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Advances Towards Inherently Safe Lithium-Ion Batteries

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Outline

- I. System level battery failure and propagation testing
- II. Diagnostics – Evaluating the condition of battery packs with a single cell under abusive conditions
- III. Not all failures are created equal – The impact of cell size and SOC on thermal runaway
- IV. What can we do? Improving failure response through material improvements.
- V. Summary

Energy Storage Safety/Reliability Issues Have Impact Across Multiple Application Sectors

System-Level Battery Safety

Field failures could include:

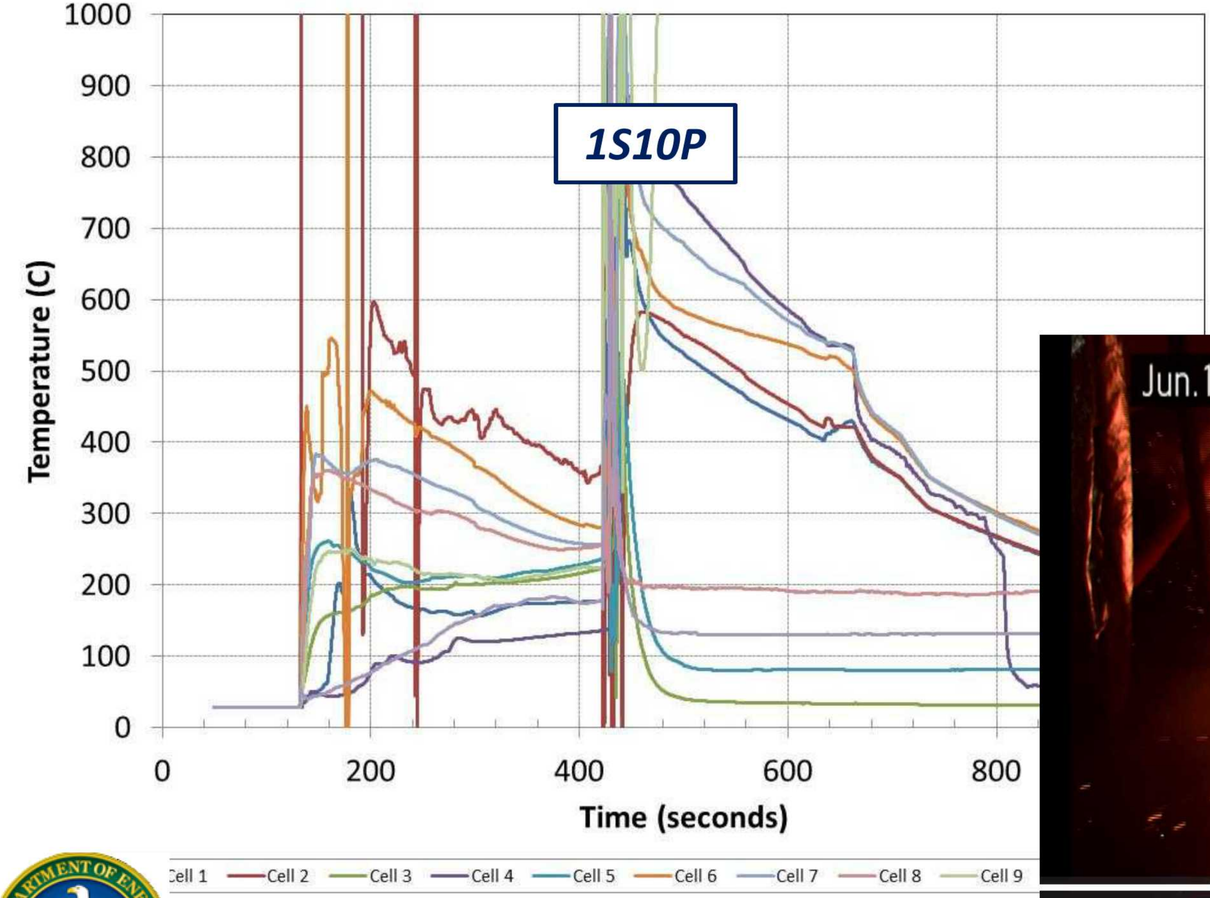
- Latent manufacturing defects
- Internal short circuits
- Misuse or **abuse conditions**
- Ancillary component issues

Any **single point failure** that **propagates** through a entire battery system is an **unacceptable** scenario to ensure battery safety

Fisker incident in the wake of Super Storm Sandy , New Jersey, 2012

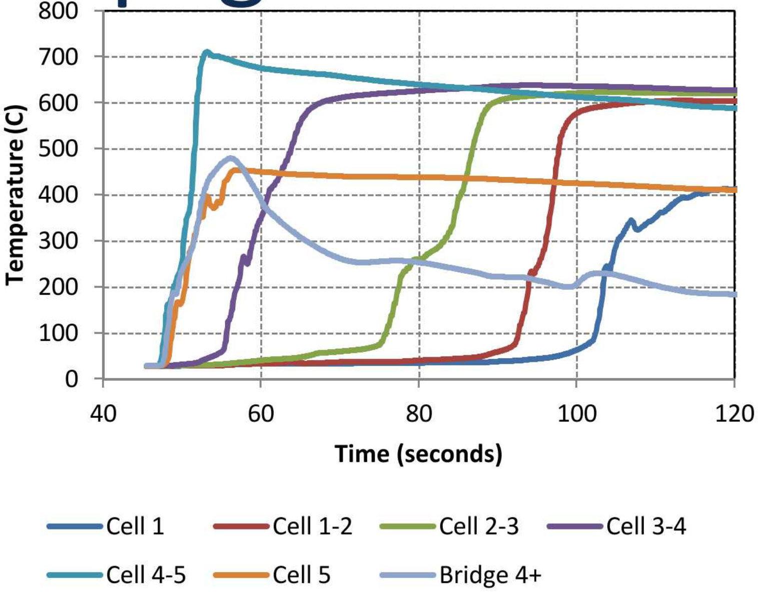
Failure Propagation Testing

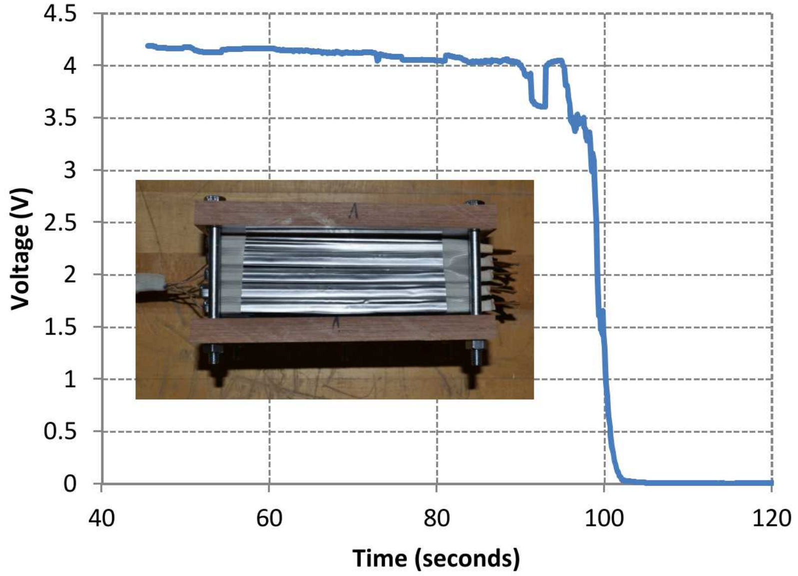
10S1P and 1S10P configurations
2.2 Ah 18650 cell packs (92 Wh at 100% SOC)
Failures initiated by mechanical insult to the center cell (#6)

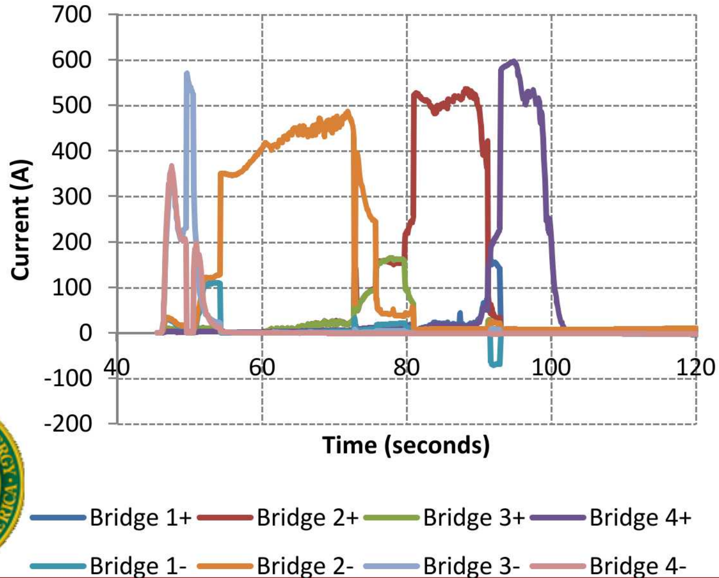


Complete propagation of a single point failure in the 1S10P pack

Propagation Testing (1S5P)

