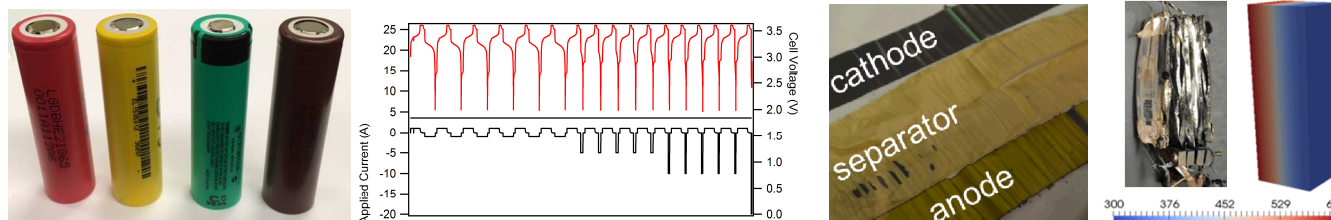


Battery Failure from a Materials, Electrochemical and Thermal Modeling Perspective



PRESENTED BY

Summer Ferreira

Gordon Research Conference – Batteries

February 27, 2018



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Impact and consequence of scale on safety

- Scale and size
- Use condition



**Consumer Cells
(0.5-5 Ah)**



**Large Format Cells
(10-200 Ah)**



**Transportation
Batteries (1-50
kWh)**

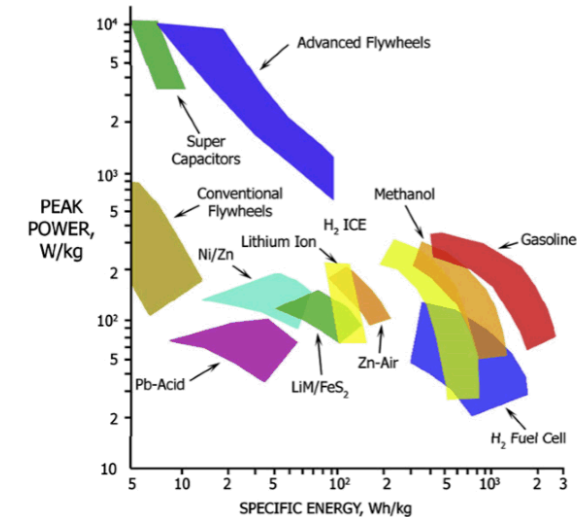
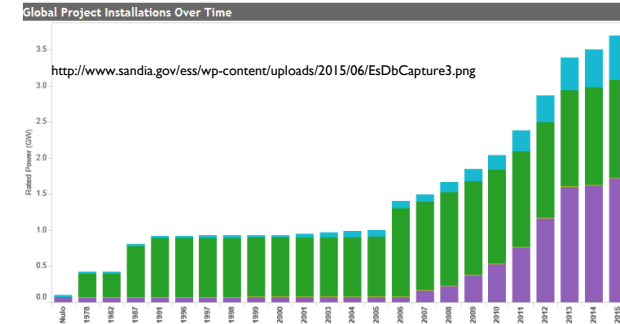


**Utility Batteries
(MWh)**

Safety issues and complexity increase with battery size

The Grid Energy Storage Safety Challenge

- Scale and size
- Use condition
- Variety of technologies
- Proximity to population
- Design considerations
- System complexity



Key Challenges:

Utility safety incidents have highlighted the **need for a focused effort** in safety.

Currently urban penetration is stalled in



Key Challenges:

Research aims to impact on near term barriers to adoption of grid storage

Safety is about reducing risk:

Where risk encompasses consequence and likelihood



Field failure

- Random
- Often the result of manufacturing defects that are difficult to predict or recreate
- Historically the greater concern to battery manufacturers

Abuse failure

- Caused by an external stimulus that pushes a cell outside its safe operating conditions
- Can generally be grouped as: Thermal, Electrical and Mechanical abuse
- Traditionally a laboratory curiosity – performed due to convenience rather than accurate recreation of conditions

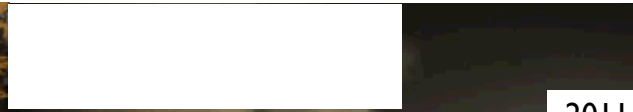


Energy Storage Safety/Reliability Issues

Have Impact Across Multiple Application Sectors



2006 Sony/Dell battery recall
4.1 million batteries



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



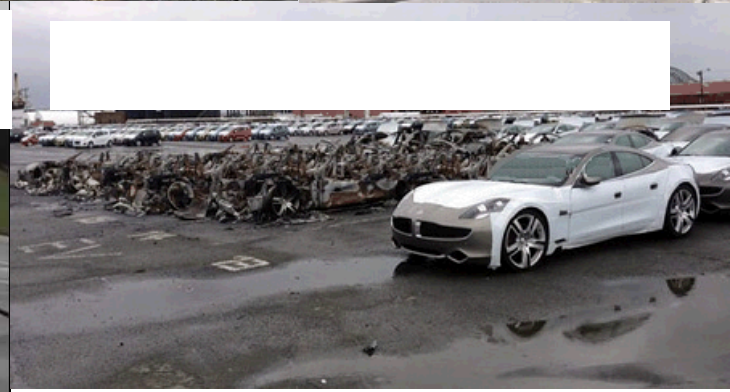
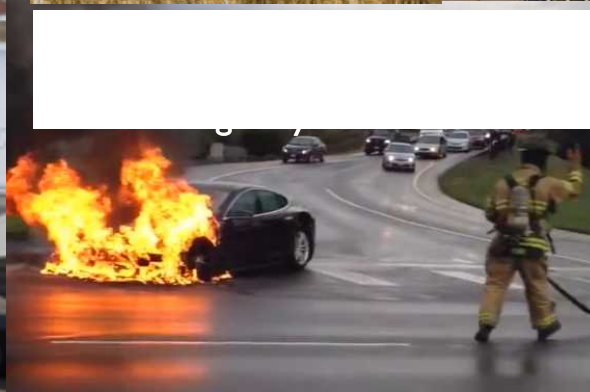
2012 GM Test Facility
Incident, Warren, MI



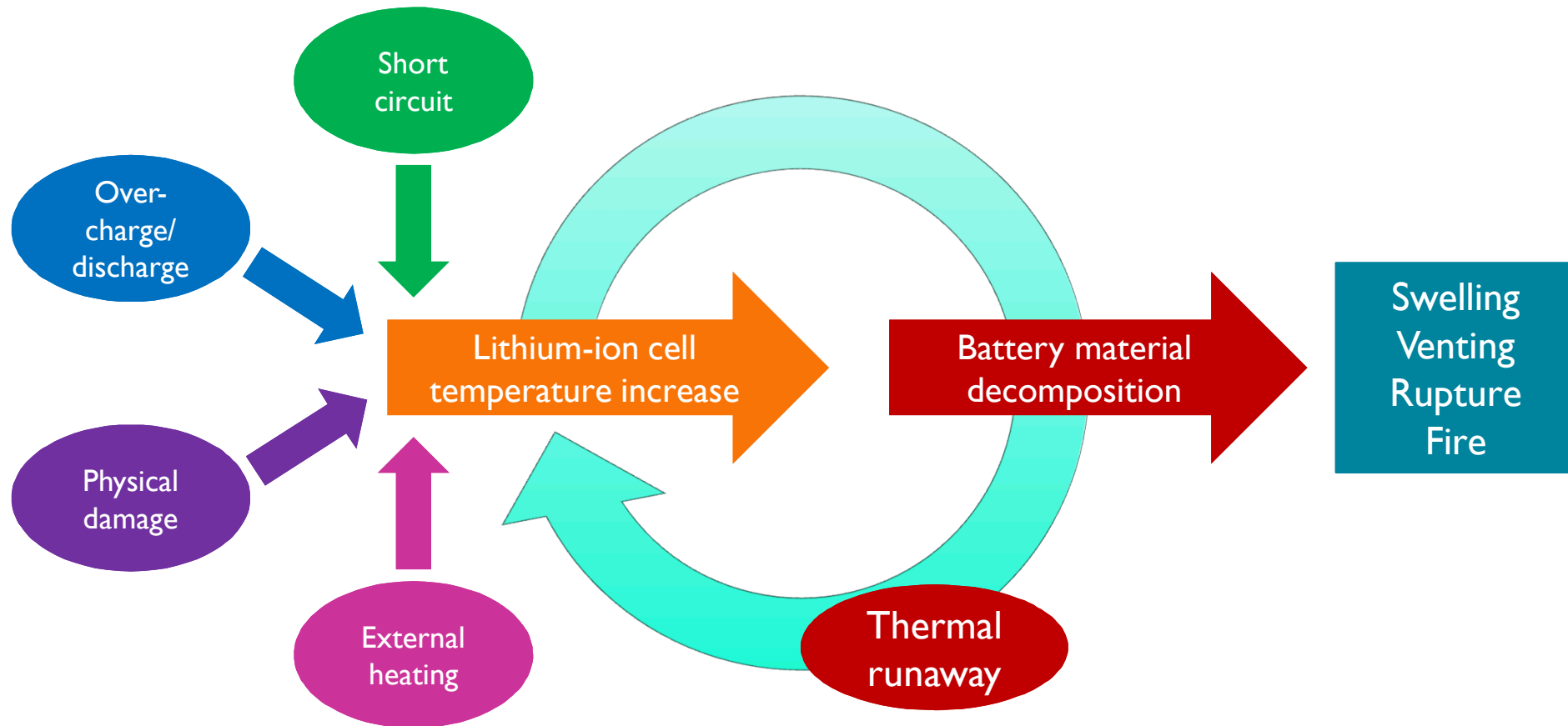
2013 Storage Battery Fire,
The Landing Mall, Port
Angeles, (reignited one week
after being "extinguished")



2013 Boeing Dreamliner Battery
Fires, FAA Grounds Fleet



Thermal runaway is cascading failure



Attention to Battery Safety is Increasing on the R&D side

Calls for attention to energy storage safety, particularly from a materials science perspective

September/October 2017

Opening the Door to Energy Storage

Challenges for Future Systems



Energy Quarterly

News and analysis on materials solutions to energy challenges
www.mrs.org/energy-quarterly

Inside:

EDITORIAL

The role of the materials scientist in battery safety

ENERGY SECTOR ANALYSIS

Manufacturing Li-ion batteries for safety and performance

ENERGY SECTOR ANALYSIS

How green is your electric vehicle?



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Images incorporated to create the energy puzzle concept used under license from Shutterstock.com.

"Manufacturing Li-ion batteries for safety and performance" title image: AllCell Technologies' Phase Change Composite

The role of the materials scientist in battery safety

There has been much negative news in the last few years about the safety of lithium batteries, from the Boeing 787 Dreamliner to hoverboards to the Samsung Note 7 phone. In each of these cases, there were multiple design and/or manufacturing problems in the batteries and control systems, which should have been identified by the manufacturer or upon importation. However, these failures occurred in less than one in a million batteries. Many manufacturers have built-in safety mechanisms. An example is the 17-in. Apple MacBook laptop, which saw many battery failures in the first 12 months. After failure, however, battery control circuits prevented any further use. There were no reported fires or human damage from these.

These problems, including notices in every airport about the Samsung Galaxy Note 7 ban, have made the public skeptical about the safety of lithium batteries. Beyond the general public, firefighters and emergency personnel worry about how to deal with high voltages in crashed electric vehicles: There have been instances of fires in electric vehicles. An upcoming concern is where to place large backup batteries in tall buildings to increase resiliency in the event of storms. The roof is out of the question, as firefighter ladders cannot reach them, and the basement is ruled out because of flooding concerns. The batteries are thus typically placed around the fourth floor, and the surrounding building has to be made fireproof.

As larger batteries become more popular, in vehicles or for energy storage in buildings, it is important for materials scientists to develop built-in sensors that can identify failures before they become critical and shut down the battery. A temperature sensor may have averted the fast charging of the batteries in the Boeing 787 and perhaps a Tesla car, when the battery was below freezing temperature. It could have stopped the charging from taking place or at least limited the initial current until the cell was warm.

The materials scientists focused inventing/developing the next generation of high

Development of
inherently safe cells



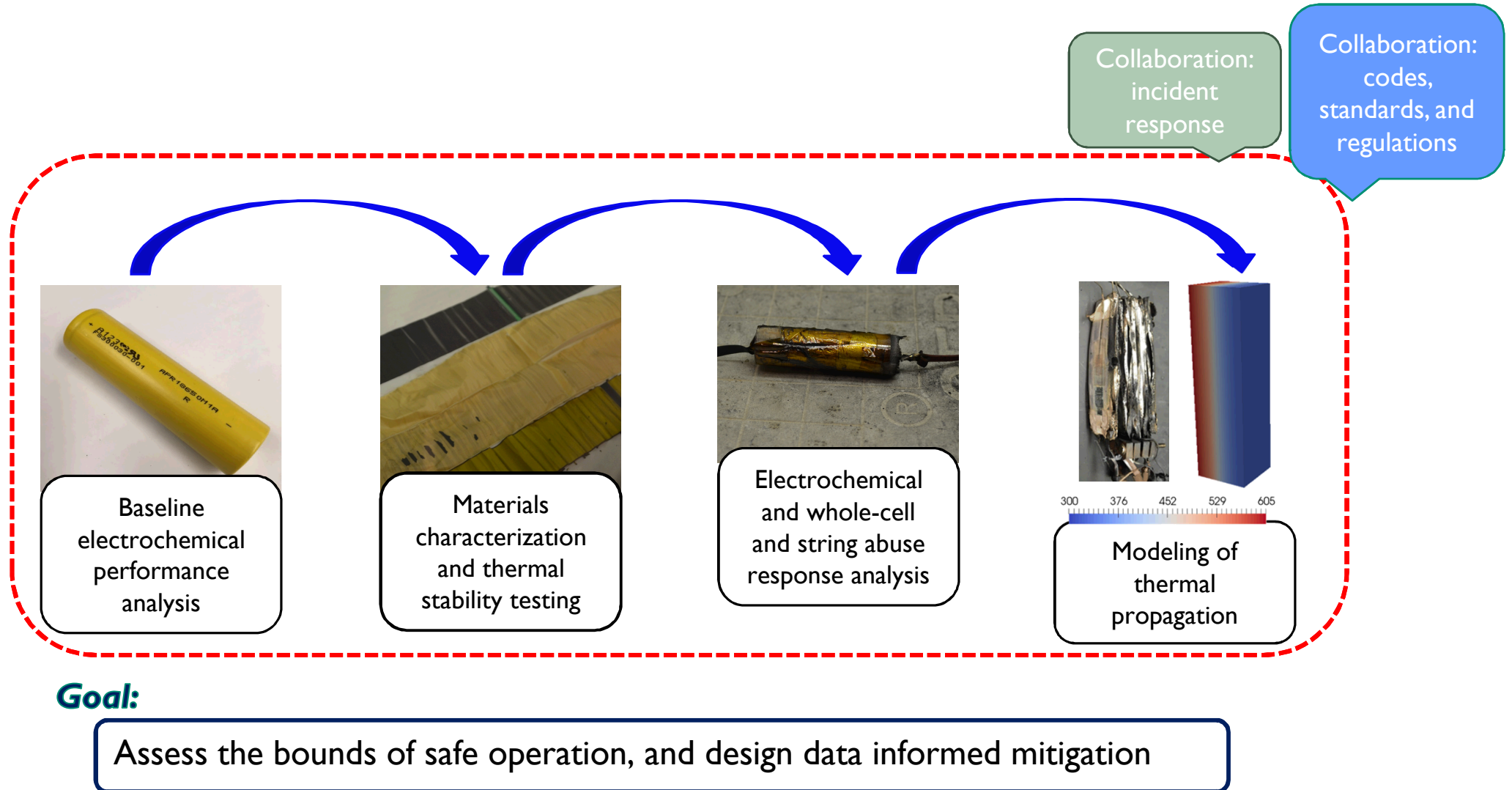
- Safer cell chemistries
- Non-flammable electrolytes
- Higher temperature and shutdown separators
- Non-toxic battery materials
- Inherent overcharge protection

Safety devices and
systems



- Cell based safety devices, ex: current interrupt devices (CID) to prevent overcharging
- Positive temperature coefficient to prevent large currents
- Circuit control through the battery management system (BMS)
- Charging systems designed to prevent overcharge conditions

Improving battery failure mitigation

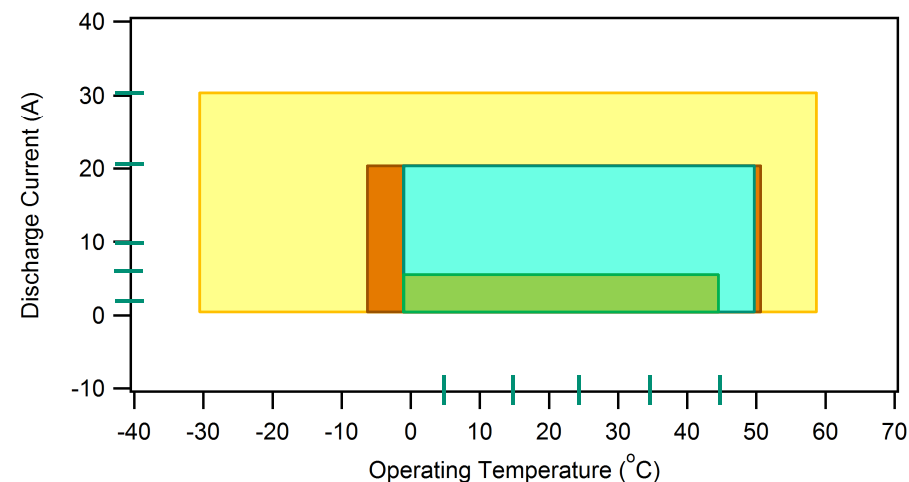


Begin with baseline performance with Li-ion cells



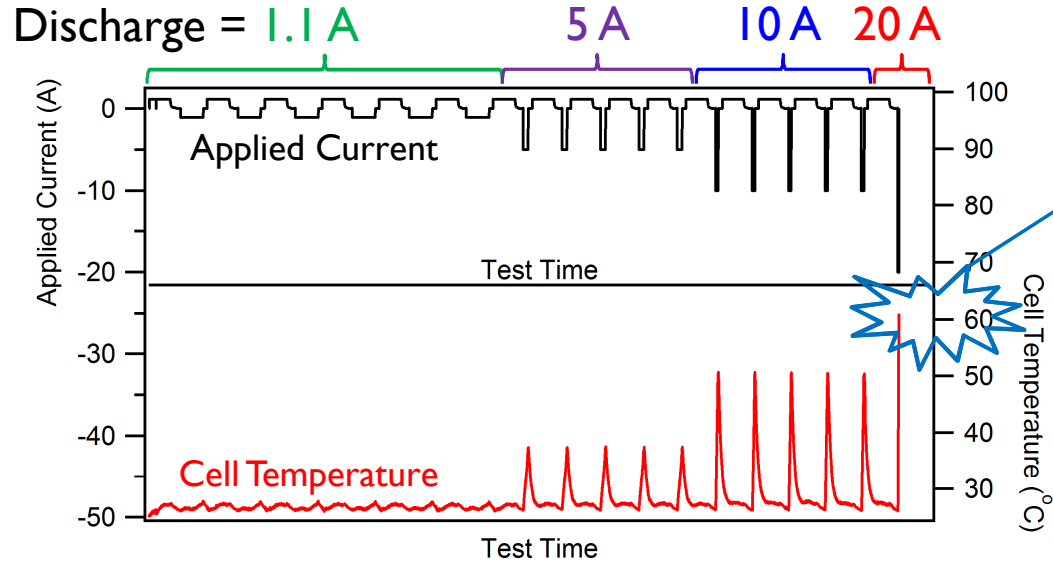
Cathode Chemistry	AKA	Specific Capacity (Ah)	Average Potential (V vs Li ⁰ /Li ⁺)	Max Discharge Current	Acceptable Temperature (°C)
LiFePO ₄	LFP	1.1	3.3	30	-30 to 60
LiNi _{0.80} Mn _{0.15} Co _{0.05} O ₂	NMC	3.0	3.6	20	-5 to 50

LCO LFP NCA NMC



Avoiding accelerated aging or abuse

LFP, 25 °C environment



Current = 20 A (max = 30 A)

Environment = 25 °C

Cell skin Temp = 60 °C

Most packs don't monitor individual cell skin temperatures.

Unintended abuse condition under 'normal' operation.

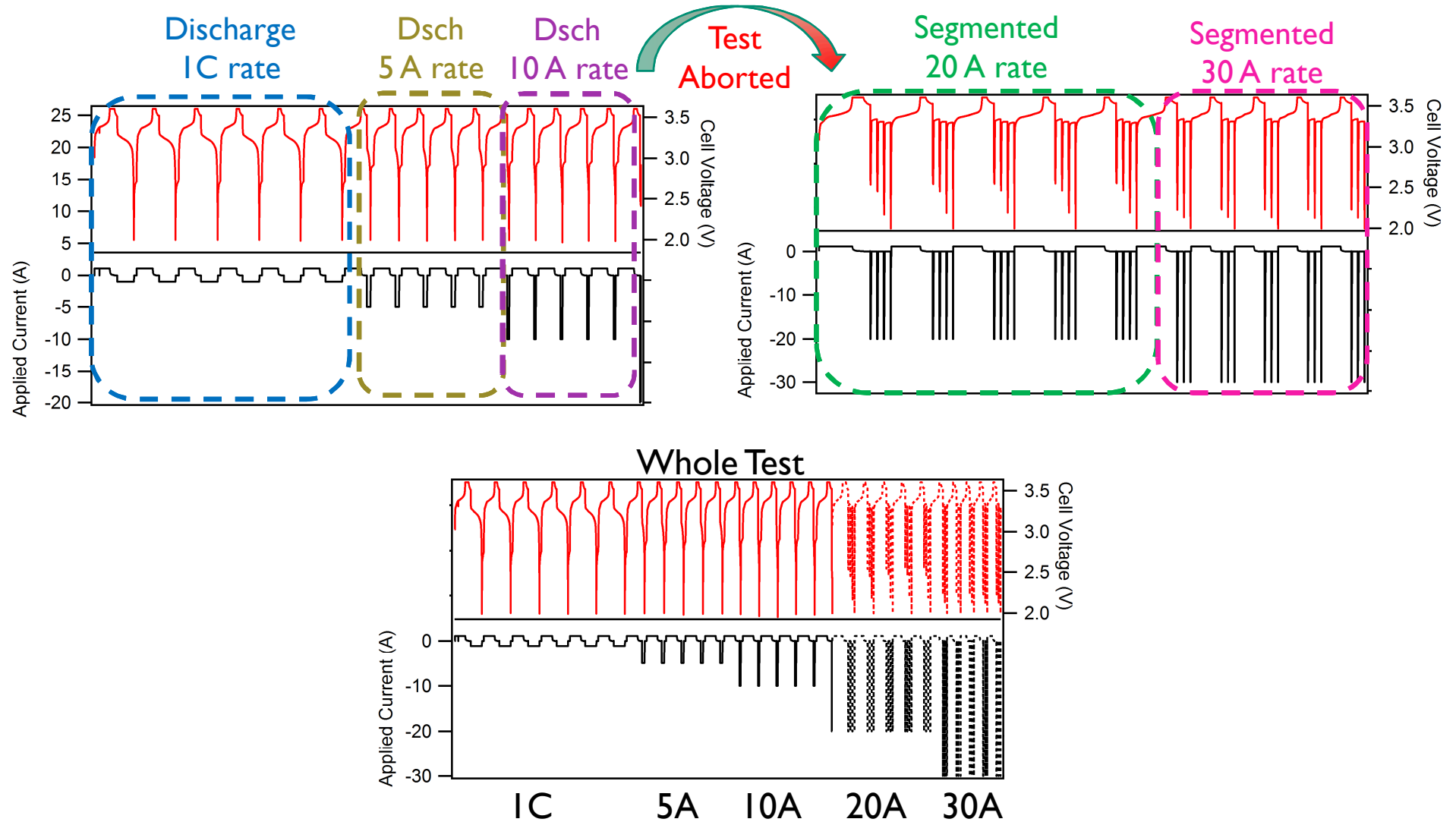
Pristine Cell



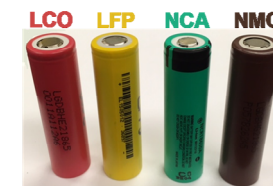
Abused Cell



Evaluating cell chemistries uniformly



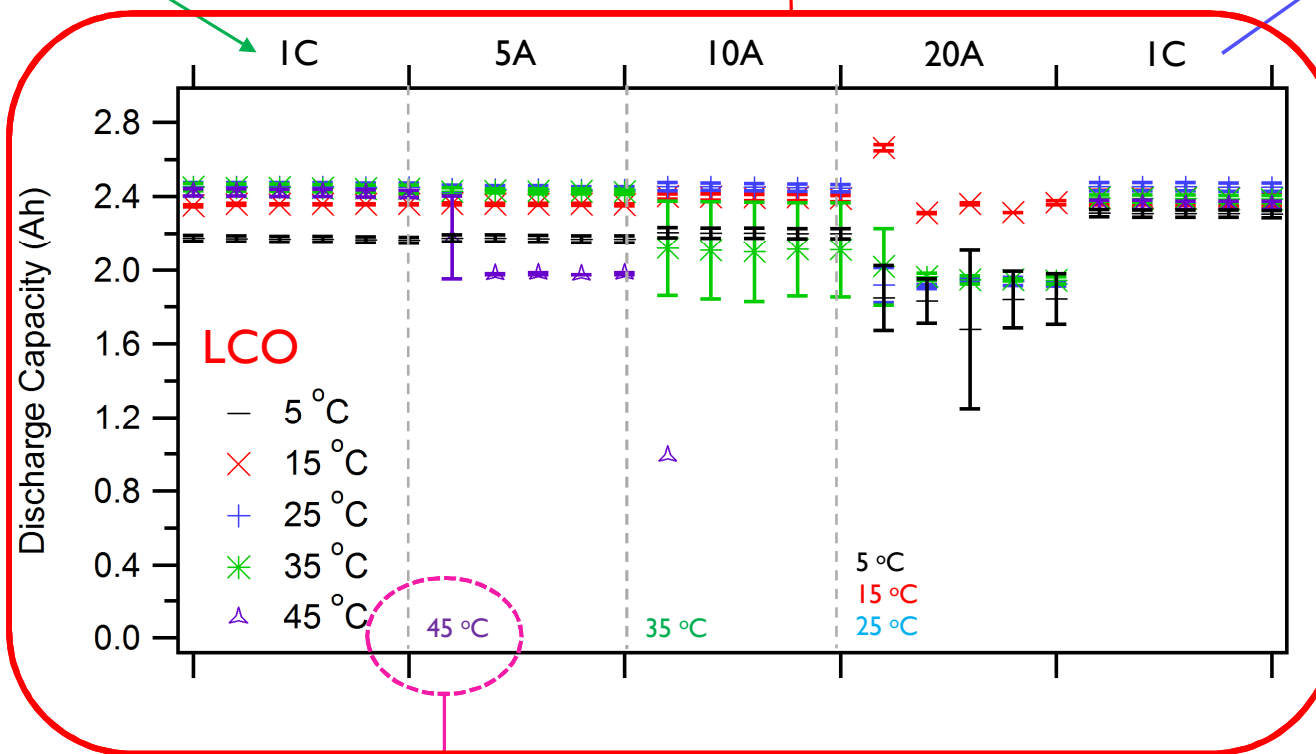
Cycling data for each chemistry is coalesced on one plot



