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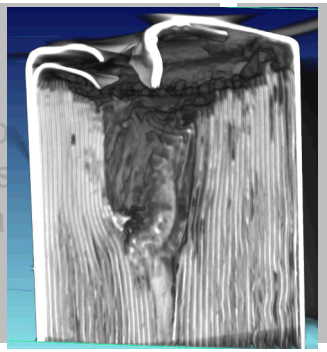

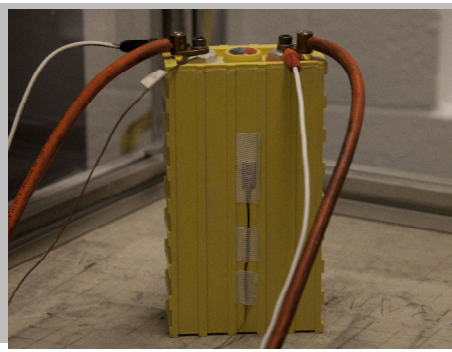

Advances Towards Inherently Safe Lithium-Ion Batteries

Joshua Lamb

AABC 2015, Detroit, MI

June 19, 2015

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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

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2006 Sony/Dell battery recall
4.1 million batteries

2008 Navy, $400M Advanced Seal Delivery Sub, Honolulu

2010 FedEx Cargo Plane Fire, Dubai

2011 NGK Na/S Battery Explosion, Japan (two weeks to extinguish blaze)

2011 Chevy Volt Latent Battery Fire at DOT/NHTSA Test Facility

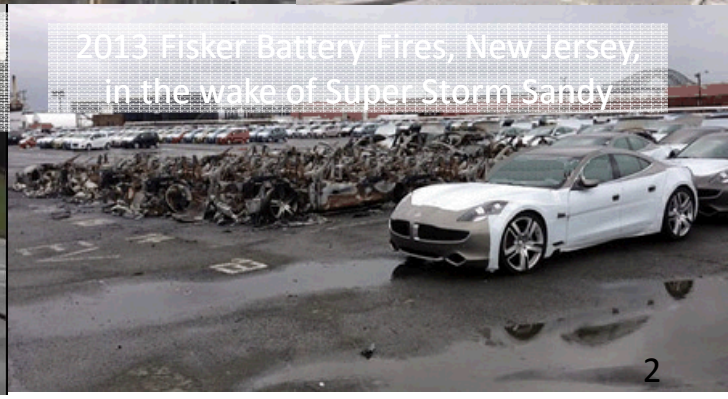
2012 Battery Room Fire at Kahuku Wind-Energy Storage Farm

2012 GM Test Facility Incident, Warren, MI

2013 Storage Battery Fire, The Landing Mall, Port Angeles, (reignited one week after being "extinguished")

2013 Boeing Dreamliner Battery Fires, FAA Grounds Fleet

2013 Tesla Battery Fires, Washington, resulting from a highway accident



2013 Fisker Battery Fires, New Jersey, in the wake of Super Storm Sandy

System-Level Battery Safety

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Field failures could include:

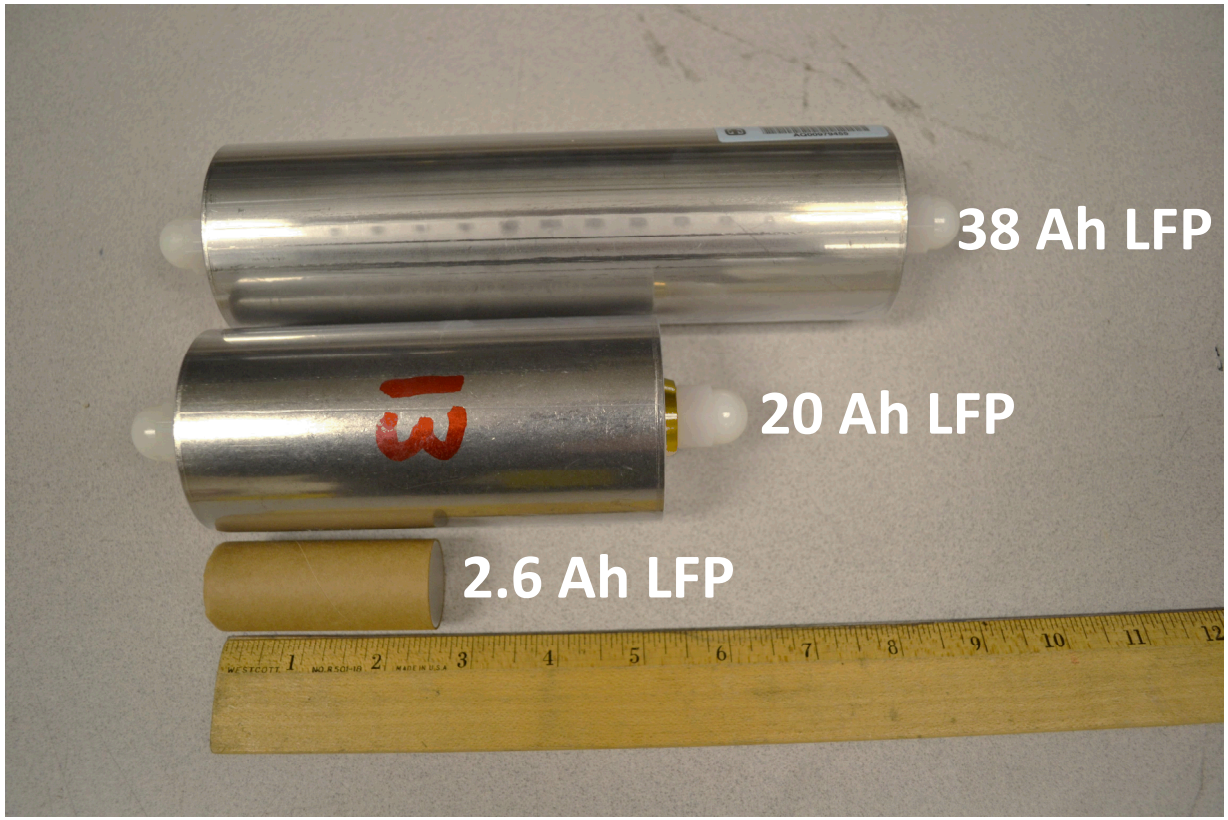
- Latent manufacturing defects
- Internal short circuits
- Misuse or **abuse conditions**
- Ancillary component issues

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

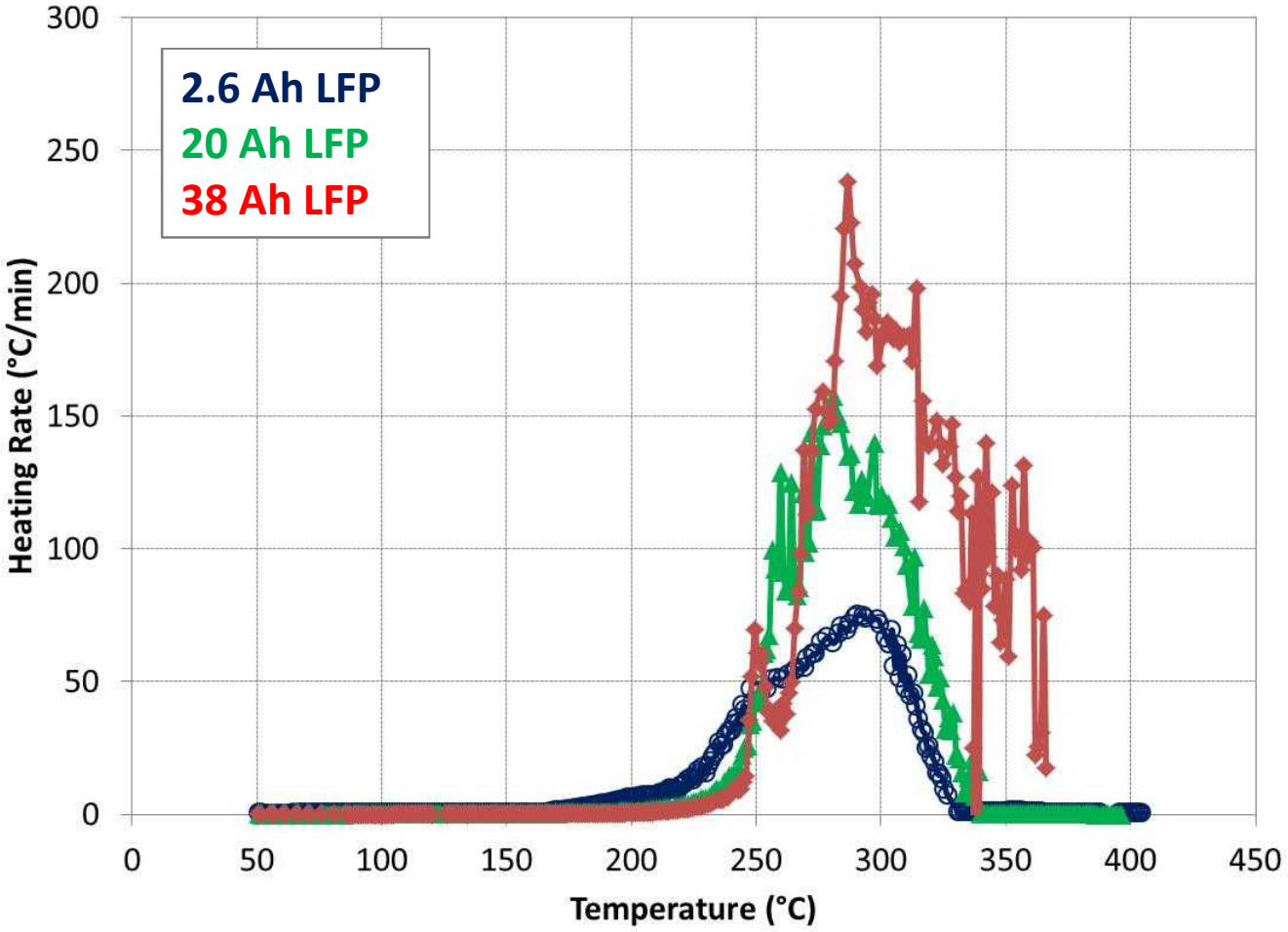
Fisker incident in the wake of Super Storm Sandy , New Jersey, 2012