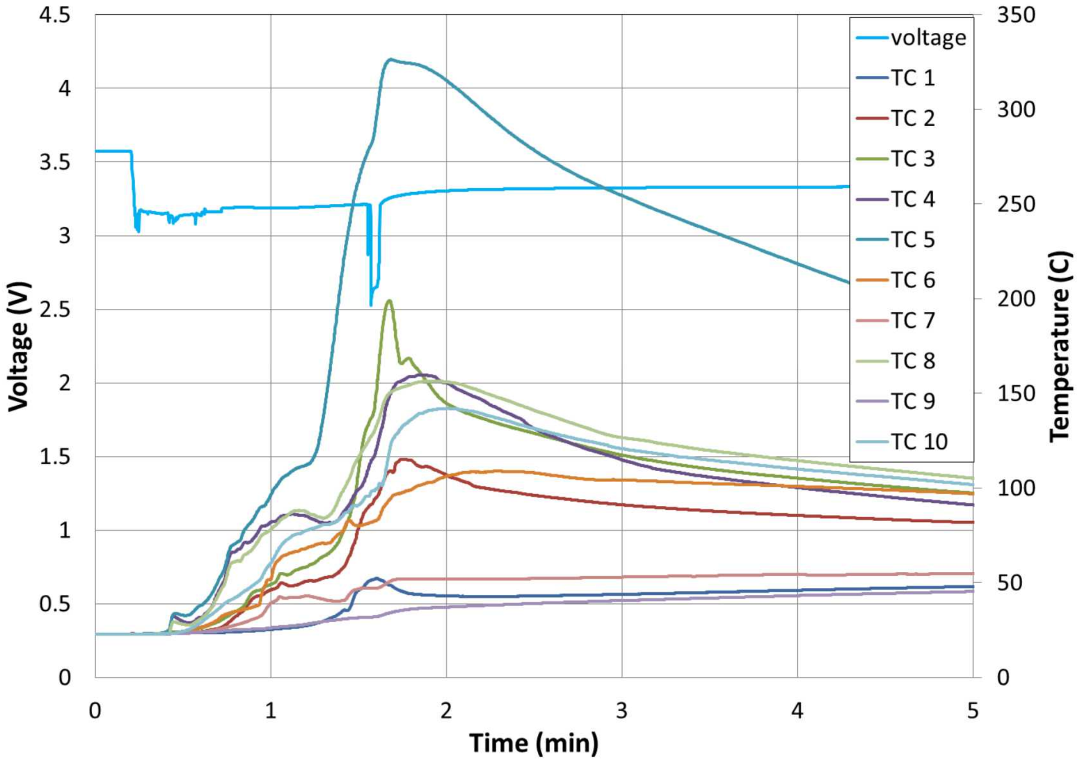






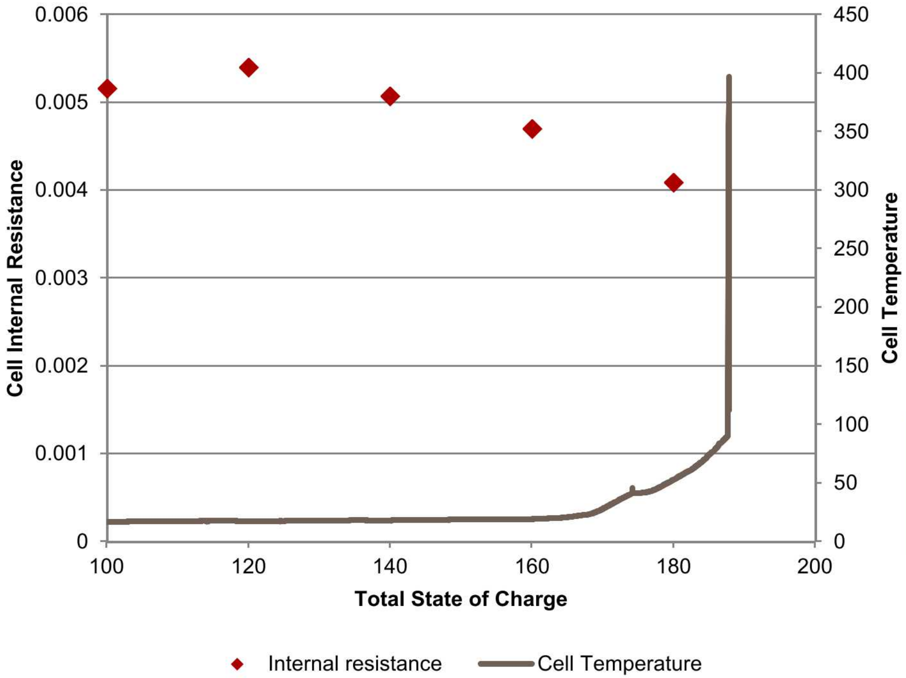
Failure and runaway initiated at Cell #1
Heat flux gauge data collected 32" from pack
Temperature corrected current flowing through bridges

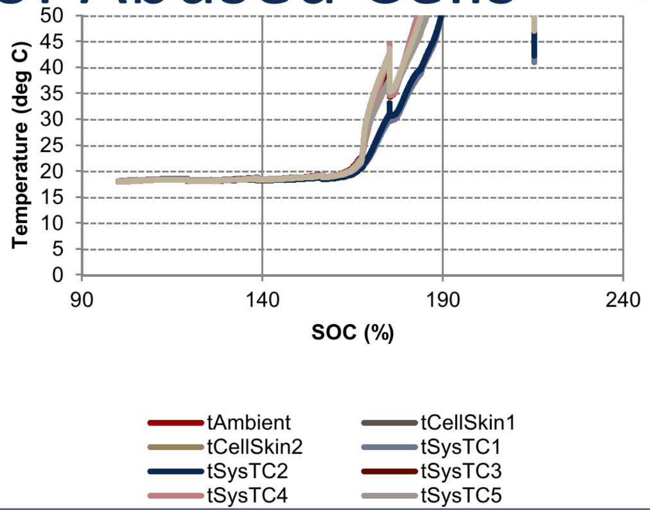
Propagation testing - LFP



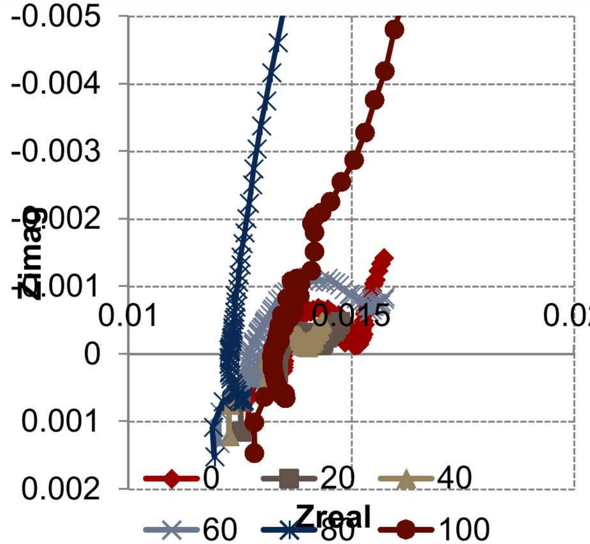
1s10p $LiFePO_4$ pack with central cell failed through nail penetration. A moderate thermal runaway was observed in the failed cell (TC 5) but did not propagate to surrounding cells. The nickel tabs used to connect the cells together were destroyed at the points where they connect to the central cell.

Safety testing- Diagnostics of Abused Cells





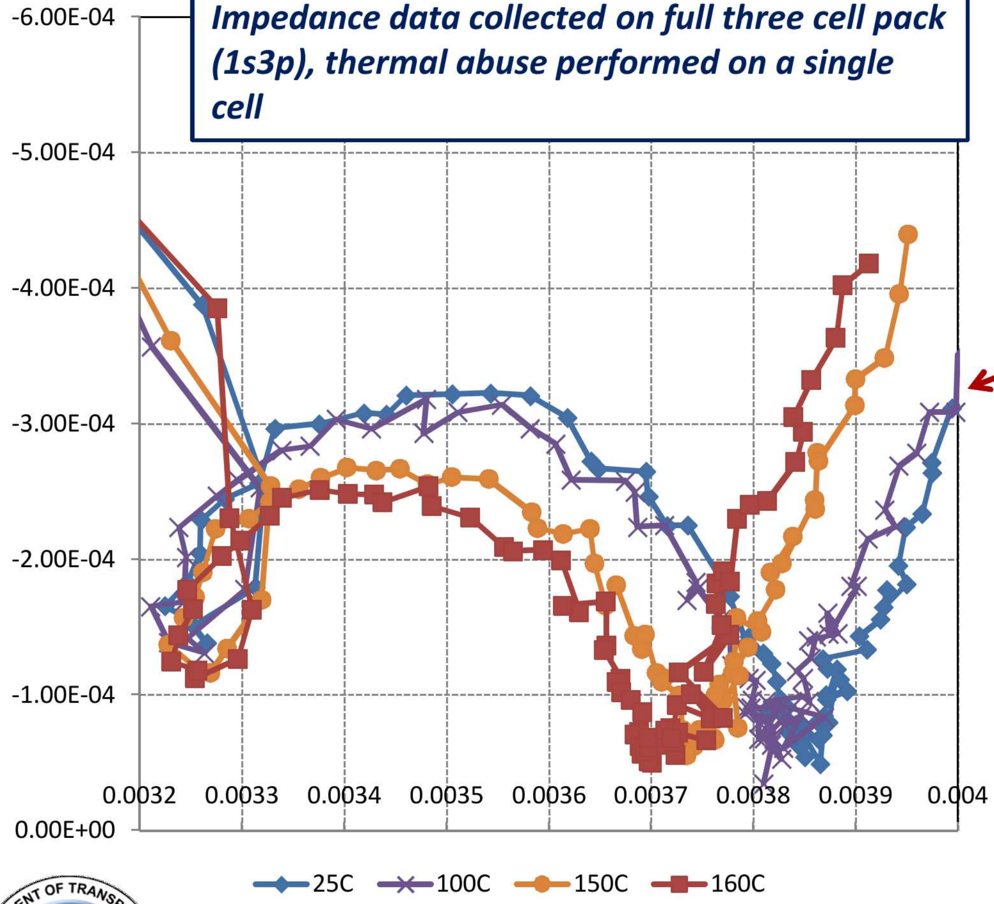
Temperature during testing- Temperature remains close to ambient up to 60% Overcharge, beginning to increase rapidly above 70% overcharge

