SAND2017-11895C

Safety Considerations of Materials at the Cell and System Level

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MRS Fall Meeting Tutorial ES05

November 26th, 2017

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Agenda Overview

- Part I Materials at the Cell to System Level for Safety Considerations
- Part II Modeling of Thermal Characteristics and Safety
- Part III Systems and Engineering Aspects including Safety and Reliability
- Part IV Research and Development Priorities for a More Resilient Energy Storage System

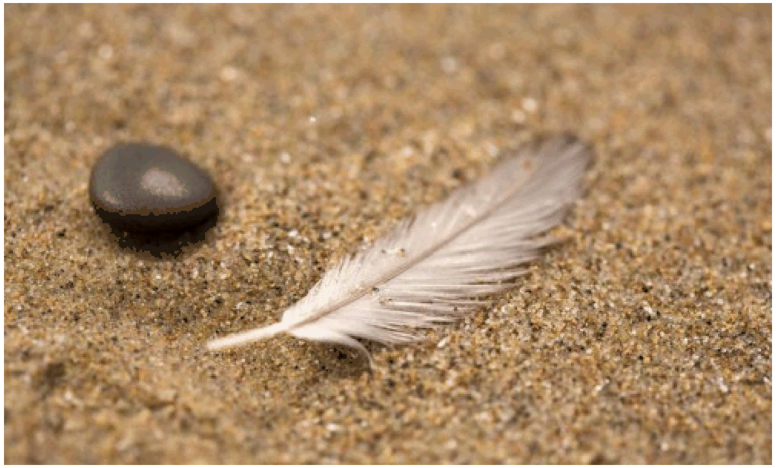
Agenda Overview

- Part I Materials at the Cell to System Level for Safety Considerations

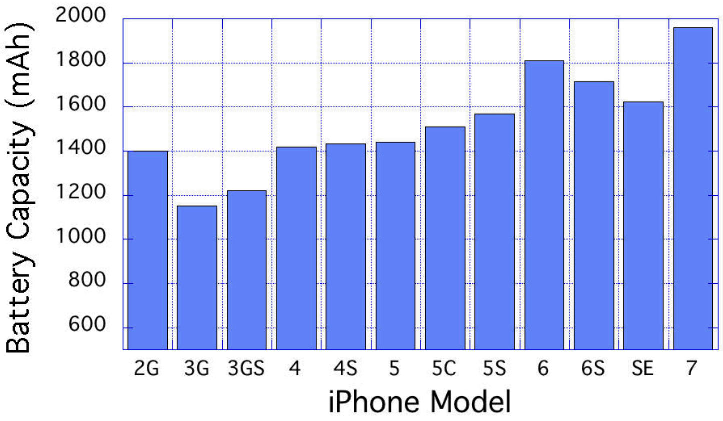
- *Safety Considerations of Materials at the Cell to System Level*
  - Why safety matters
  - Consequences of failure
  - Modes of failure
  - How cells fail – materials perspective (what are the dominoes and in what order do they fall)
  - Inherently safe batteries "the dream"
    - Shutdown separator
    - Electrolyte
    - Electrode (anode) decomposition prevention

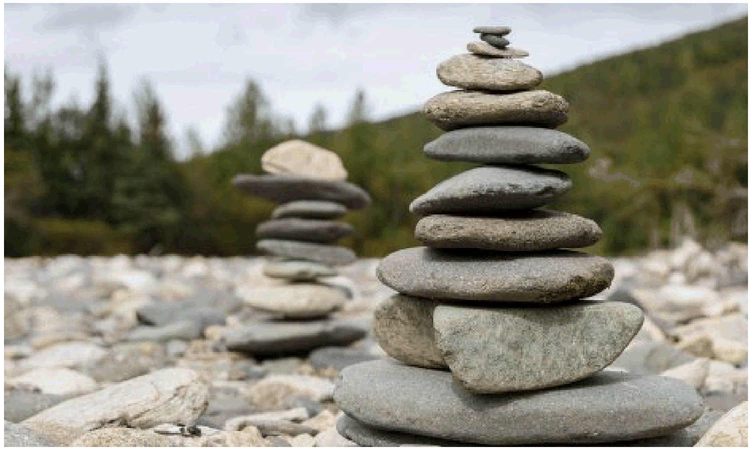
Safety risks consequences scales with …

Density



Size





iStockphoto.com/AJ_Mascari
https://www.dailydot.com/debug/iphone-2g-vs-iphone-7/
Shutterstock.com/Menno Schaefer

Safety risk likelihood scales with…

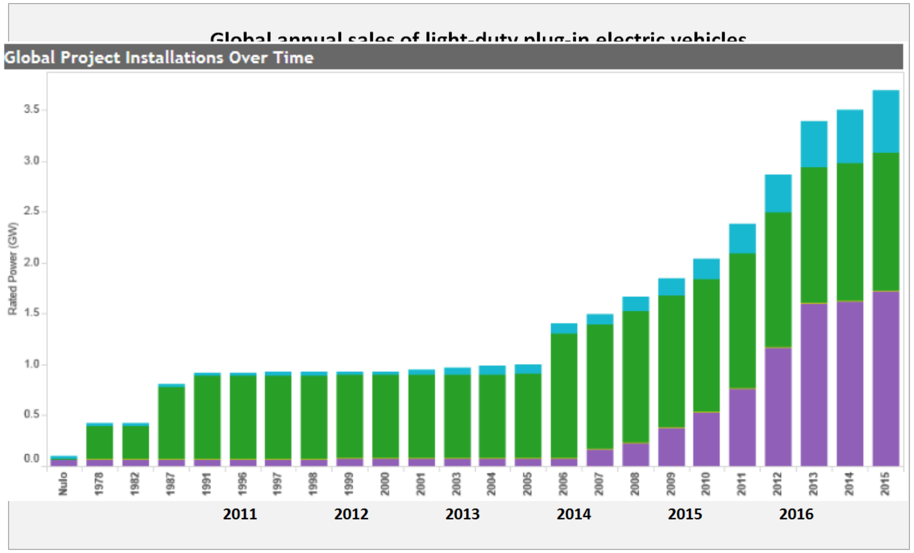
Proximity and quantity

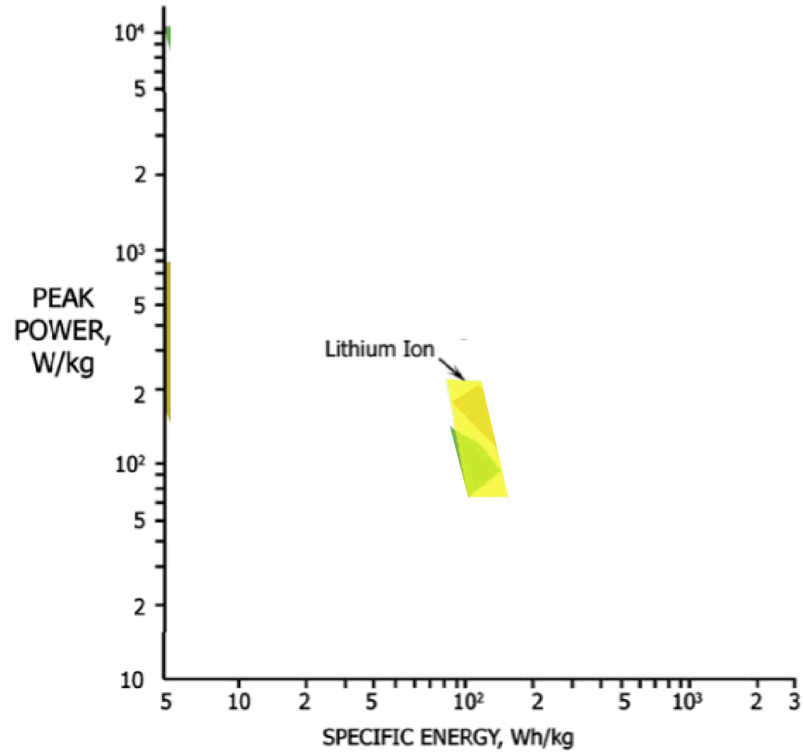
http://i2.cdn.cnn.com/cnnnext/dam/assets/160816161739-earbuds-thumbnail-large-169.png
http://a.abcnews.com/images/GMA/140728_gma_schiavocampo3_0743_16x9_992.jpg
http://www.trustedreviews.com/news/samsung-galaxy-s7-edge-overheating-catch-fire

Risk encompasses consequence and likelihood

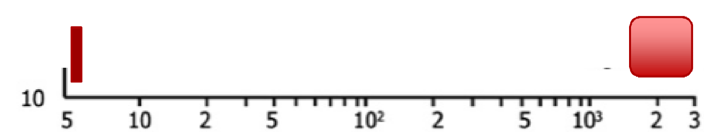
https://commons.wikimedia.org/w/index.php?title=User:EvanS