Discharge current

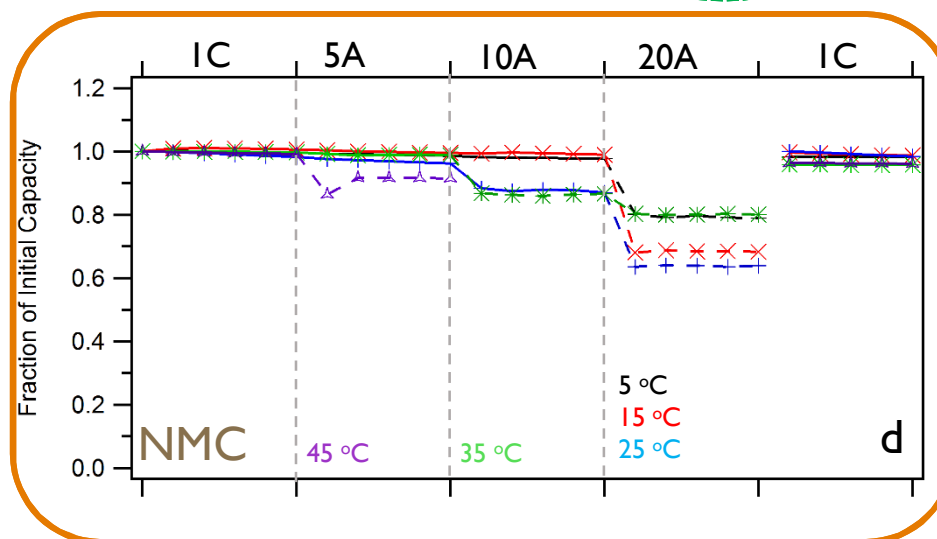
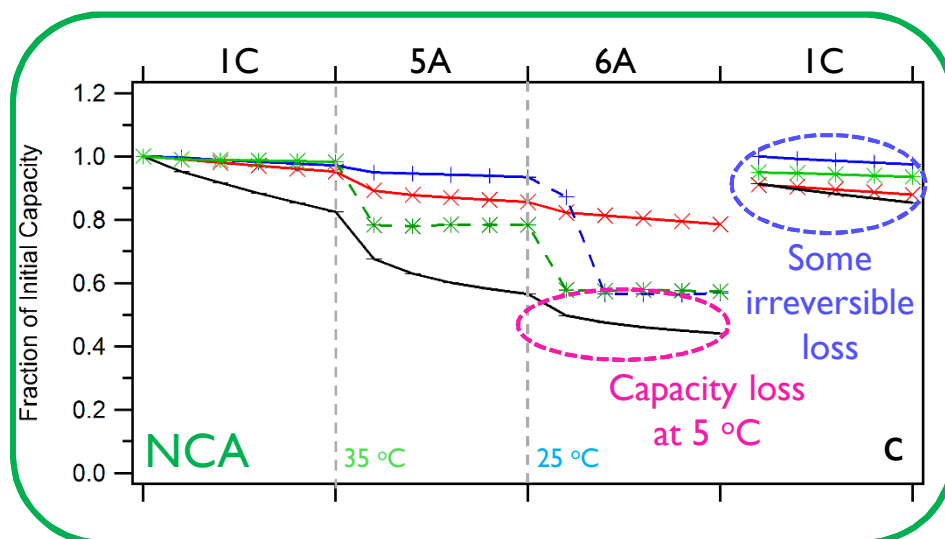
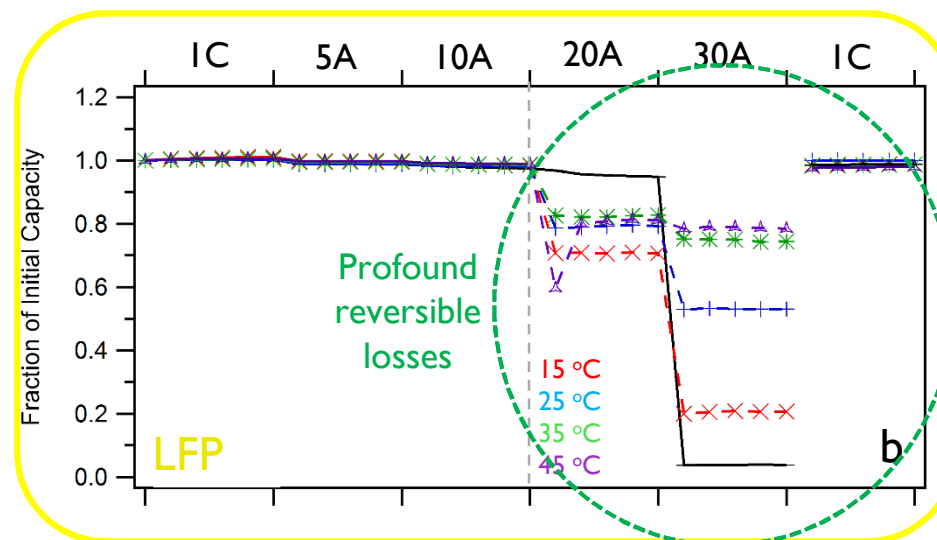
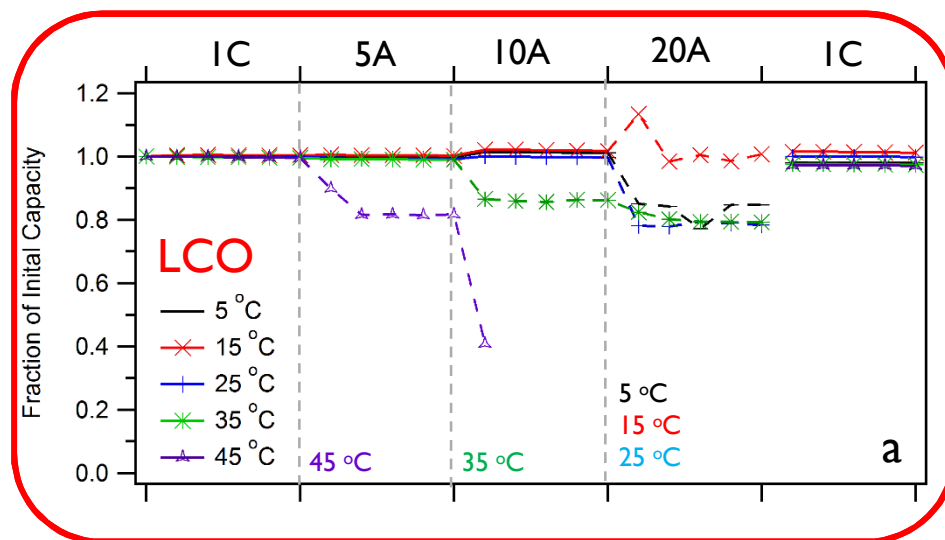
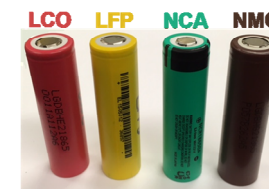
Corresponds to red LCO

@ 25 °C



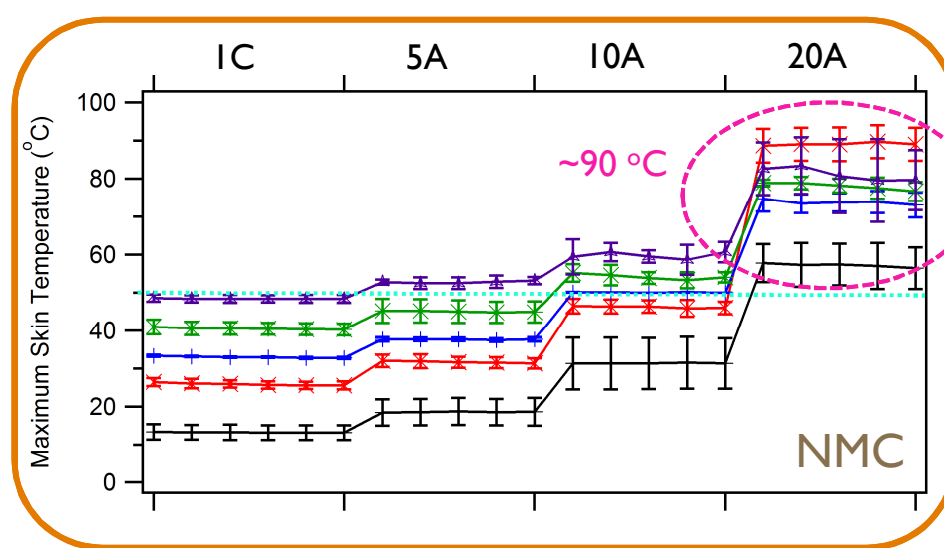
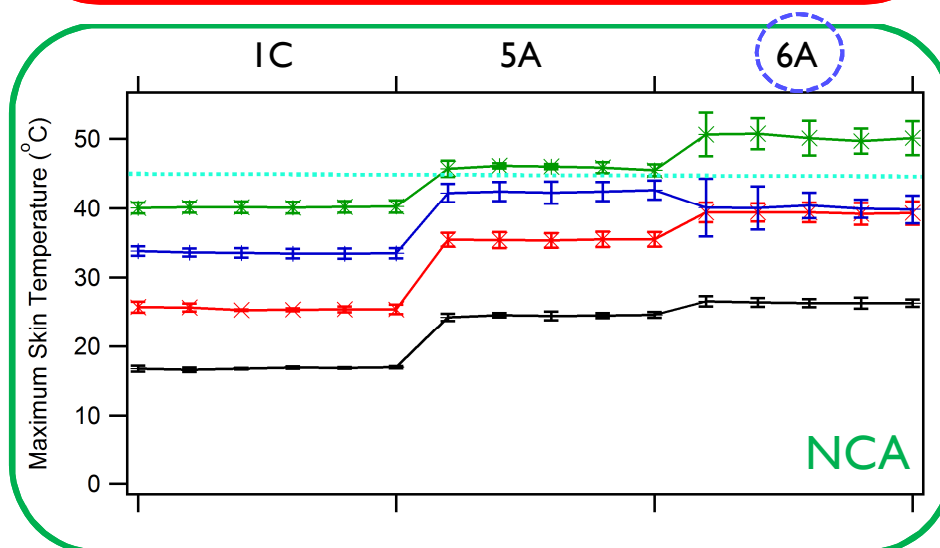
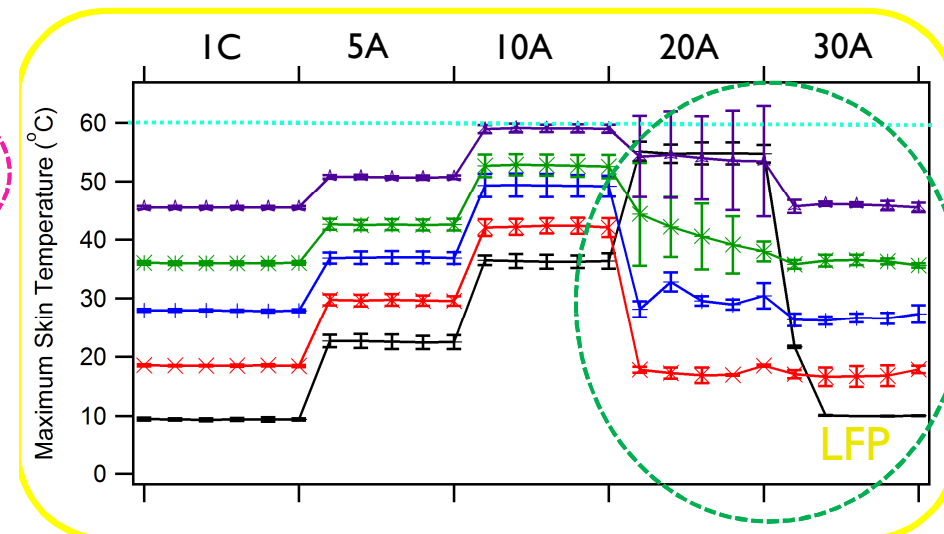
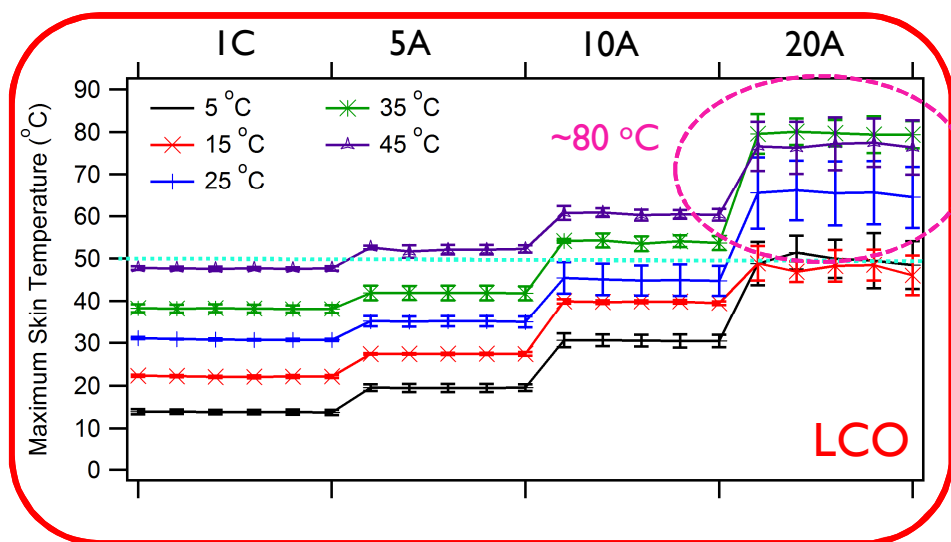
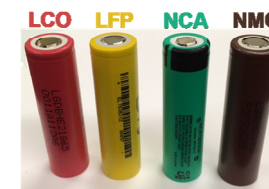
Segmented discharging began at 45 °C

NCA experiences lasting capacity losses after cycling



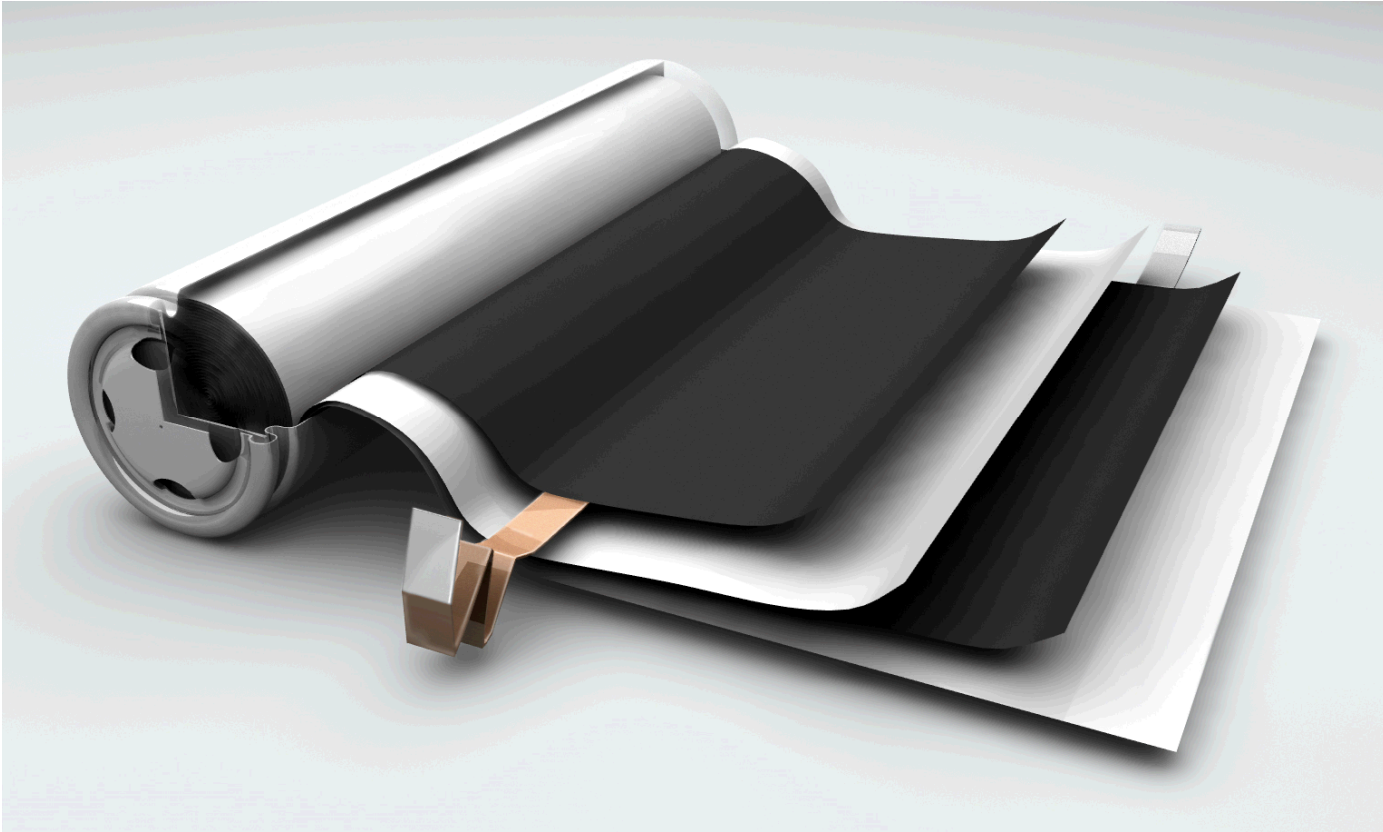
Operating conditions combine to produce unintended abuse and accelerated aging

Significant self-heating can occur if cells are unmonitored



- NCA experiences aging, likely from Li plating at low temperatures
- Small losses quantified here can be extrapolated to rapid cell death

Challenges with lithium-ion battery safety



If we can figure out where issues are coming from, we can design better batteries



Intolerance of Abuse



Electrolyte Flammability



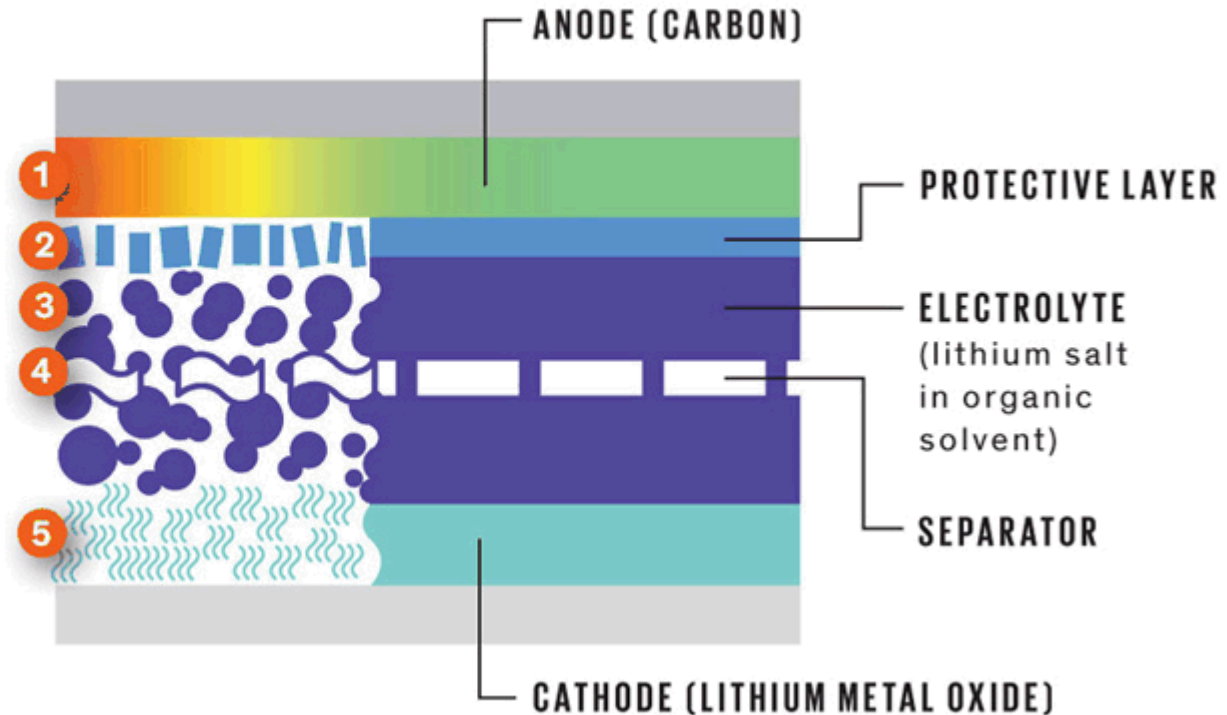
Thermal Stability



Energetic Decomposition

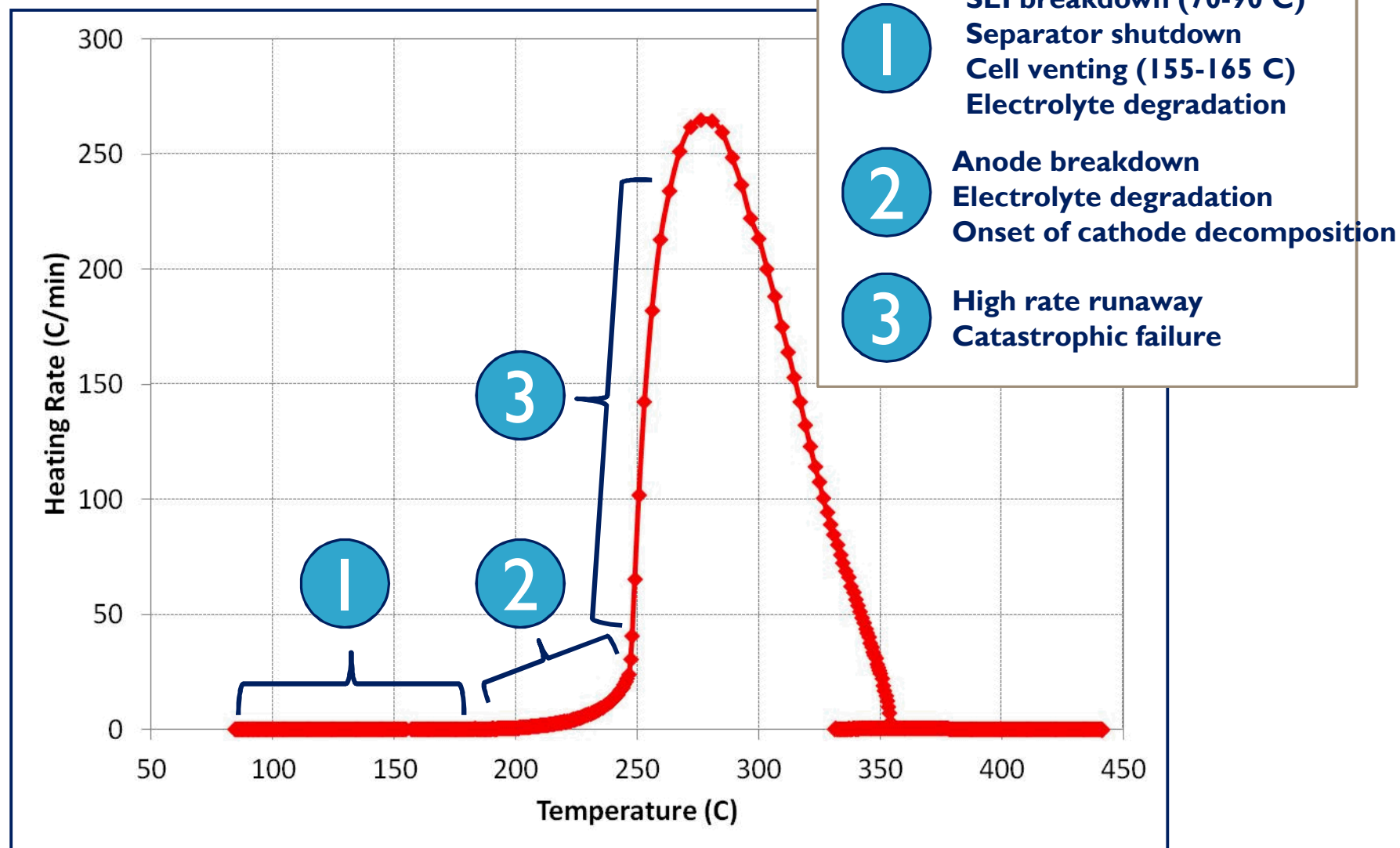
Thermal Runaway in a Lithium-Ion Battery

1. Heating starts.
2. Protective layer breaks down.
3. Electrolyte breaks down into flammable gases.
4. Separator melts, possibly causing a short circuit.
5. Cathode breaks down, generating oxygen.