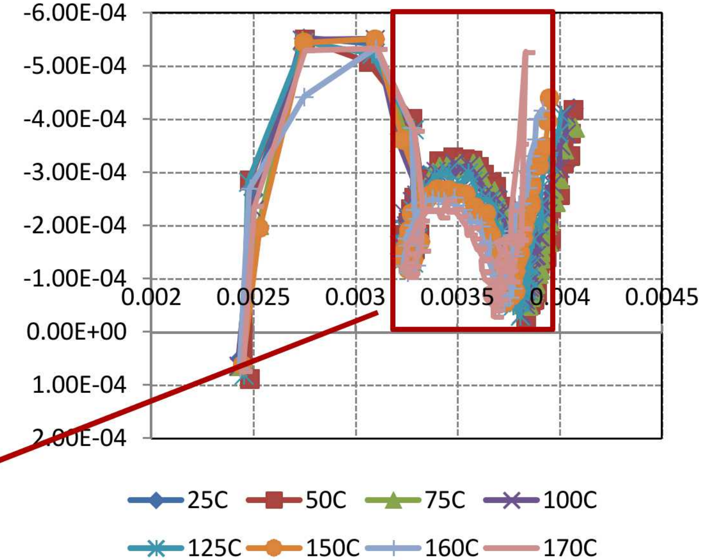


Impedance spectra at increasing states of overcharge Reduction in charge transfer resistance (radii of semicircles) from 0-40% overcharge, similar to impedance changes seen in normal charging, increasing over 60% overcharge.

Parallel Pack Testing

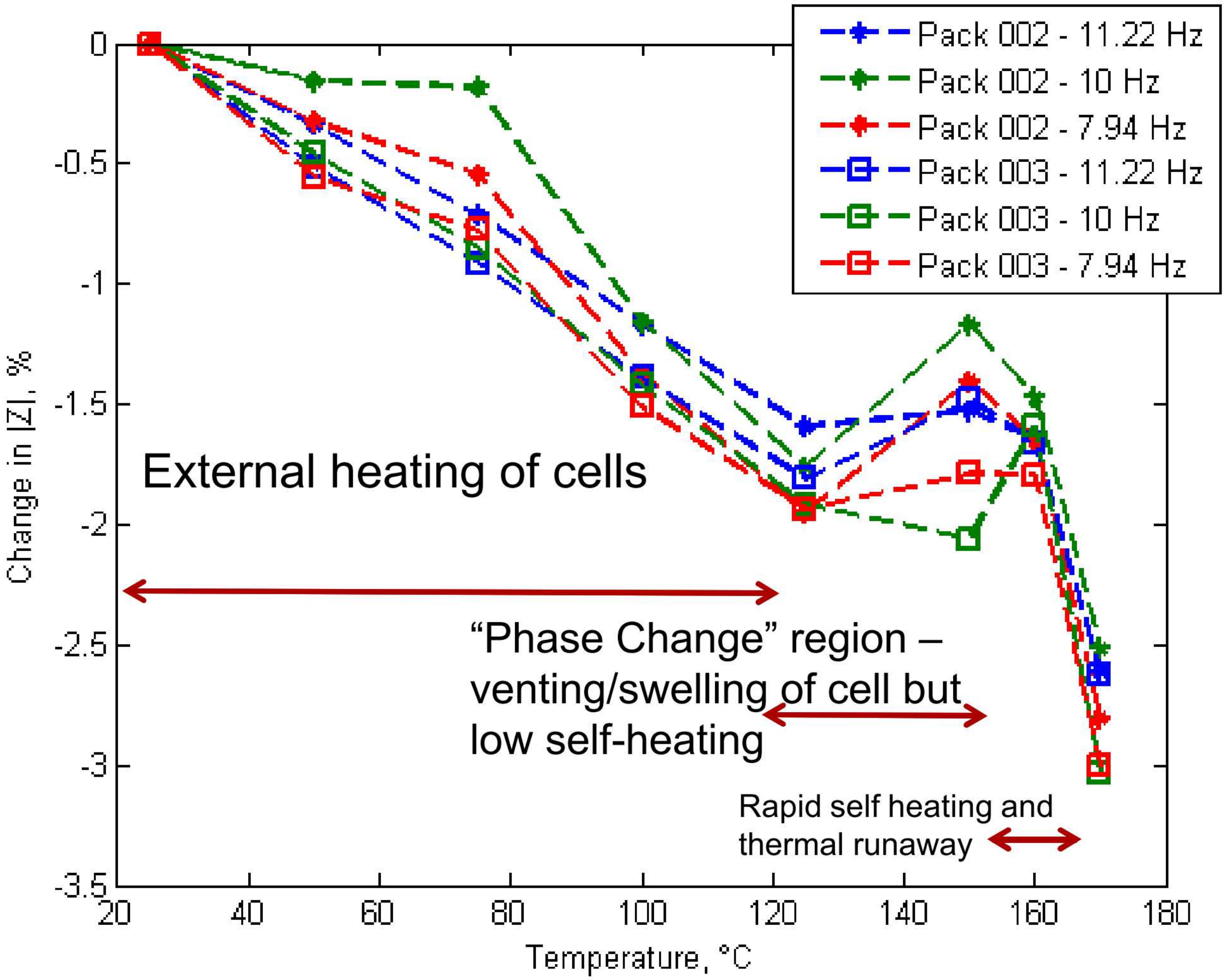
Impedance data collected at 25 °C intervals up to 150 °C, then 10 °C intervals until failure
Impedance data collected on full three cell pack (1s3p), thermal abuse performed on a single cell





Little change observed up to 100 °C.
Shifts in RCT observed as temperature increases above 100 °C.
Thermal runway observed during data collection at 170 °C

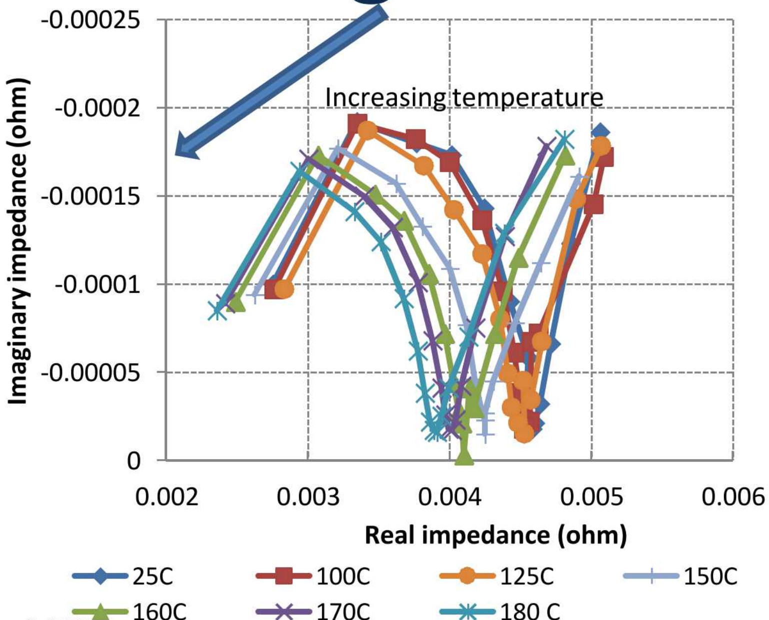
Three cell parallel testing

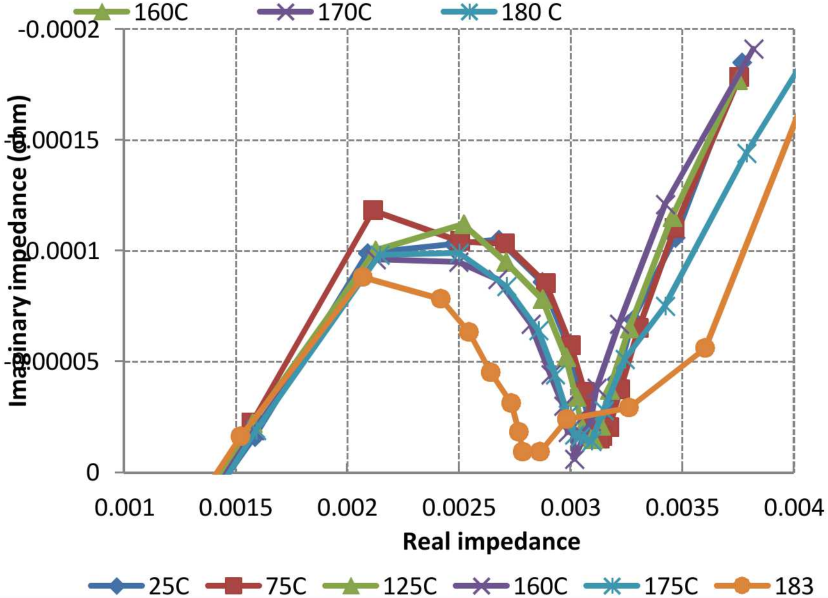


Impedance measurement of entire pack, thermal abuse applied to a single cell within the pack until runaway