Systems have more complex risks





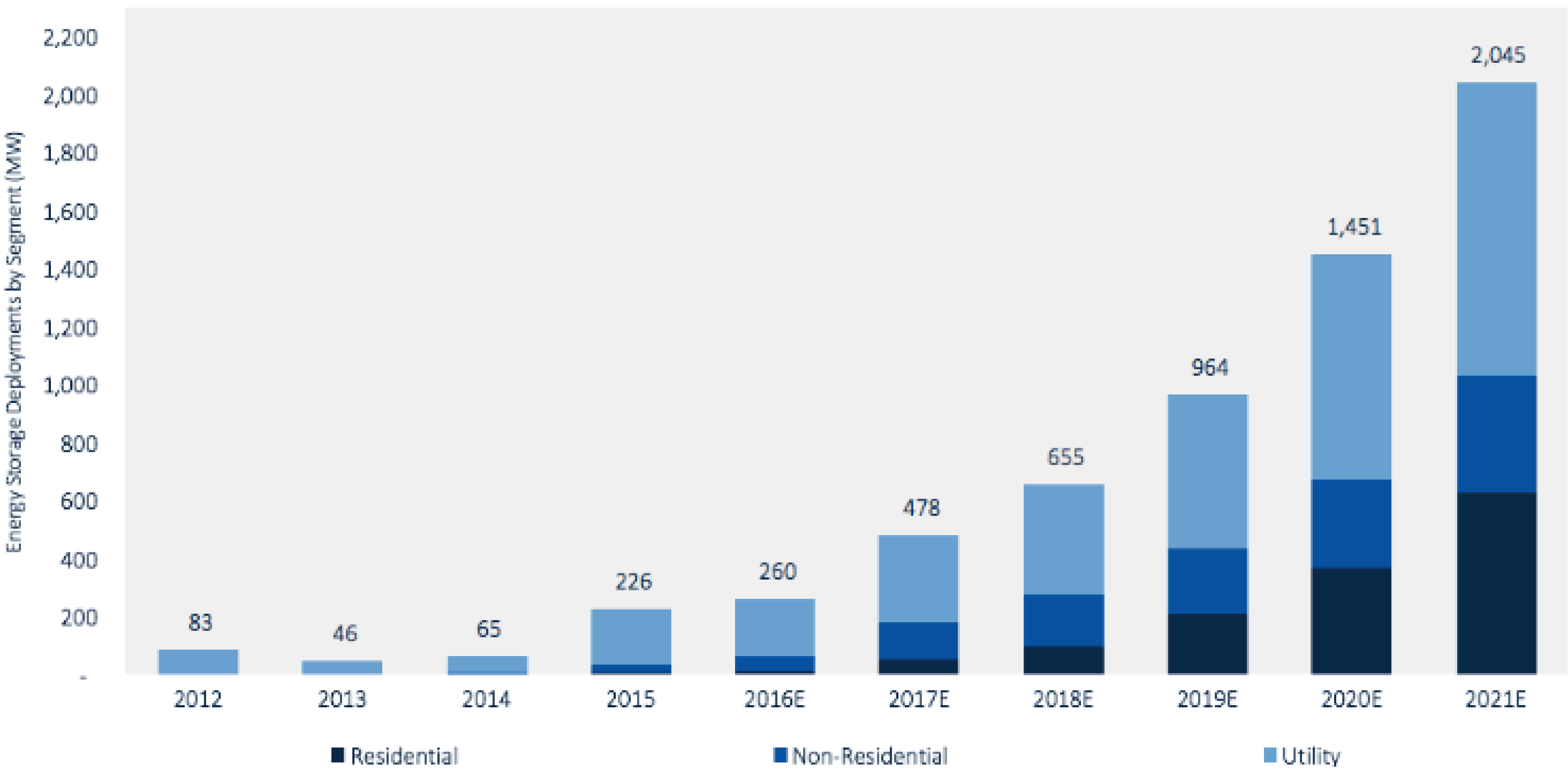
Use	Average Capacity (Ah)	Minimum (Ah)	Maximum (Ah)
cellphone	2	1	2
laptop	6	4	6
Hybrid	1500	1500	1600
PH	10000	4400	20000
EV	25000	16000	100000
Stationary	?	5000	100000000



CAPACITY, Ah

https://www.statista.com/statistics/274774/forecast-of-mobile-phone-users-worldwide/
http://www.sandia.gov/ess/wp-content/uploads/2015/06/EsDbCapture3.png
A.F. Ghoniem / Progress in Energy and Combustion Science 37 (2011) 15e51
https://en.wikipedia.org/wiki/Electric-vehicle_battery

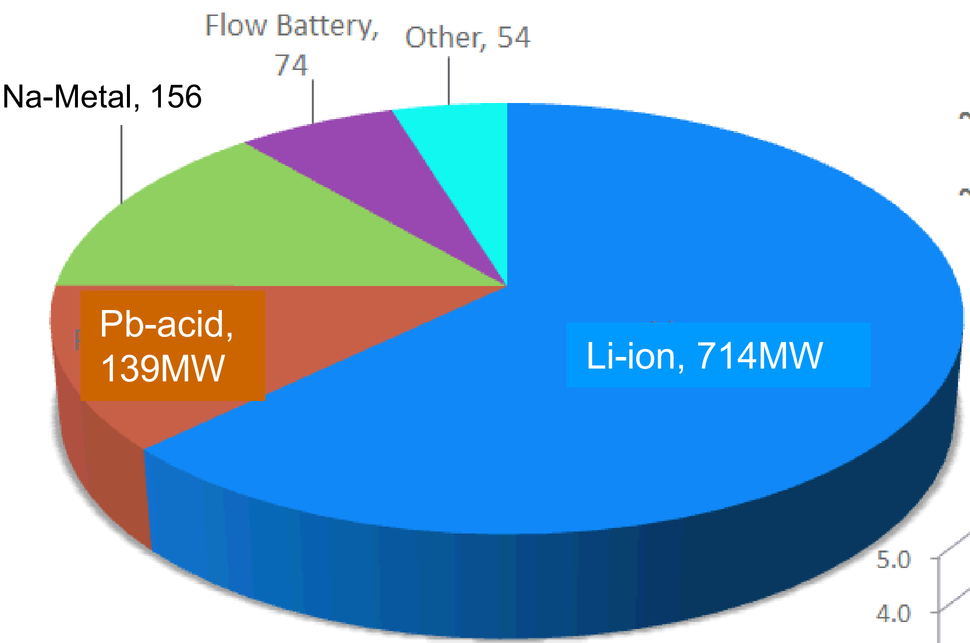
Energy Storage – Projected Deployment



Source – Green Tech Media Inc

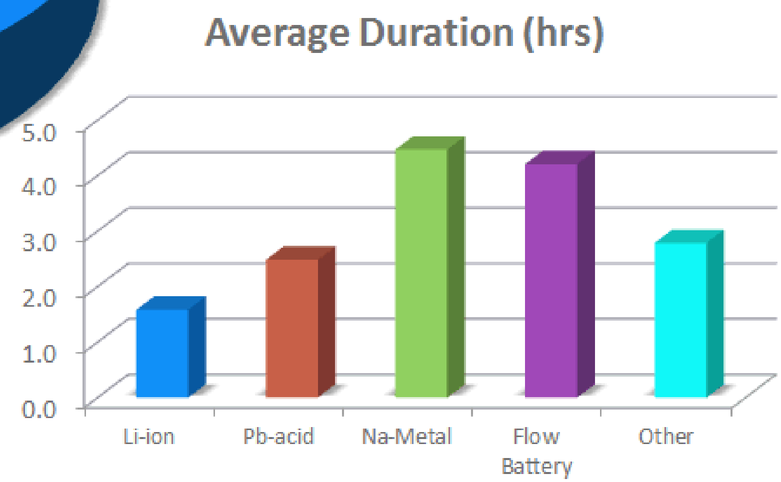
Global Energy Storage Deployments (Battery Only)

BASICS



~ 1.1 GW of Battery Energy Storage

~110 GW of Pumped Hydro



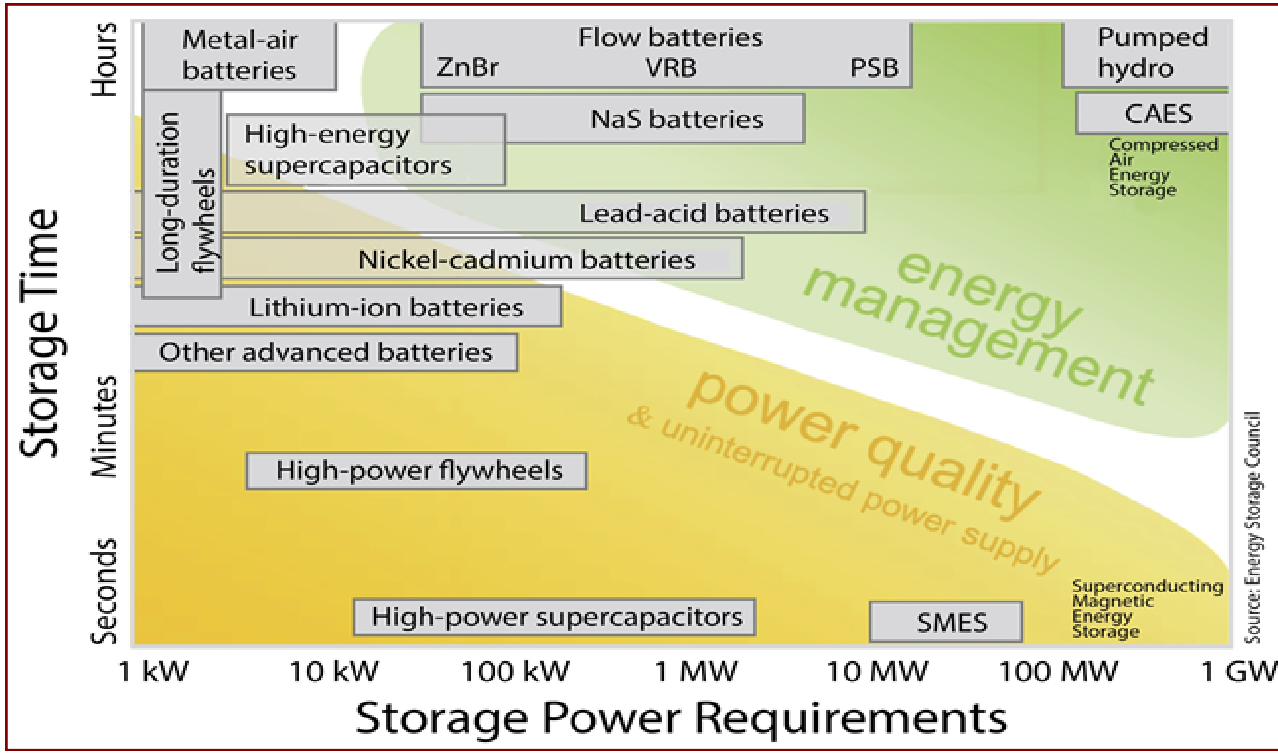
Source: *DOE Global Energy Storage Database http://www.energystorageexchange.org/*
July 2015

Energy Storage Technologies

BASICS

Energy – long discharges (min to hr) ala a “10K”

- Pumped Hydro
- Compressed Air Energy Storage (CAES)
- Electrical Storage (Batteries)
- Sodium Sulfur (NaS)
  - Flow Batteries
  - Lead Acid
  - Advanced Lead Carbon
  - Lithium Ion
- Flywheels
- Electrochemical Capacitors



Power – short discharges (sec to min) ala a “100 m sprint”

DRIVERS

Policy Incentives and Mandates

The demand for energy storage can be accelerated through policy initiatives and incentives that provide needed support until the market matures.