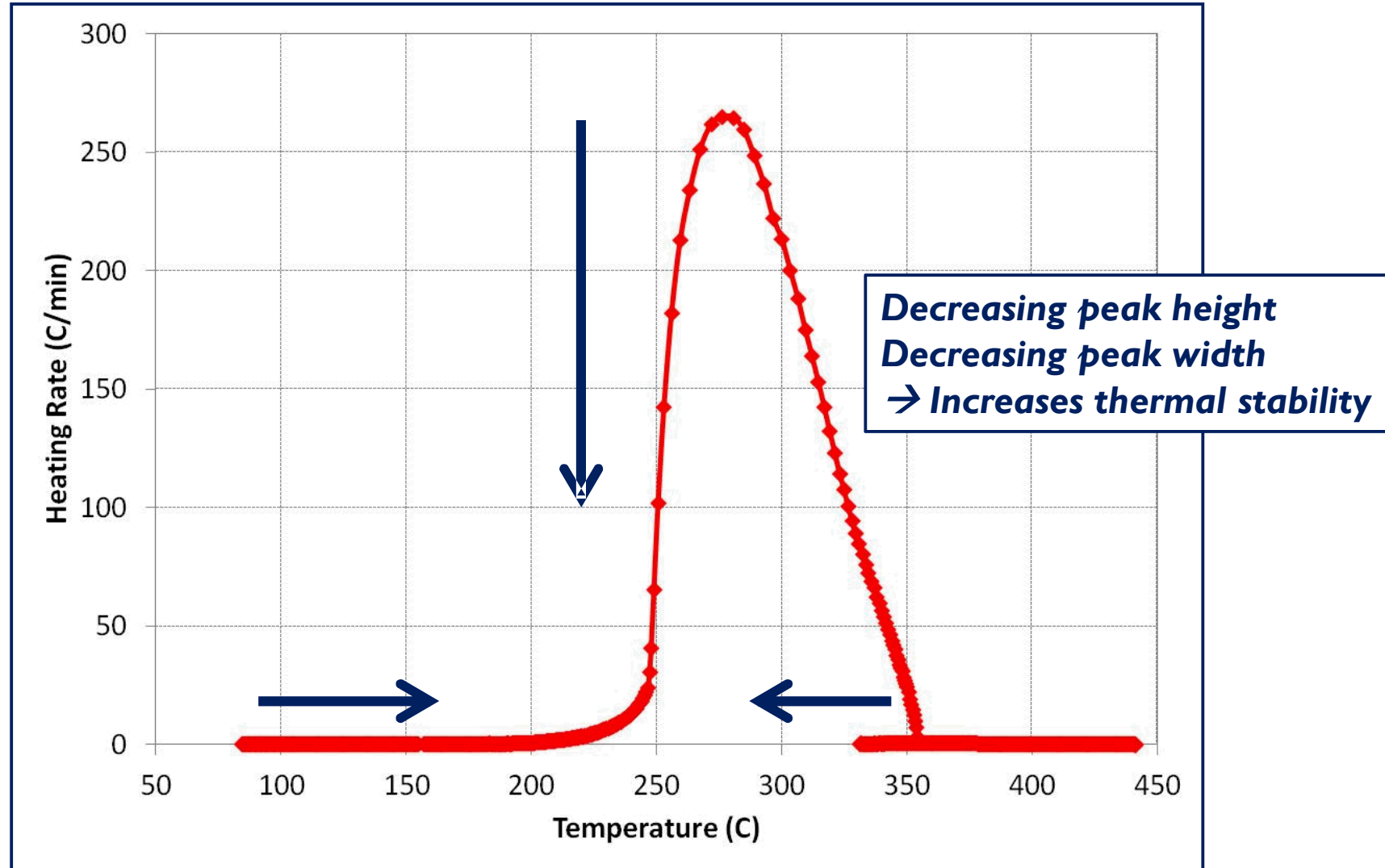


Stages of Lithium-ion Cell Runaway

Accelerating Rate Calorimetry (ARC) of a Li-ion Cell

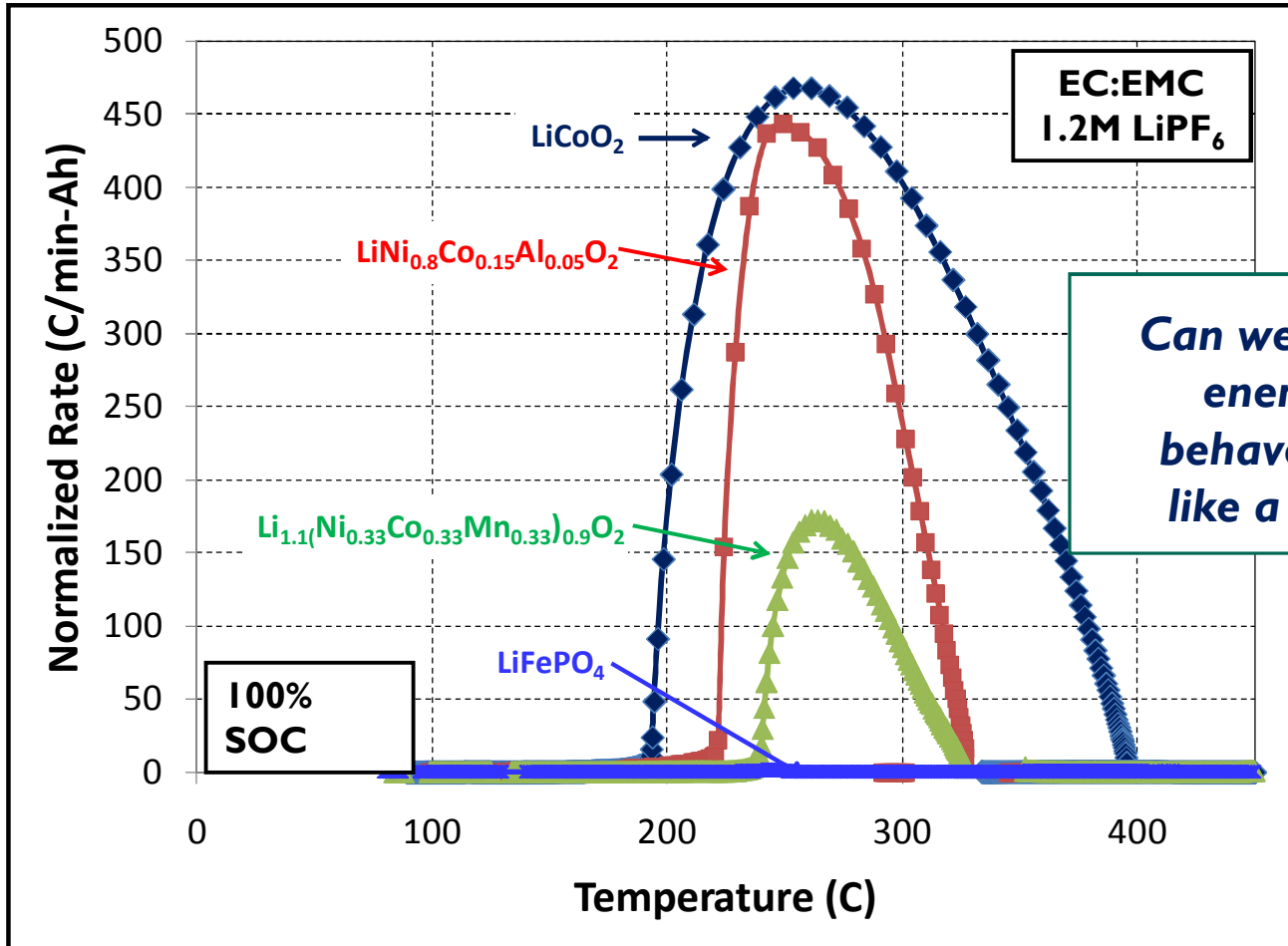


Stages of Lithium-ion Cell Runaway



Changing Cathode Chemistry

ARC of cells with different cathode chemistries

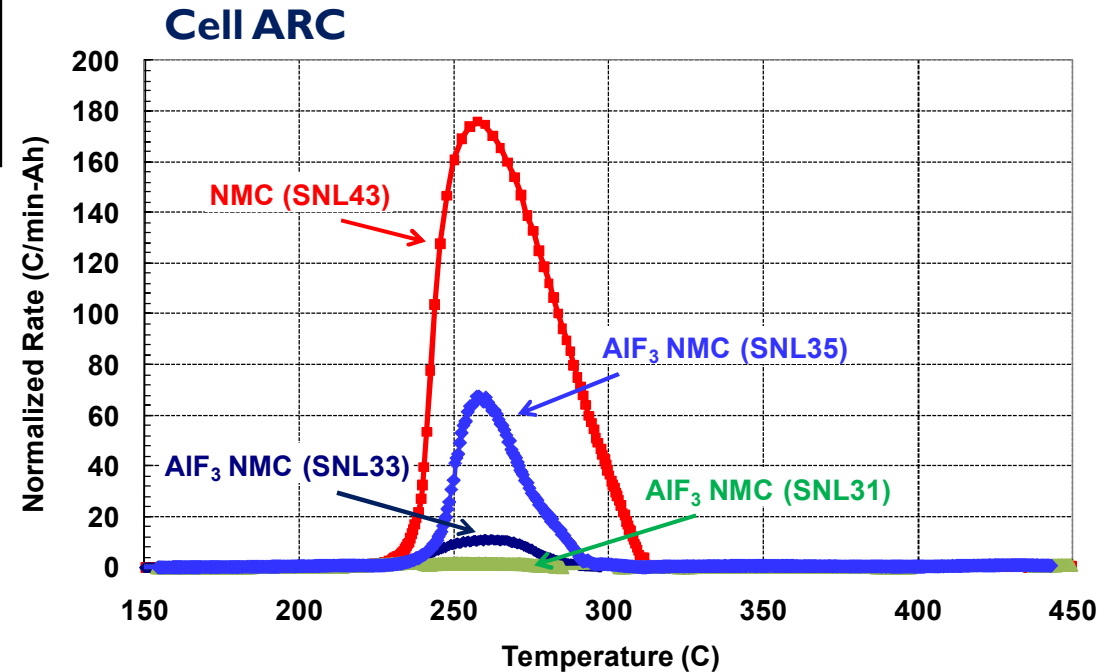
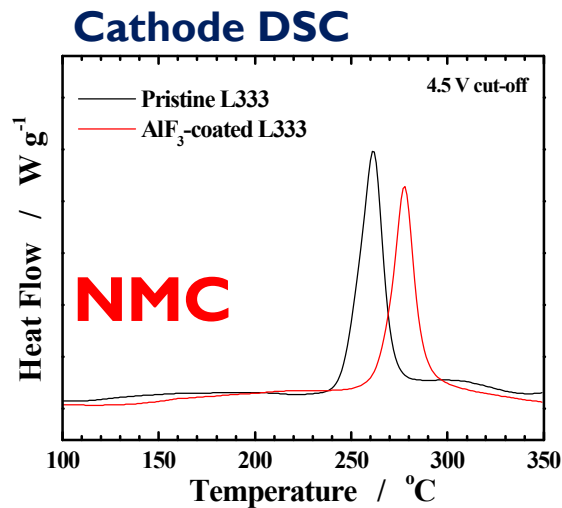
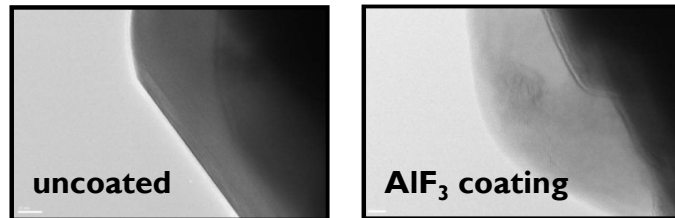


Differences in runaway enthalpy and reaction kinetics are related to oxygen release from the cathode and the electrolyte combustion

Coating Active Materials

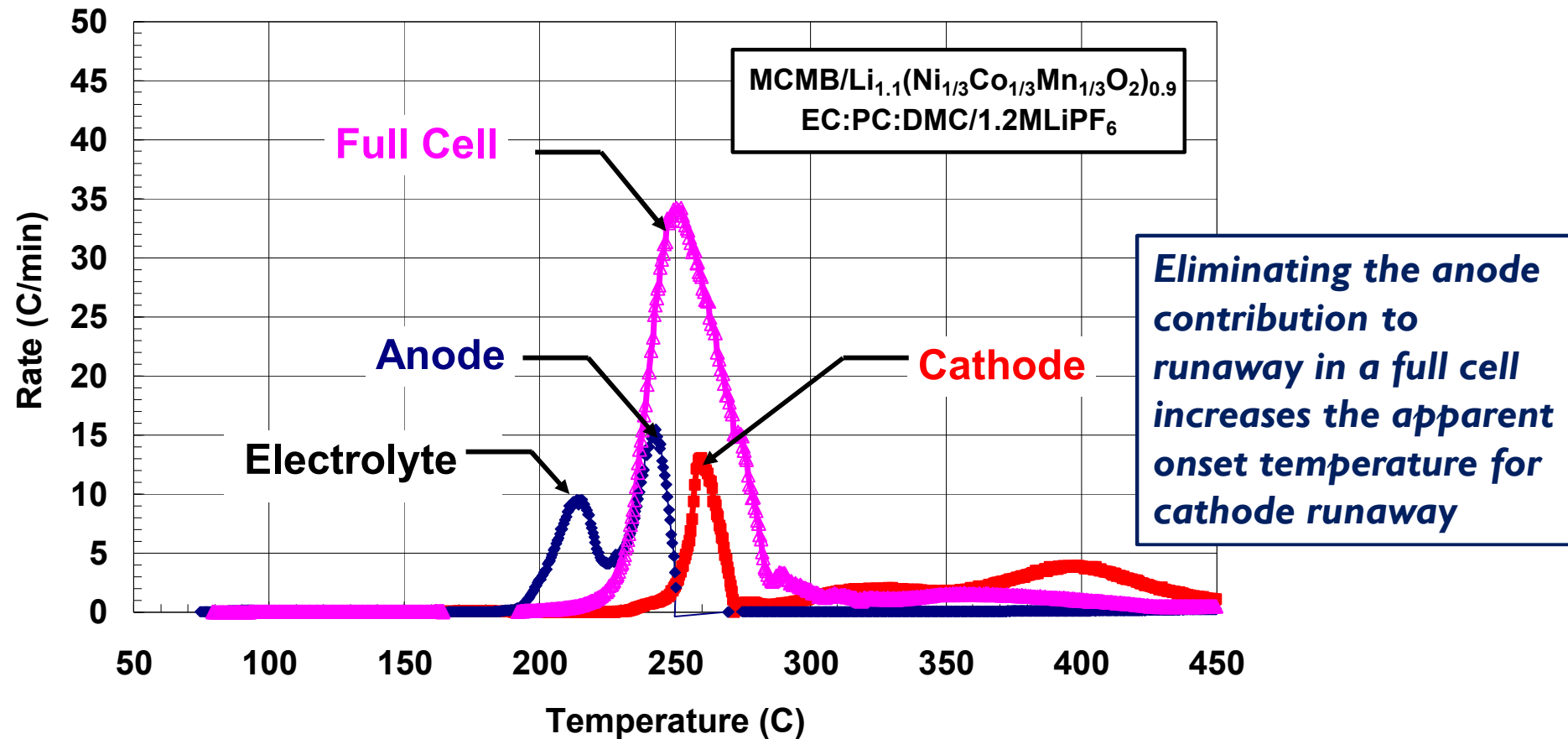
Collaboration with Khalil Amine and Zonghai Chen (ANL)

Inert coatings are used to stabilize the surface of active materials



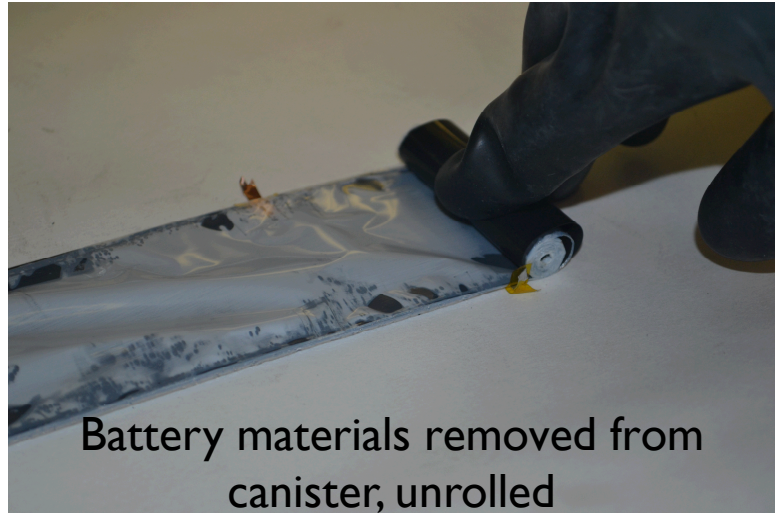
Reduction in NMC cell runaway kinetics with 2% (wt) AlF₃ coatings

Anode and Cathode Runaway

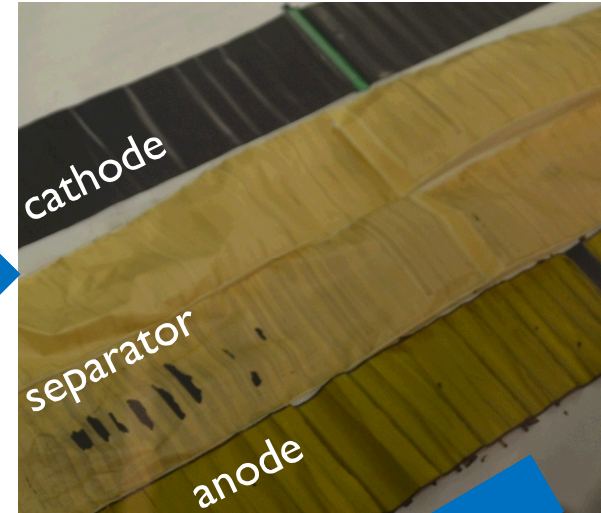


Results are consistent with stabilized anode response to thermal runaway when alumina coated by ALD

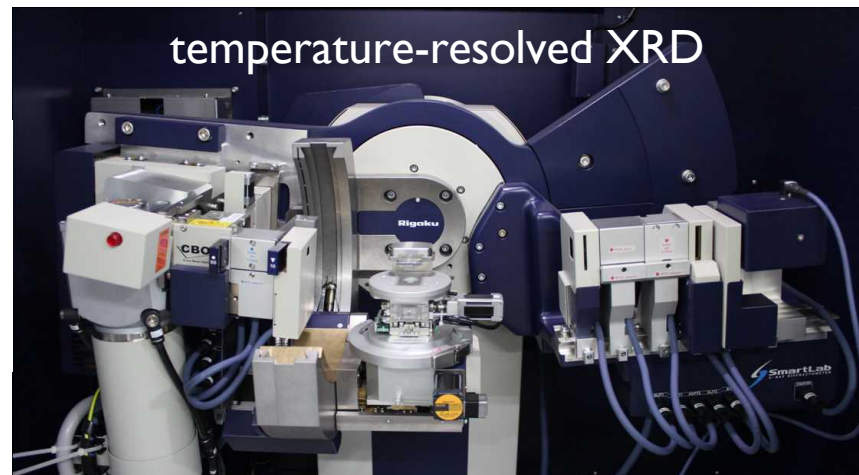
Batteries are disassembled to reveal steps of failure

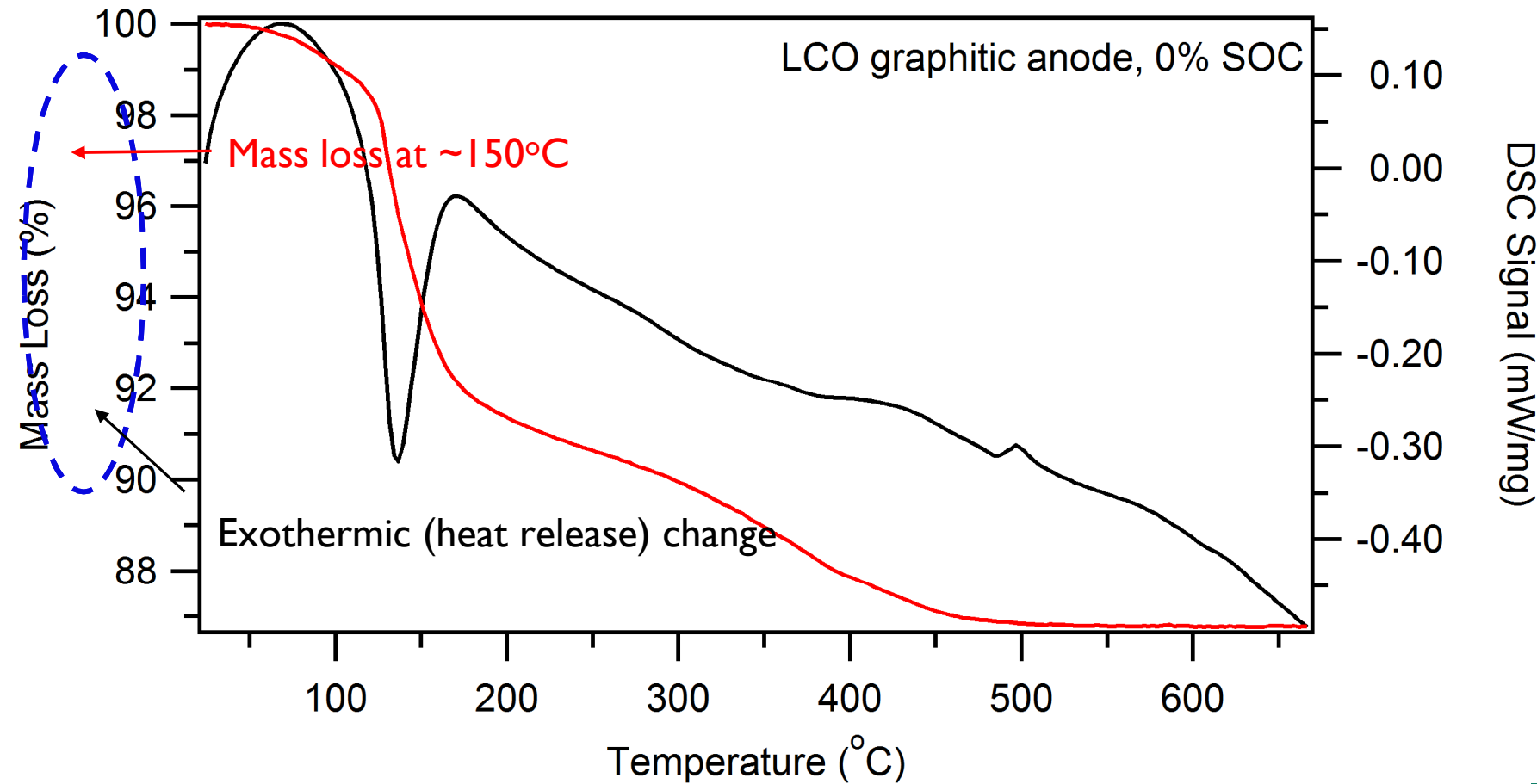


Disassembly



Temperature-resolved
XRD shows how the
material changes with
temperature



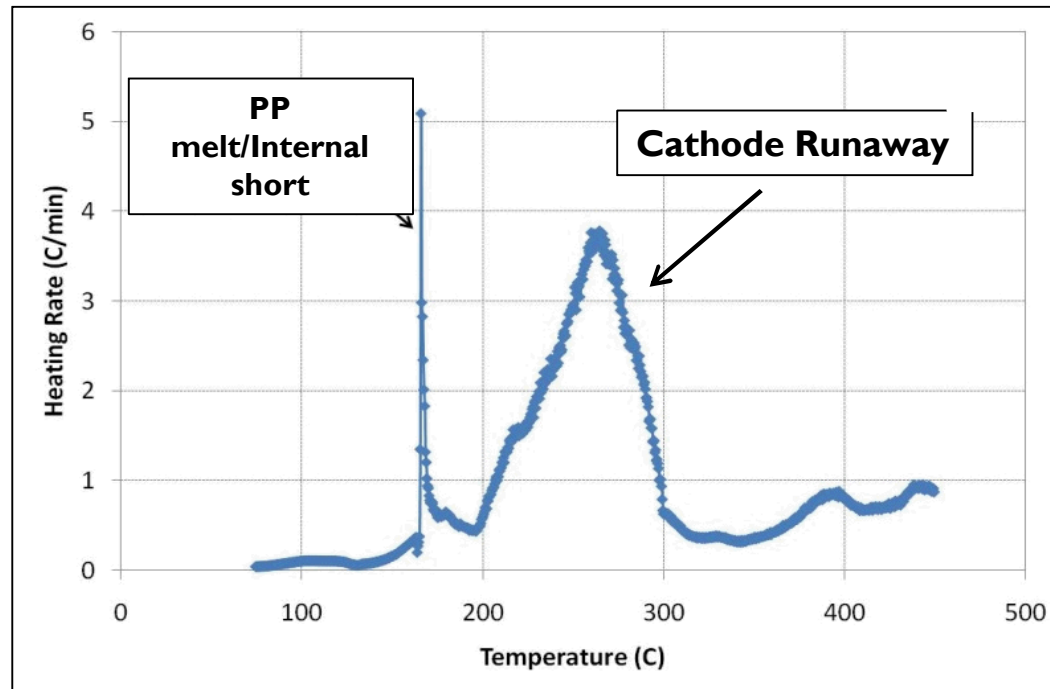


We have learned that the anode loses mass at 150°C and this also releases heat

Advanced Separator Materials

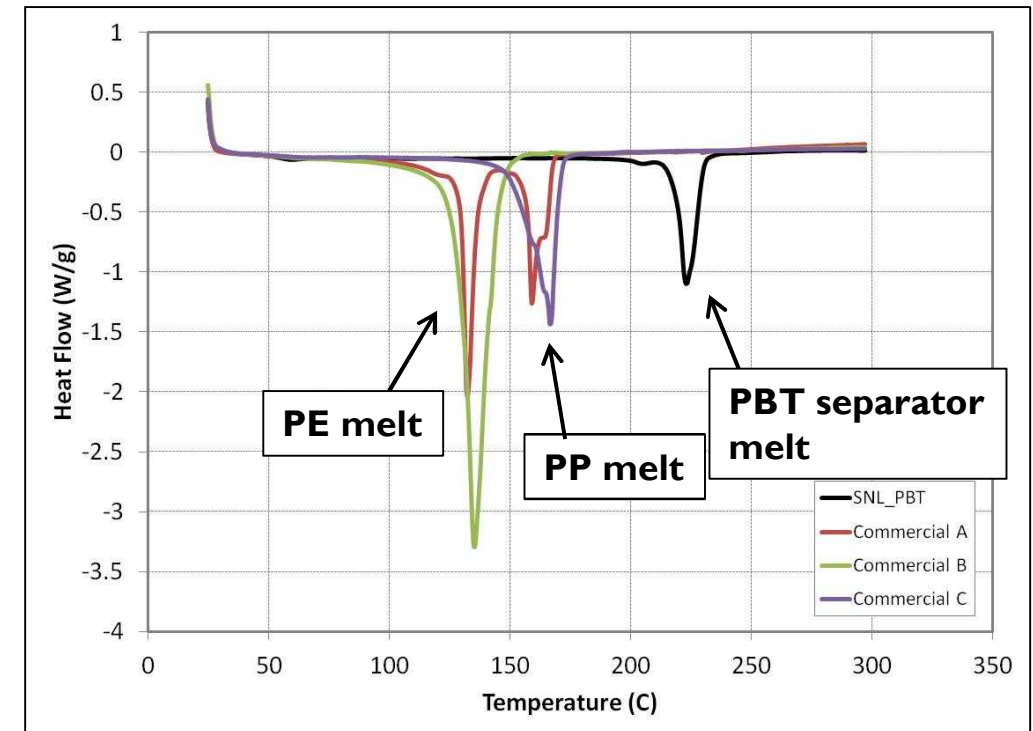
Closing the gap between separator phase transition and cathode runaway temperature