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*

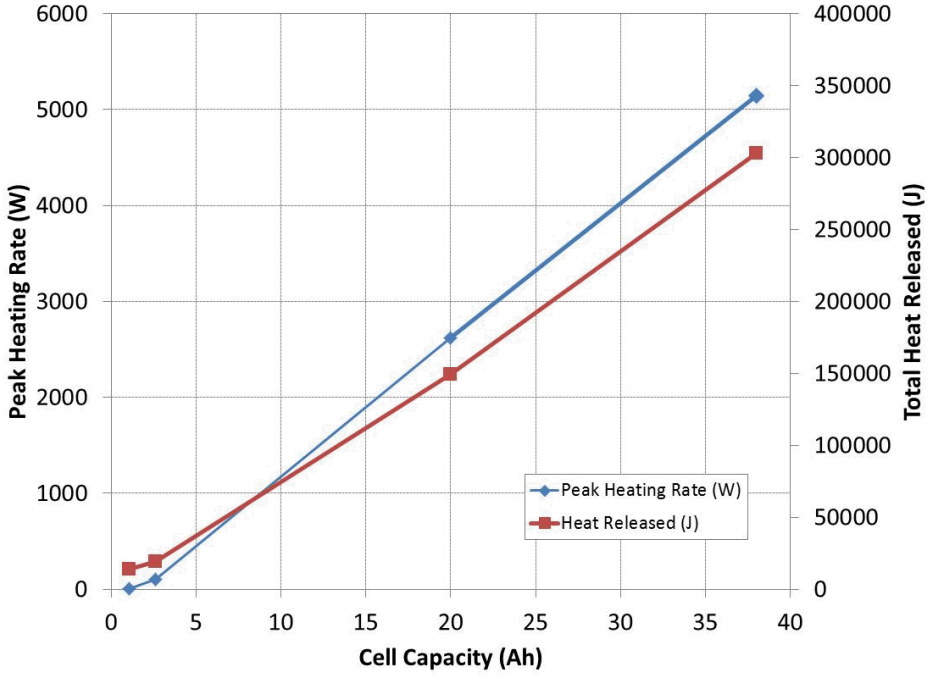


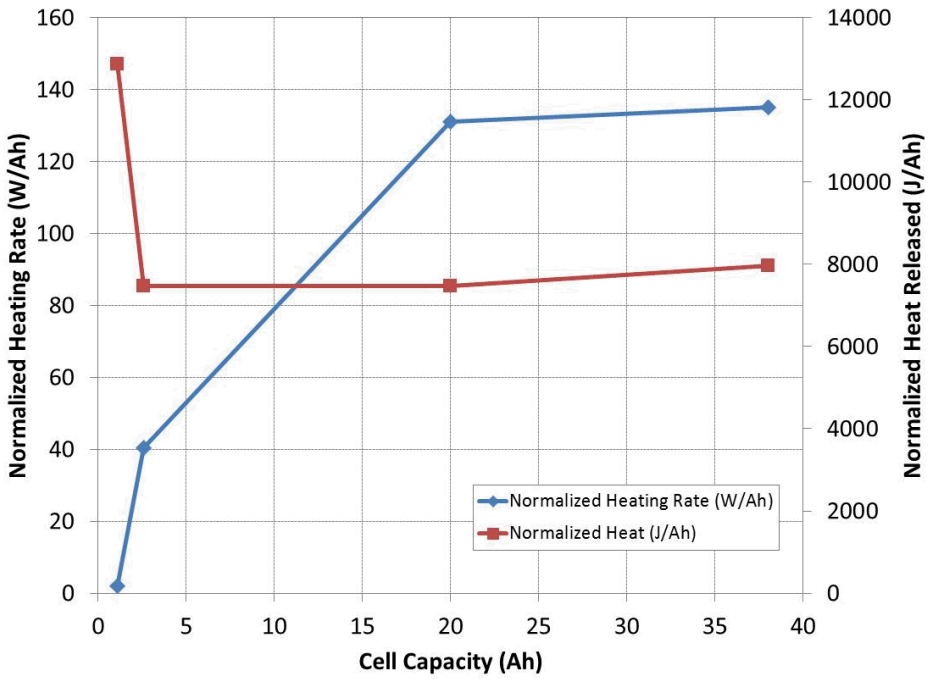
Impact of Cell Size on Runaway



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

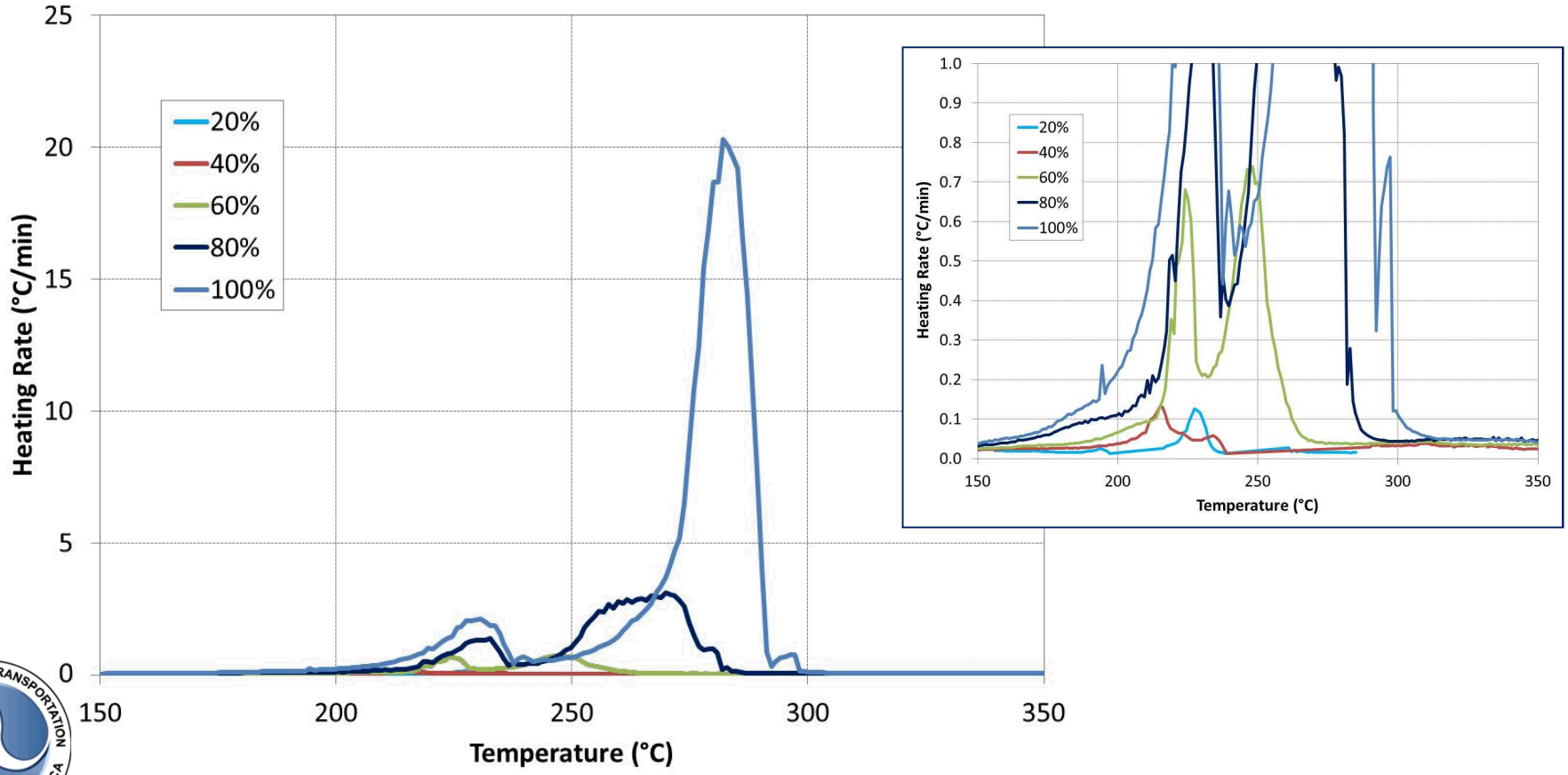




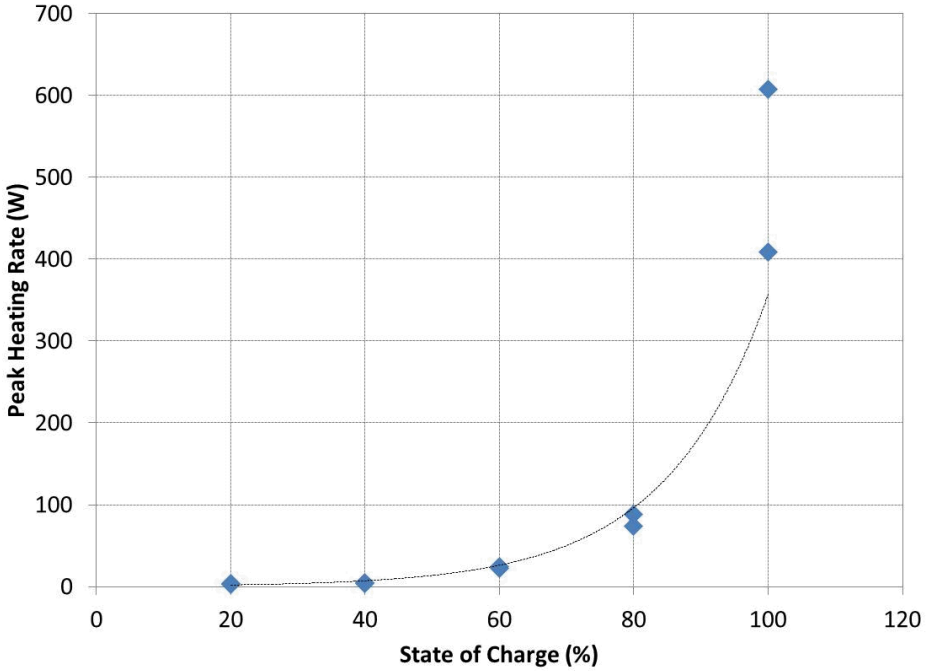
Total heat output and heating rate both scale with increasing cell capacity
Normalized heat output (J/Ah) is almost constant at ~7500-8000 J/Ah for 2.6-38 Ah cells

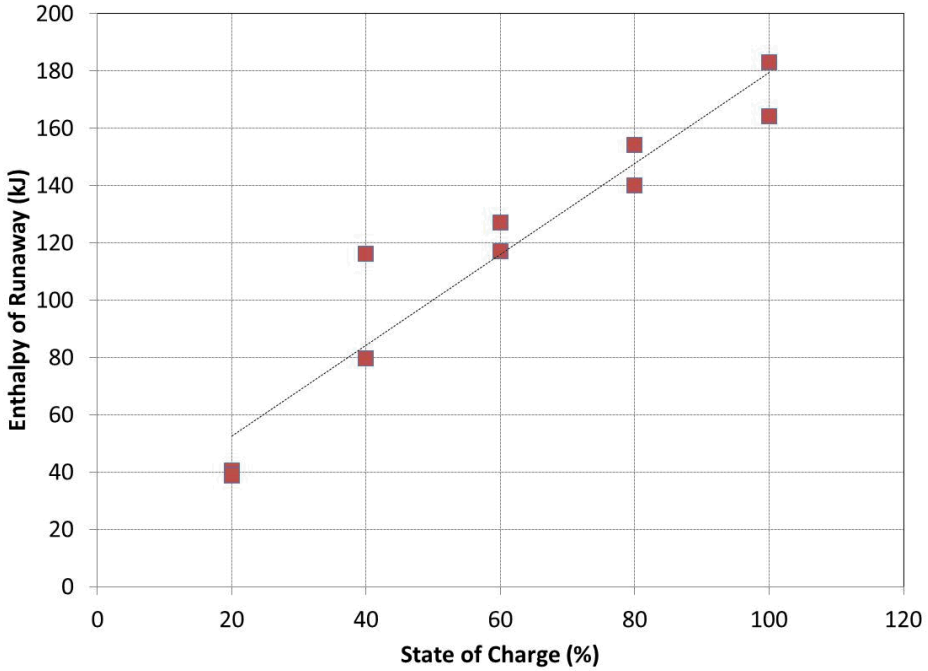
Impact of SOC on Runaway