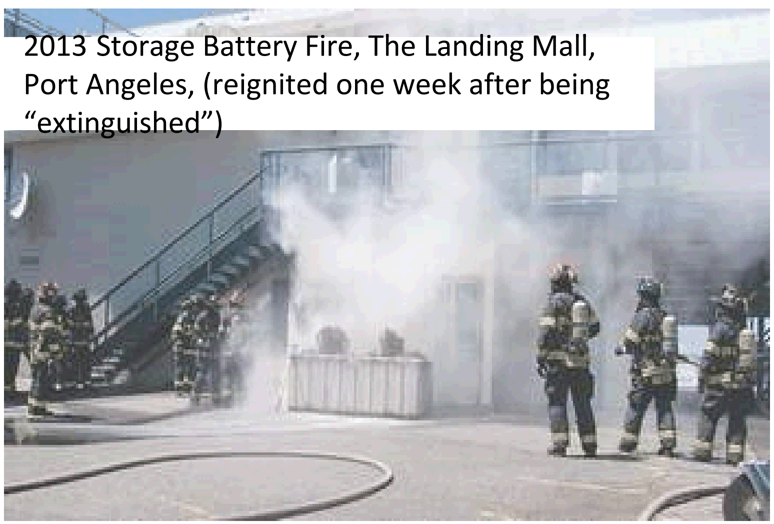
- Install 1.4 gigawatts of storage capacity in New York City
- CA PUC initiative
- MA storage requirement
- OR storage requirement

Energy Storage Safety

2011 Beacon Power Flywheel Failure

2012 Battery Room Fire at Kahuku Wind-Energy Storage Farm

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



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

2012 GM Test Facility Explosion, Warren, MI

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

Energy Storage Hazard Identification

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The risk of safety incidents will increase as a function of ESS deployment

Damage to Facilities

2012 Battery Room Fire at Kahuku Wind-Energy Storage Farm

- There were two fires in a year at the Kahuku Wind Farm
- There was significant damage to the facility
- Capacitors in the power electronics are reported to be associated with the failure

Impact to First

2013 Storage Battery Fire, The Landing Mall, Port Angeles WA

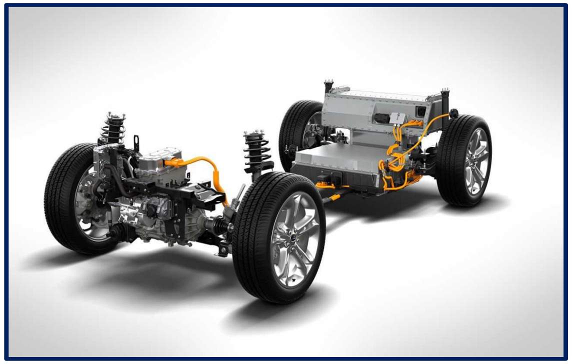
- First responders were not aware of the best way to extinguish the fire
- The fire reignited a week after it was thought to be extinguished

Safety and Reliability

- Unlike batteries for consumer electronics and battery packs for electric vehicles, the scale and complexity of large stationary applications in the electric grid impose a complex set of requirements on the safety and reliability of grid-scale energy storage systems.
- Safety aspects of grid energy storage and how this safety is connected to the electrochemistry of materials, cell-level interactions, packaging and thermal management at the cell and system level, and the overall engineering and control architecture of large-scale energy storage systems.

Impact and consequence of scale on safety

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


Consumer Cells (0.5-5 Ah) → Large Format Cells (10-200 Ah) → Transportation Batteries (1-50 kWh) → Utility Batteries (MWh)

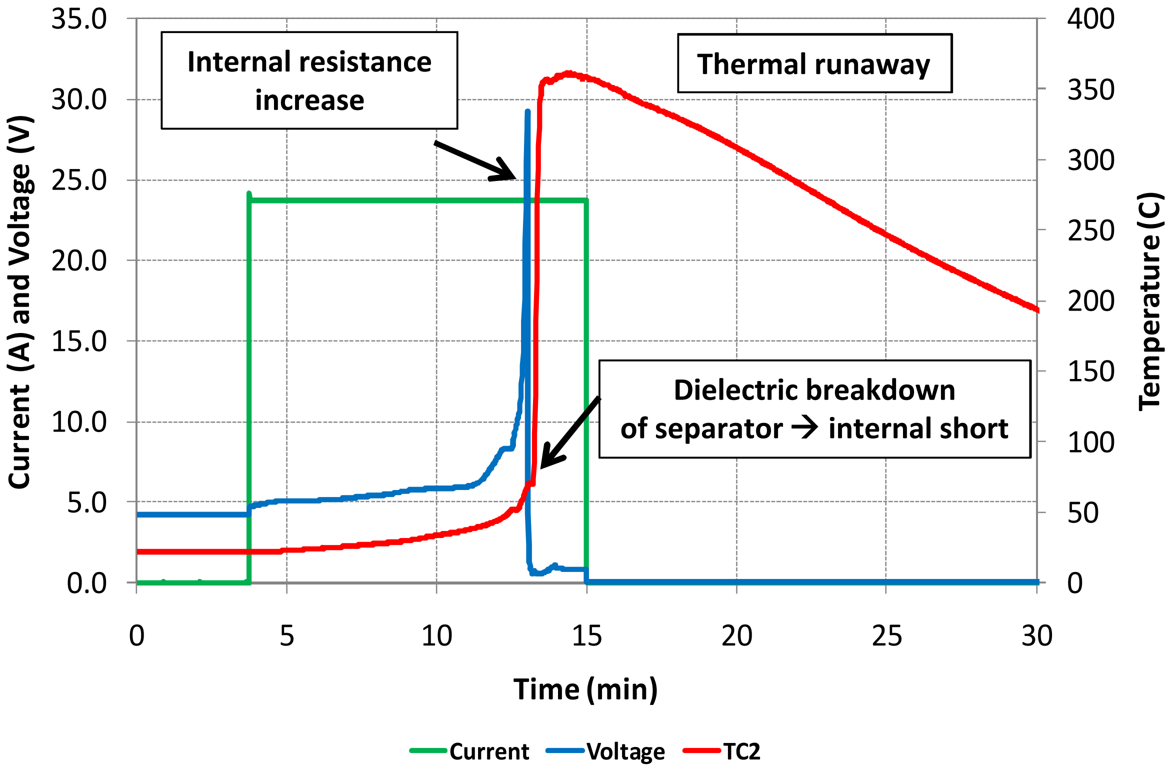
Safety issues and complexity increase with battery size

Currently urban penetration is stalled

Key Challenges:

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

12 Ah (~50 Wh) Overcharge Abuse



PL-8570170-2C_01 fire.mpg

Internal temperature limited due to ejection of cell contents

500 Wh battery failure? 5000 Wh battery failure?

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Properties in Battery Systems that Can Develop Hazards

Voltage

Arc-Flash/Blast

Fire

Combustion

Toxicity

Voltage

- *The number of battery cells per string in grid energy storage can be higher than in mobile applications, resulting in higher DC voltage and a need for additional precautions.*
- *In the voltage range 100-1000V DC, the NFPA Standard 70E on electrical safety in the workplace establishes a limited approach boundary for unqualified workers at 1.0m.*
- *This boundary is to prevent those who are unable to avoid hazards from coming within arms reach of the exposed electrical conductors.*

Source: NFPA70E

Properties in Battery Systems that Can Develop Hazards

Voltage

Arc-Flash/Blast

Fire

Combustion

Toxicity

Arc-Flash/Blast

High string voltage affects both the potential for shock and the potential for arc-flash/blast. The equations below show the maximum power point method for calculating the incident energy in DC arc-flash. Incident energies calculated by this equation are described as "conservatively high" and other methods are being explored for calculating and classifying the potential harmful energy in a DC arc-flash. Arc-blast results from explosive components of an electric arc (e.g. vaporized copper) and depends greatly on the equipment and environment involved in the arc. Common controls to prevent injury from arc flash include increasing separation between positive and negative conductors, regular maintenance to prevent equipment failure, and arc-rated PPE for electrical workers.

$$I_{arc} = 0.5 I_{bf}$$

$$IE = 0.01 V_{sys} I_{arc} T_{arc} / (D^2)$$

Source: NFPA70E

Where:
Iarc = Arcing current (amps)
Ibf = System bolted fault current (amps)
IE = incident energy at a given working distance (cal cm□2)
Vsys = System voltage (volts)
Tarc = Arcing Time (sec)
D = working distance (cm)