Cell ARC

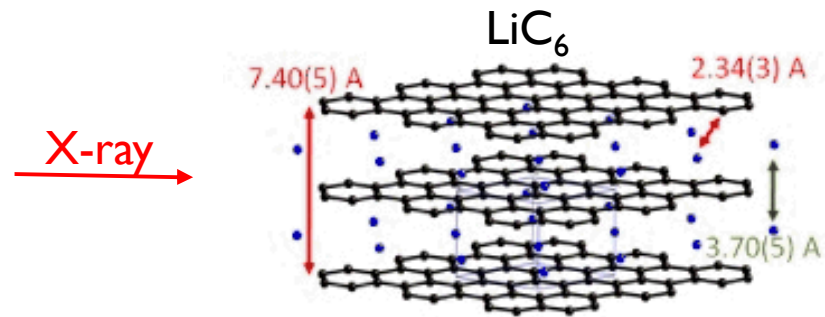


- *PE and PP melt between 135 and 160 °C*
- *Cathode runaway between 190 and 240 °C*
- *Should target higher melting temperature separators to improve cell stability*

Separator DSC

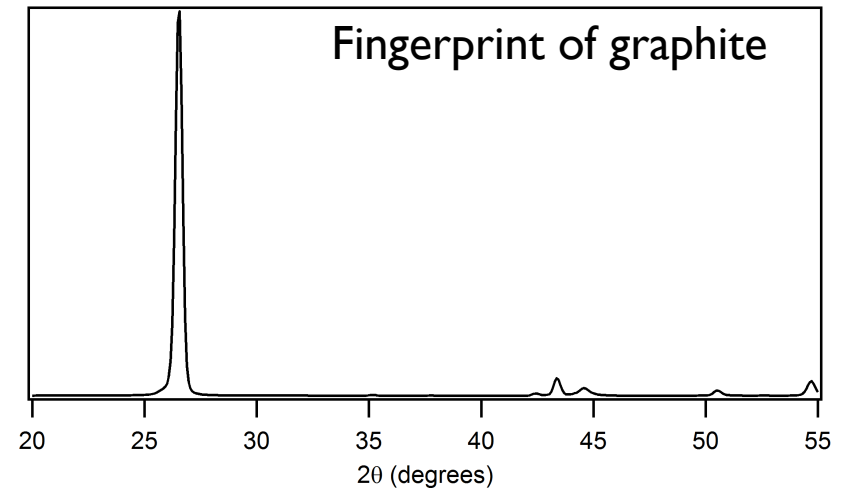
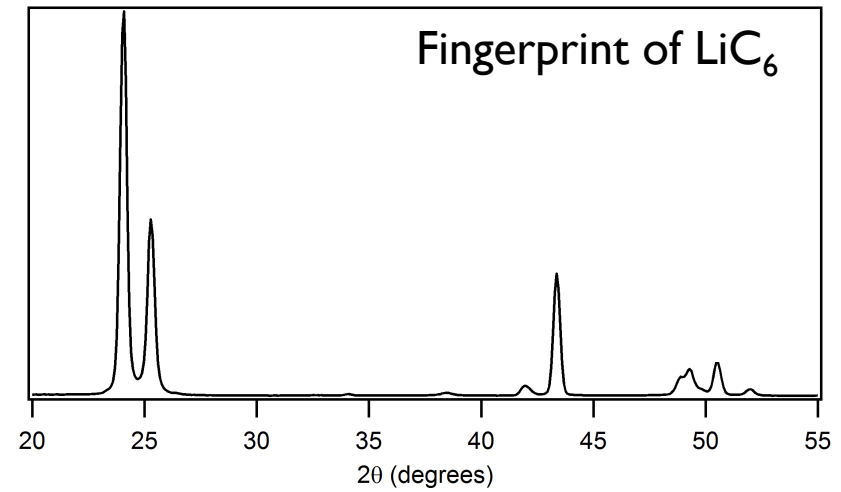
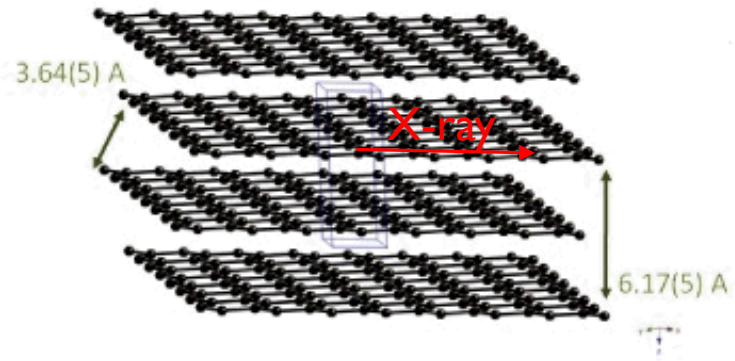


Temperature-resolved XRD exposes decomposing structure

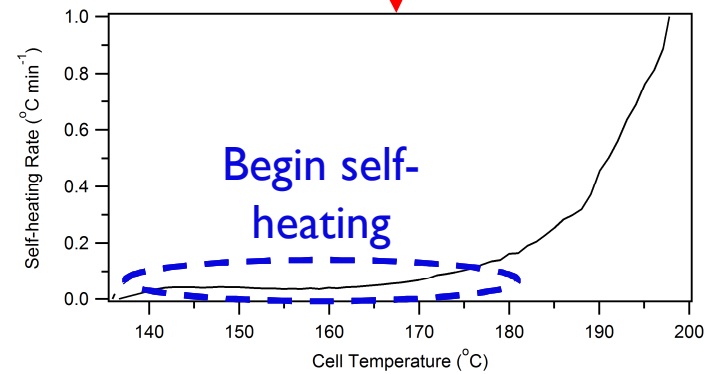
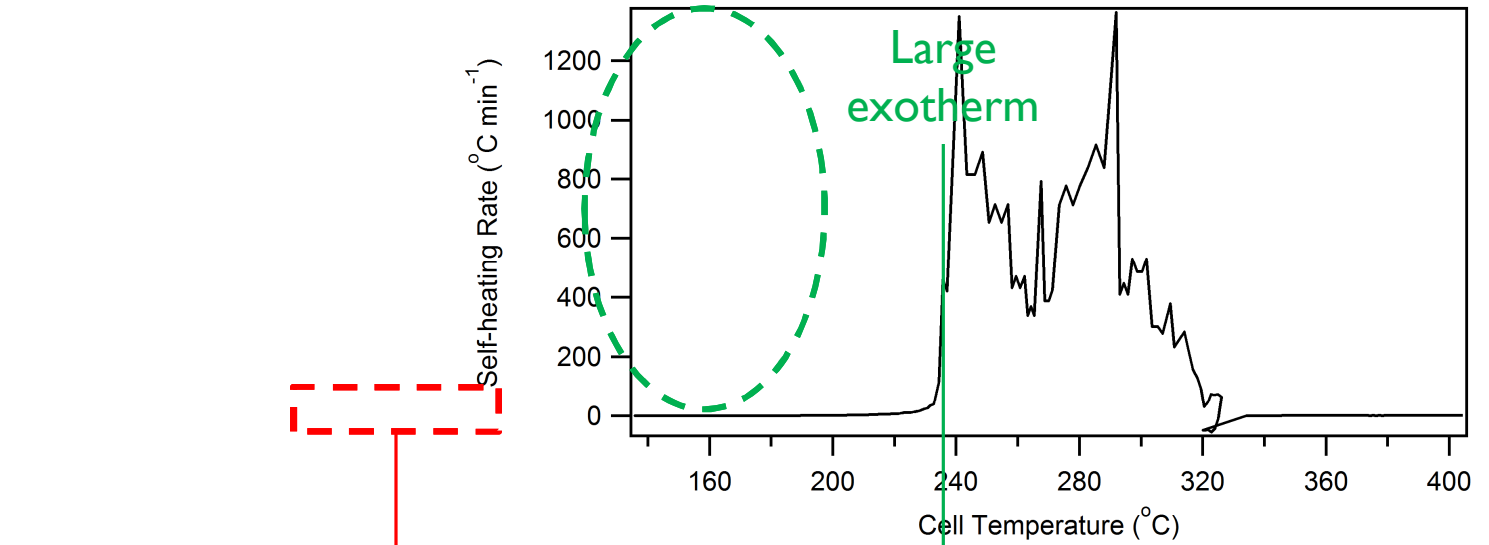
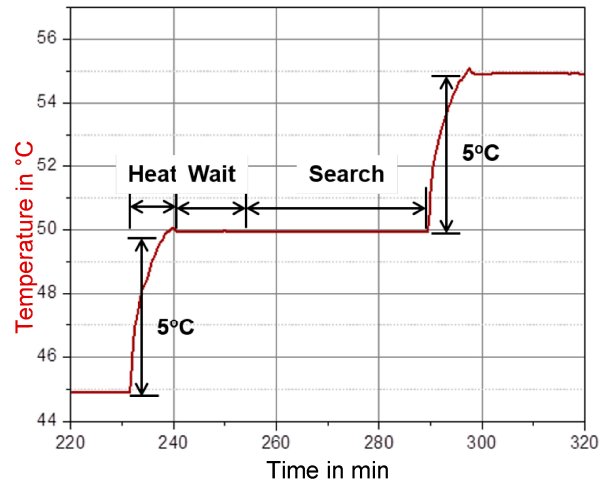
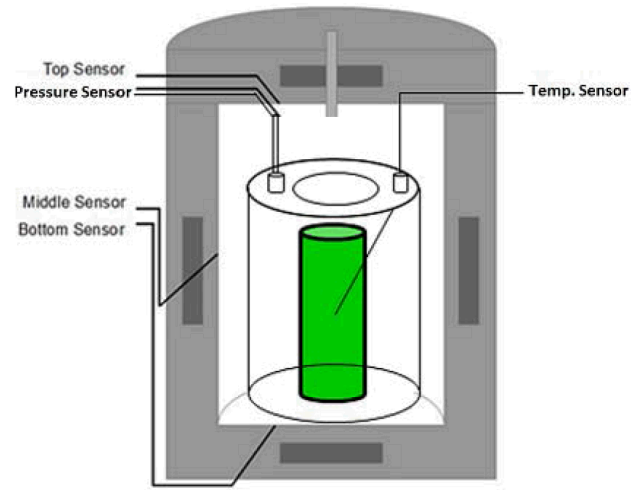


heat the
battery

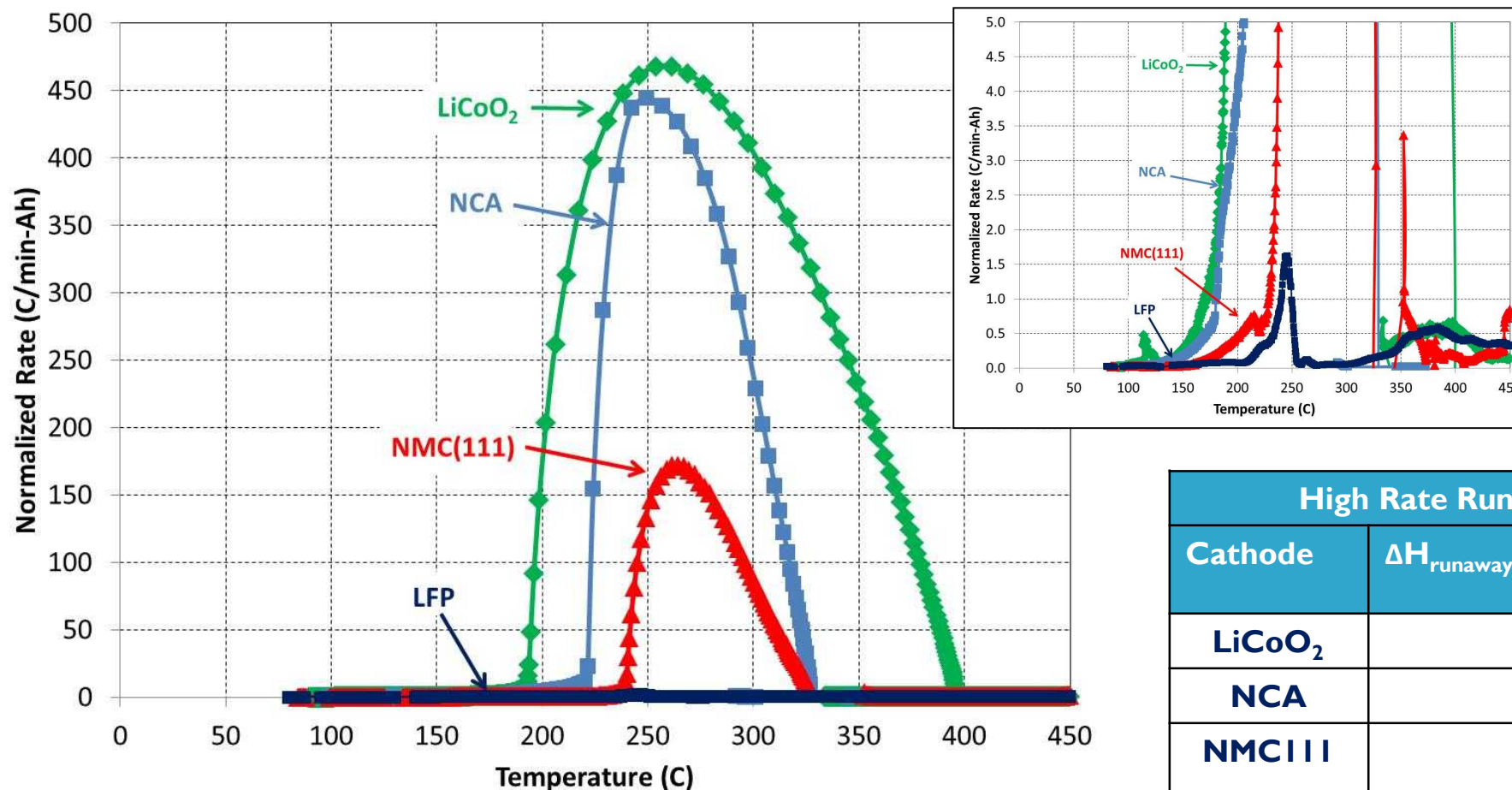
graphite



Accelerating Rate Calorimetry (ARC) demonstrates thermal runaway



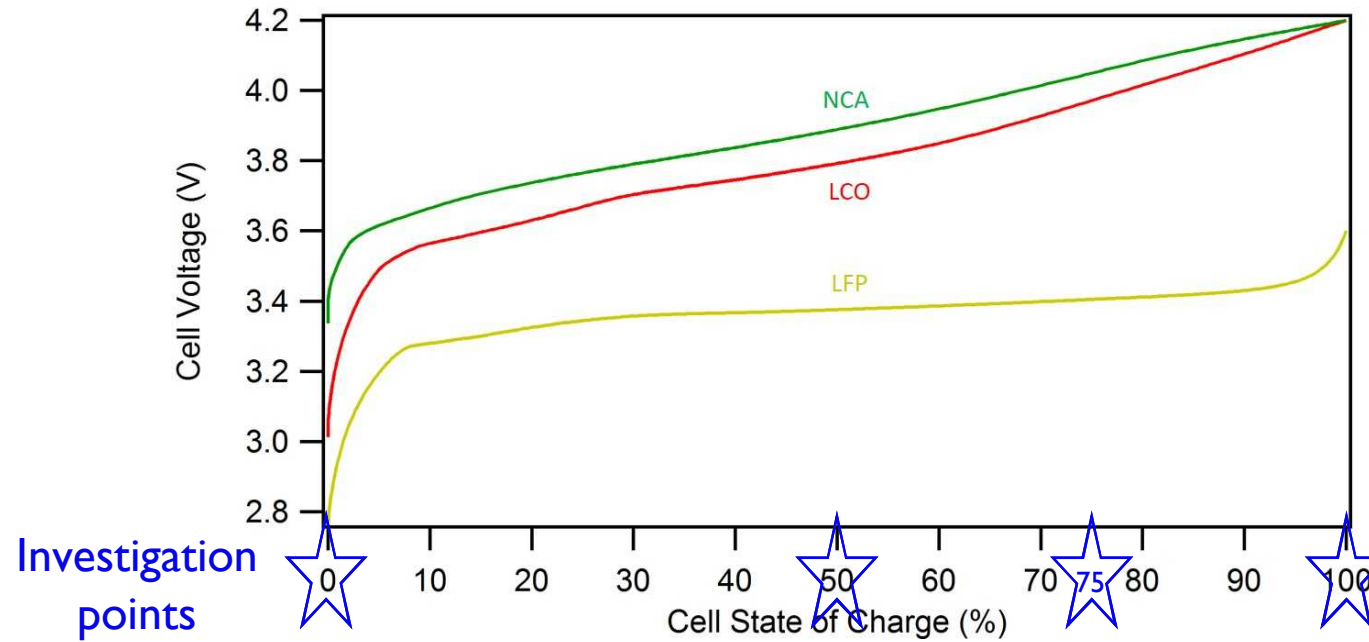
Accelerating rate calorimetry (ARC) of 18650 cells with different cathode materials



High Rate Runaway	
Cathode	$\Delta H_{\text{runaway}}$ (kJ/Ah)
LiCoO ₂	15.9
NCA	9.8
NMC(111)	8.3
LFP	2.4

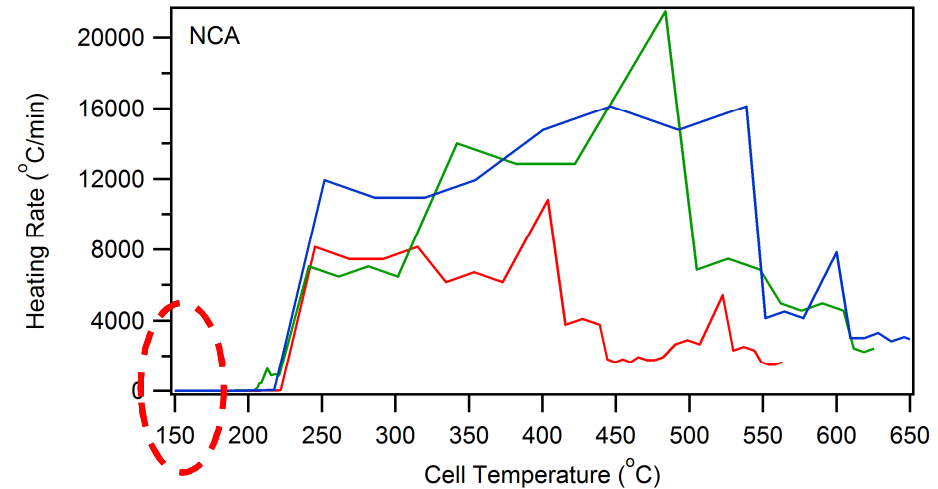
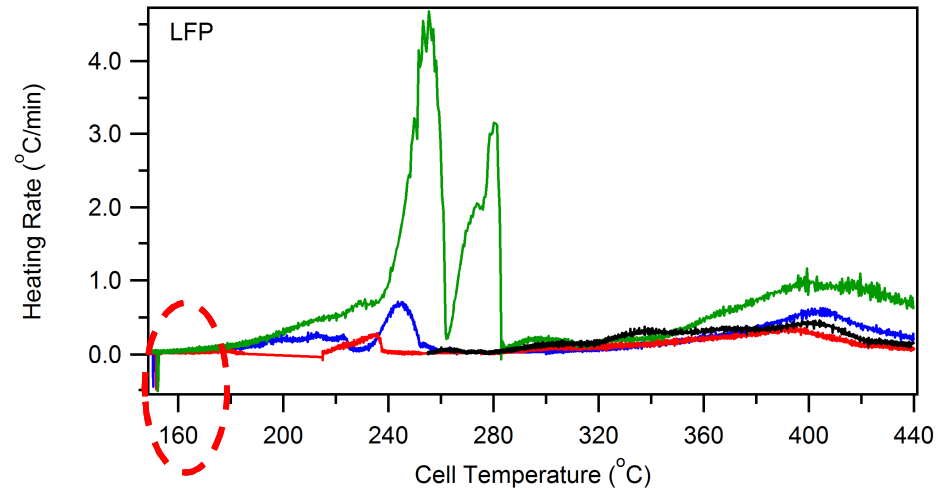
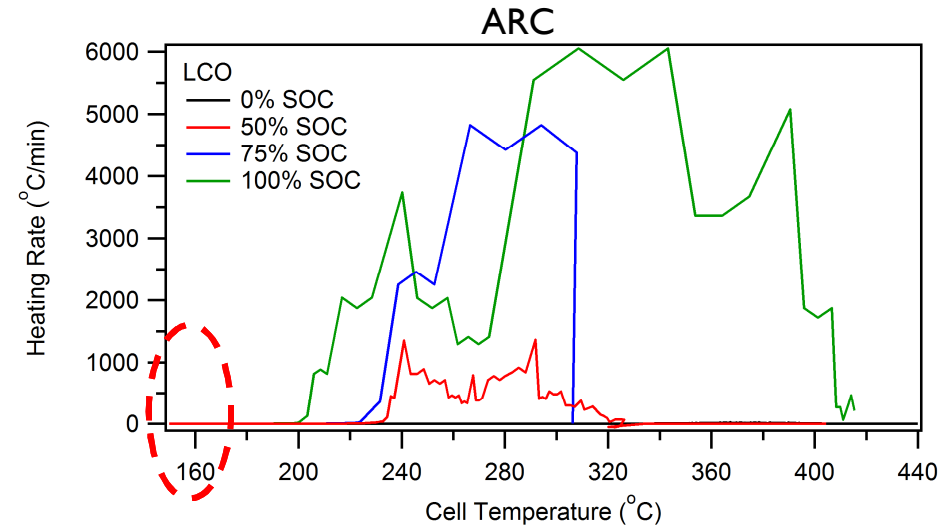
- Develop an understanding of how the runaway response scales with cell size.
- Traditionally testing performed at 100% SOC; how does this change at lower SOC?