- ***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)***



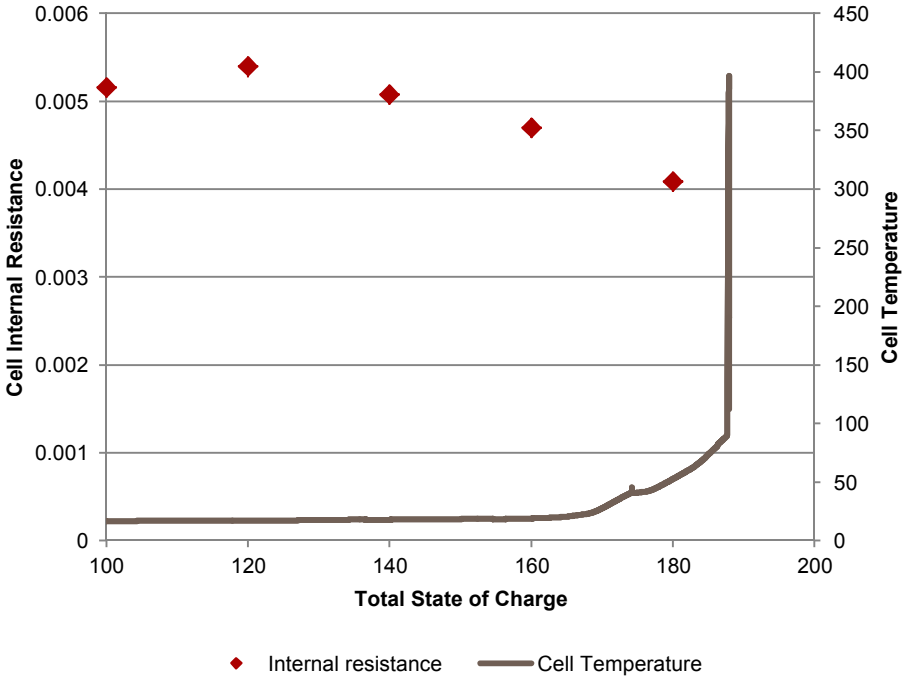
Impact of SOC on Runaway

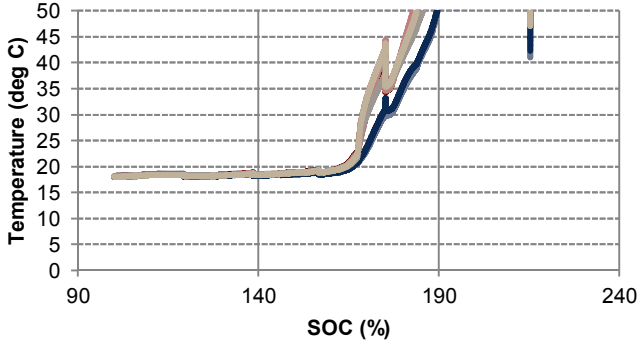


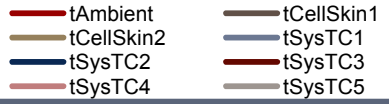


Results show a nearly linear relationship between total heat release (kJ) and cell SOC
Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC
Results show a significant reduction in heat release rate between 40-60% SOC (validates a best practice of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