Properties in Battery Systems that Can Develop Hazards

- Voltage
- Arc-Flash/Blast
- Fire
- Combustion
- Toxicity

Fire

As a Fuel Source

- *Plastic burns, some electrolytes are flammable.*

Thermal Runaway

- *Thermal runaway is chemical process where self-heating in a battery exceeds the rate of cooling causing high internal temperatures, melting, off-gassing/venting, and in some cases, fire or explosion.*
- *Thermal, mechanical, and electrical abuse can lead to thermal runaway; internal short circuit from manufacturing defects; or the development of metallic dendrites that form an internal short over time.*

Source: David Rosewater, Adam Williams, Analyzing system safety in lithium-ion grid energy storage, Journal of Power Sources, Volume 300, 30 December 2015, Pages 460-471, ISSN 0378-7753

Properties in Battery Systems that Can Develop Hazards

- Voltage
- Arc-Flash/Blast
- Fire
- Combustion
- Toxicity

Combustion

Hydrogen buildup from charging

- *Charging aqueous batteries can crack water into hydrogen and oxygen.*
- *Without proper ventilation this hydrogen can build up in an enclosed space.*
- *The Lower Explosive Limit (LEL) for hydrogen is 4% concentration in air.*
- *Battery system with this hazard must be equipped with alarm systems.*

Vent gas combustion from thermal runaway

- *Lithium-ion batteries undergoing thermal runaway can vent their internal contents in the form of gas.*
- *Without proper ventilation a combination of gases can build up in an enclosed space.*
- *The LEL for this mixture can very.*
- *Oxygen starvation fire suppression in lithium-ion battery systems is not recommended.*

Properties in Battery Systems that Can Develop Hazards

- Voltage
- Arc-Flash/Blast
- Fire
- Combustion
- Toxicity

Toxicity

Smoke

- *Smoke can be toxic and smoke from batteries is no exception.*
- *Use of a positive pressure breathing apparatus is recommended whenever responding to battery system fires.*

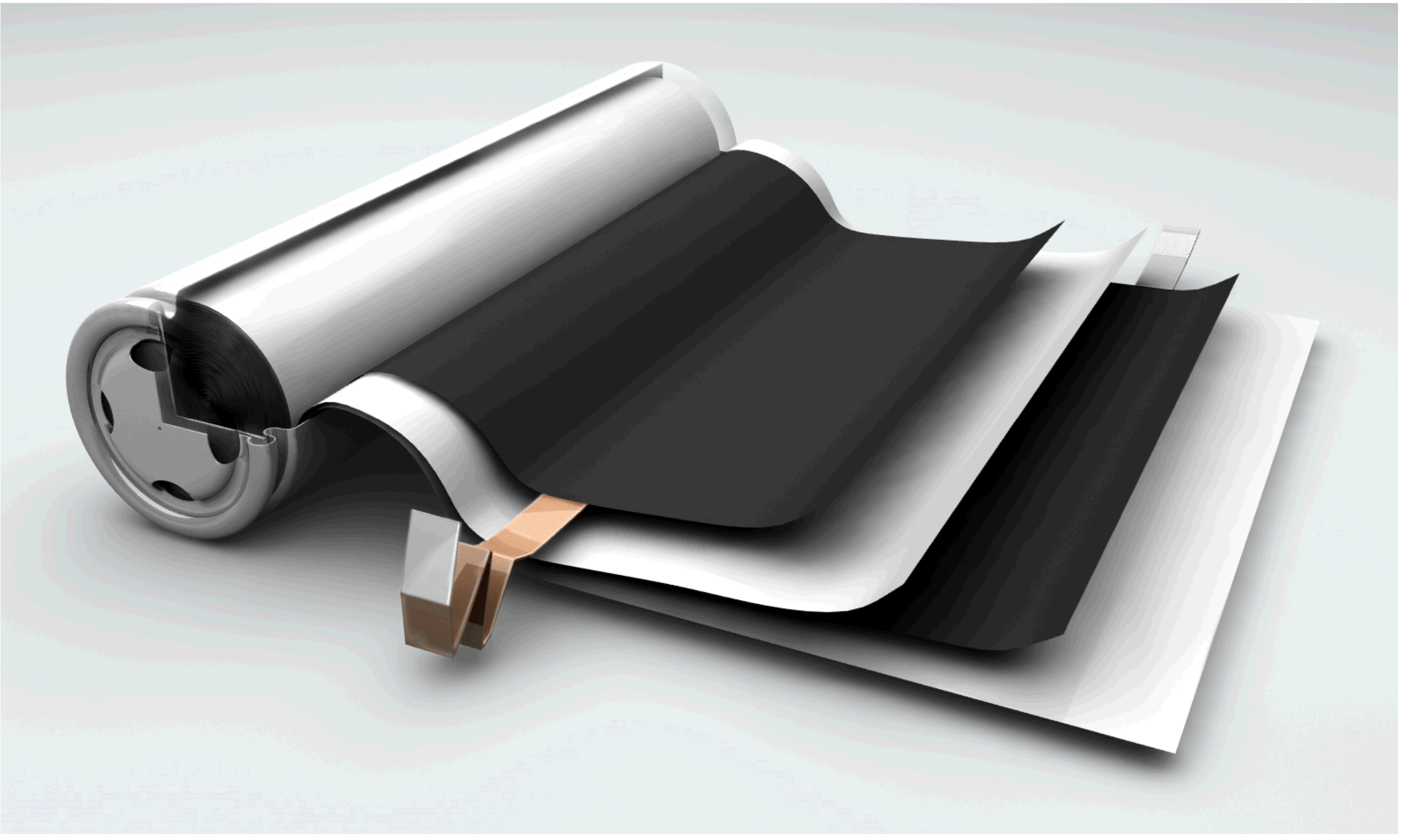
Liquid Electrolyte

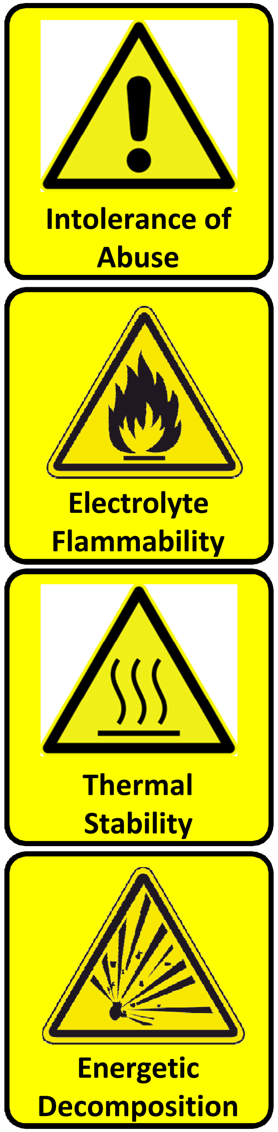
- *Some flow-batteries contain electrolyte which can be toxic to the environment or to people.*
- *The MSDS should provide proper safety measures for handling and exposure.*
- *Liquid electrolyte can also be corrosive so avoid contact with the skin or eyes.*

Exposure to high temperature causes smoke and fire (thermal runaway)