State of charge (SOC) matters



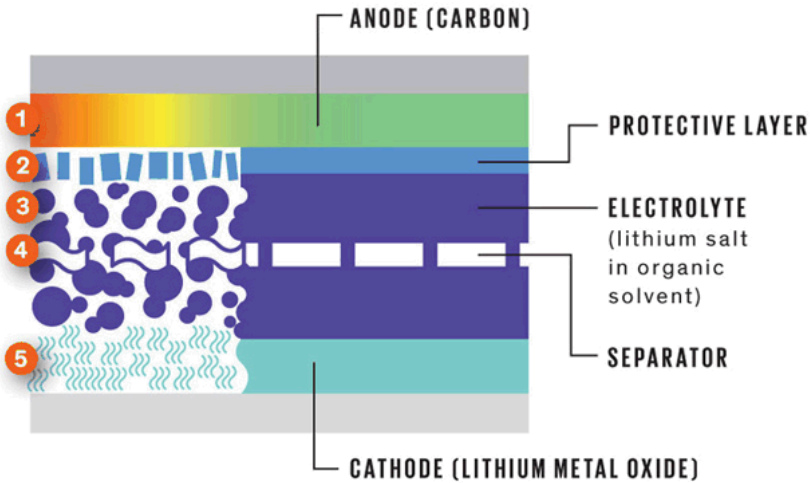
Derated batteries can address safety and cycle life, but increase costs

Thermal runaway behavior changes with chemistry and SOC



Onset temperature is $\sim 150^{\circ}\text{C}$ for all chemistries

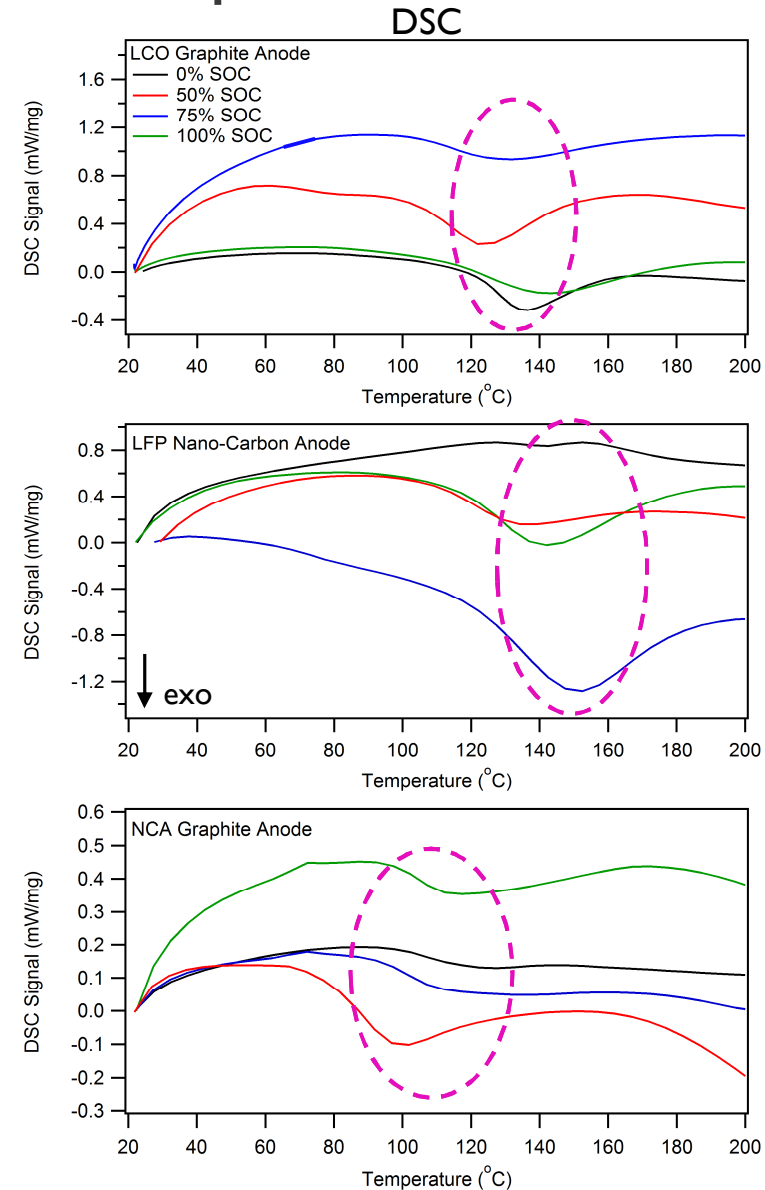
Thermal runaway begins with anode decomposition



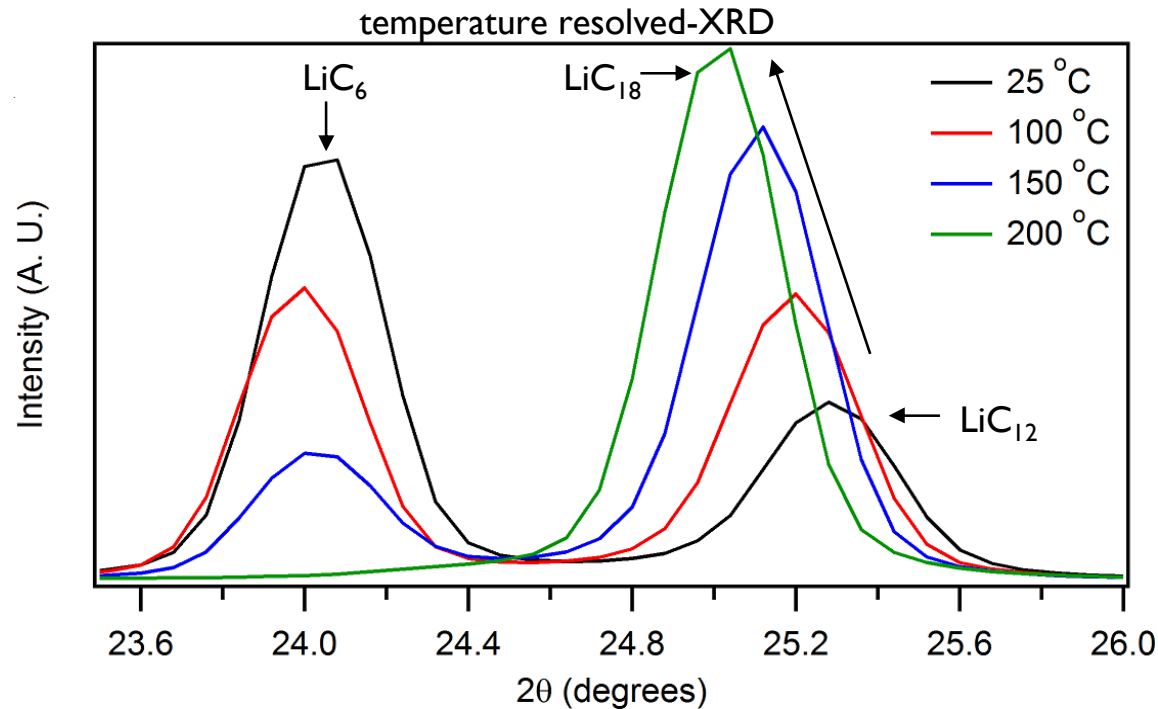
Protective layer (2) breaks down, releasing heat (exotherm).

Underlying anode (1) is no longer protected, and reacts with the electrolyte (3) also releasing heat (exotherm).

This is the onset of thermal runaway detected in the ARC

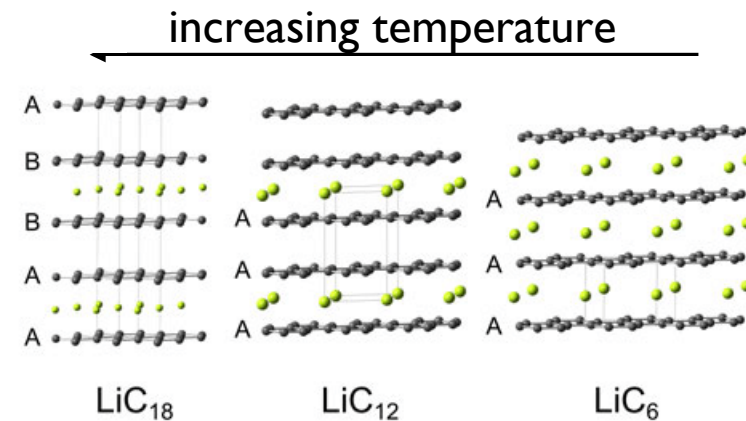


Charged anodes decompose with temperature

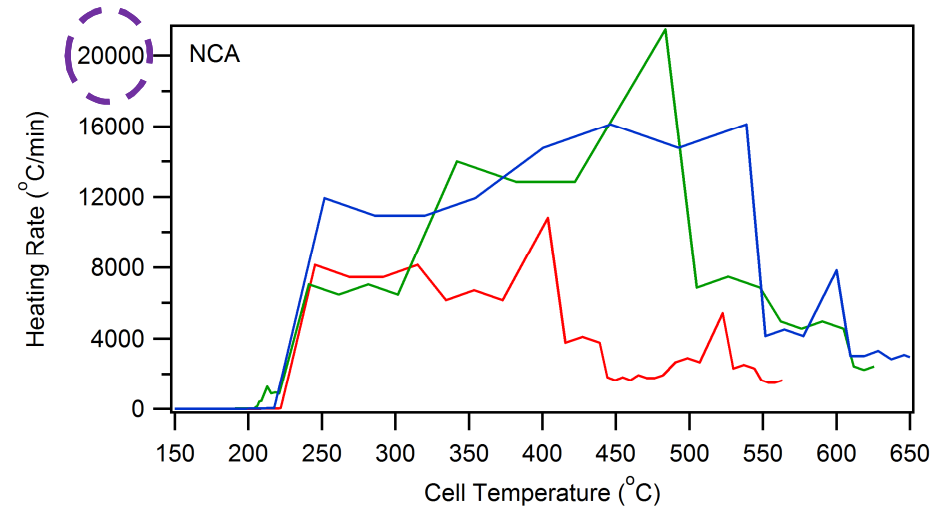
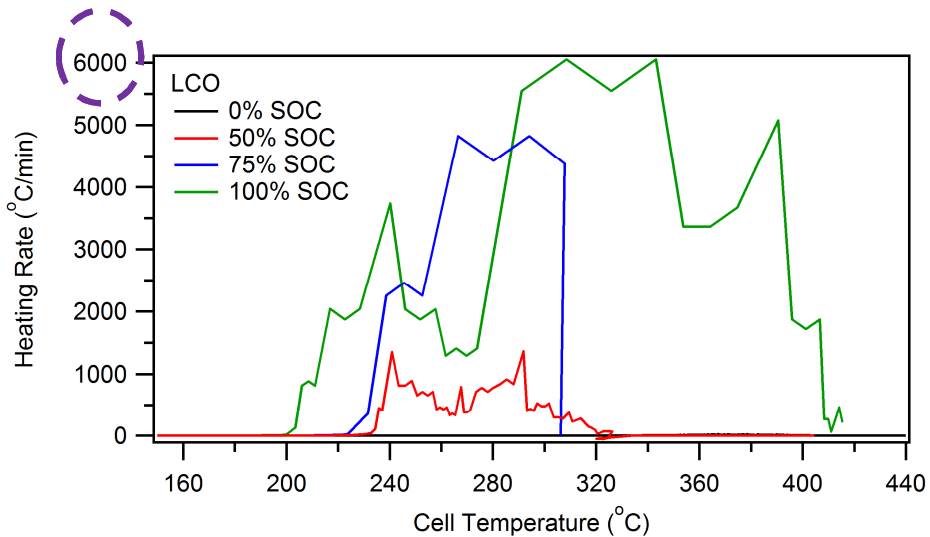
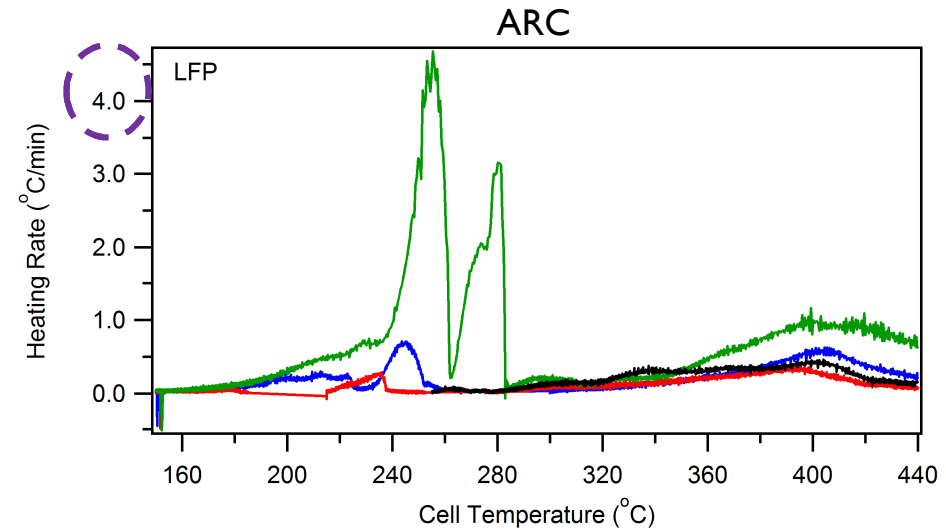


As temperature increases, lithium reacts and is pulled out of the anode.

This de-lithiation process is exothermic (generates heat) and corresponds to the peak in DSC and onset of thermal runaway observed in ARC.

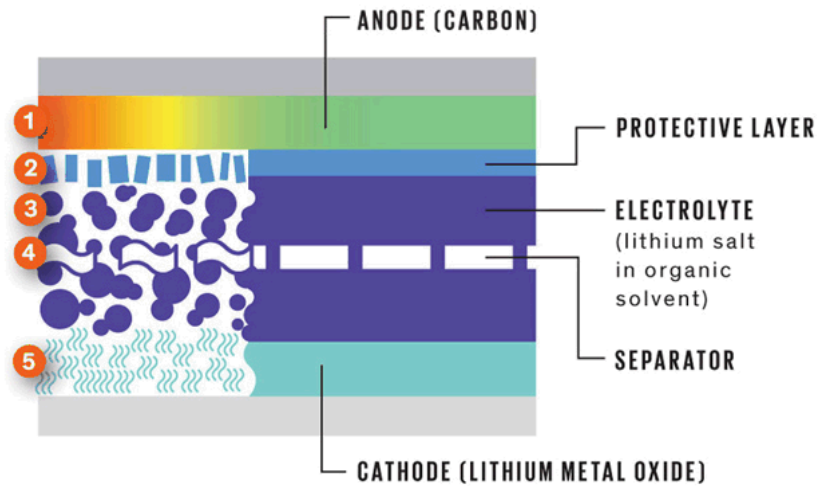


Thermal runaway behavior changes with chemistry and SOC



Maximum heating rate is chemistry dependent

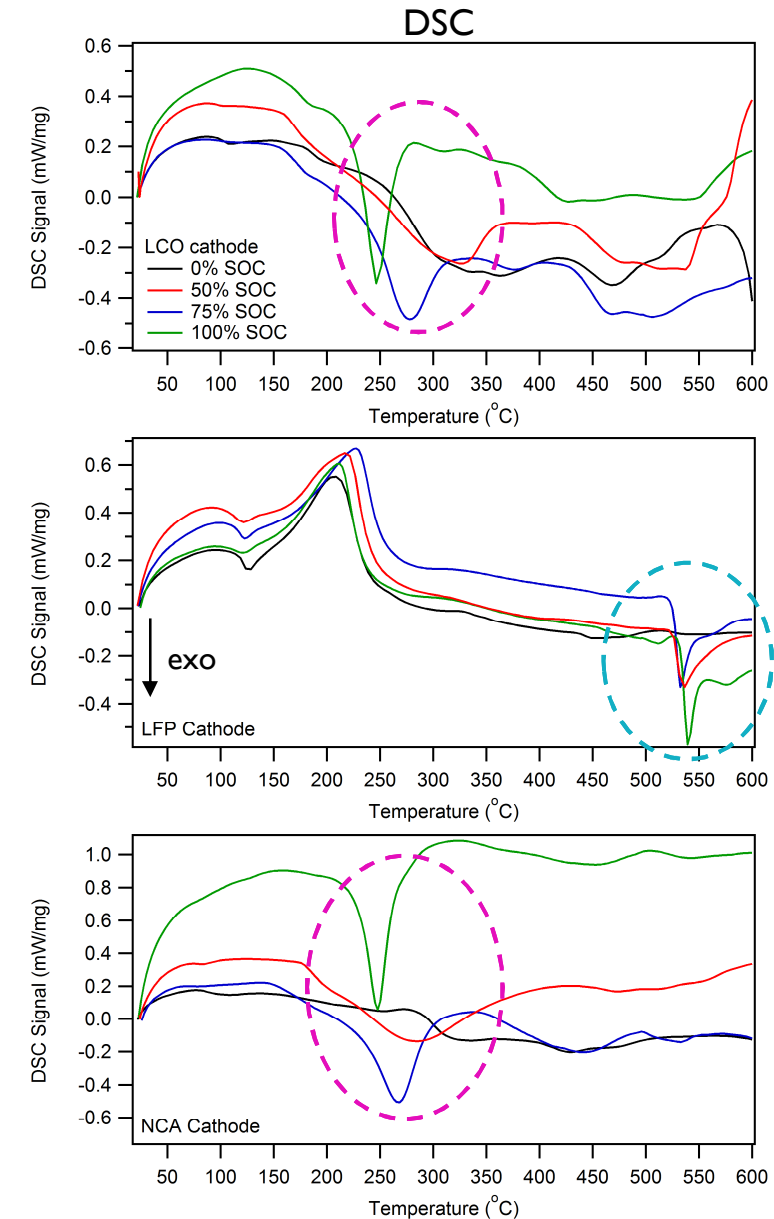
Cathode decomposition releases a lot of heat



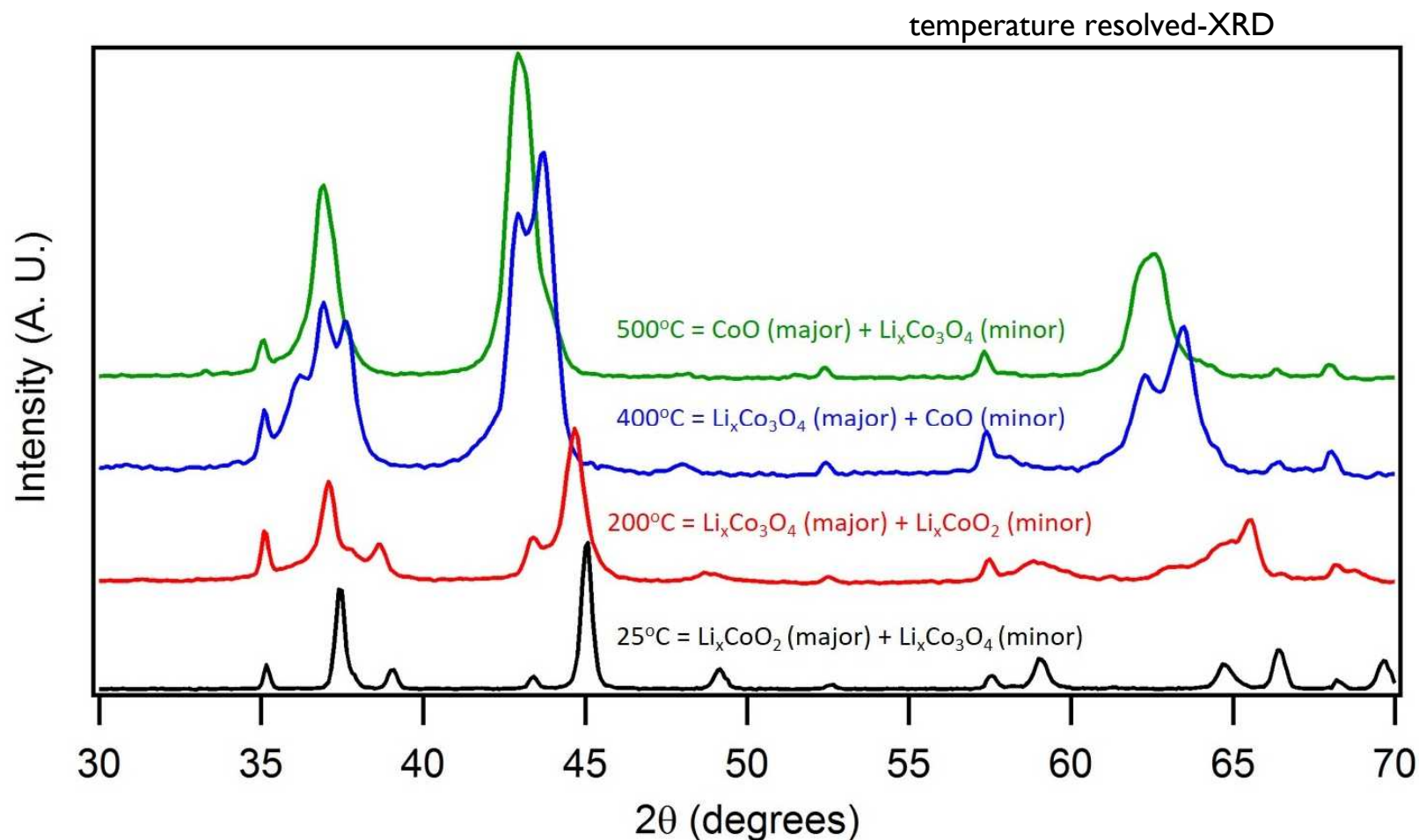
At higher temperatures, the LCO and NCA cathodes (5) break down, releasing a lot of heat (exotherm).

The LFP cathode is stable to very high temperatures

This is the peak of thermal runaway detected in the ARC (or how much heat is released).

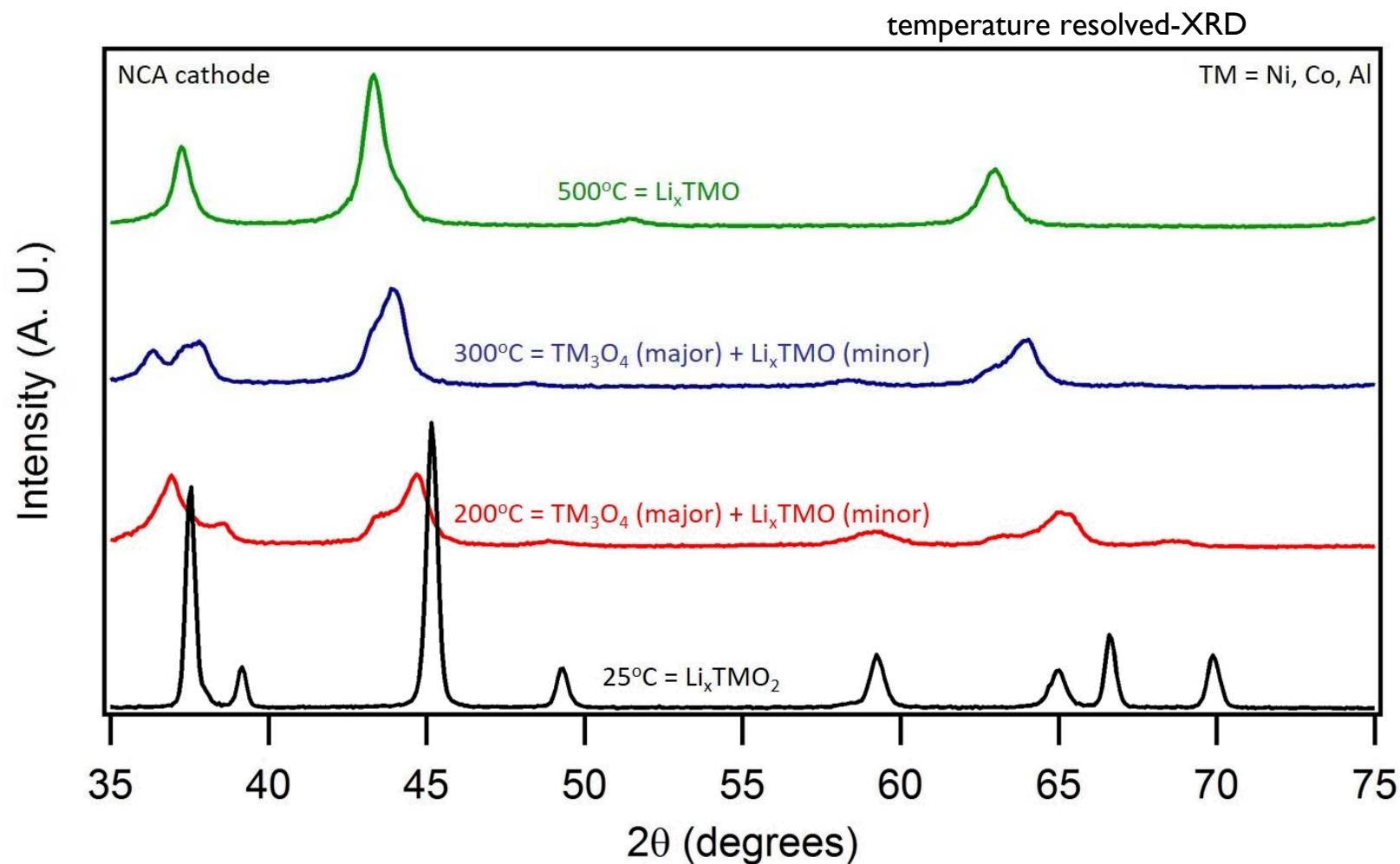


LCO cathode decomposes slowly



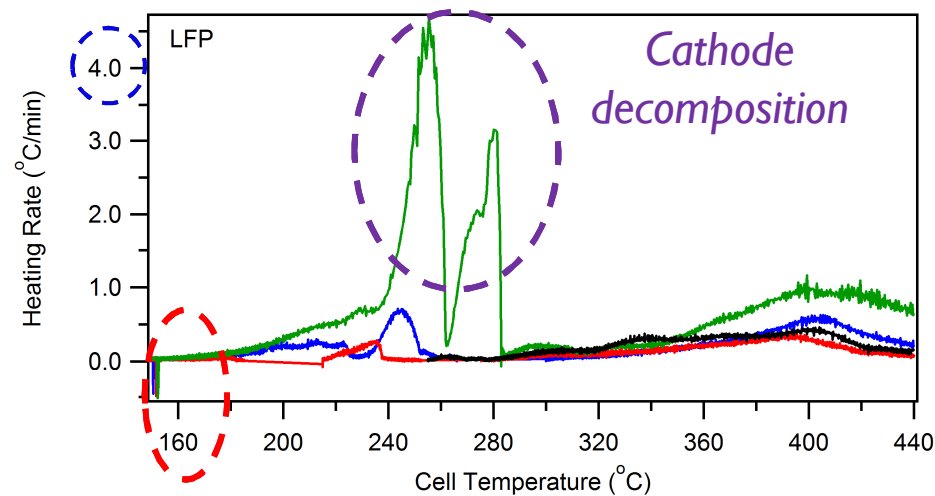
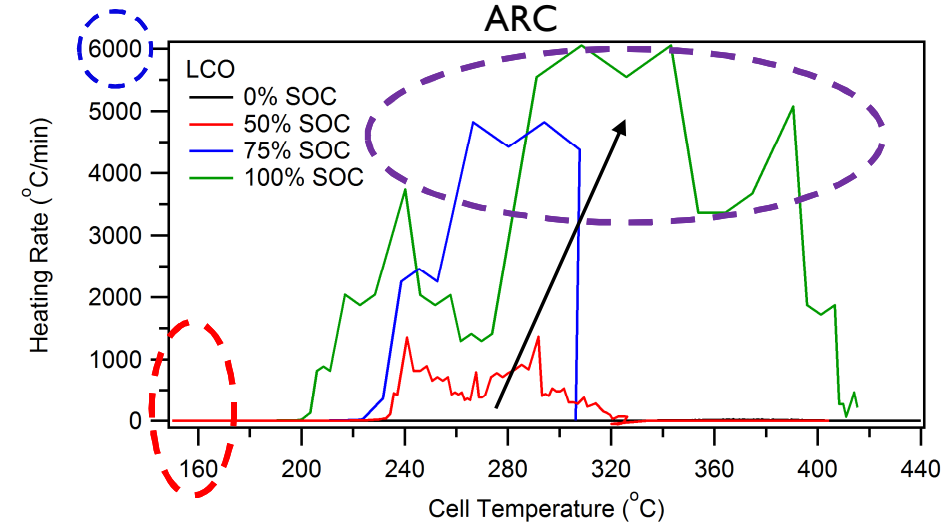
Cathode decomposition releases oxygen and heat.
Slower LCO decomposition results in lower heating rates in ARC.