Safety testing- Diagnostics of Abused Cells

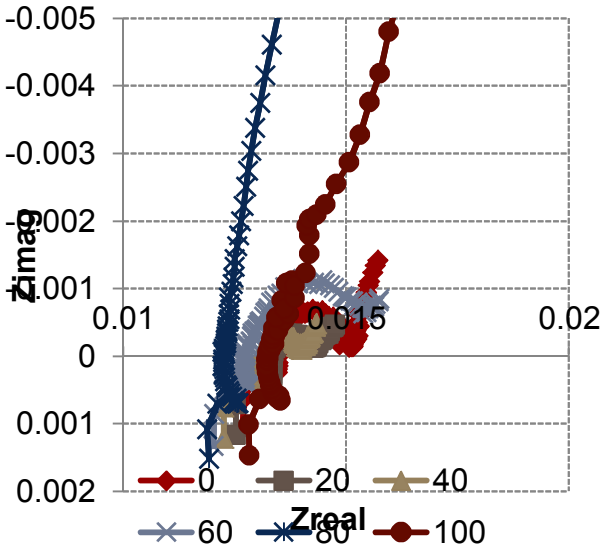






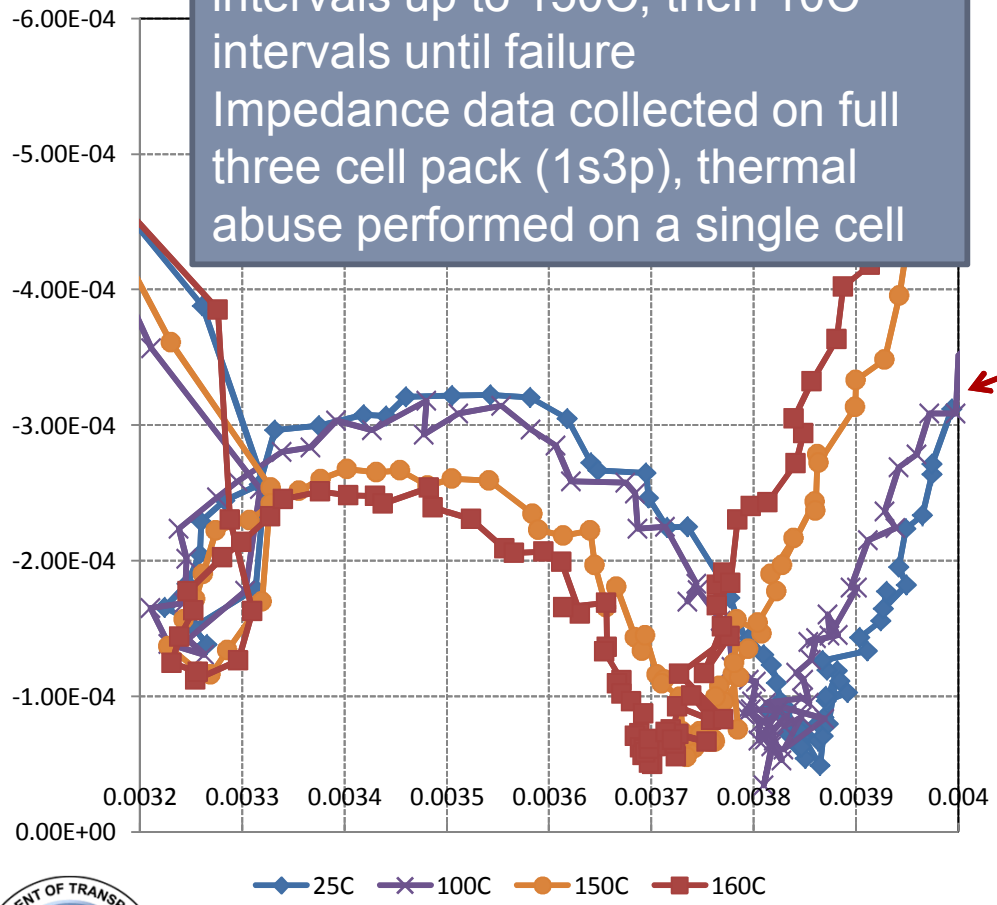
Temperature during testing- Temperature remains close to ambient up to 60% Overcharge, beginning to increase rapidly above 70% overcharge

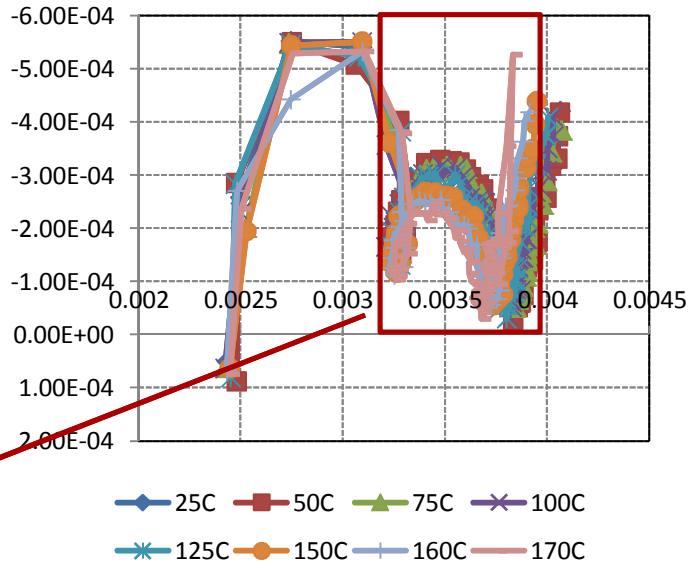
Impedance spectra at increasing states of overcharge Reduction in charge transfer resistance (radii of semicircles) from 0-40% overcharge, similar to impedance changes seen in normal charging, increasing over 60% overcharge.



Parallel Pack Testing

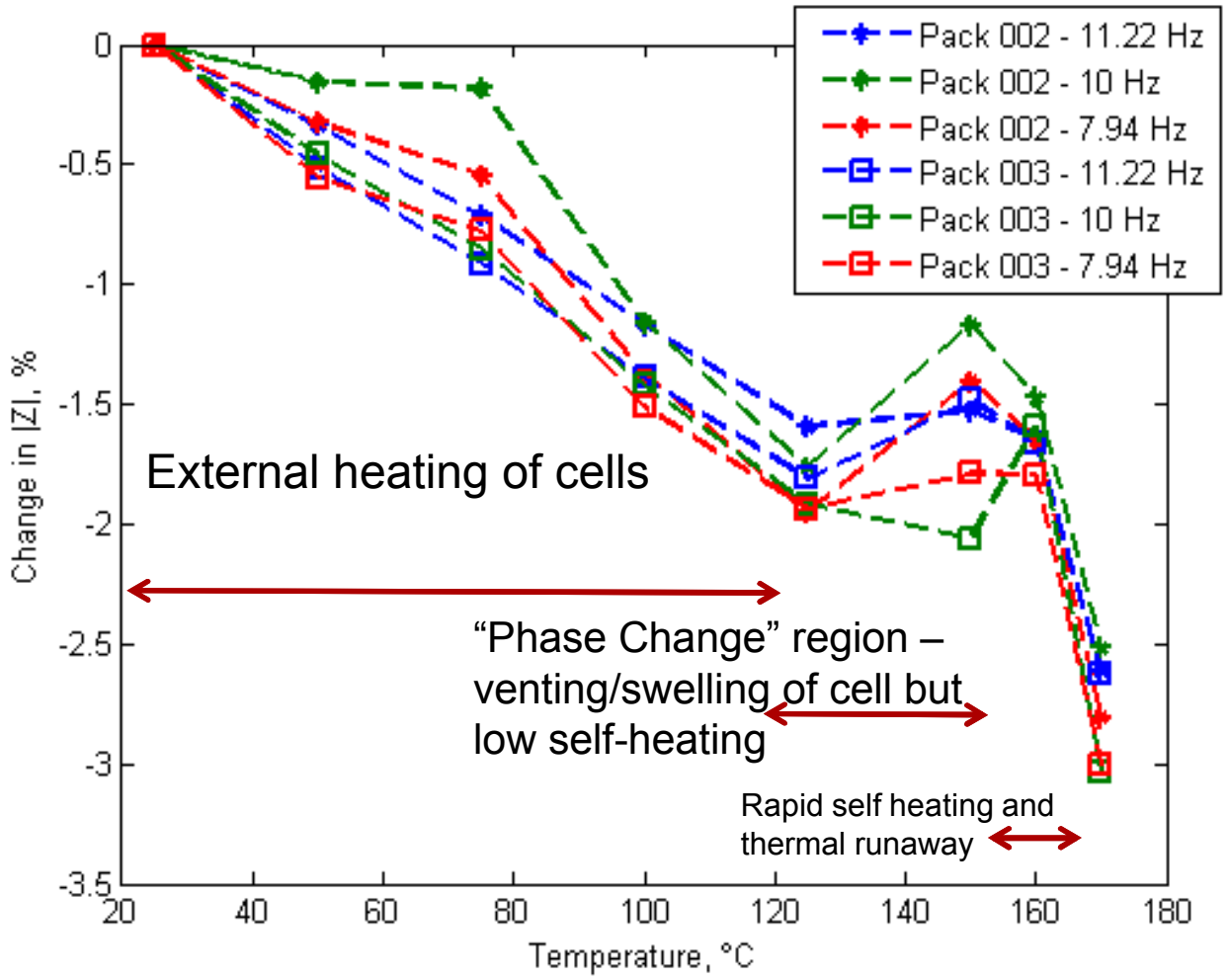
Impedance data collected at 25 C intervals up to 150C, then 10C intervals until failure
Impedance data collected on full three cell pack (1s3p), thermal abuse performed on a single cell





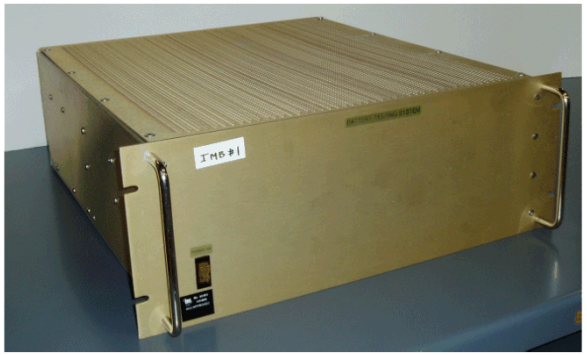
Little change observed up to 100C.
Shifts in R_{CT} observed as temperature increases above 100C.
Thermal runway observed during data collection at 170C