- Video of thermal runaway

Challenges with lithium-ion battery safety





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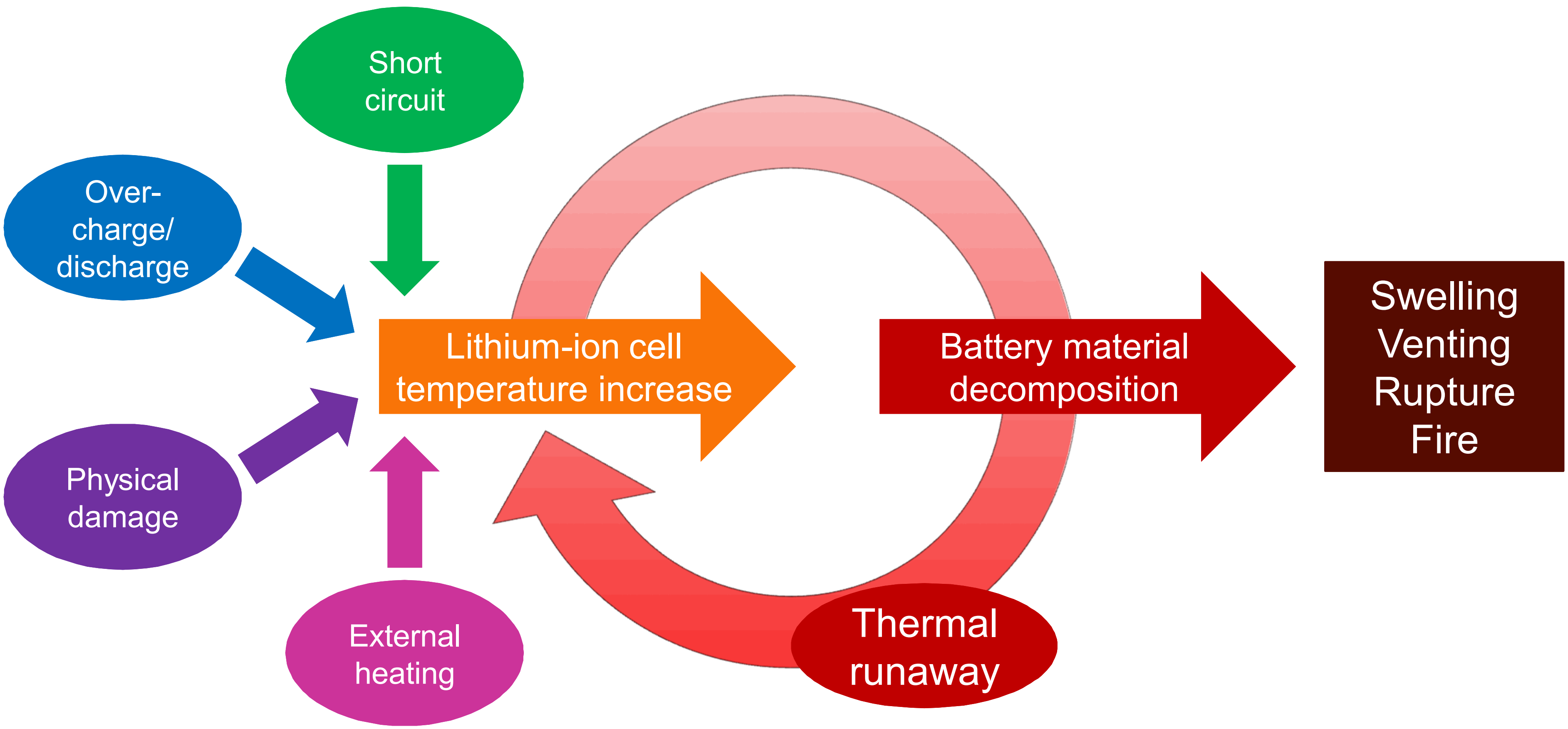
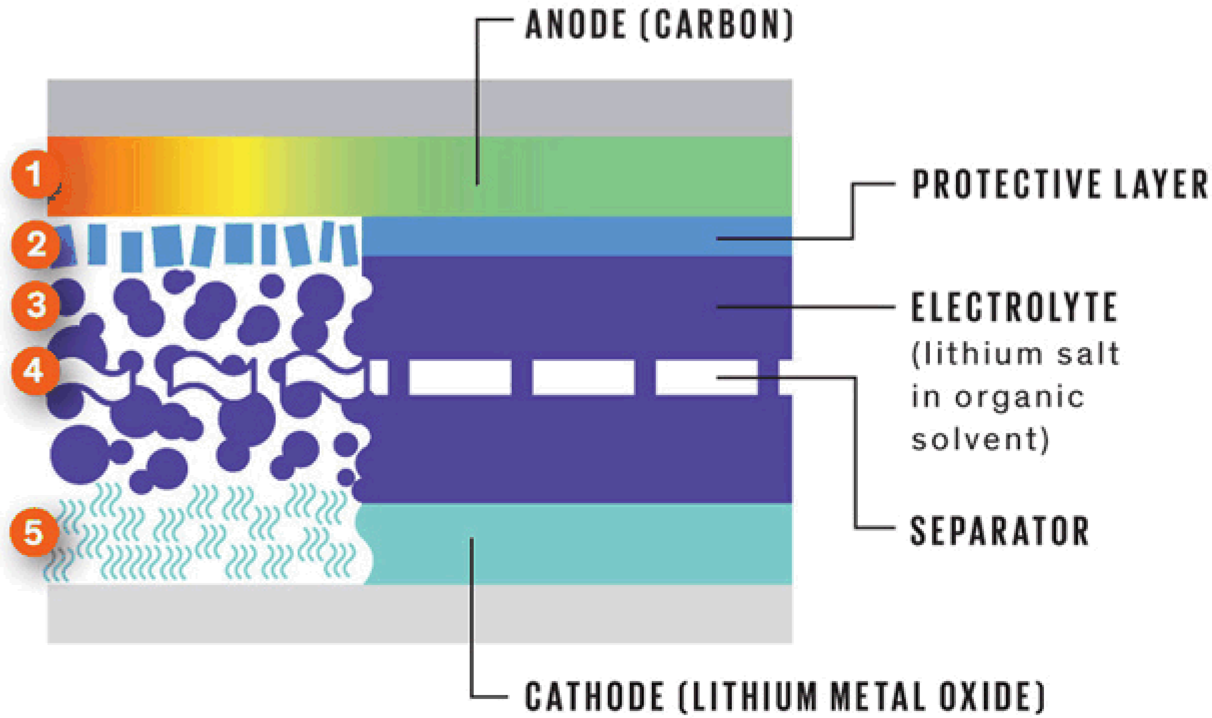
Thermal runaway is cascading failure



Cell materials are responsible for thermal runaway behaviors

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.



https://www.extremetech.com/extreme/208888-doping-lithium-ion-batteries-could-prevent-overheating-and-explosion

Improving battery safety

Development of Inherently Safe Cells →

- Safer cell chemistries
- Non-flammable electrolytes
- Shutdown separators
- Non-toxic battery materials
- Inherent overcharge protection

Challenges with inherent cell safety

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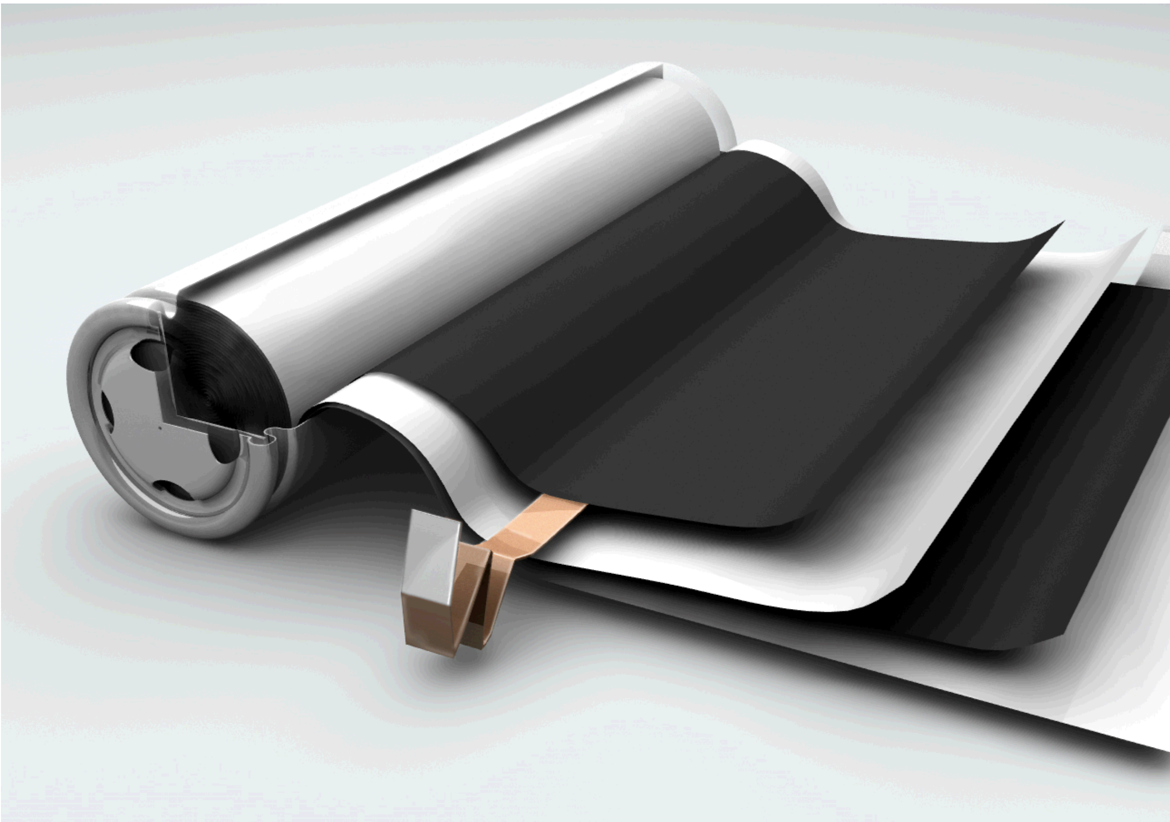
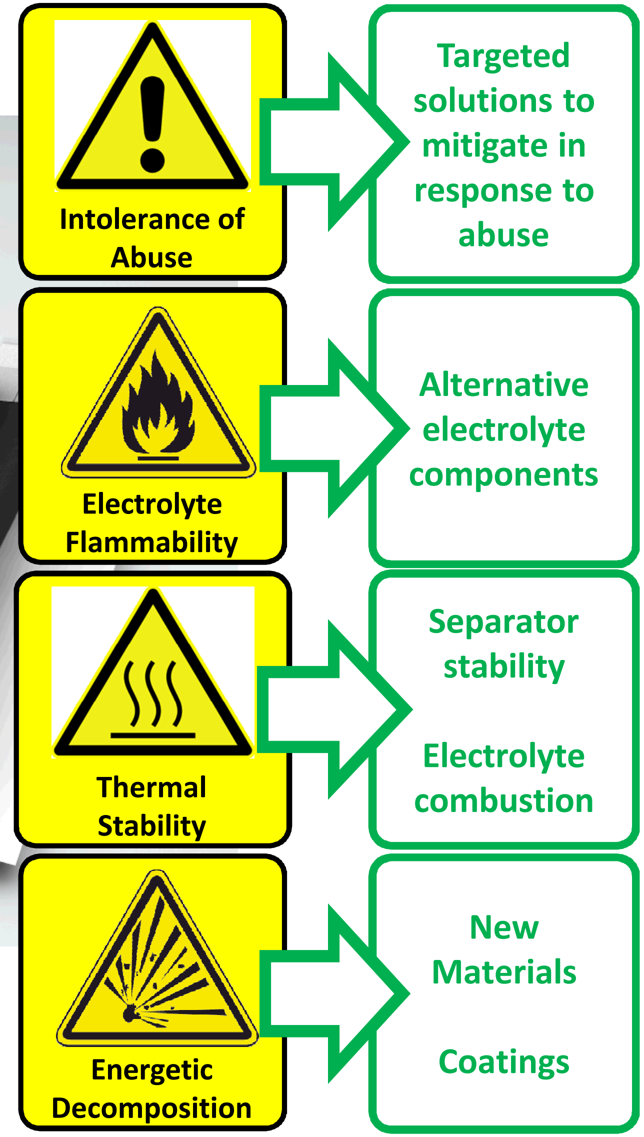
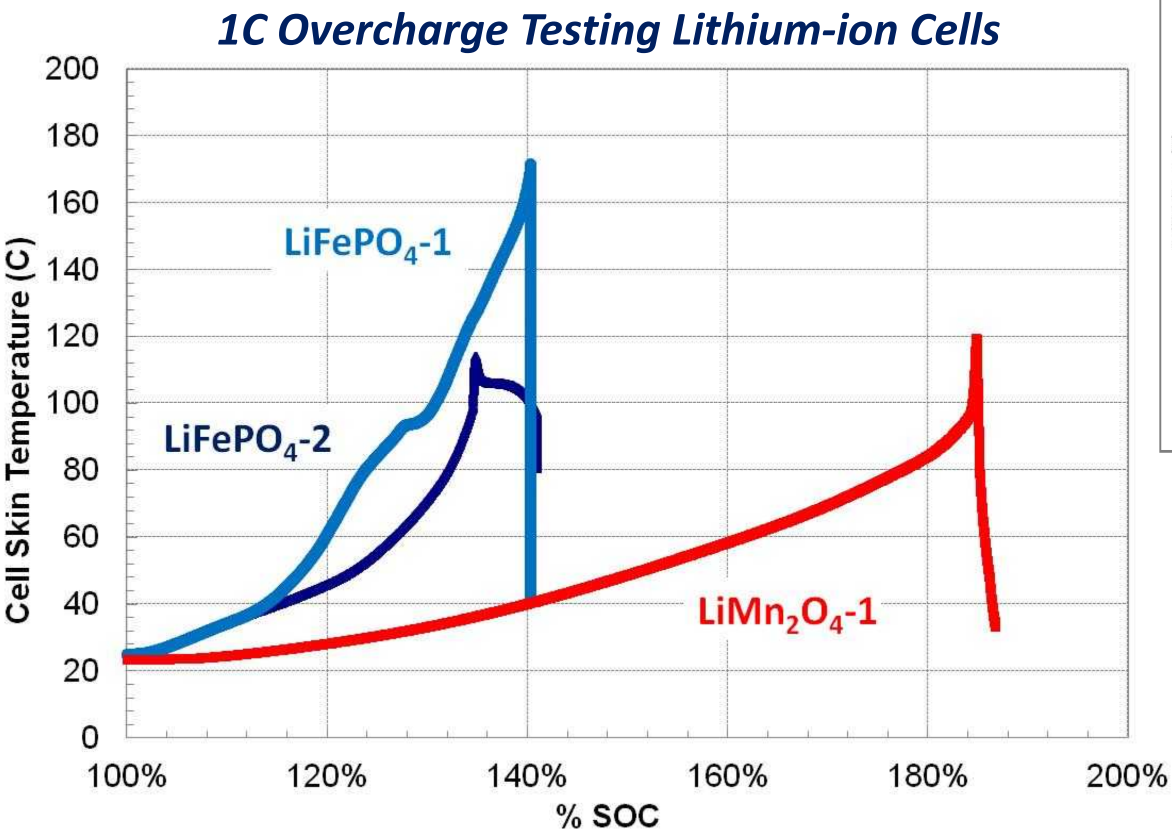