NCA cathode decomposes rapidly



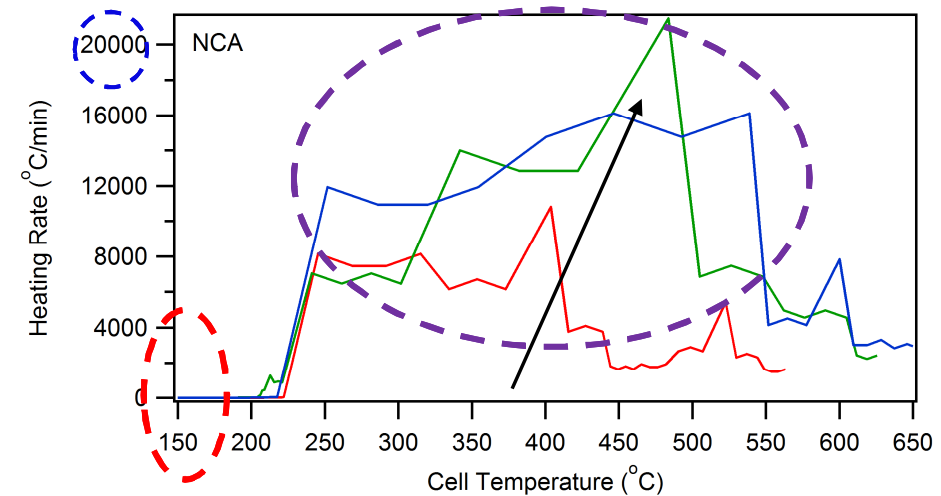
Cathode decomposition releases oxygen and heat.
Faster NCA decomposition results in higher heating rates in ARC.

Thermal runaway behavior changes with chemistry and SOC



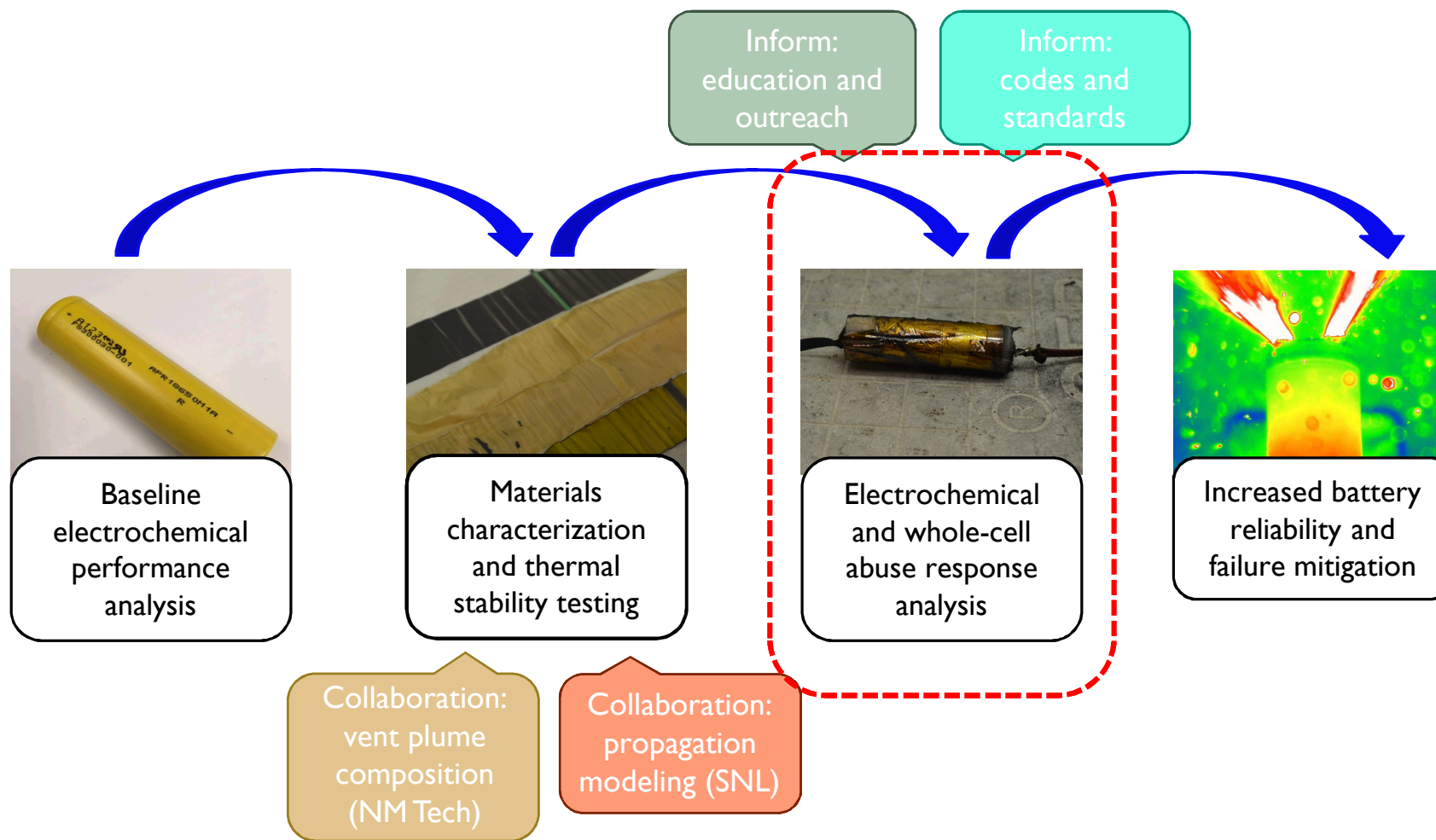
Anode decomposition

Cathode chemistry affects heat release rates

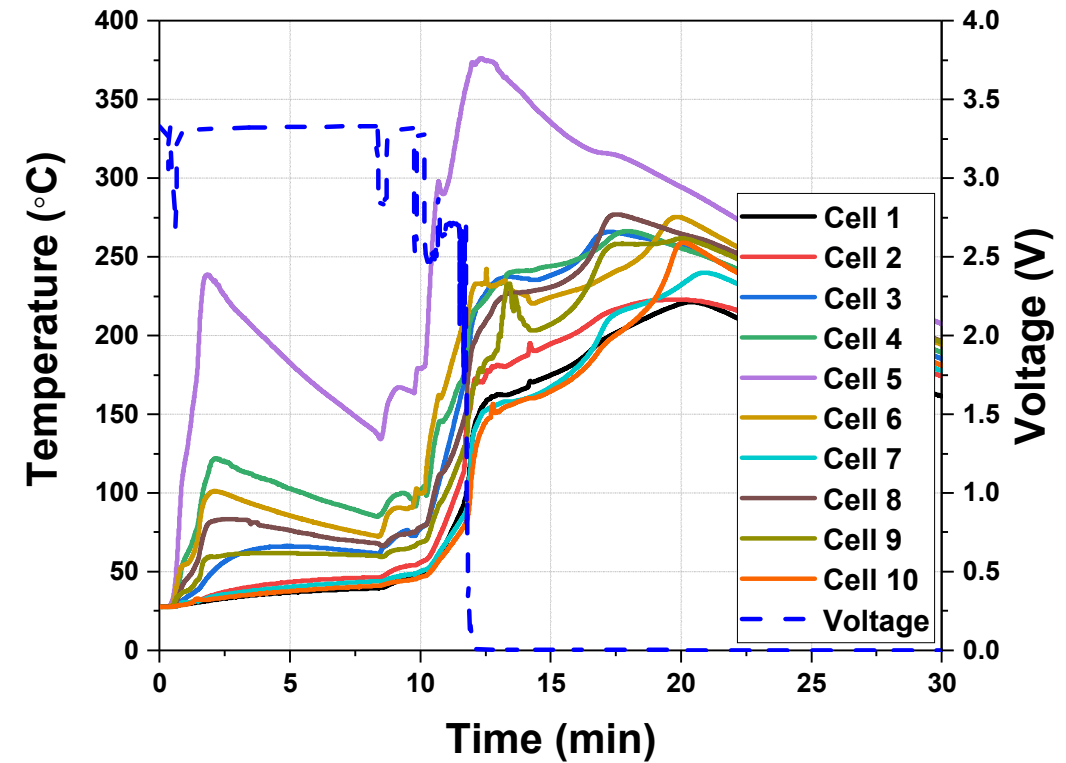
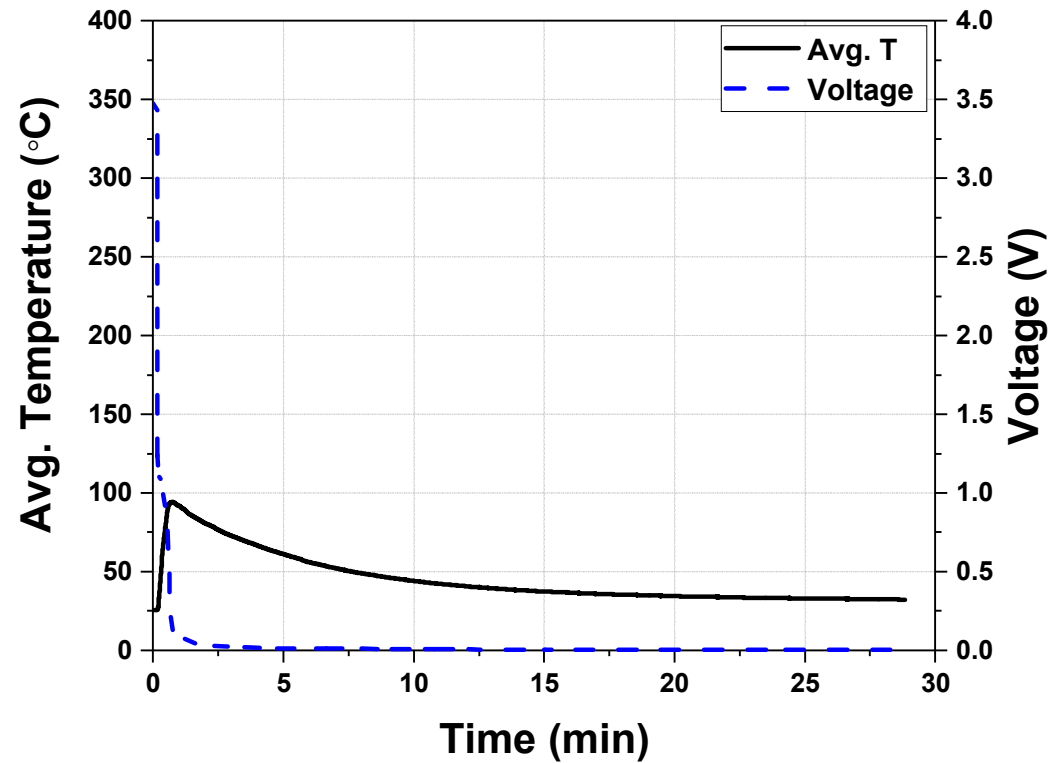


SOC effects heat release rates

Project Goal is Battery Failure Mitigation

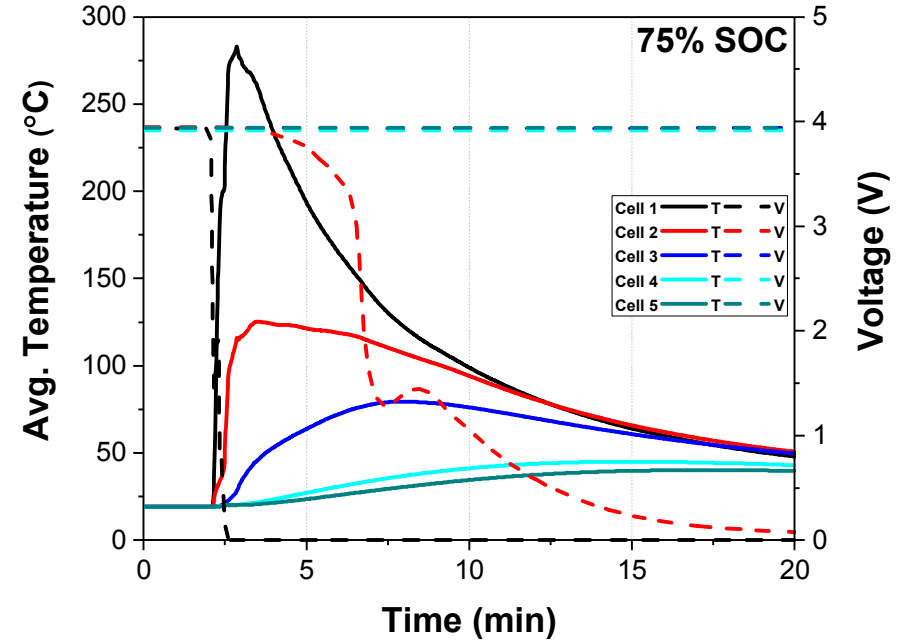
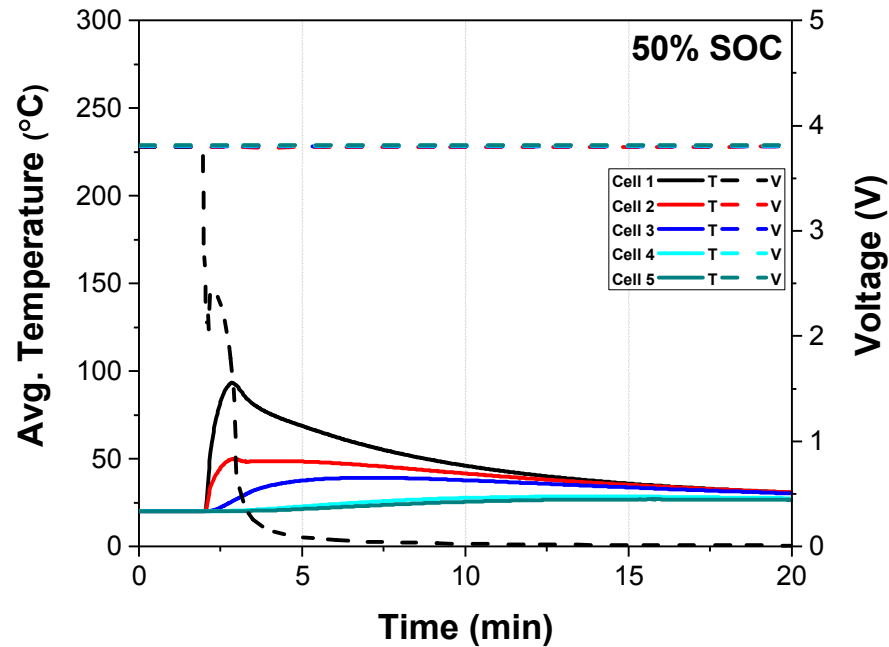


Motivation for propagation testing



- *Results of single cell nail penetration and ISI0P propagation test*
- *26650 LFP cell*
- *Single cell has relatively minor failure*
- *Significant increase in intensity with a 10 cell pack*

Mitigation through de-rating cells



- **50% SOC no cell to cell propagation observed**
 - Thermal runaway of initial cell failure also fairly minimal
- **Limited propagation at 75%**
 - Cell 2 went into thermal runaway following the failure of cell 1
 - Some other cell damage was observed but no high rate thermal runaway events seen in cells 3-5

Failure propagation with passive thermal management

Methodology:

Experimentally determine a reproducible thermal runaway initiator for each cell type

Use this initiator to trigger a single cell thermal runaway failure in a battery

Evaluate the propagation of that failure event

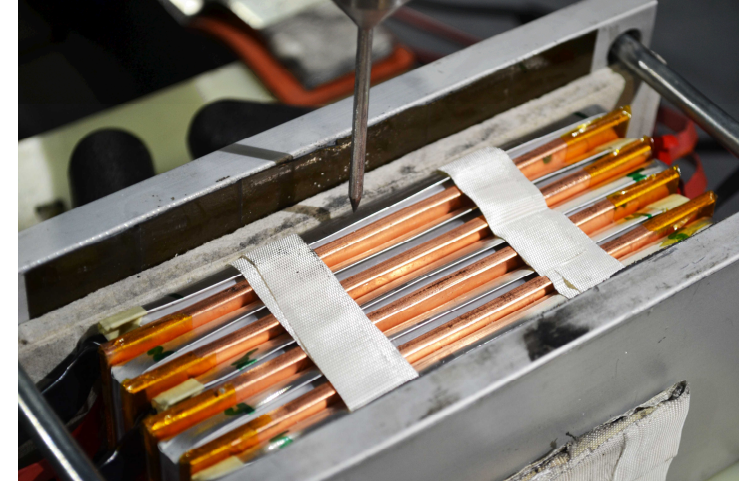
Experiment

COTS LiCoO₂ 3Ah pouch cells

5 cells closely packed

Failure initiated by a mechanical nail penetration along longitudinal axis of edge cell (cell 1)

The current effort is focused on understanding extent of propagation with inclusion of passive thermal management in the form of heat sinks between pouch cells (aluminum and copper)

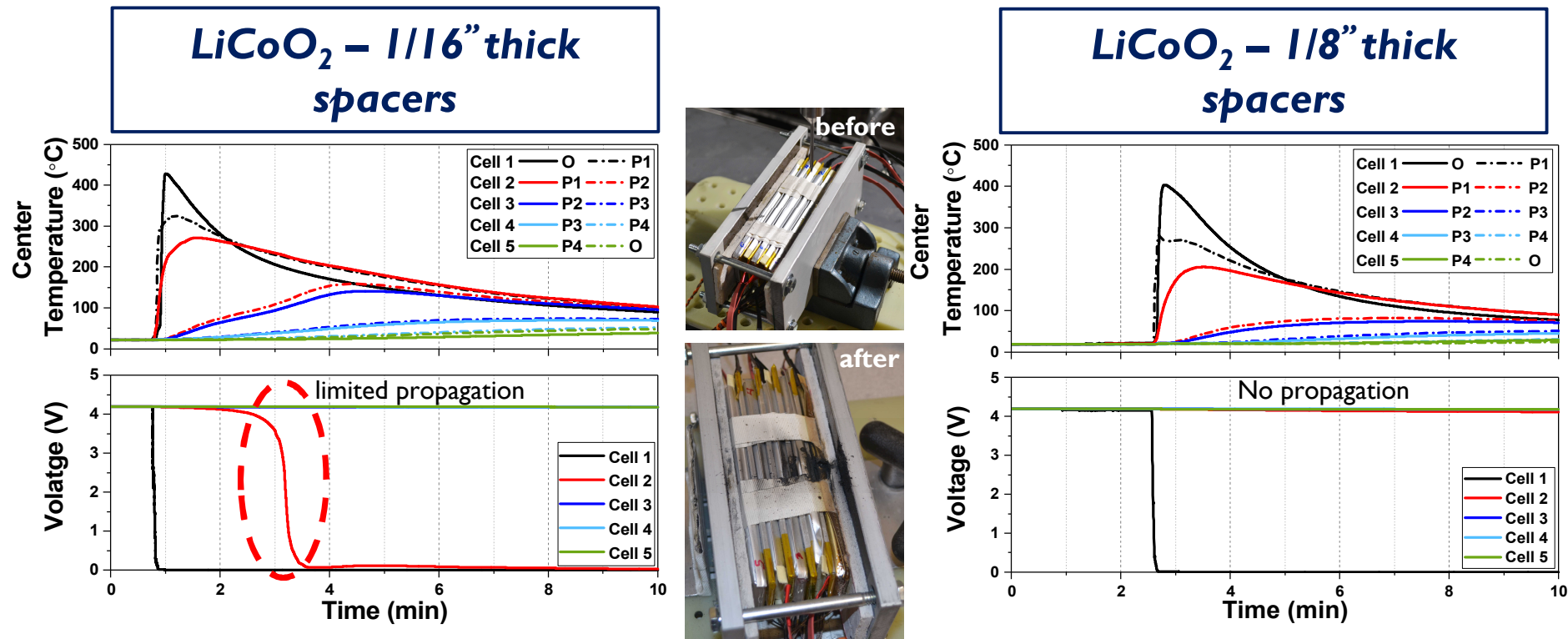


5 cell pack with aluminum or copper spacers between cells



Failure Propagation: Aluminum spacer

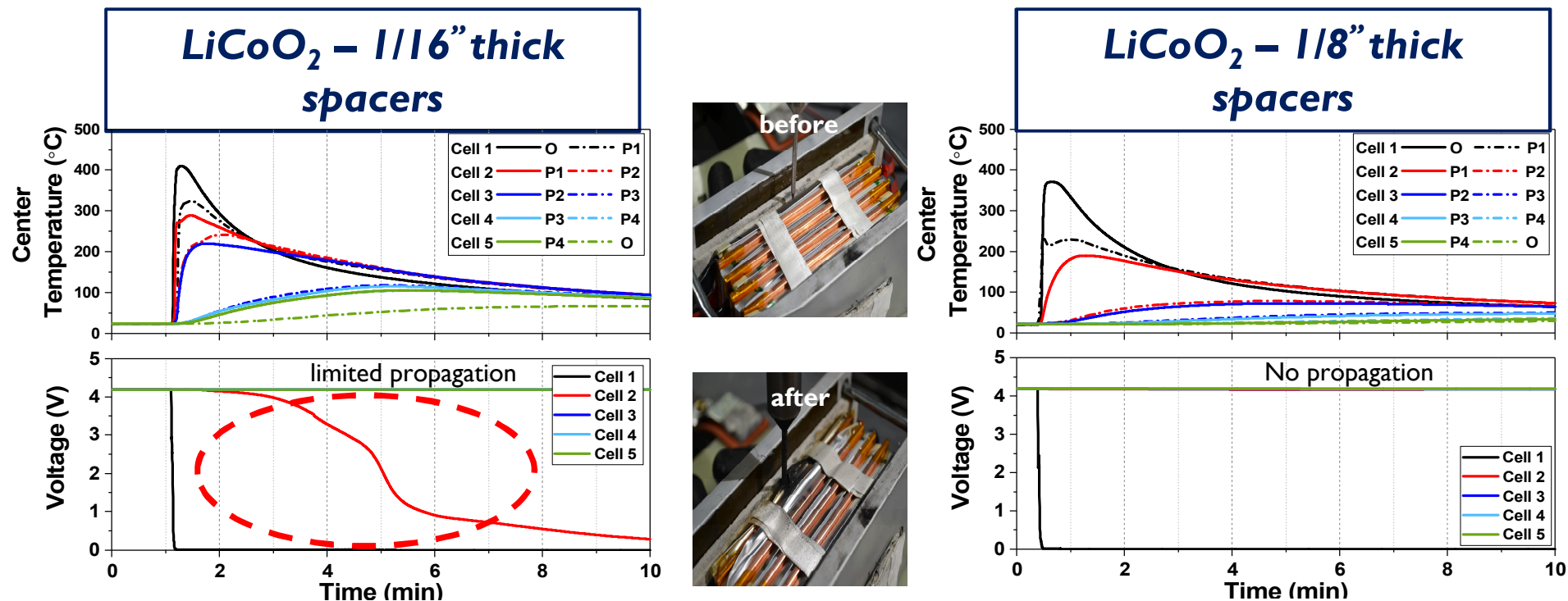
Failures initiated by mechanical insult to edge cell of COTS LiCoO₂ packs



- Failure of cell 1 in both cases were consistent and peak temperatures reached ~400 °C
- Limited propagation (from cell 1 to 2) occurred with the thinner material (1/16")
- No propagation was realized when space thickness was increased to 1/8"