Three cell parallel testing

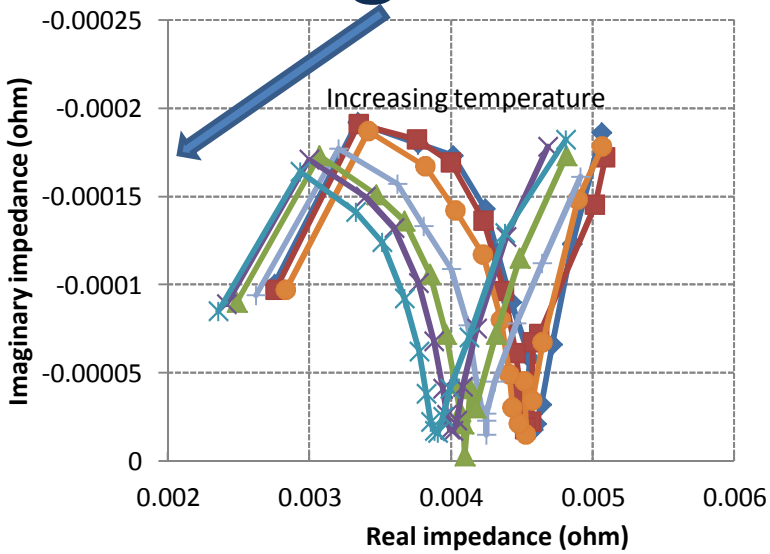


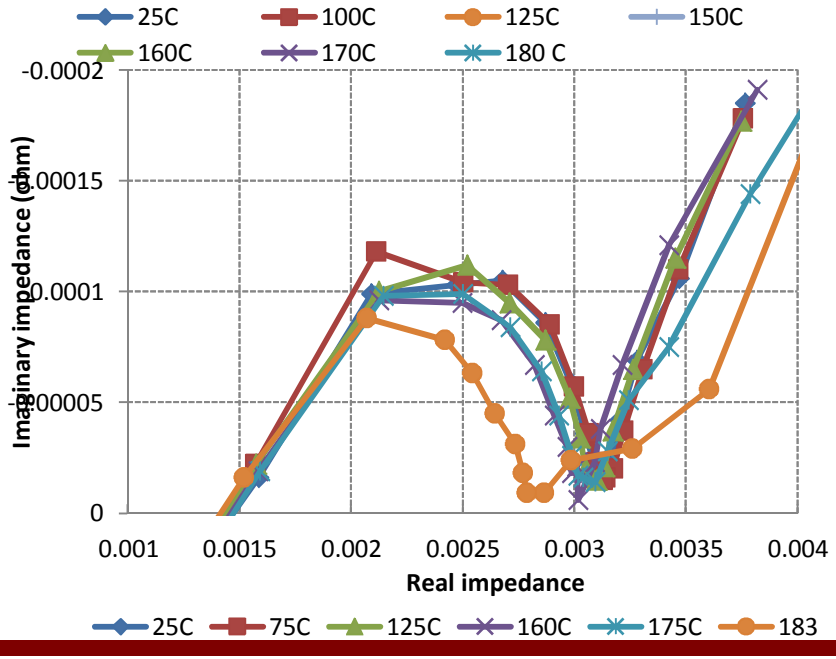
Impedance measurement of entire pack, thermal abuse applied to a single cell within the pack until runaway

Fast impedance monitoring



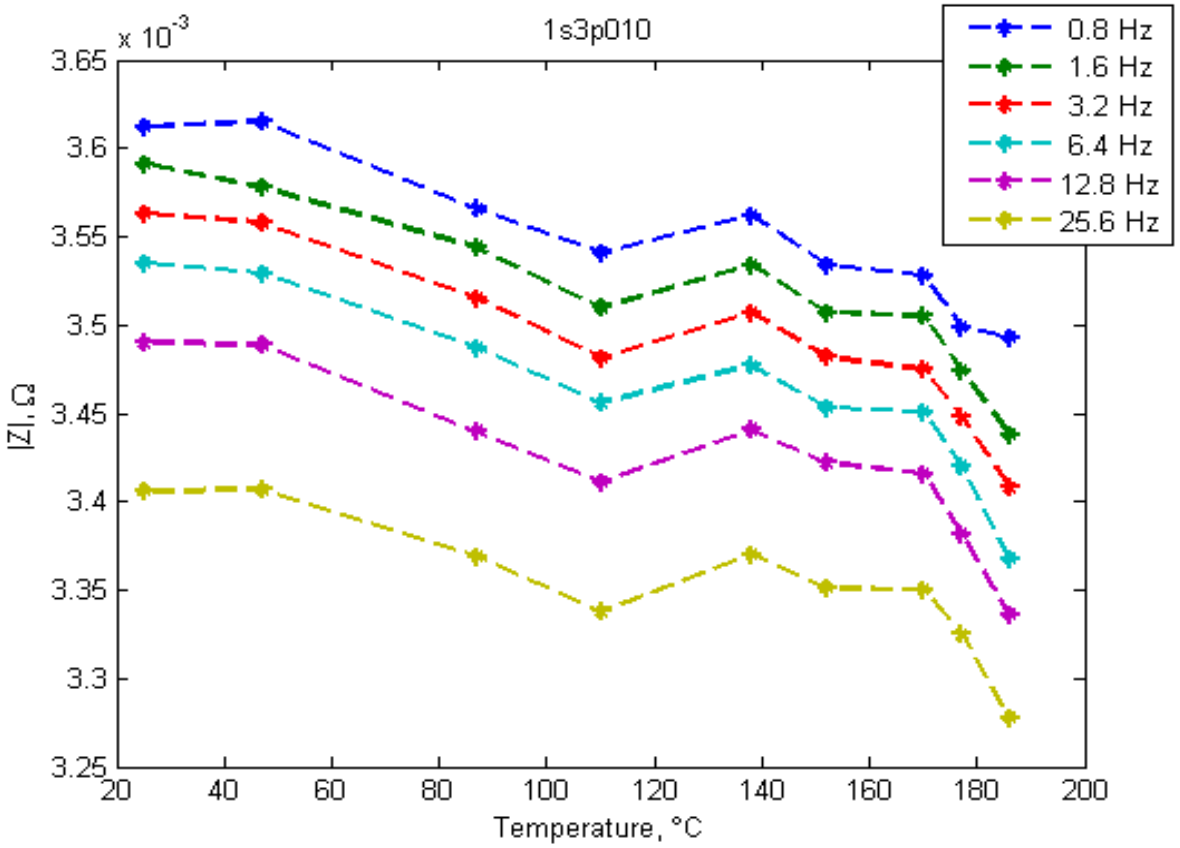
Impedance measurement box developed by INL





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

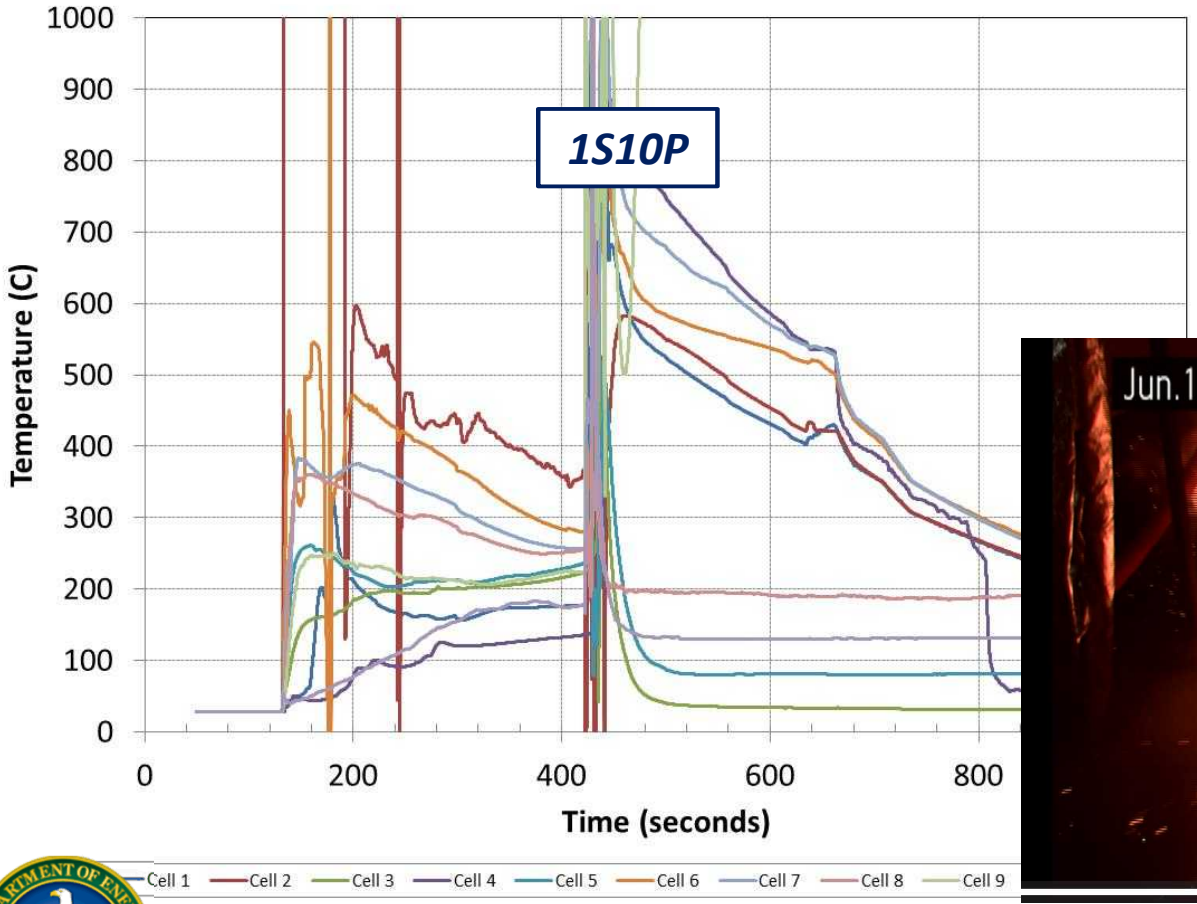
Three cell parallel continuous monitoring

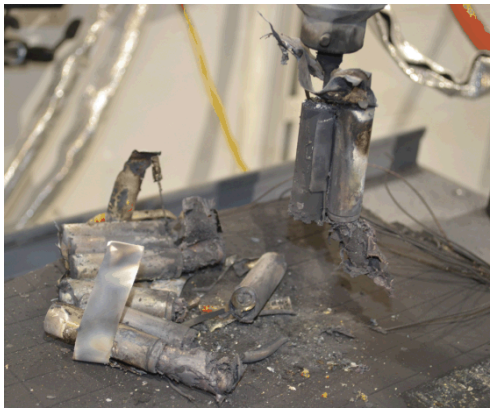


Impedance measurement of entire pack, thermal abuse applied to a single cell within the pack until runaway at a constant rate of 3 °C/min. Similar to behavior observed during step-by-step measurements.