Fast impedance monitoring

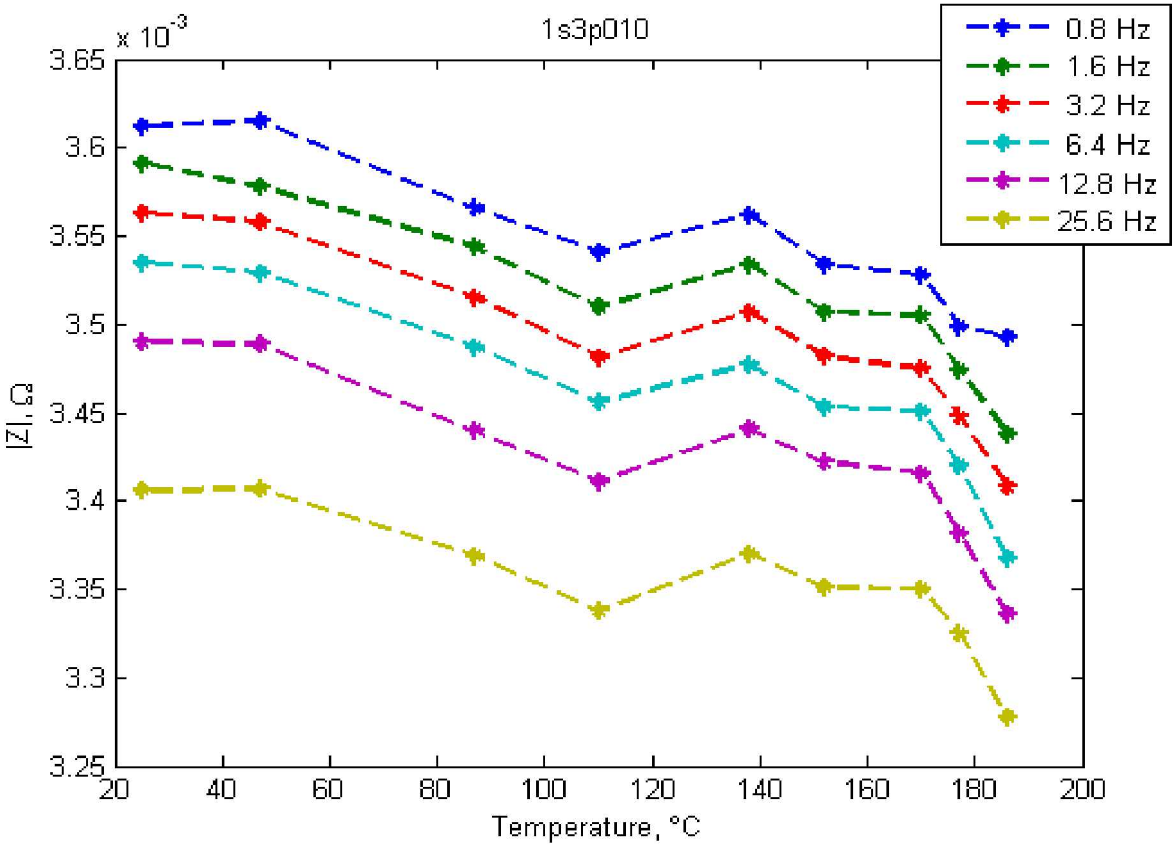
Impedance measurement box developed by INL





Impedance data collected after temperature is allowed to equilibriate vs. scans taken every 20 seconds during a 3 °C/min thermal ramp test

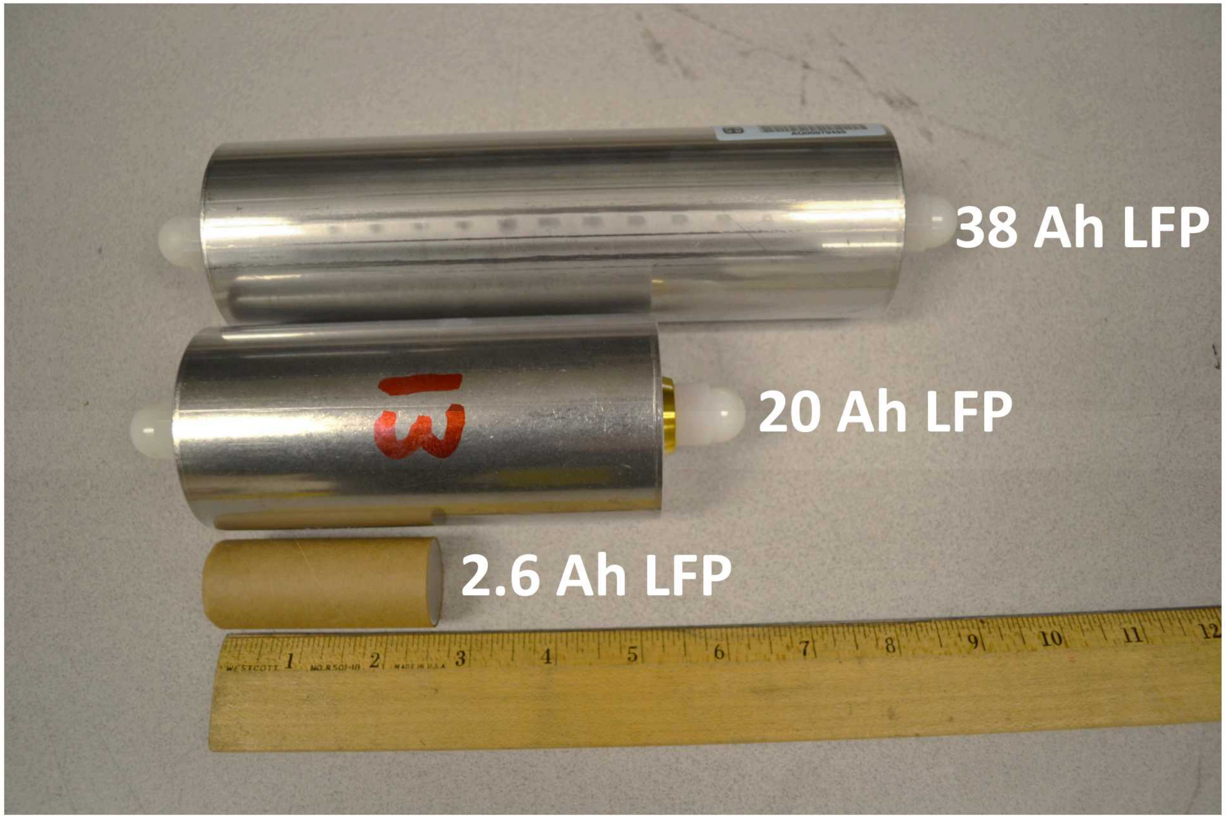
Three cell parallel continuous monitoring



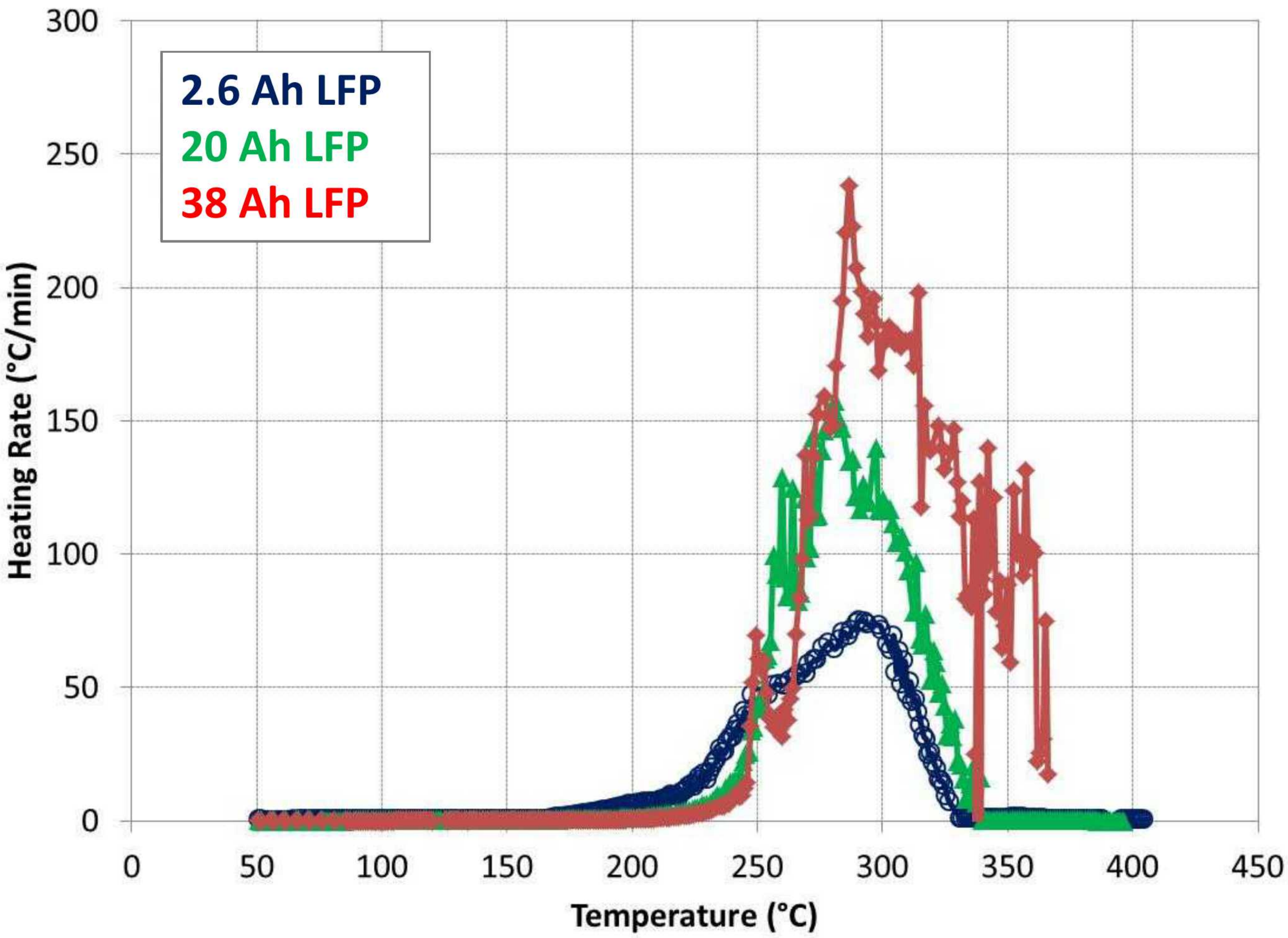
Impedance measurement of entire pack, thermal abuse applied to a single cell within the pack until runaway at a constant rate of 3 °C/min. Similar to behavior observed during step-by-step measurements.