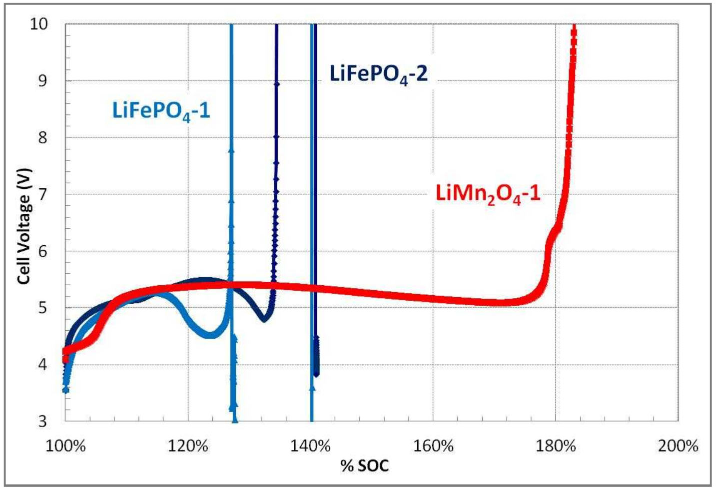
G. Nagasubramanian et al. J. Power Sources 196 (2011) 8604-8609
G. Nagasubramanian et al. (2013) http://dx.doi.org/10.1016/j.electacta.2012.09.065
Chen, Z. et al. Energy Environ. Sci. 4 (2011) 4023-4030
C. J. Orendorff et al. Adv. Energy Mater (2013) DOI: 10.1002/aenm.201200292

Abuse Tolerance Improvements

Overcharge Abuse Tolerance



E.P. Roth, DOE Annual Merit Review 2008



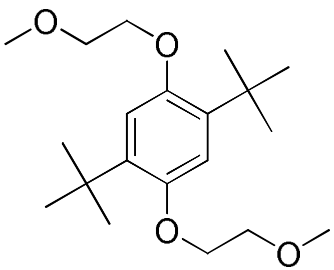
Cathode	x @ 100% SOC	Onset (SOC)
Li_xFePO_4	0	100%
$Li_xMn_2O_4$	0.1	110%
NCA	0.36	125%
NMC (111)	0.48	150%
Li_xCoO_2	0.5	160%

$LiFePO_4$ is inherently intolerant of overcharge because it is completely delithiated at 100%SOC

RS2 Overcharge Shuttle

Collaboration with ANL (Khalil Amine, Greg Krumdick) and A123 (Leslie Pinnell, Tony Gozdz)

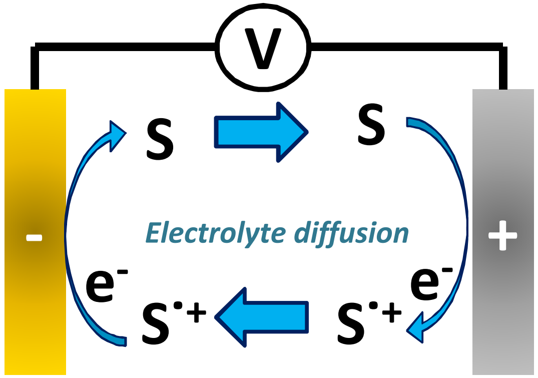
ANL RS2



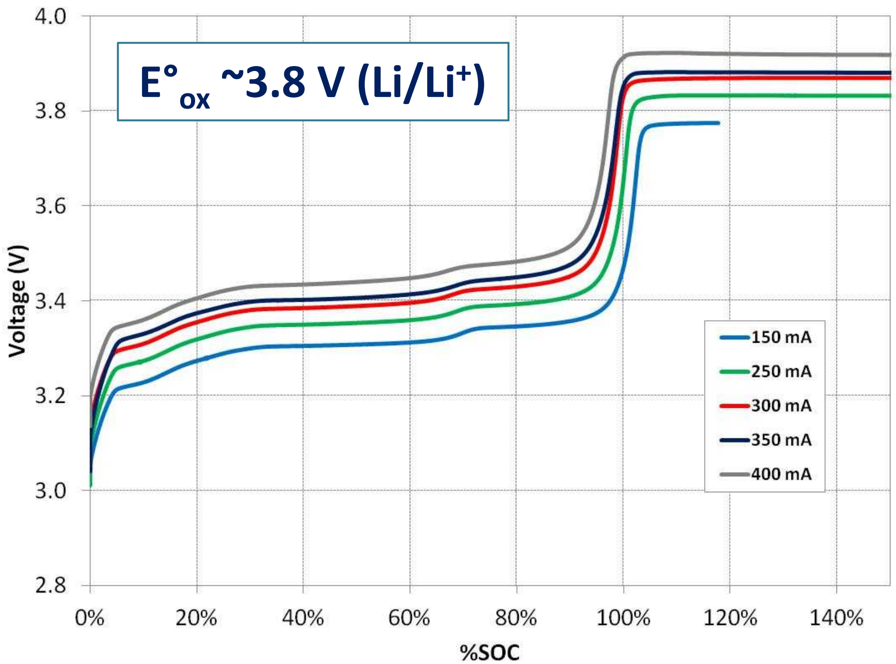
(1,4-Bis(2-methoxyethoxy)-2,5-di-*tert*-butylbenzene)

LFP 18650 Cells
1.2 M $LiPF_6$ in EC:EMC (3:7)
+ 0.2 M RS2

How the shuttle principle works:



18650 Cell Charging



Does this actually work for cell balancing?
What is the heat output during shuttle activation?
Does this improve overcharge abuse tolerance?

