the EIS data as wells as introducing dQ/dV work as another electrochemical marker

Research Outputs

- Upcoming Presentations:
    - ECS Fall 2020: Correlating Materials Degradation Trends to Electrochemical Indicators in Systematic Long-Term Cycling of Commercial Li-Ion Batteries, Wittman et al
    - MRS Spring 2020 (moved to Fall 2020): Materials Degradation Trends from Systematic Long-Term Cycling of Commercial Li-Ion Batteries, Wittman et al.
- Upcoming Publications:
    - Materials Degradation in Long Term Cycling of Commercial Li-ion Batteries
    - Correlating Materials Changes to Electrochemical Markers during Cycling of Commercial Li-ion Batteries

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Slide 1

TL6 Top figure is a bit blurry. The 9 matrix figure doesnt have a x axis label. What are the different lines in the figures? There is no legend.
Torres-Castro, Loraine, 9/14/2020

TL7 I understand what you are saying because I am familiar with the work but it may be confusing to other people. For example, when you say EIS by SOC, I could think that you are evaluating the EIS at different SOCs.
Torres-Castro, Loraine, 9/14/2020