Impact of Cell Size on Runaway

- ***Evaluation of heat and gas generation as a function of cell size from 2-50 Ah***
- ***Using COTS cells and controlling cell chemistry and format as much as practical***
  - ***3 cylindrical LFP cells and 3 cylindrical NCA cells***

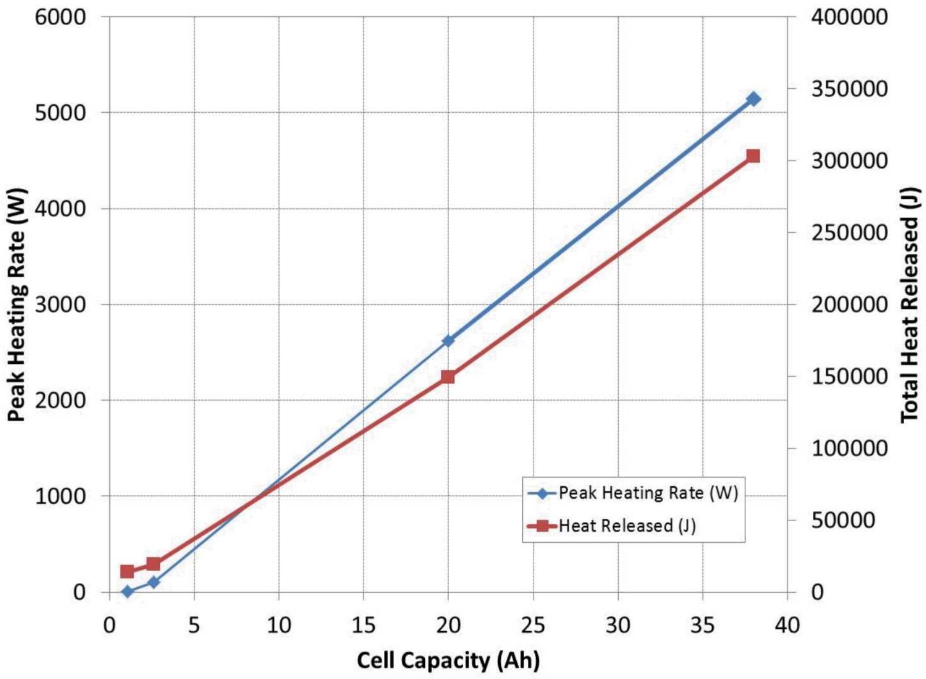


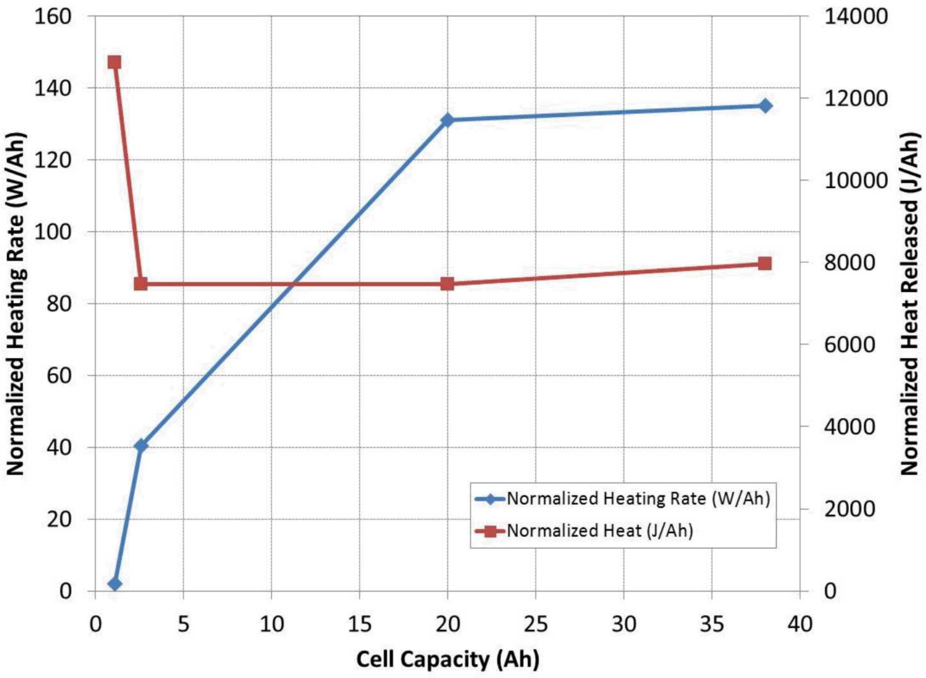
Impact of Cell Size on Runaway



As measured, the LFP cells show the expected trends where larger capacity cells show larger heating rates and larger temperature rise during thermal runaway