Failure Propagation Testing

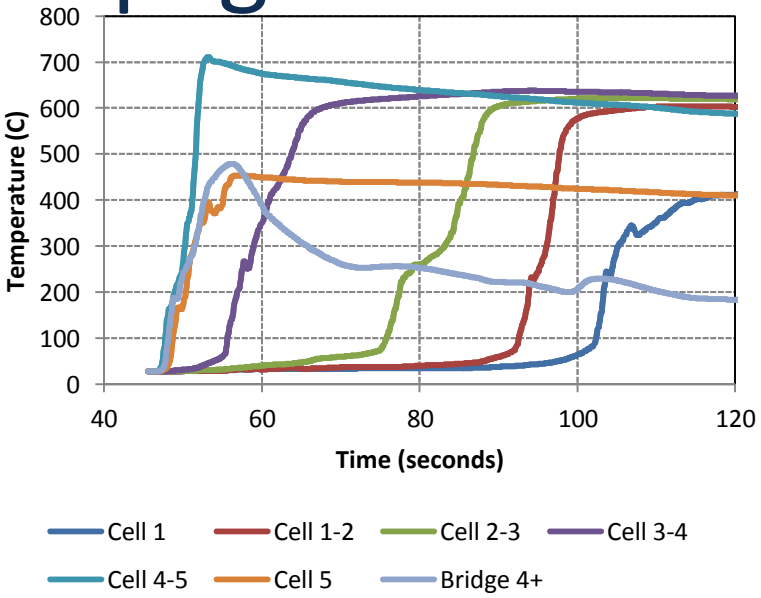
10S1P and 1S10P configurations
2.2 Ah 18650 cell packs (92 Wh at 100% SOC)
Failures initiated by mechanical insult to the center cell (#6)

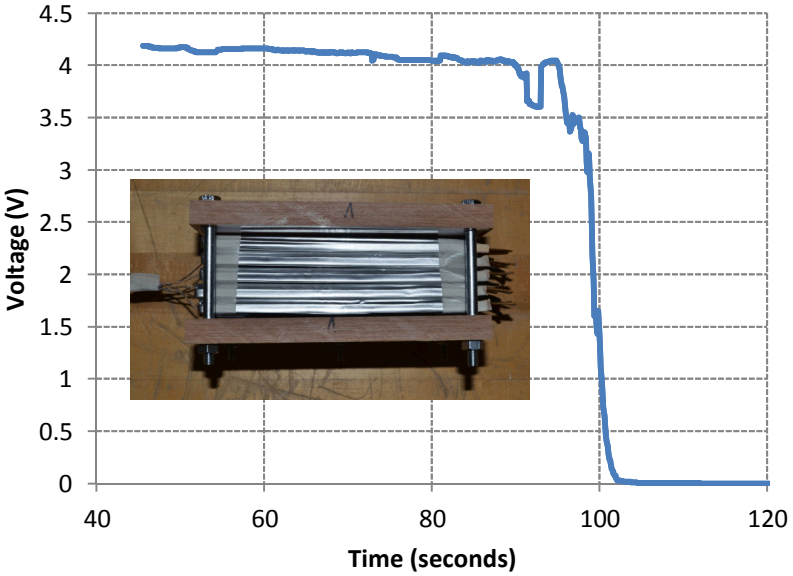


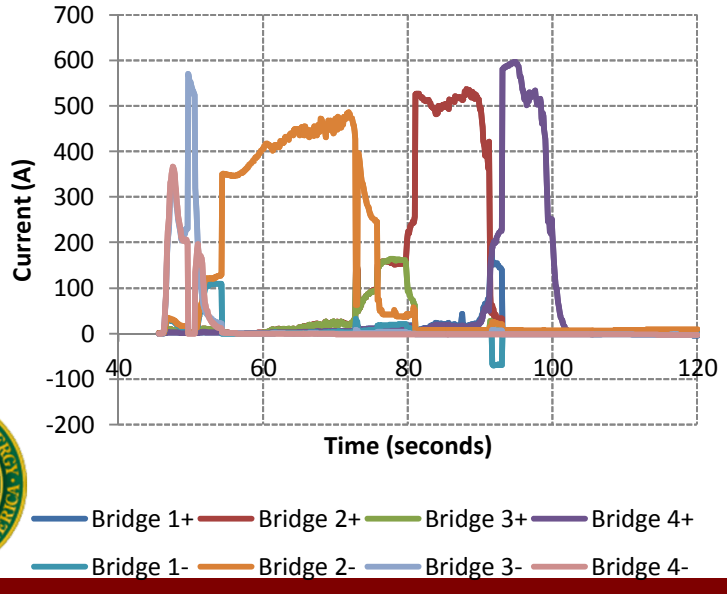


Complete propagation of a single point failure in the 1S10P pack

Propagation Testing (1S5P)



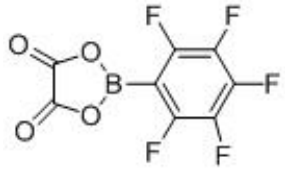




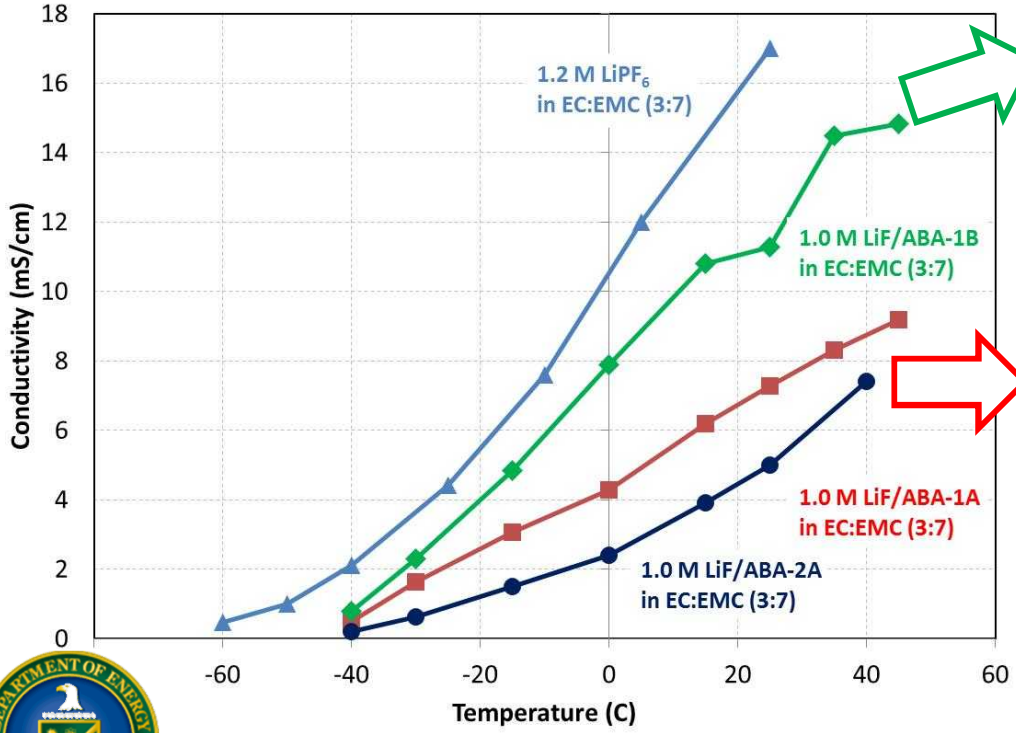
- Failure and runaway initiated at Cell #1
- Heat flux gauge data collected 32” from pack
- Temperature corrected current flowing through bridges

Abuse Resilient Components

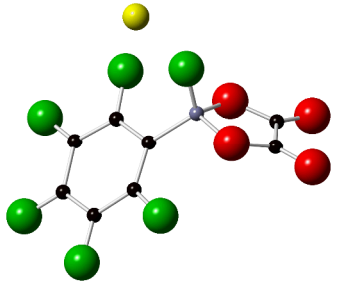
Electrolytes based on LiF and anion binding agents (ABAs)