Cell Balancing with RS2

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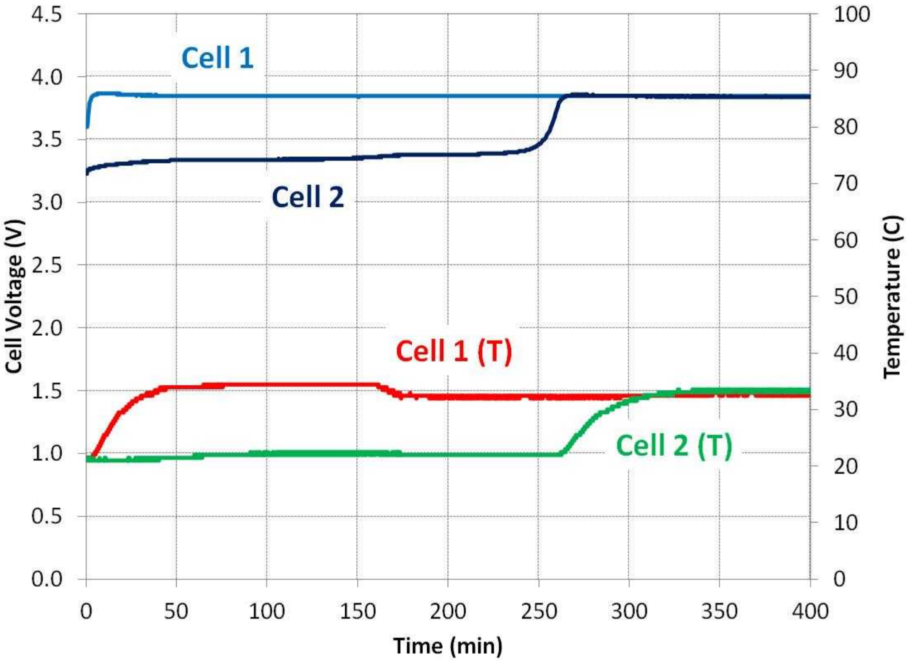
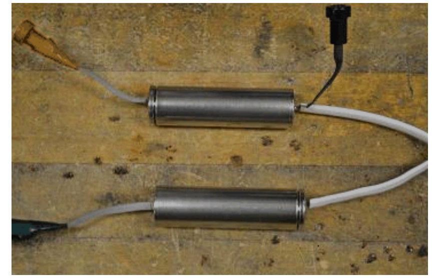
200 mA Charge (C/5)



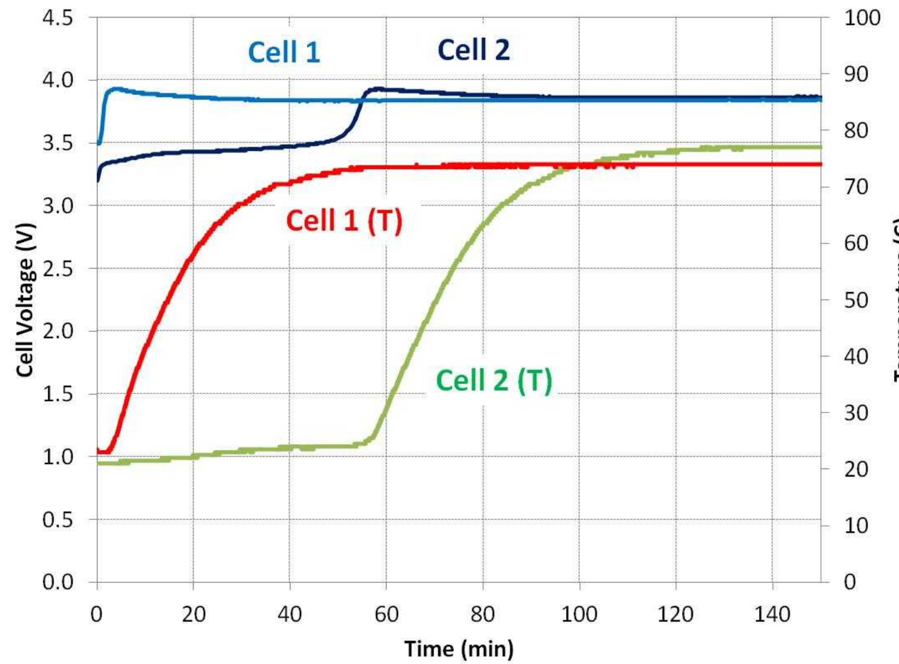
2 imbalanced cells in series



Cell 1, V_o = 3.60 V

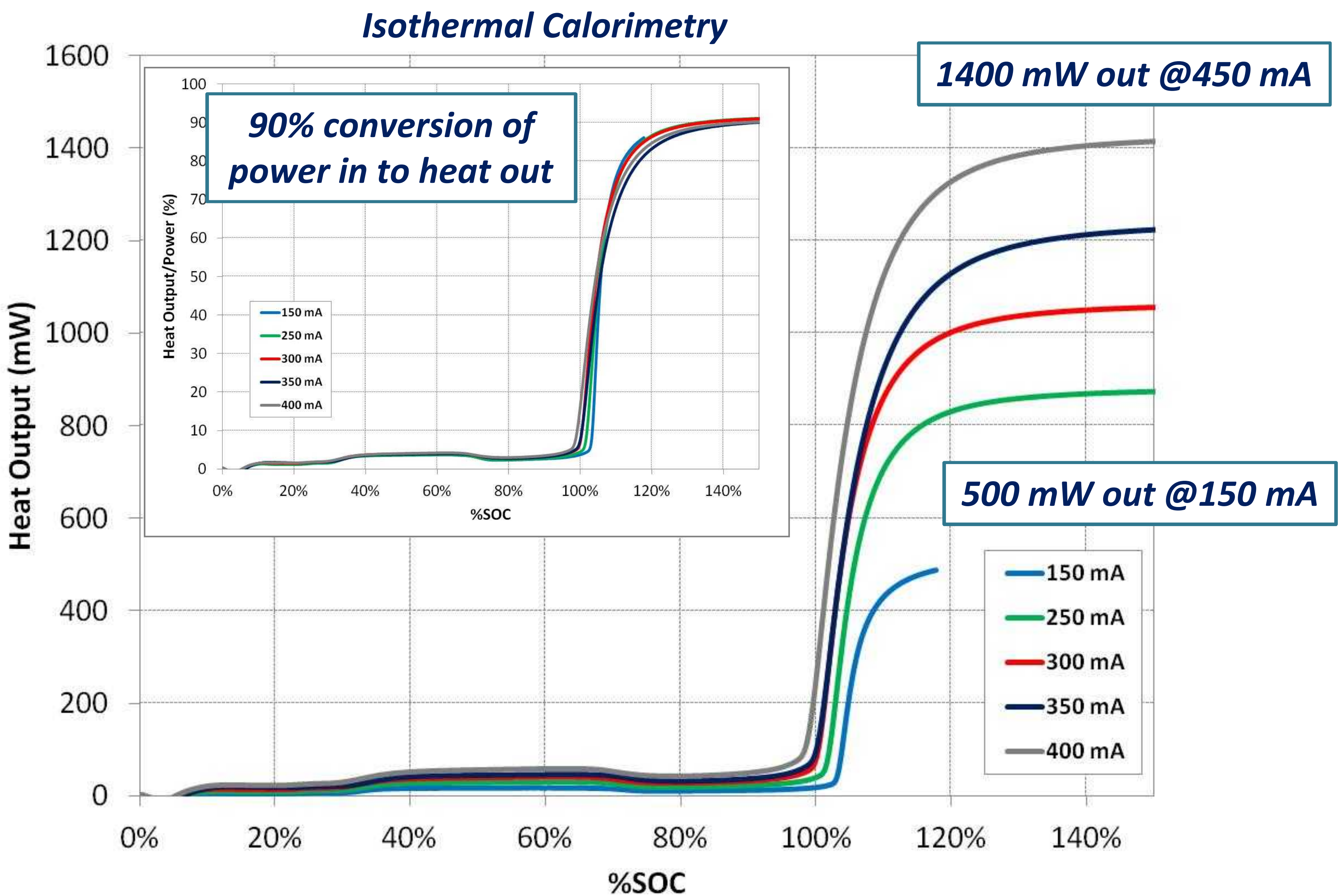
Cell 2, V_o = 3.25 V

1 A Charge (1C)



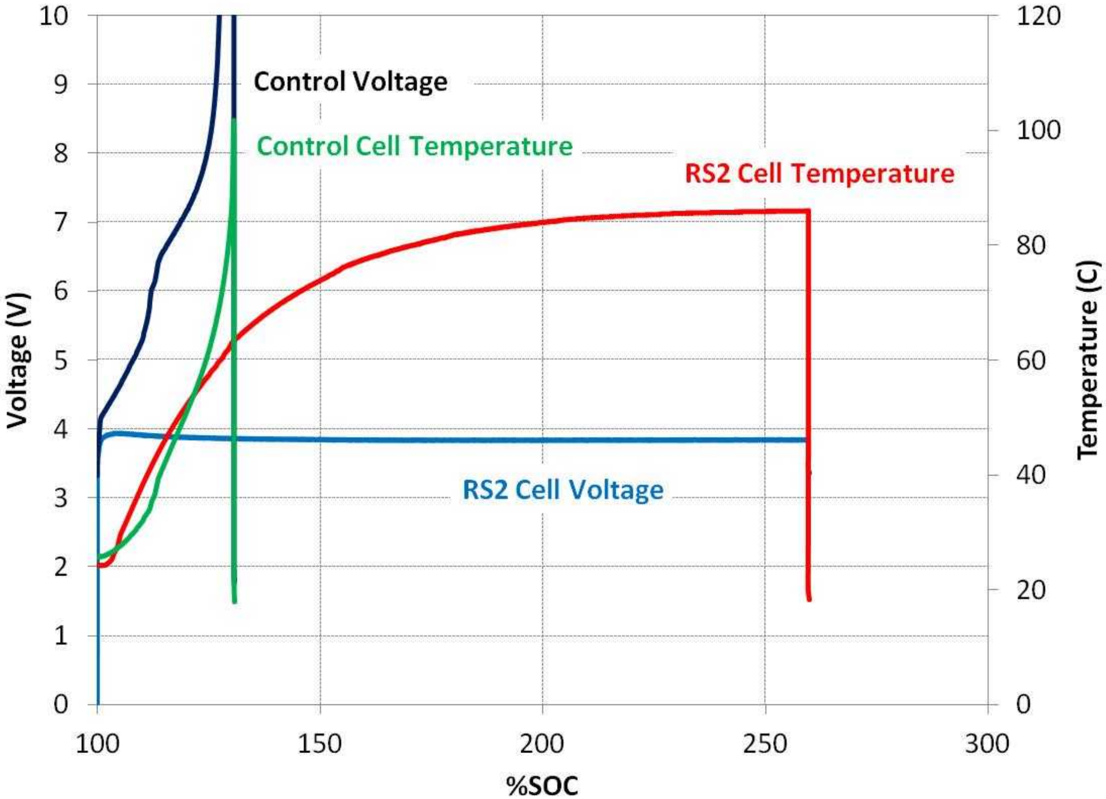
- ***Balanced in 4.5 hrs at 200 mA with a max. temperature of 32 °C***
- ***Balanced in 1.5 hrs at 1 A with a max. temperature of 85 °C***
- ***RS2 could theoretically be used for cell balancing, but it is very inefficient***