Impact of Cell Size on Runaway

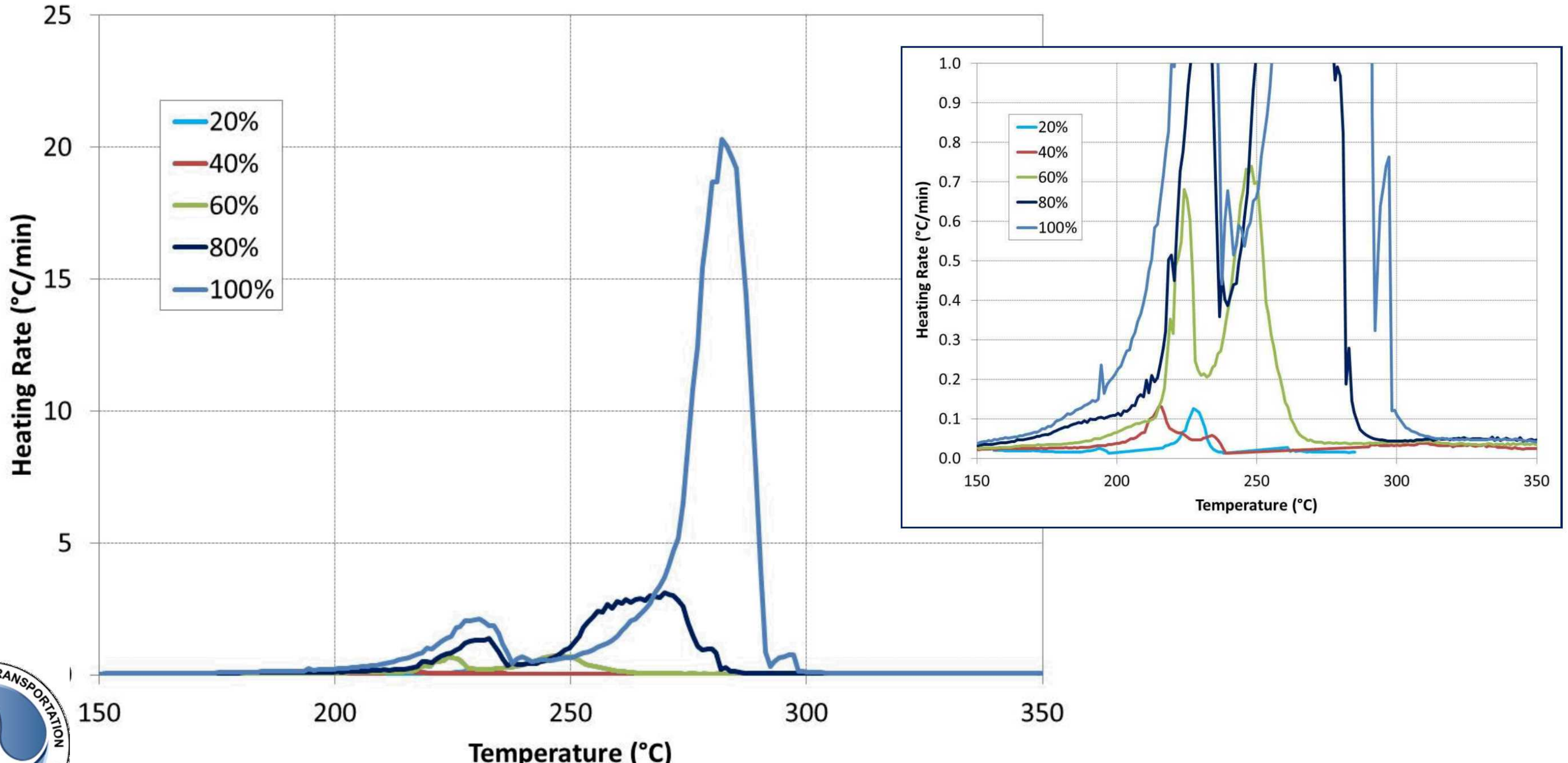




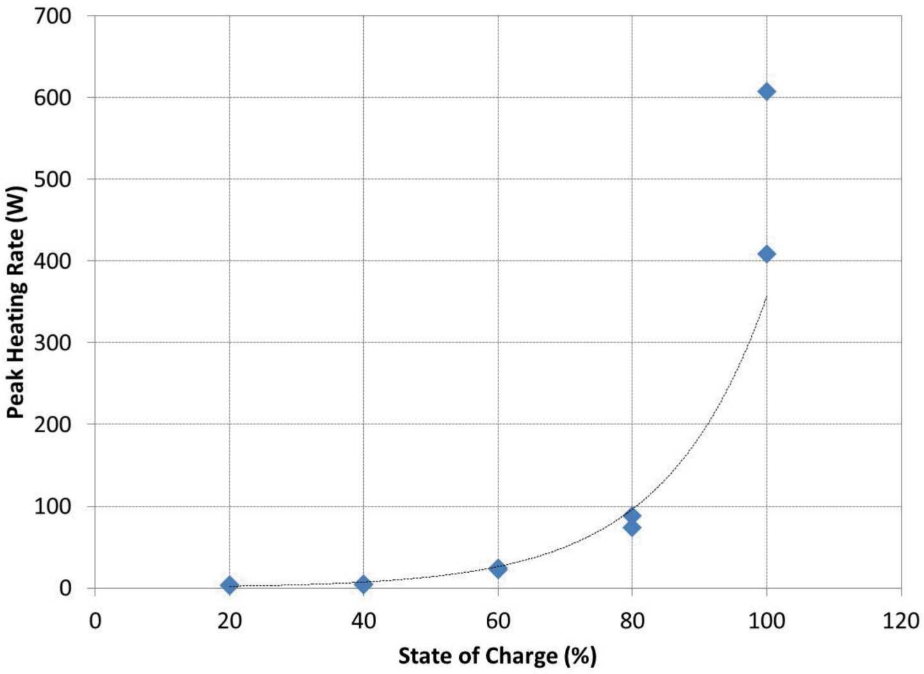
Total heat output and heating rate both scale with increasing cell capacity
Normalized heat output (J/Ah) is almost constant at ~7500-8000 J/Ah for 2.6-38 Ah cells

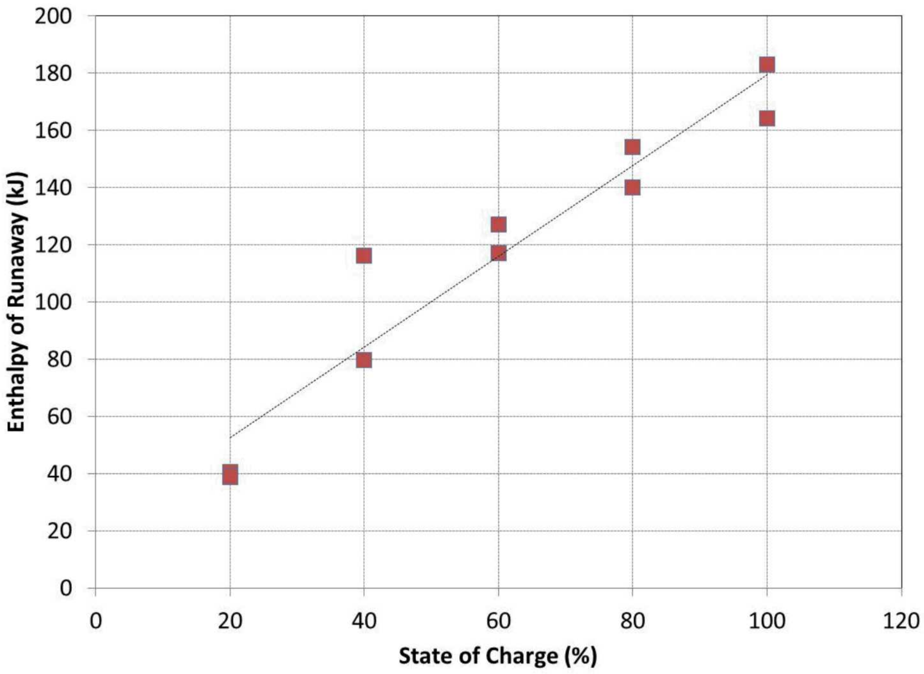
Impact of SOC on Runaway

- ***16 Ah automotive (PHEV) pouch cells (mixed $LiMn_2O_4$ spinel)***
- ***The objective is to provide data to support an acceptable discharge state in dealing with stranded energy in a rechargeable energy storage system (RESS)***



Impact of SOC on Runaway

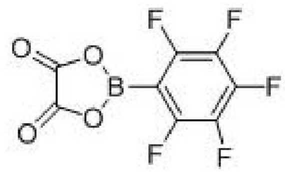




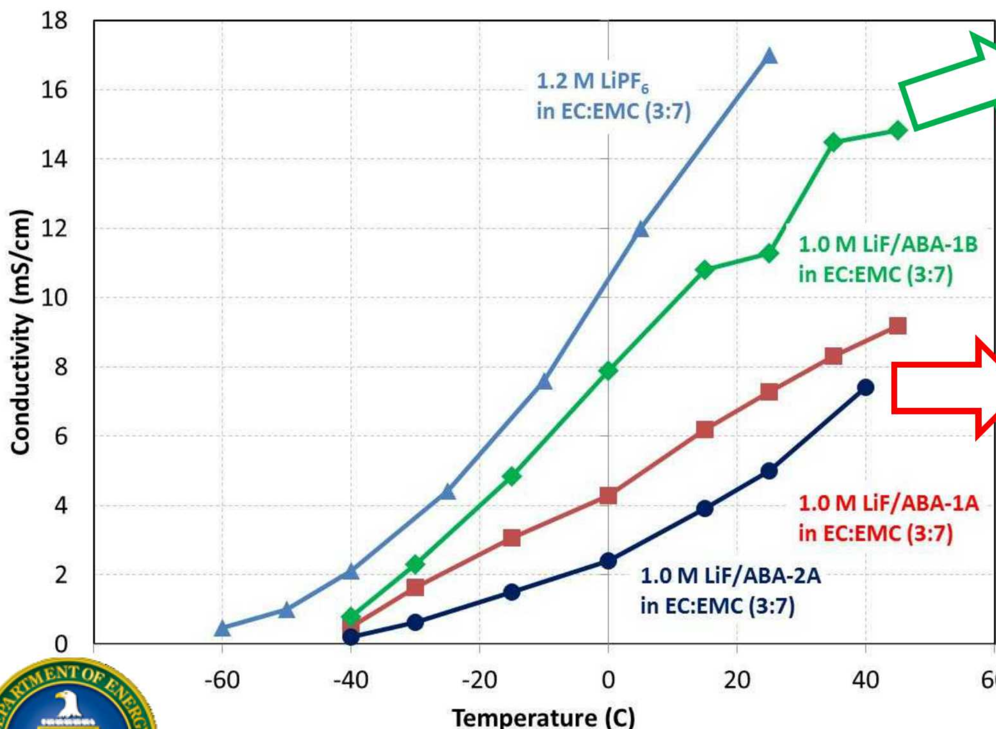
Results show a nearly linear relationship between total heat release (kJ) and cell SOC
Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC
Results show a significant reduction in heat release rate between 40-60% SOC (validates a best practice of handling and shipping cells at ~50% SOC)

Abuse Resilient Components

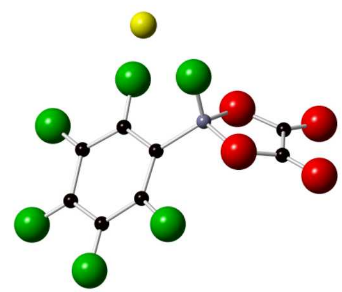
Electrolytes based on LiF and anion binding agents (ABAs)



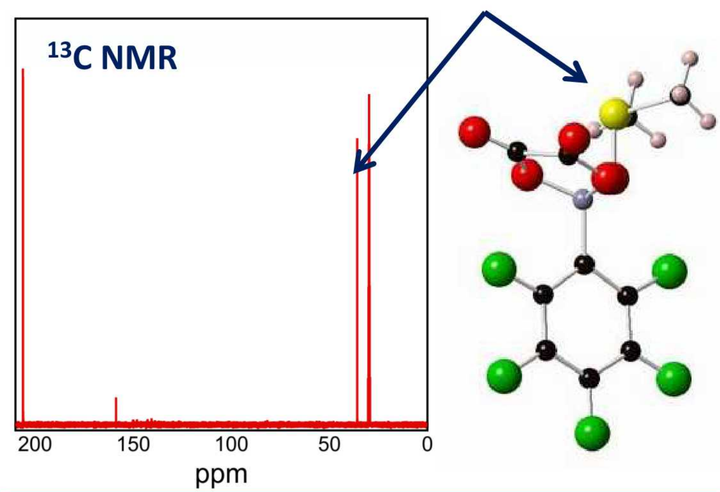
Perfluorophenyloxaltoborate (ABA -1)