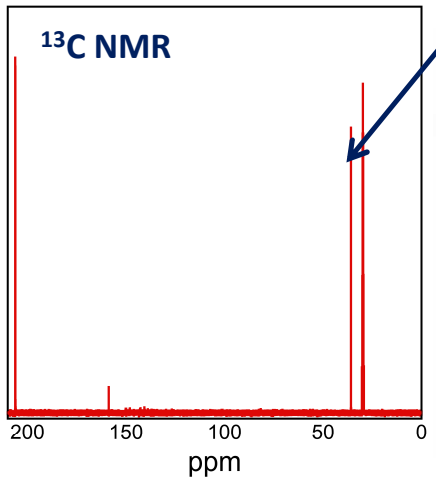
Perfluorophenyloxaltoborate (ABA -1)



Free LiF-ABA



DMSO coordinated to ABA-1A

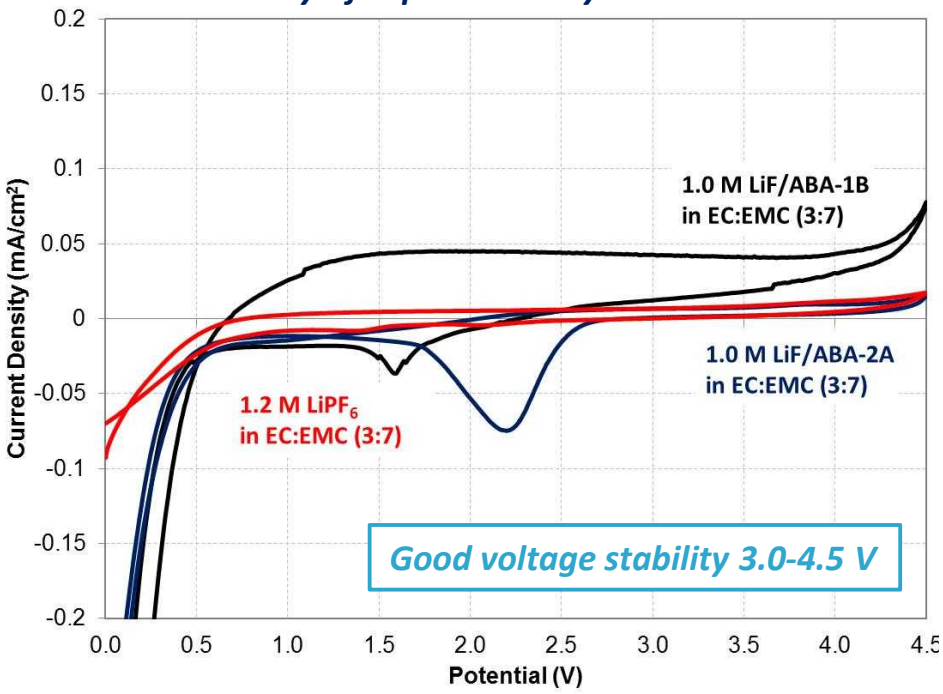


Improved performance of new ABA-based electrolytes

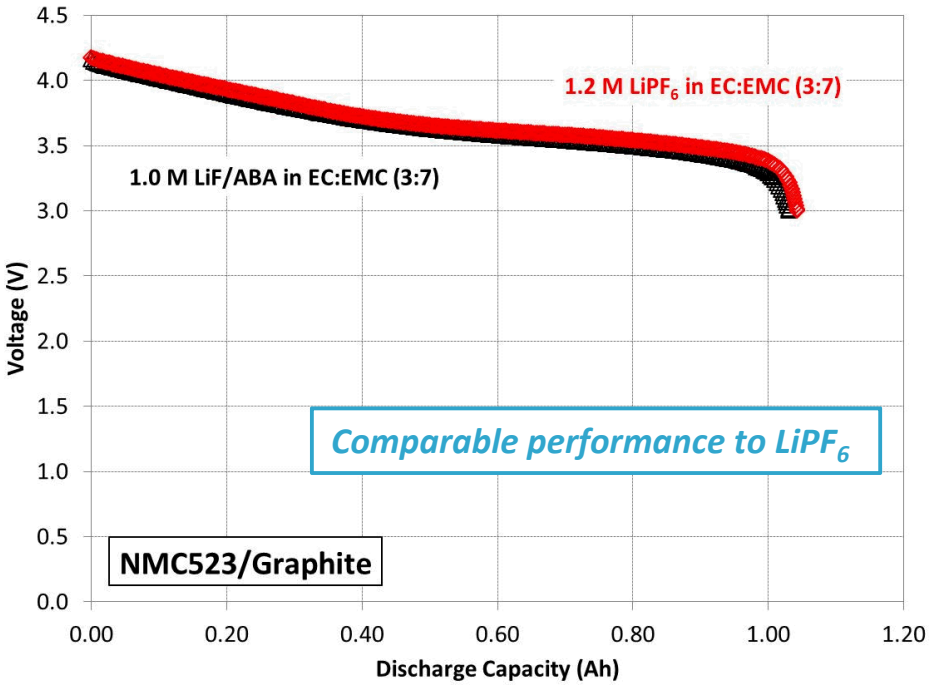
Abuse-Resilient Components

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

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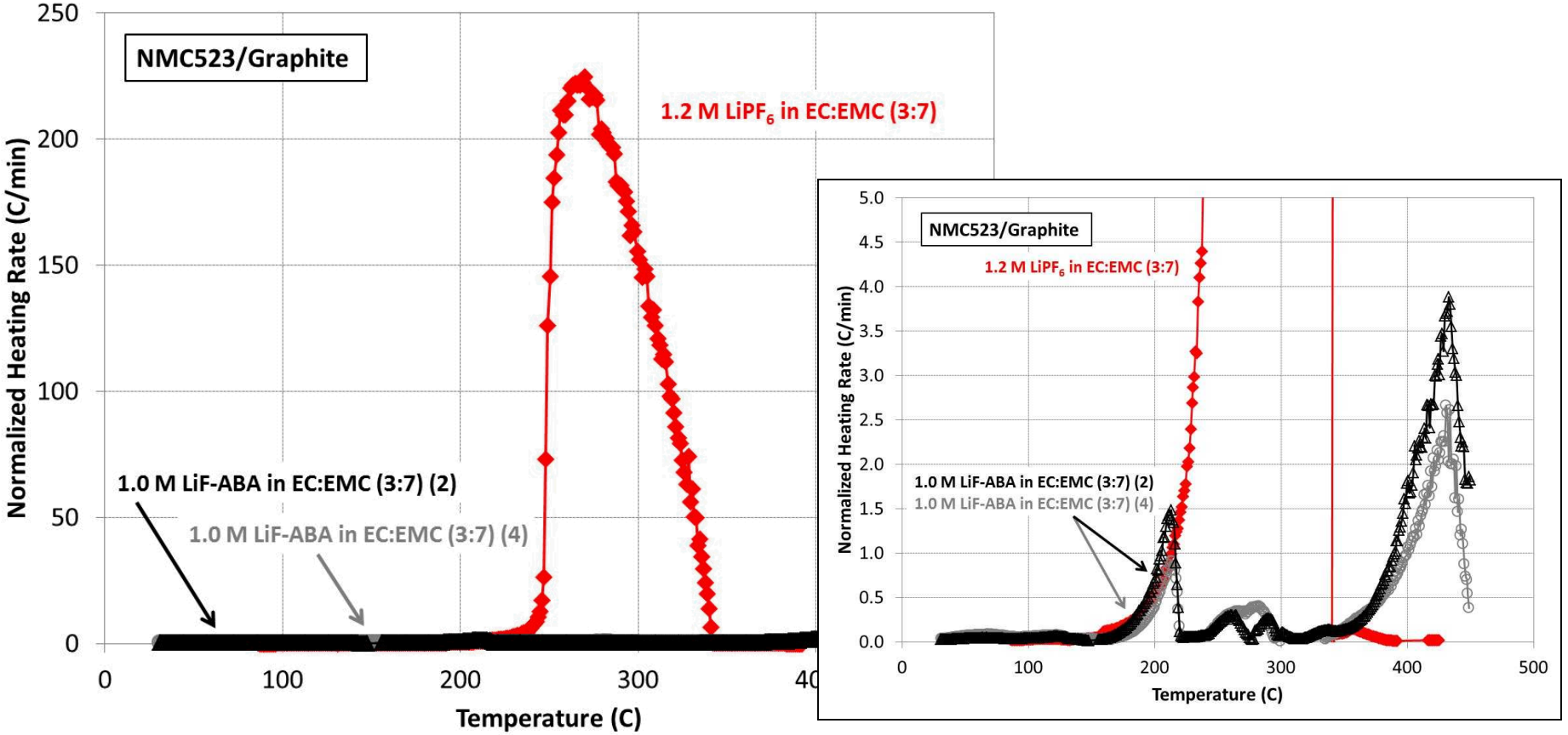
LiF/ABA Impact on Cell Thermal Runaway Response