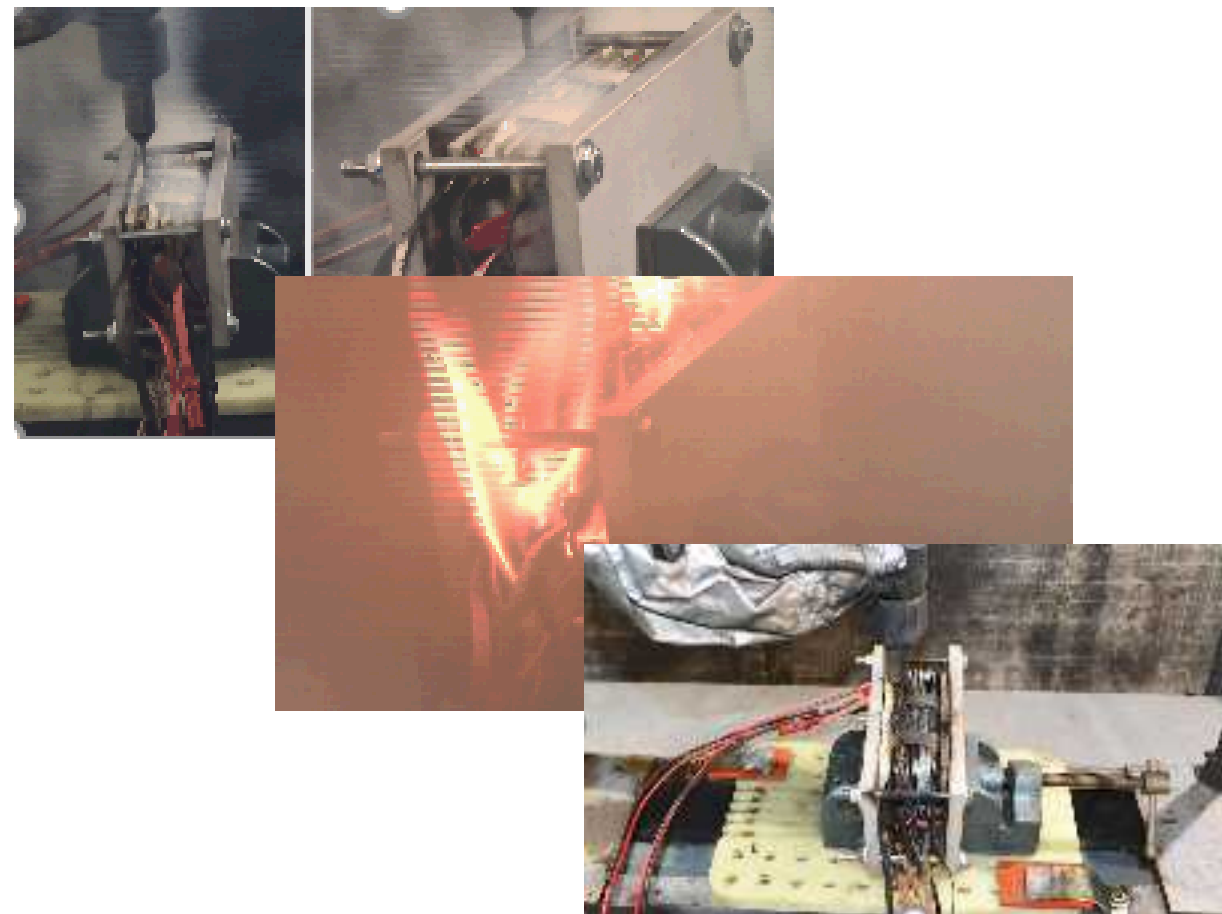
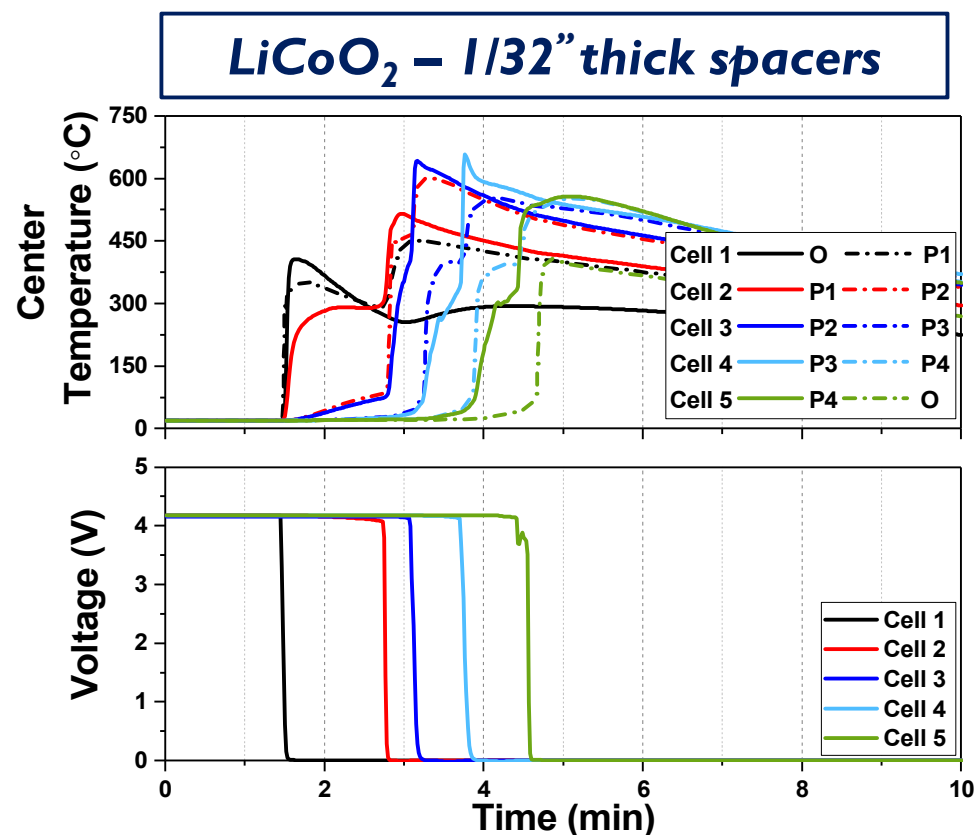
Failure Propagation: Copper spacer

Failures initiated by mechanical insult to edge cell of COTS LiCoO₂ packs



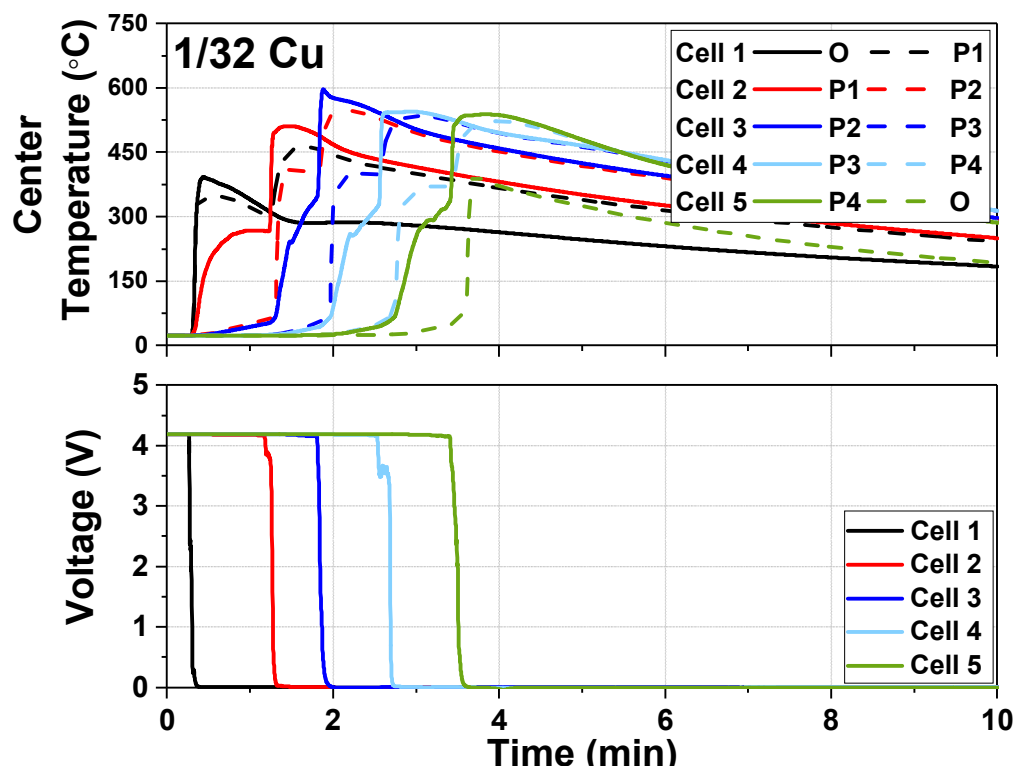
- Failure of cell 1 in all cases were consistent and peak temperatures reached ~400 °C
- Limited propagation (from cell 1 to 2) occurred with the thinner material (1/16")
- No propagation was realized when space thickness was increased to 1/8"

Failure propagation – Aluminum spacer

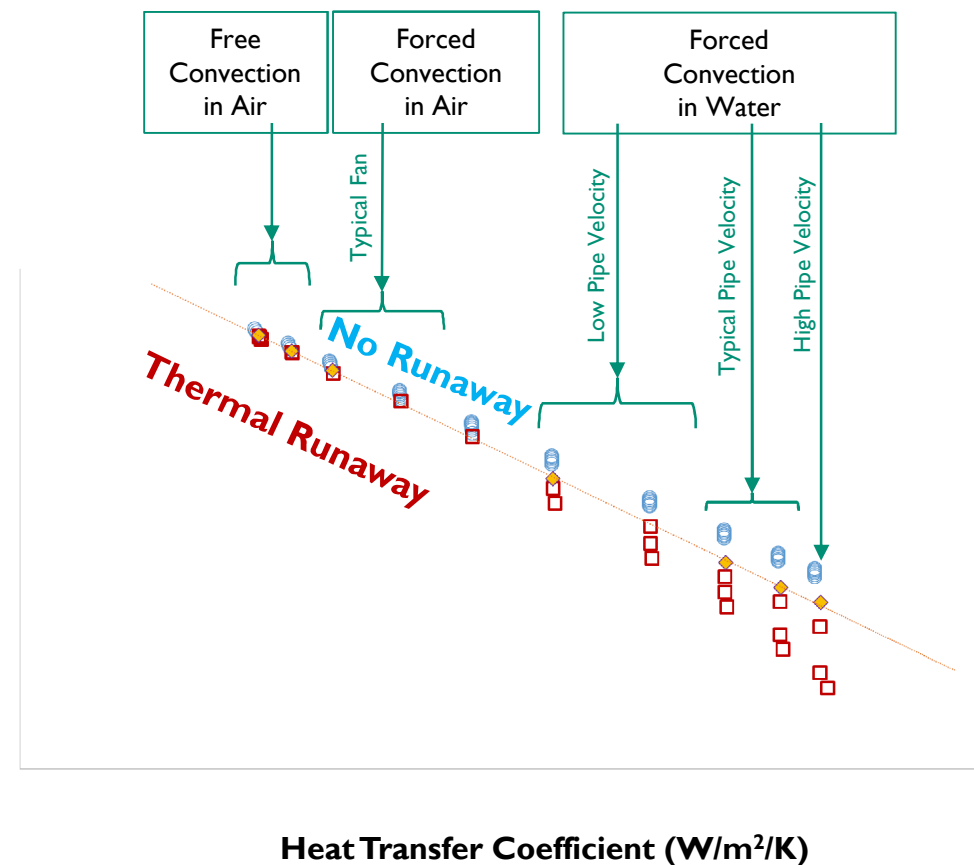


- Failure of Cell 1 observed initially
- Pulsing propagating failure behavior observed over the next several minutes
- Entire pack consumed ~4 minutes after initial cell failure

Failure propagation – Copper spacer

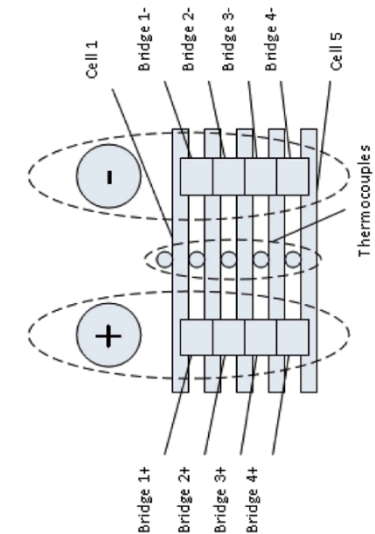
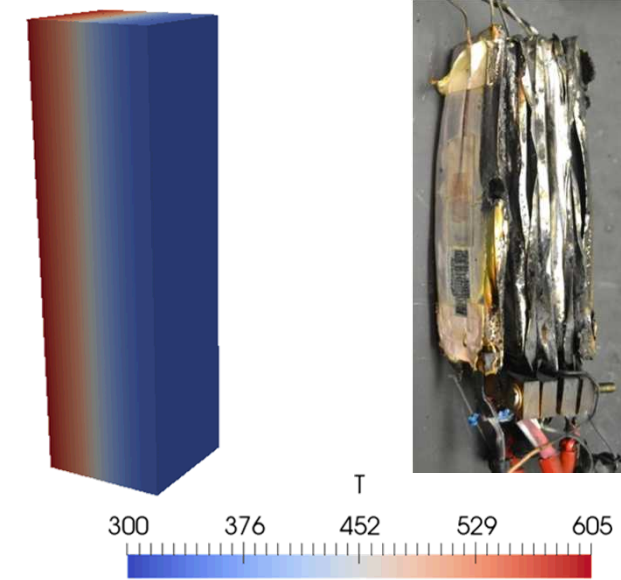
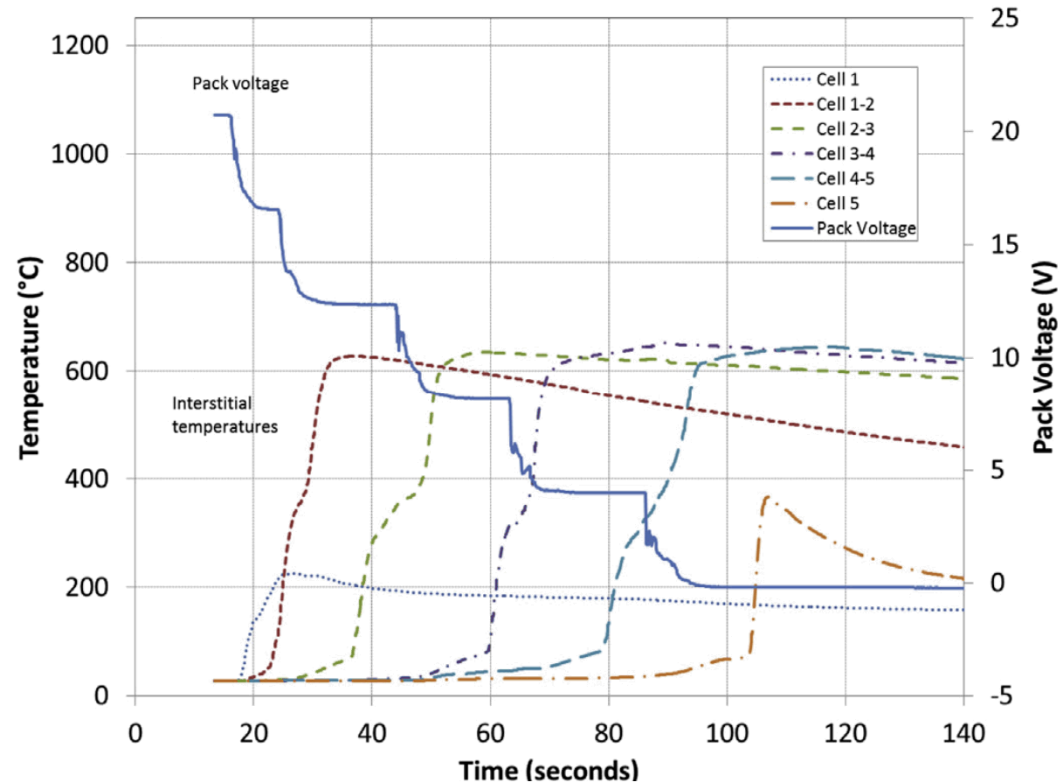


Short Circuit Resistance (ohms)



- Identified limits of mitigating thermal propagation with passive thermal management
- Next step is active cooling assessment

Cascading Propagation Observed in Li-Ion Packs



Experimental propagation in 5 stacked pouch cells at Sandia

Investigating effects of

- State of charge
- Intermediate layers
- Cell geometry

Good pack-scale model validation cases

Classic model as foundation for model development

Preliminary chemistry model from literature

- Based on Dahn group from 2000, 2001
- Derived from calorimetry data (ARC and DSC)
- Model calibrated to a specific material set

Empirical chemical reactions

- SEI decomposition $2 \text{ROCO}_2\text{Li} \rightarrow \text{Li}_2\text{CO}_3 + \text{prod}$
- Cathode-electrolyte $\text{CoO}_2 + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \frac{1}{3}\text{Co}_3\text{O}_4 + \text{prod}$
- Electrolyte-salt $\text{C}_3\text{H}_4\text{O}_3 + \text{LiPF}_6 \rightarrow \text{prod}$
- Anode-electrolyte $\text{C}_6\text{Li} + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{prod}$

This model form has been utilized repeatedly, but requires calibration for each system because it is not expressed in terms of fundamental cell characteristics.

Works well for determining onset

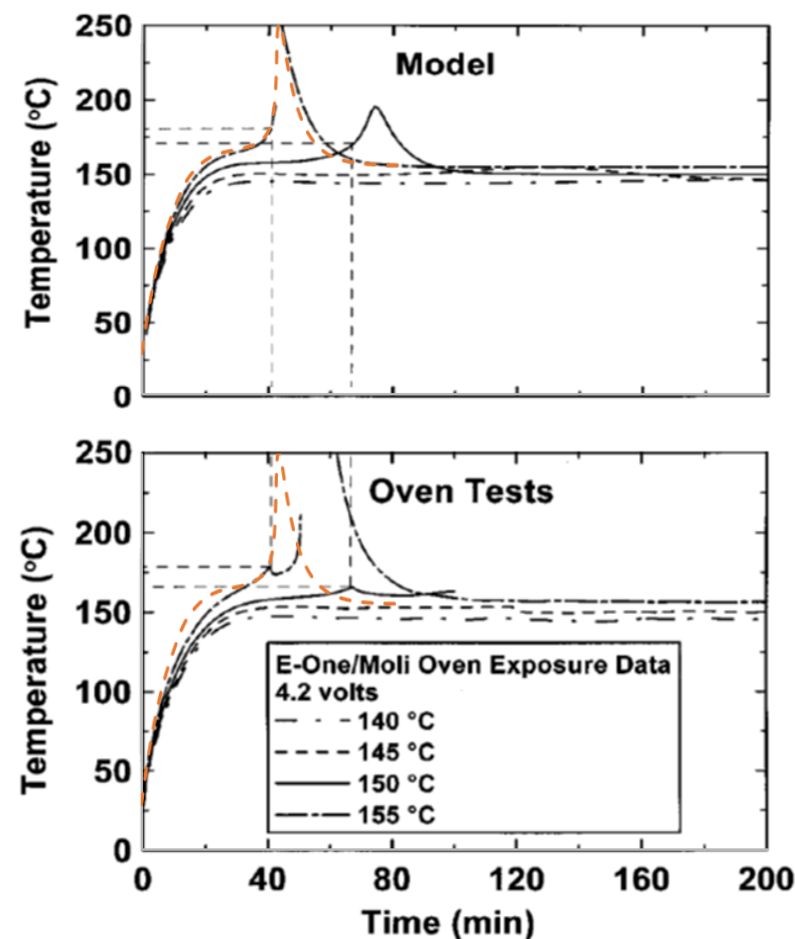
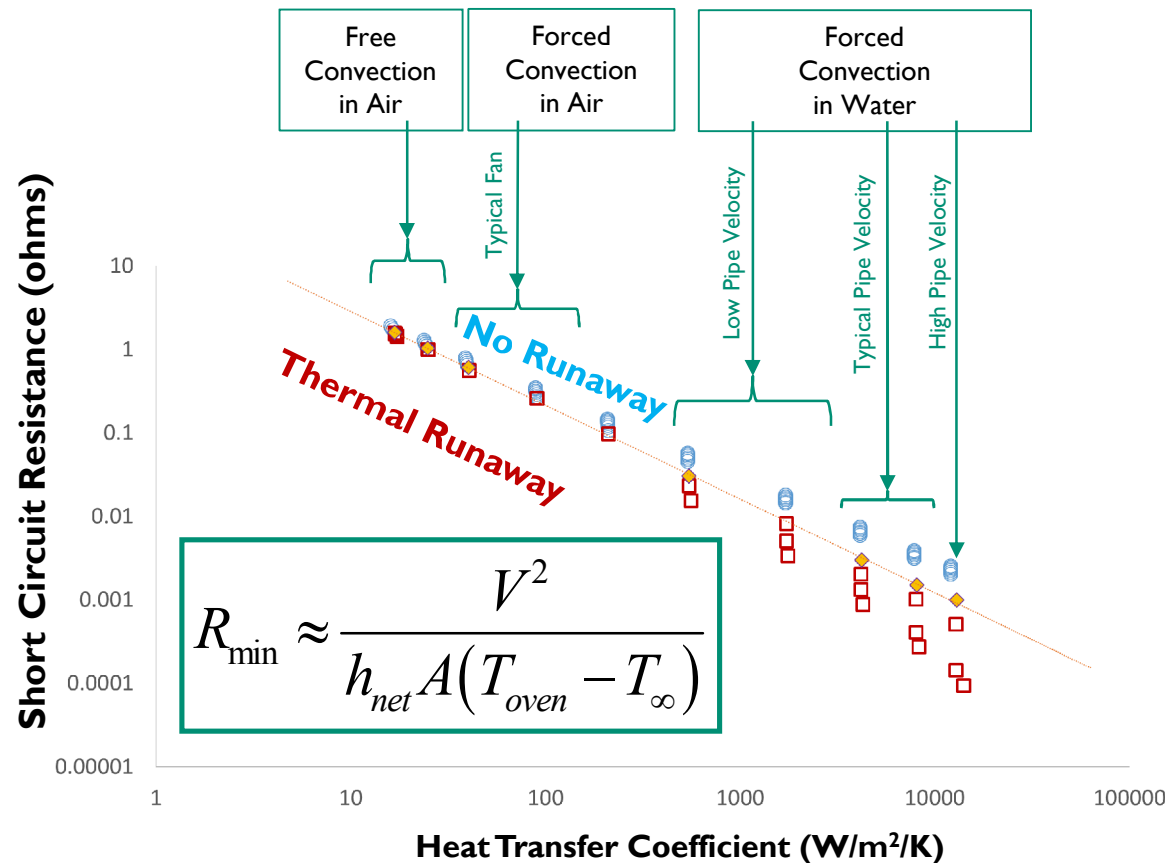
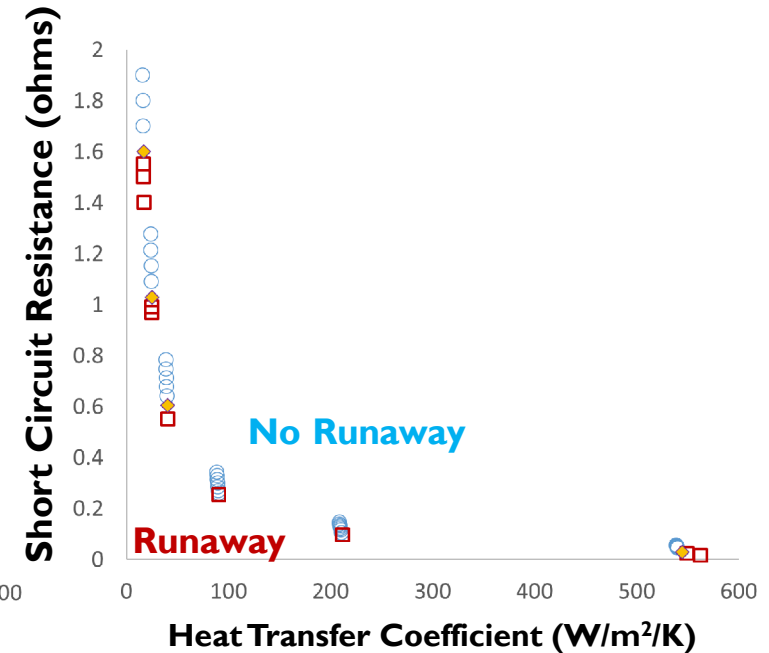


Figure 2. A comparison of oven exposure test results to model predictions: (top) model predictions and (bottom) oven test results for Energy cells charged to 4.2 V.

How Much Cooling to Suppress Runaway with Internal Short Circuit?



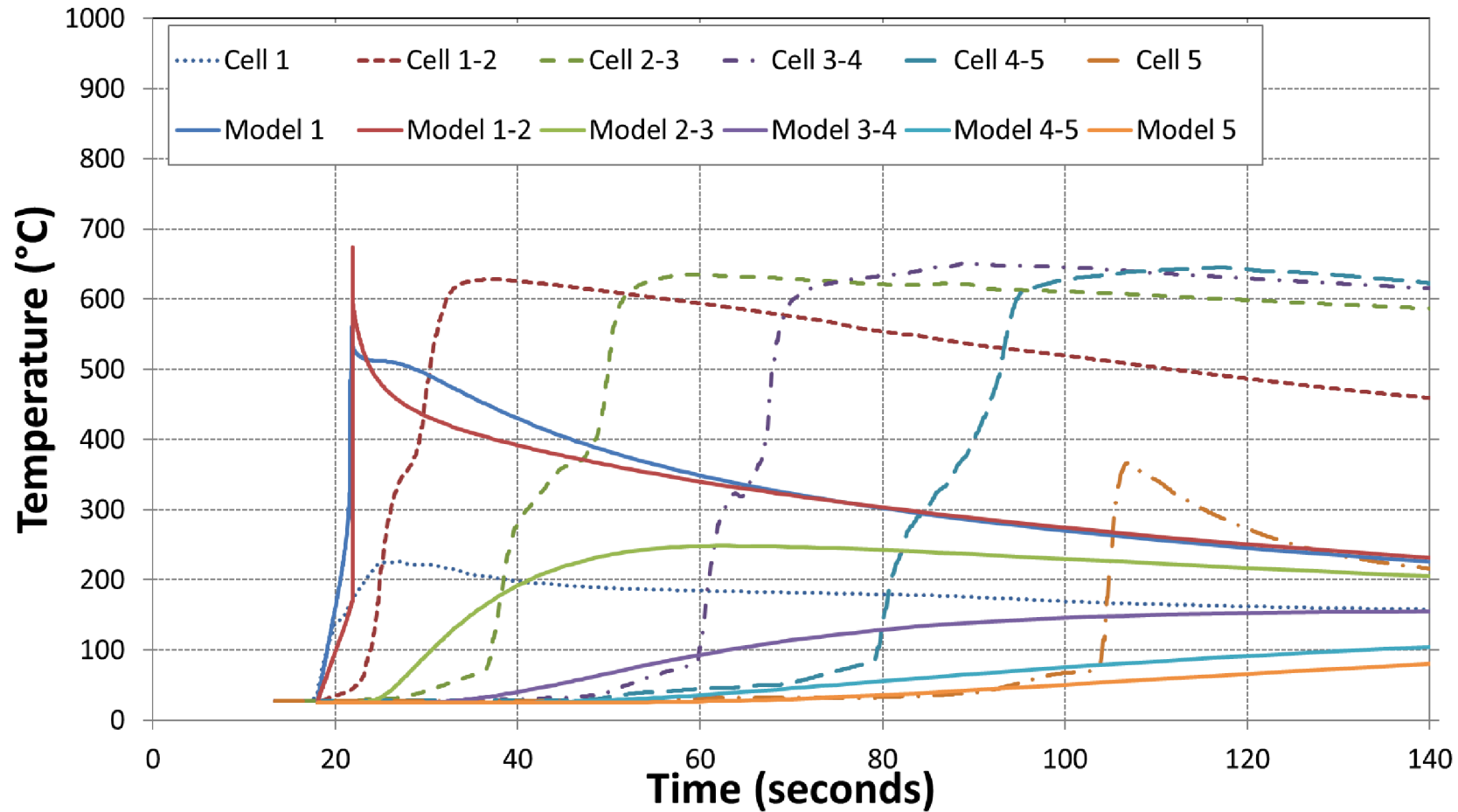
$$T_{\text{eff}} = T_{\infty} + P / h_{\text{net}} A \quad P = \frac{V^2}{R}$$



- Models can be used to estimate cooling requirements
 - Simulation shows homogeneous heating of 18650 cells (varying short resistance and cooling)
 - Internal temperature variation will be worse for large format systems and localized shorts –didn't resolve spatially (lumped capacitance limit)
 - Uses Dahn model on that specific battery to determine where thermal runaway – scenario with short circuit and cooling.