Free LiF-ABA



DMSO coordinated to ABA-1A

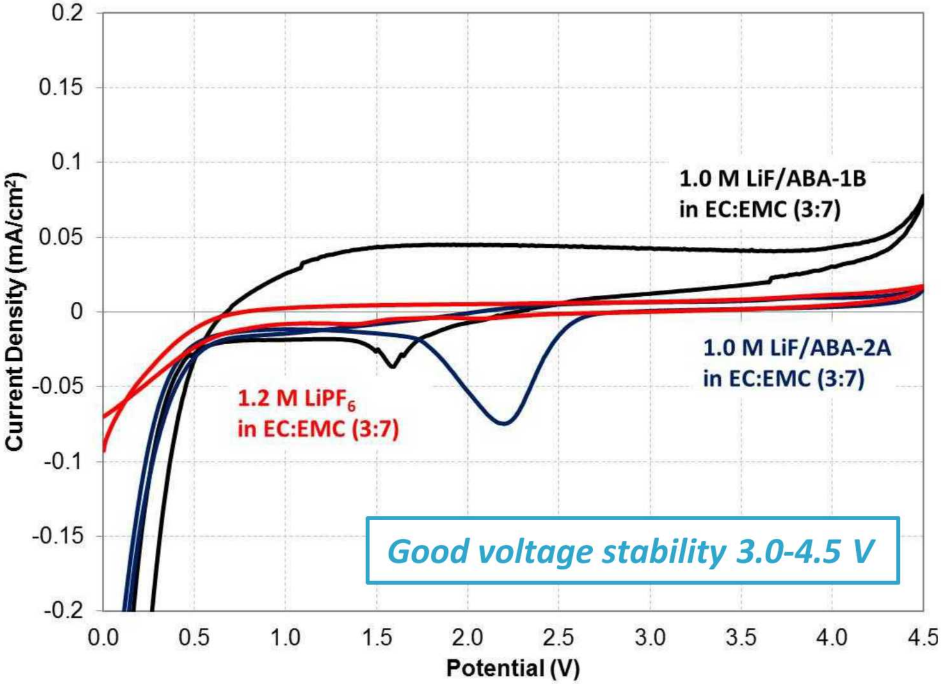


Improved performance of new ABA-based electrolytes

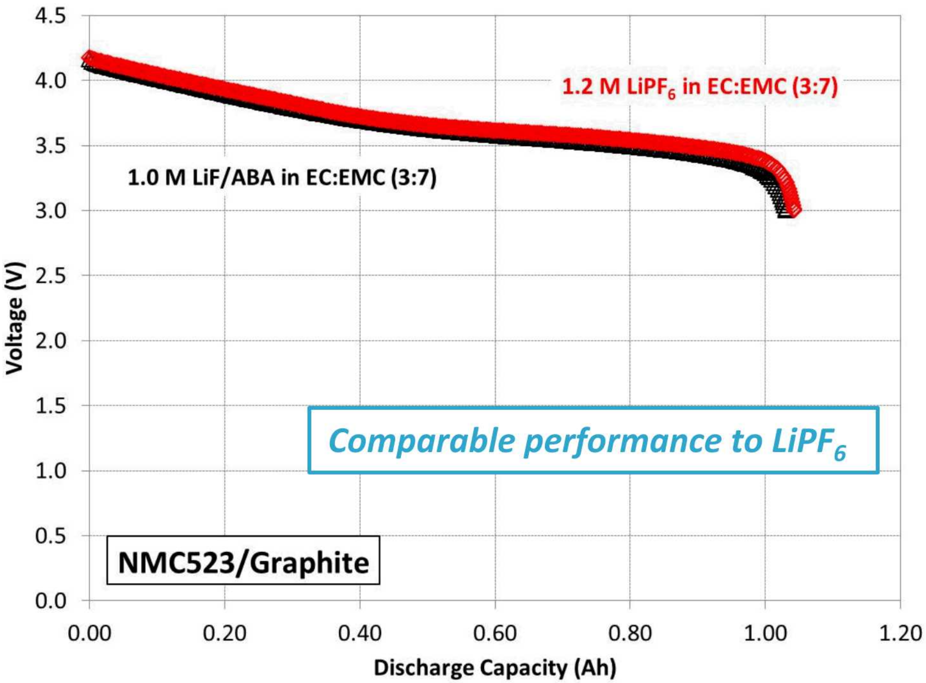
Abuse-Resilient Components

LiF/ABA Electrochemical Performance

Voltammetry of Liquid Electrolytes



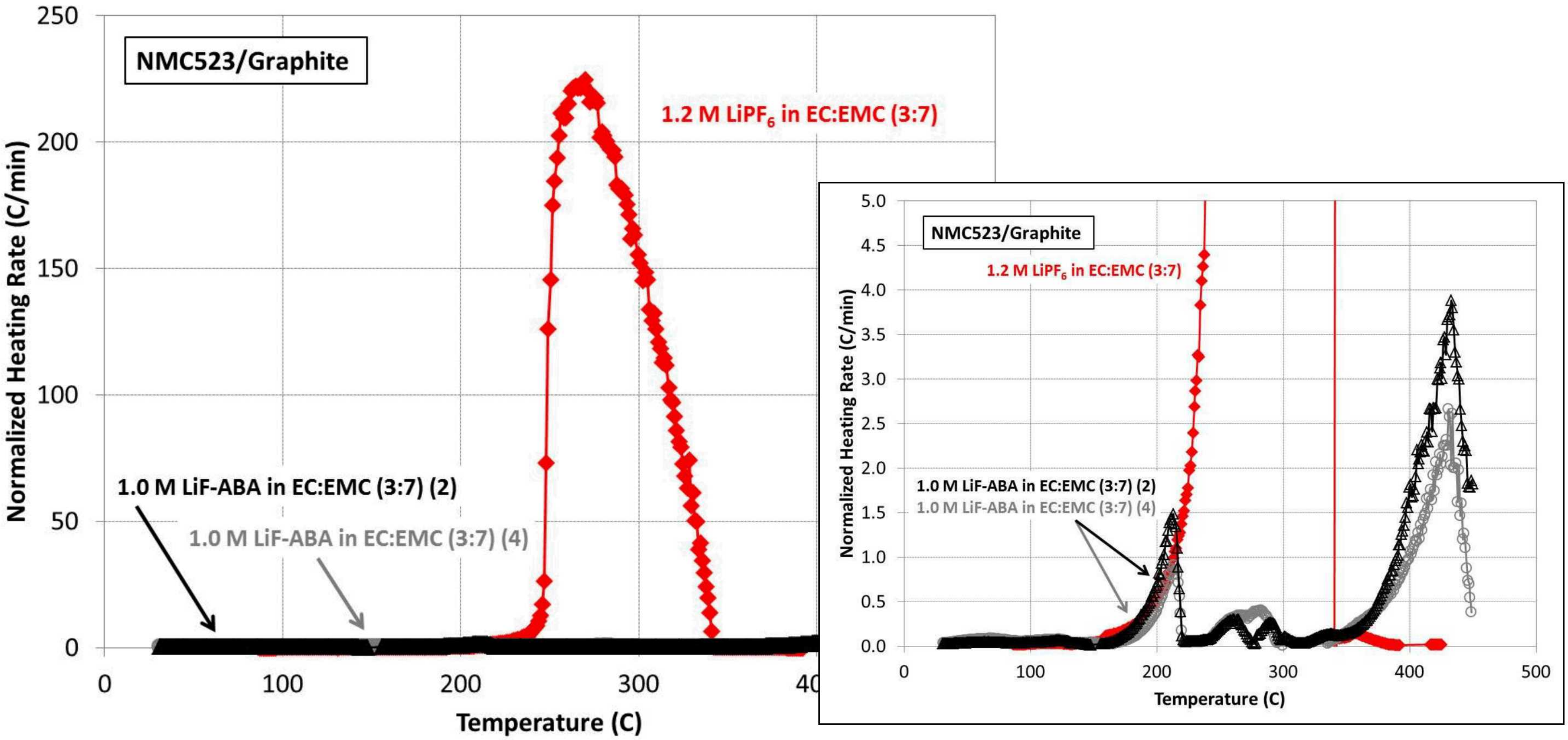
18650 Cell Performance



LiF/ABA electrochemical performance comparable to $LiPF_6$ during 18650 cell formation
ABA-2A voltage stability comparable to $LiPF_6$ at 4.5 V

Abuse-Resilient Components

LiF/ABA Impact on Cell Thermal Runaway Response



High rate cathode thermal runaway is almost completely eliminated with LiF/ABA electrolytes