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

Advanced Electrolytes

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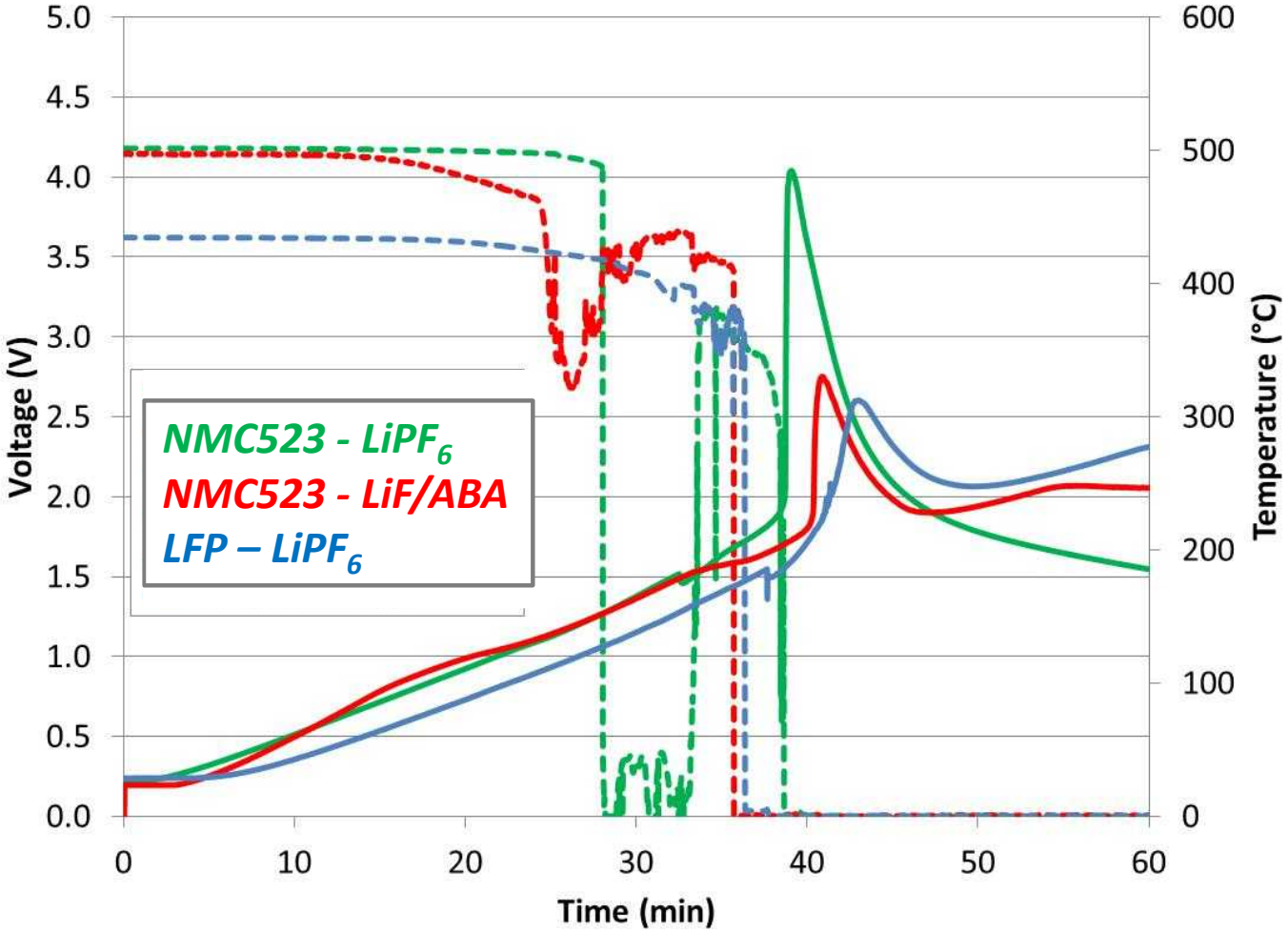
Thermal Abuse Tolerance of LiF/ABA



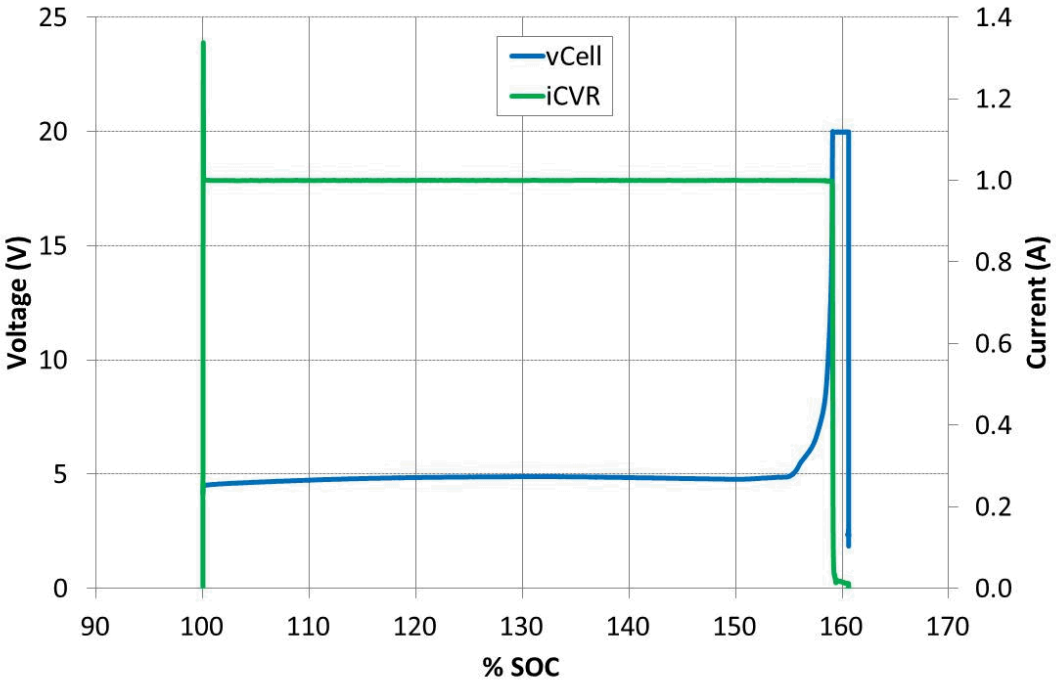
LiF/ABA NMC cells show thermal abuse tolerance comparable to LFP cells

Advanced Electrolytes

Sandia National Laboratories

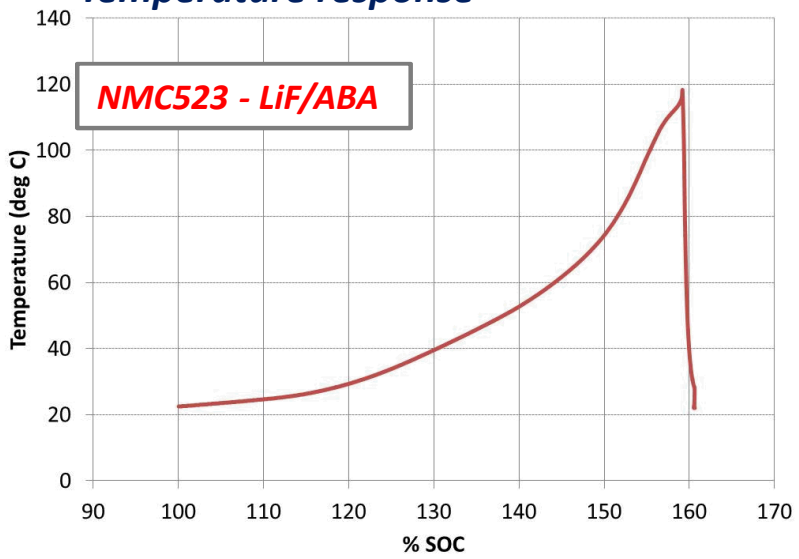
Overcharge Abuse Tolerance of LiF/ABA

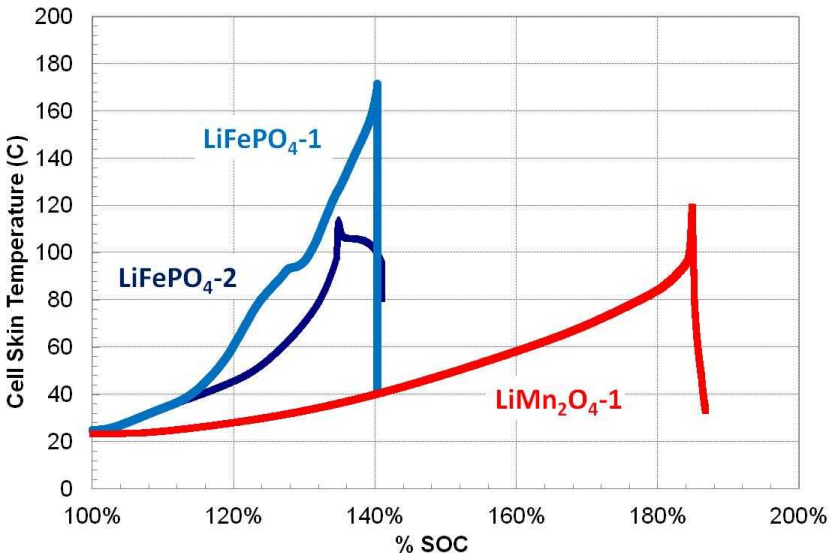
Voltage and Charge Current



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

Temperature response





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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