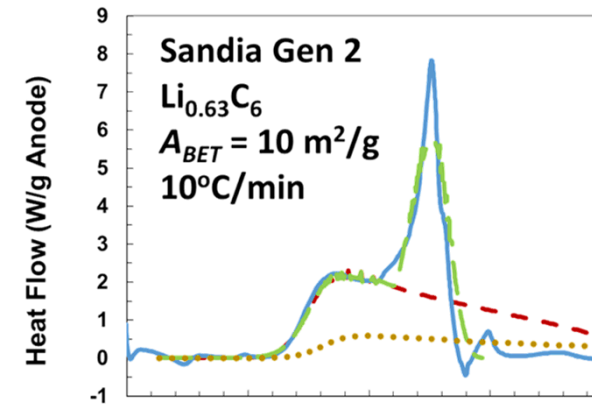
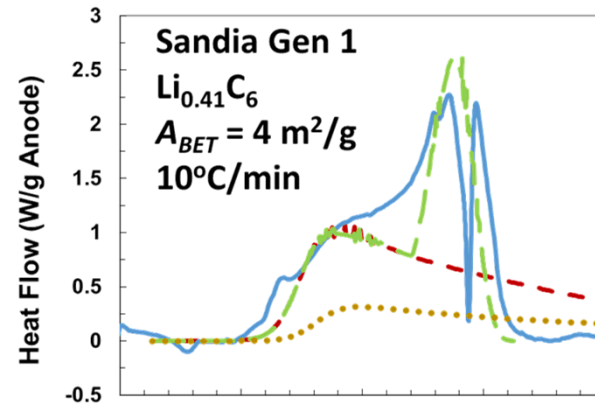
High-Fidelity Models Required for Cascading Failure

Decrease high-temperature reaction rate by 2x again

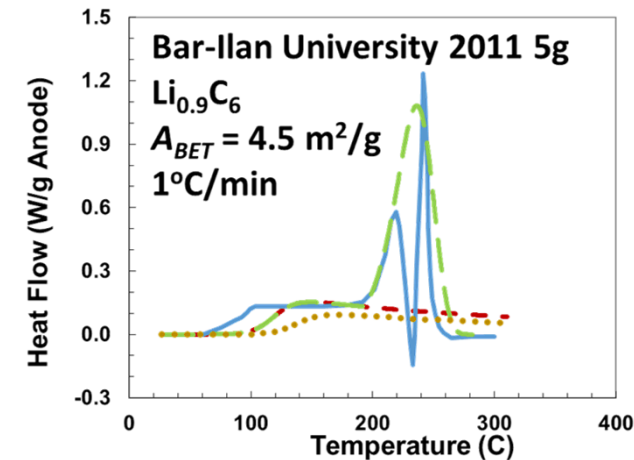
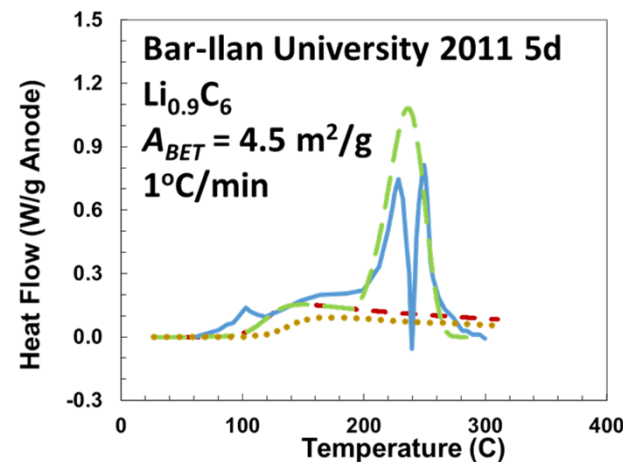


- Propagation predictions will improve with fidelity of high-temperature chemistry

Model dependent on thermodynamics/material properties



Data **Dahn Model** **One Rxn Step Area-Scaled** **Two Rxn Step Area-Scaled**



E. P. Roth and D. H. Doughty, *J. Power Sources*, **128**, 308 (2004).

O. Haik, S. Ganin, G. Gershinsky, E. Zinigrad, B. Markovsky, D. Aurbach and I. Halalay, *J. Electrochem. Soc.*, **158**, A913 (2011). – different electrolytes – not first order effect

Approaches to designing in safety

The current approach is to test our way into safety*

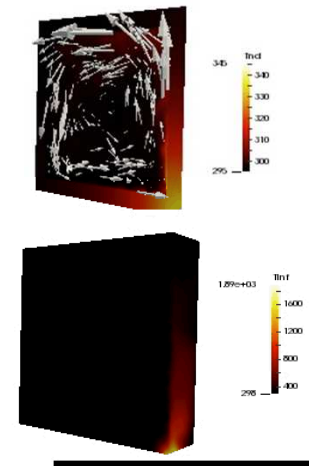
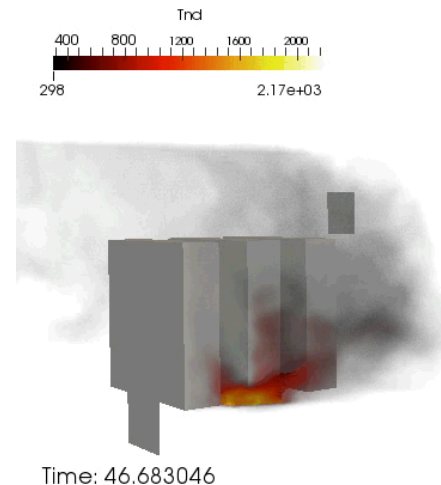
- Large system (>1MWh) testing is difficult and costly.

Consider supplementing testing with predictions of challenging scenarios and optimization of mitigation.

Develop multi-physics models to predict failure mechanisms and identify mitigation.

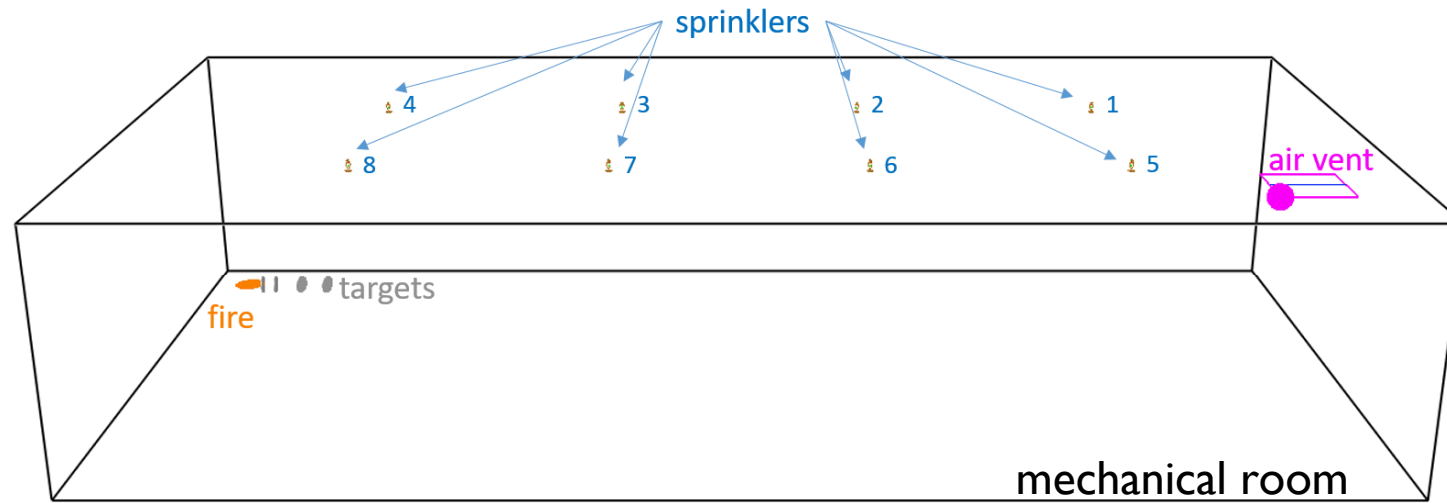
Build capabilities with small/medium scale measurements.

Still requires some testing and validation.



* 'Power Grid Energy Storage Testing Part I.' Blume, P.; Lindenmuth, K.; Murray, J. EE – Evaluation Engineering. Nov. 2012.

Batteries in buildings need to be controlled by sprinkler systems



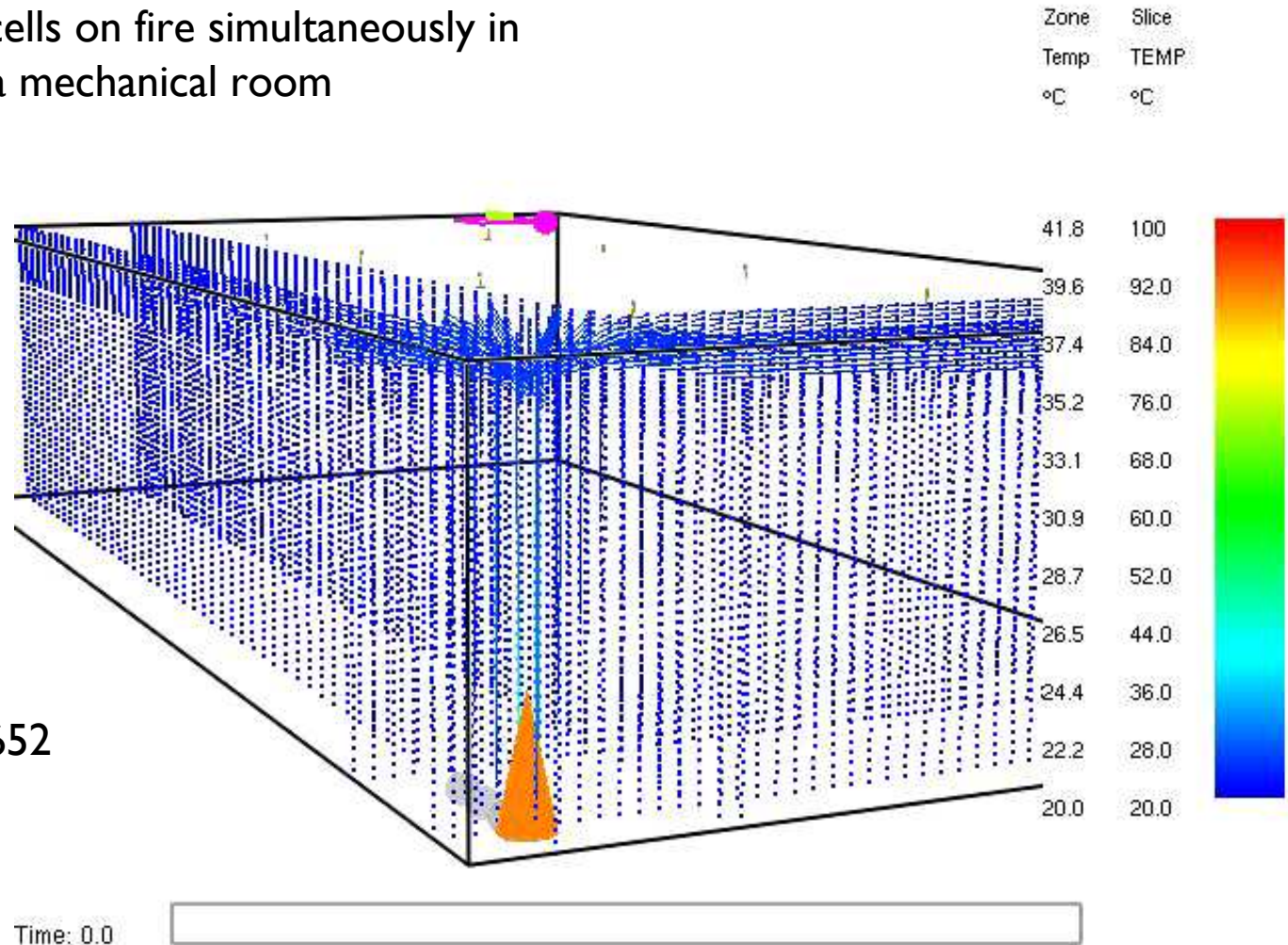
Sprinkler systems are designed to control the fire until firefighters can arrive.

More than one sprinkler activation is considered a “failed” test.

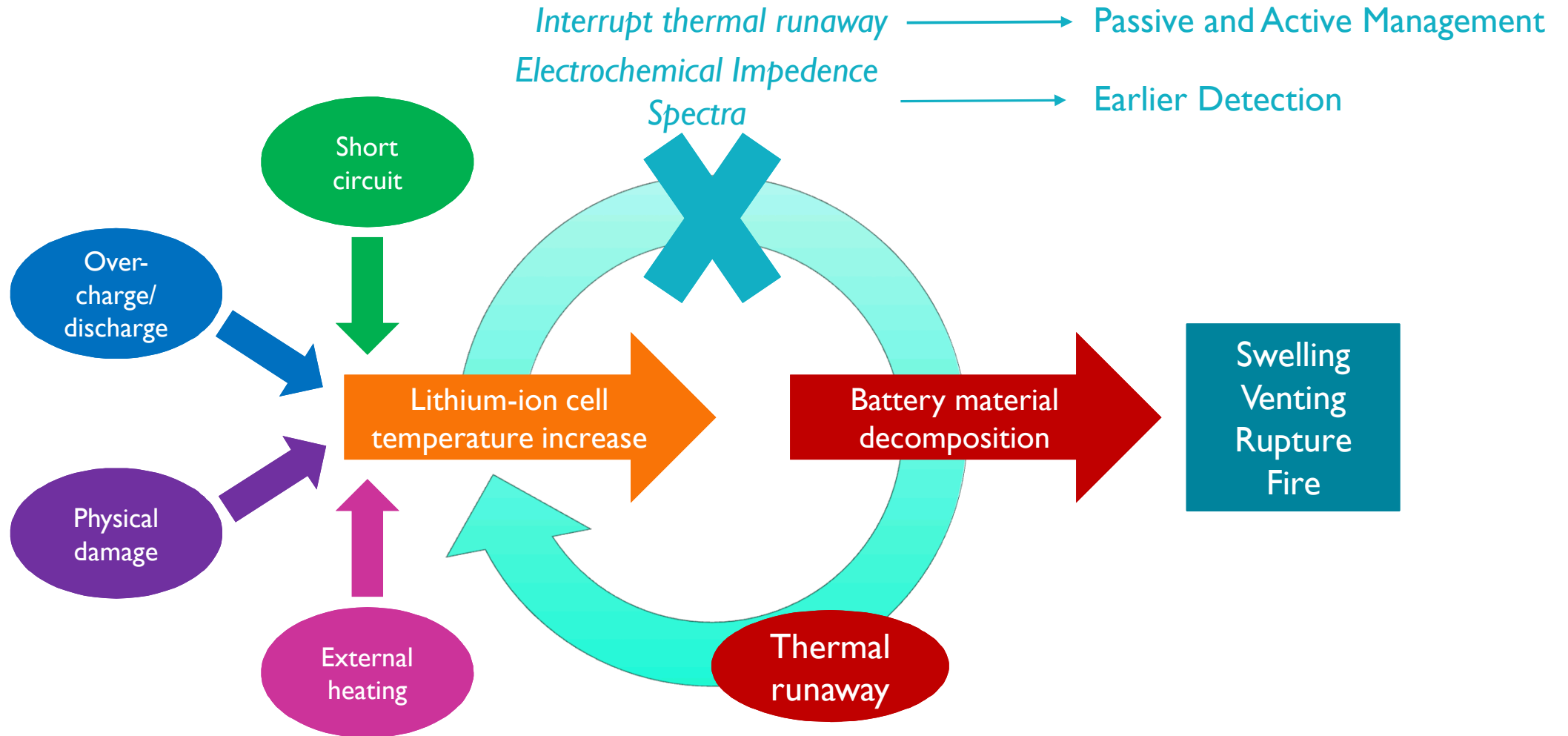
Rapid sprinkler response can control small battery fires

100 LCO cells on fire simultaneously in
a mechanical room

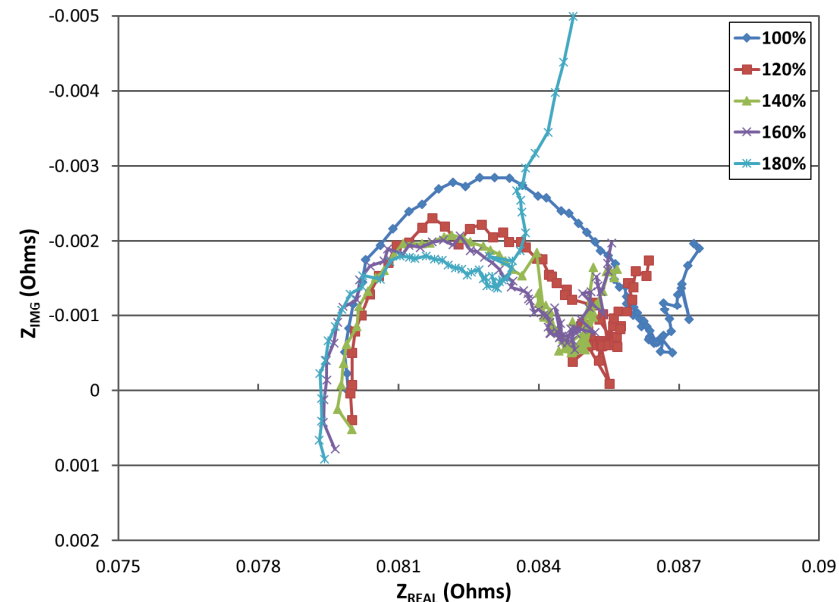
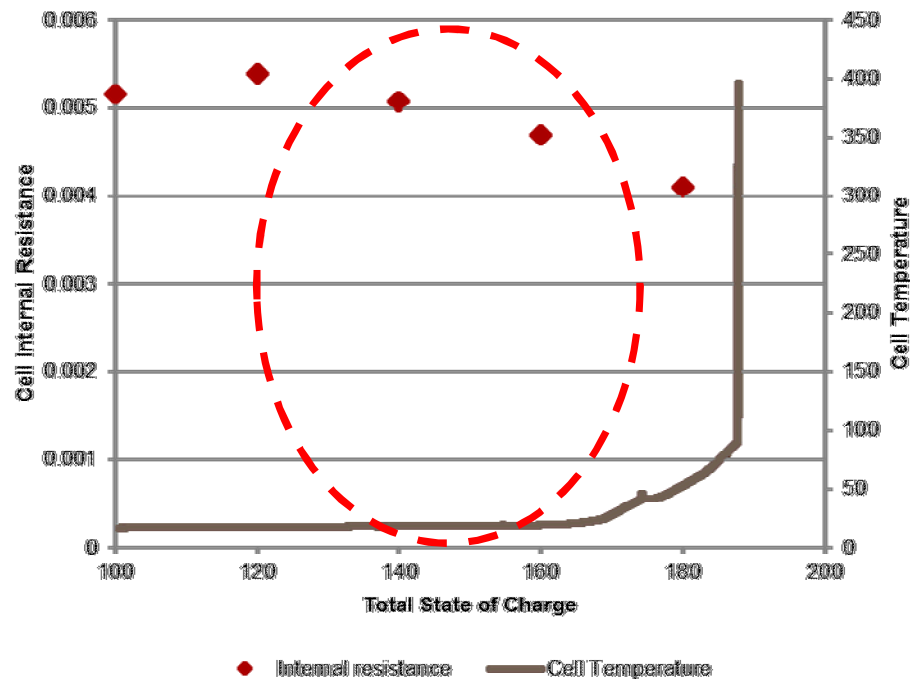
One sprinkler activates at 652
seconds



Can we prevent a battery fire?

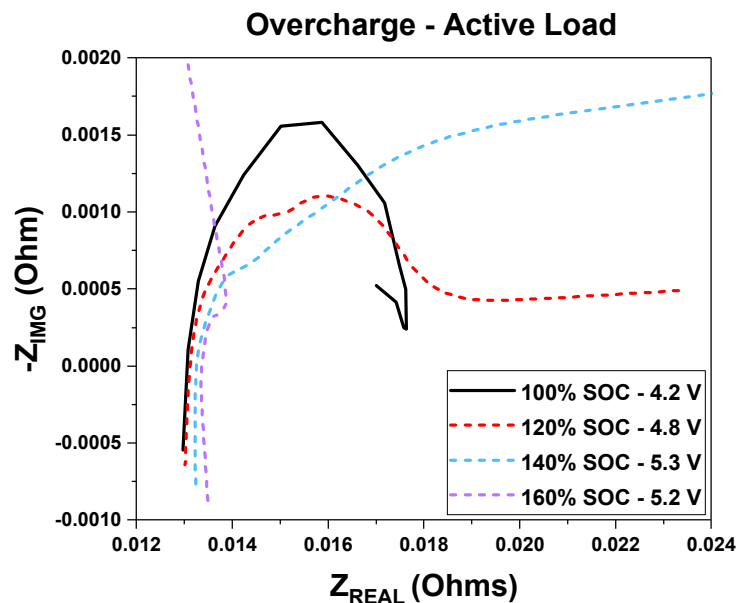
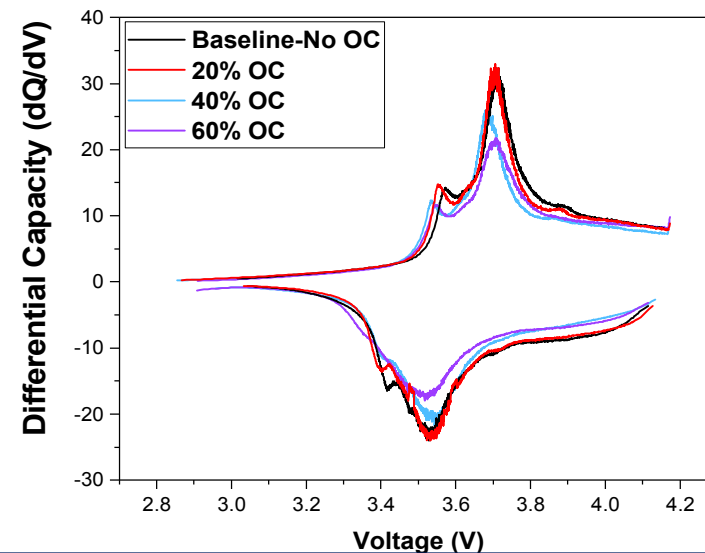
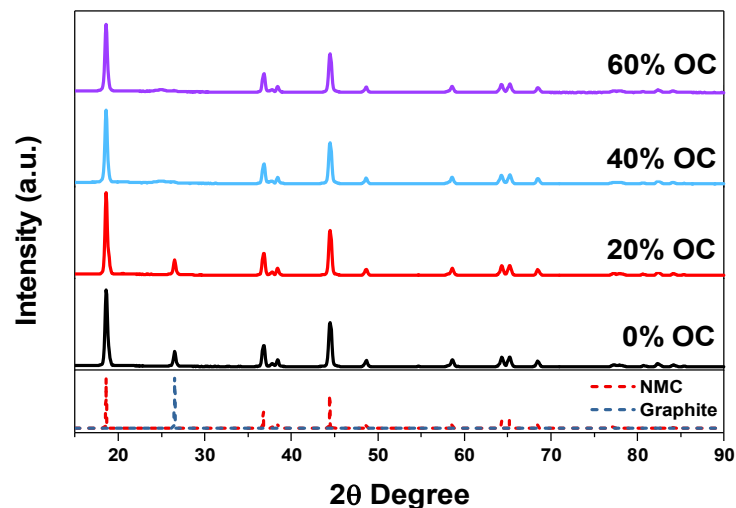


Is early detection with EIS a realistic option



- Temperature changes often lag severe damage to the cell
- Changes in internal resistance appear more indicative of abuse than external temperature
- 3SIP data shows data as single cell within a 3 cell series pack is overcharged

Understanding materials consequence of diagnostic markers



- **Overcharge is applied to 10 AH NMC cells**
- **Fast impedance hardware allows for collection of EIS data while cell is under active load**
- **Cycling performed after overcharge test to observe differential capacity behavior**
- **Anode and Cathode materials harvested post test for materials analysis (Harvested at 0% SOC, cathode results shown)**
- **Coupling electrochemical measurement and materials analysis to create a predictive measurement technique**

Summary

Field the most inherently safe chemistries and designs

Testing failure propagation to understanding vulnerabilities

Research informed by materials understanding is critical to:

- **Containment** of storage across scales and chemistries
- Effective **suppressants** identification and use
- Appropriate **hardware and software controls** to mitigate failures and propagation of failures

Through integrated R&D into failure behavior and consequences using **experimental** and **modeling** efforts across scale.

ESS Safety Team

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Armando Fresquez

Sergei Ivanov

Jill Langendorf



Acknowledgements

Battery Safety R&D Program at Sandia: http://energy.sandia.gov/?page_id=634

DOE Office of Electricity Dr. Imre Gyuk for supporting energy storage safety work

Office of Vehicle Technologies

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Los Alamos National Laboratory (Contract DE-AC52-06NA25396) and Sandia National Laboratories (Contract DE-AC04-94AL85000).