Advanced Electrolytes

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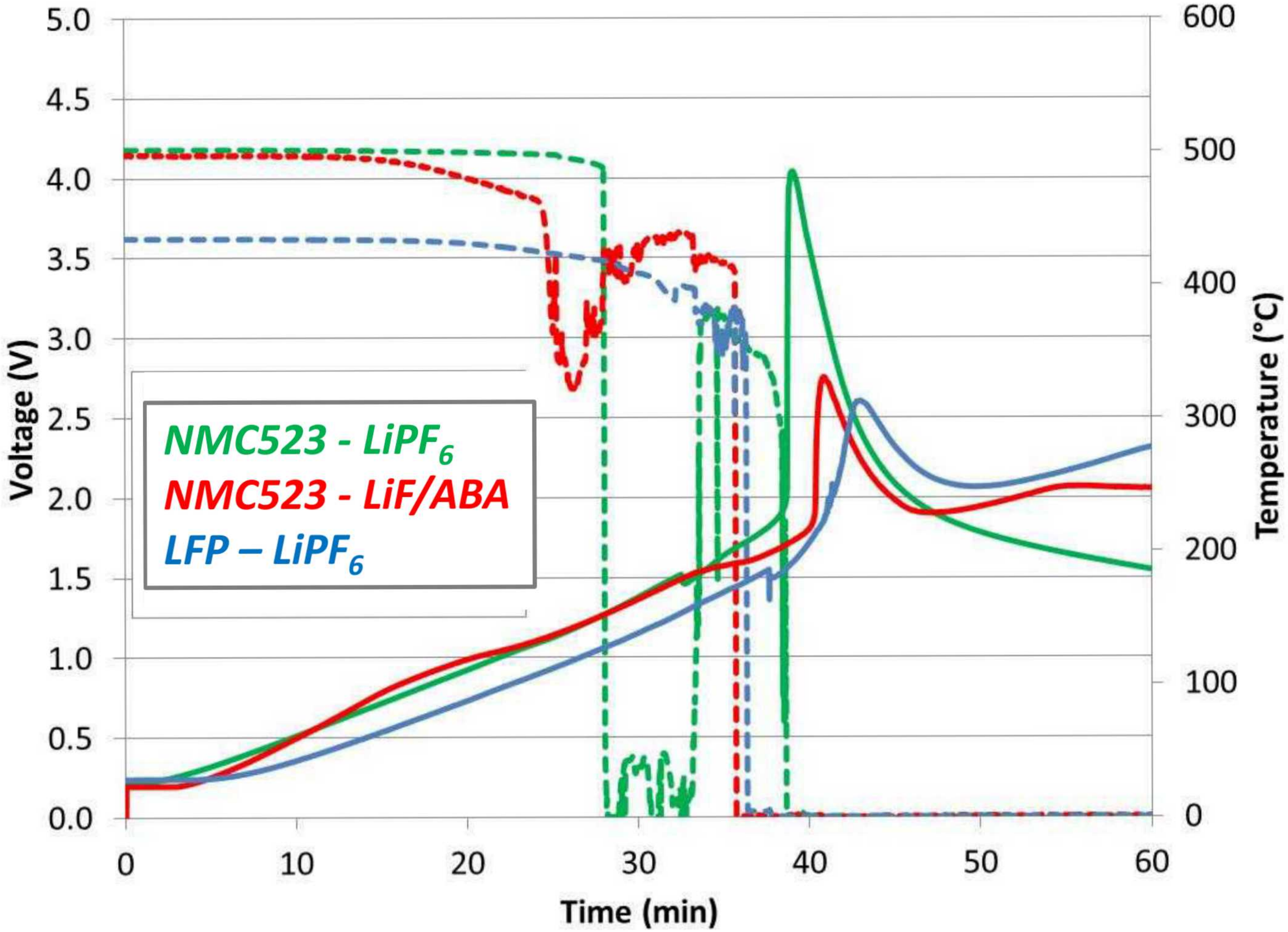
Thermal Abuse Tolerance of LiF/ABA

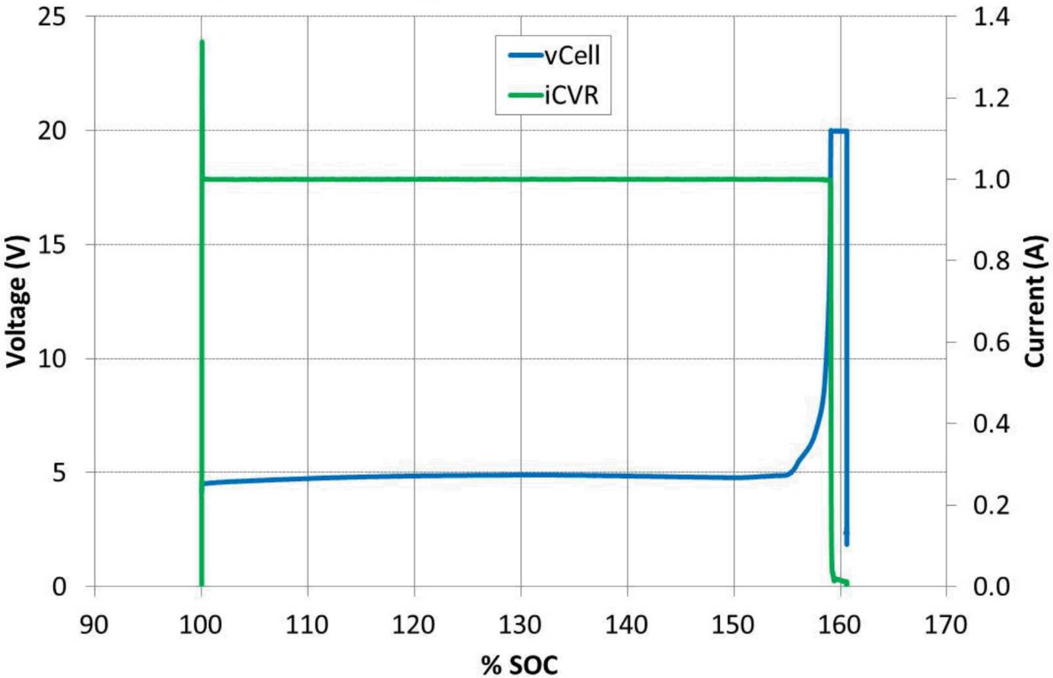


LiF/ABA NMC cells show thermal abuse tolerance comparable to LFP cells

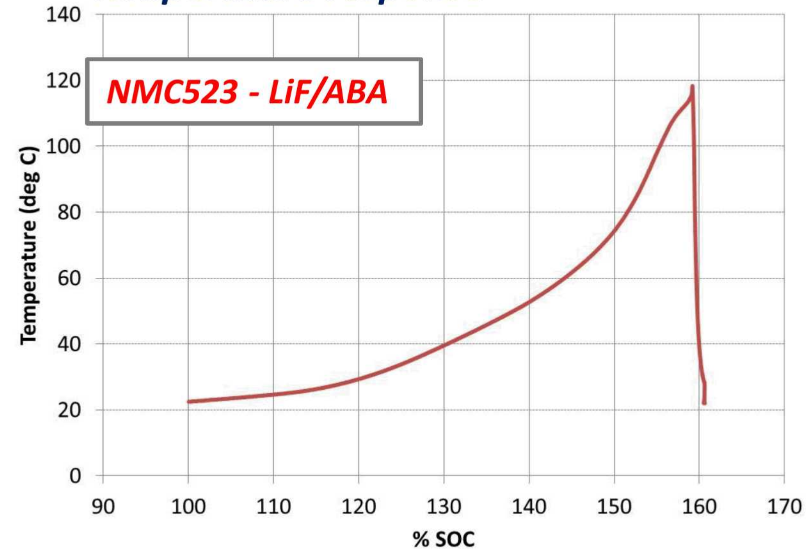
Advanced Electrolytes

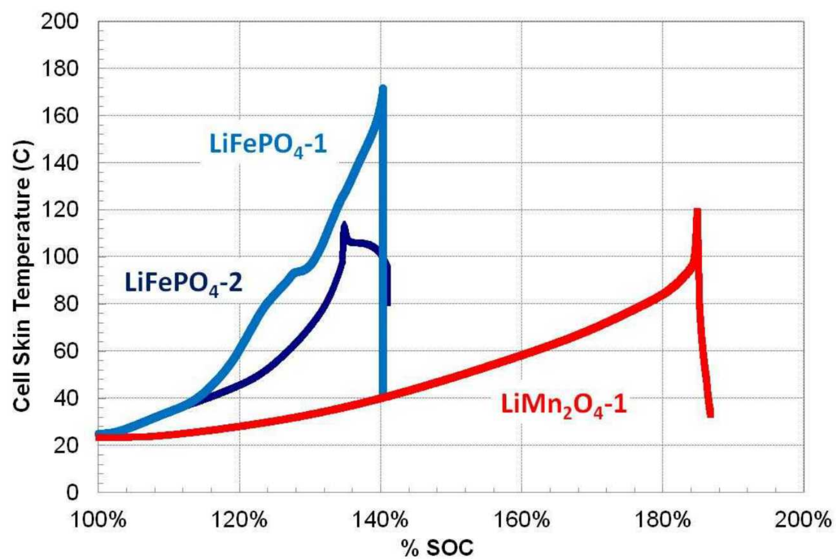
Overcharge Abuse Tolerance of LiF/ABA

Voltage and Charge Current



Temperature response





LiF/ABA NMC cells show consequences of overcharge abuse comparable to LFP cells

Summary

- The total heat output observed from the thermal runaway of LFP cells scaled with increasing capacity; at larger sizes both the heat output and peak heating rate remained fairly constant when normalized to capacity
- Peak heating rates increased rapidly as the cell state of charge increased above 60%, but remained fairly low below that.
- Impedance analysis of abused cells show strong trends in internal resistance for single cells, but changes become more subtle as the cell increases in complexity
- Comparisons of single frequency in the 1-12 Hz range of 1s3p packs have behaviors that correlate to observed abusive behavior
- Parallel configurations of cells show significant discharge through the electrical connections during a single cell failures
  - Contributes significantly to runaway in 18650 packs
- LiF/ABA NMC cells were observed to have overcharge abuse response similar to that of LFP cells

Acknowledgements

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