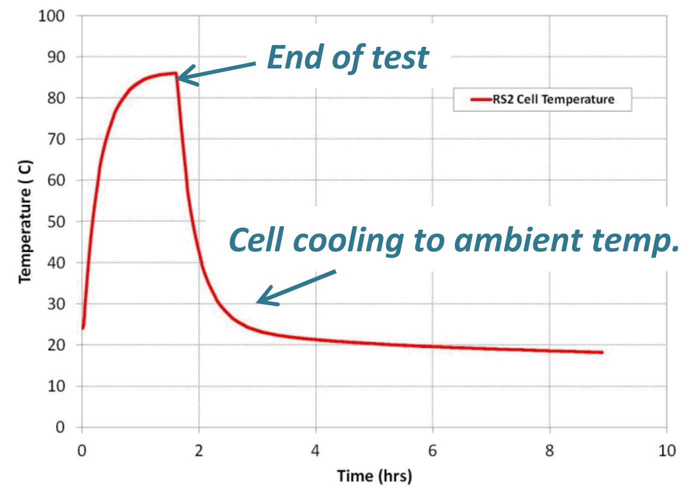
RS2 Overcharge Shuttle

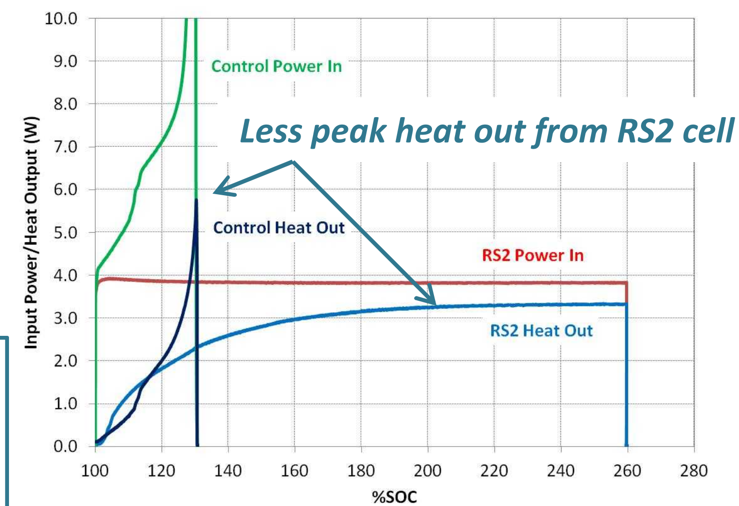


Overcharge Abuse

1 A Constant Current (1C) Overcharge Abuse Test

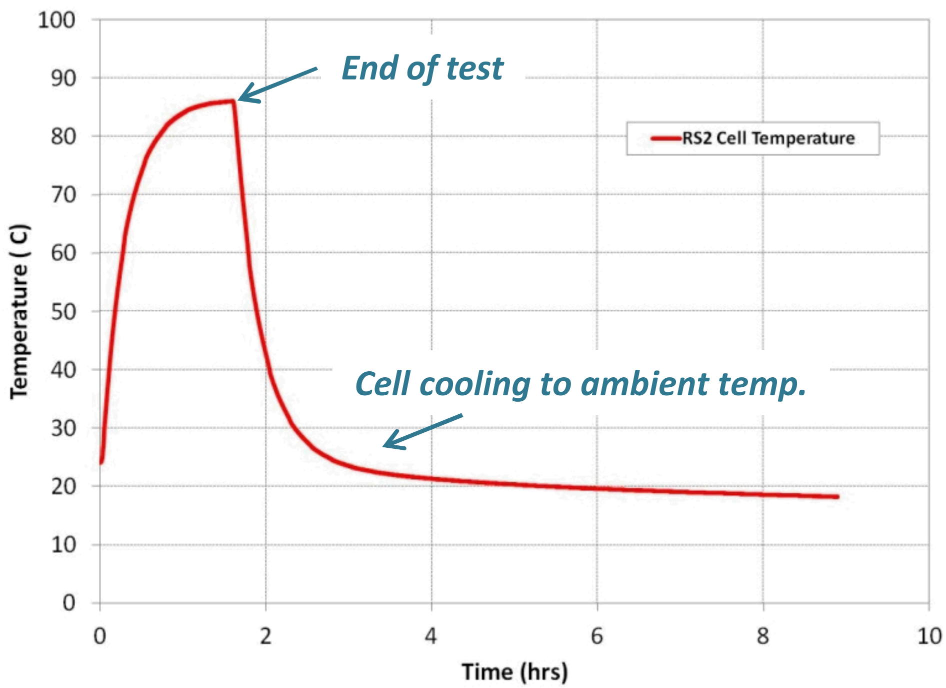




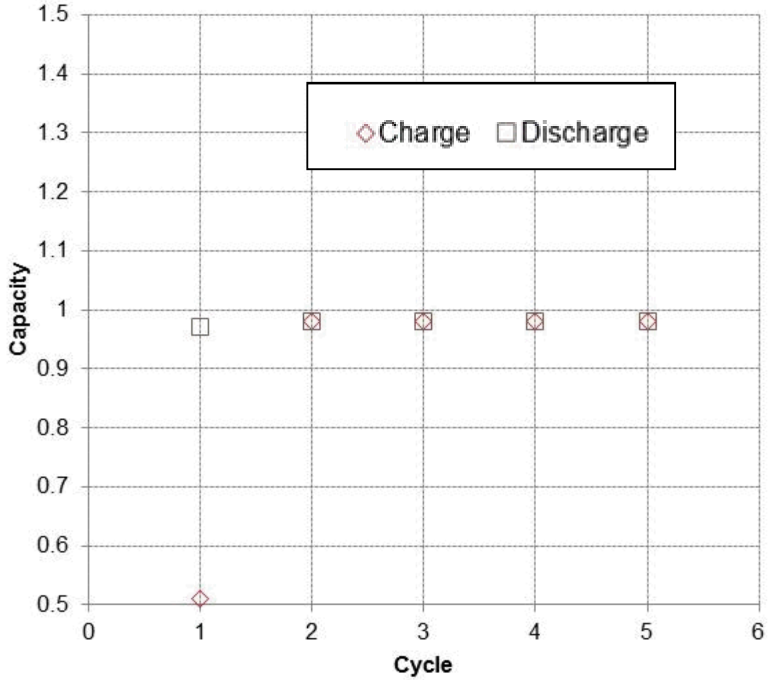


Control cell failure at 130% SOC
RS2 cell test stopped at 260% SOC with no failure event
RS2 cell temperature ~90 °C at 260% SOC

Functionality Post-Test



Post-OC test cell capacity



6% capacity loss after OC to 260% SOC

Demonstrates not only improved abuse tolerance, but retention of functionality

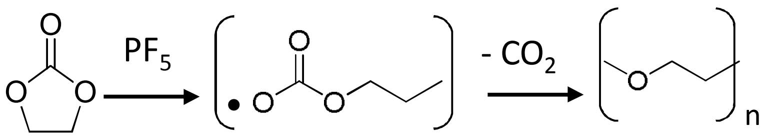
Electrolyte Flammability

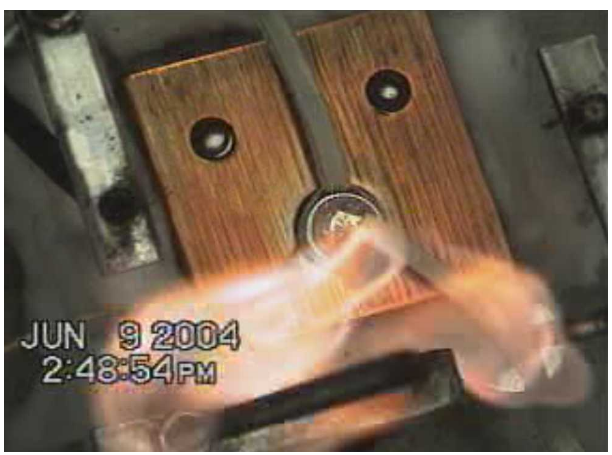
Electrolyte Flammability

Challenges with conventional electrolytes

- Additive approach has had limited success
- High solvent combustion enthalpy, low autoignition temperature, low flash point, etc.
- PF_6^- decomposition of solvent to generate CO_2

$LiPF_6 \rightarrow \rightarrow PF_5 + POF_3$ .....



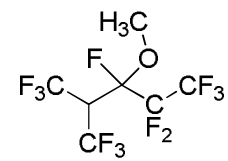


Thermal ramp test of an 18650 Li⁺ cell containing $LiPF_6$ electrolyte with ~5% "flame retardant" additive

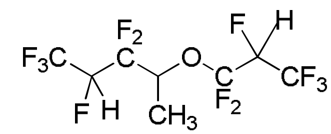
Opportunities for advanced electrolytes

- Nonflammable cosolvent approach*
- High flashpoint solvent choices
- Alternatives to PF_6^-

Hydrofluoro ether (HFE) cosolvents:



TMMP



TPTP

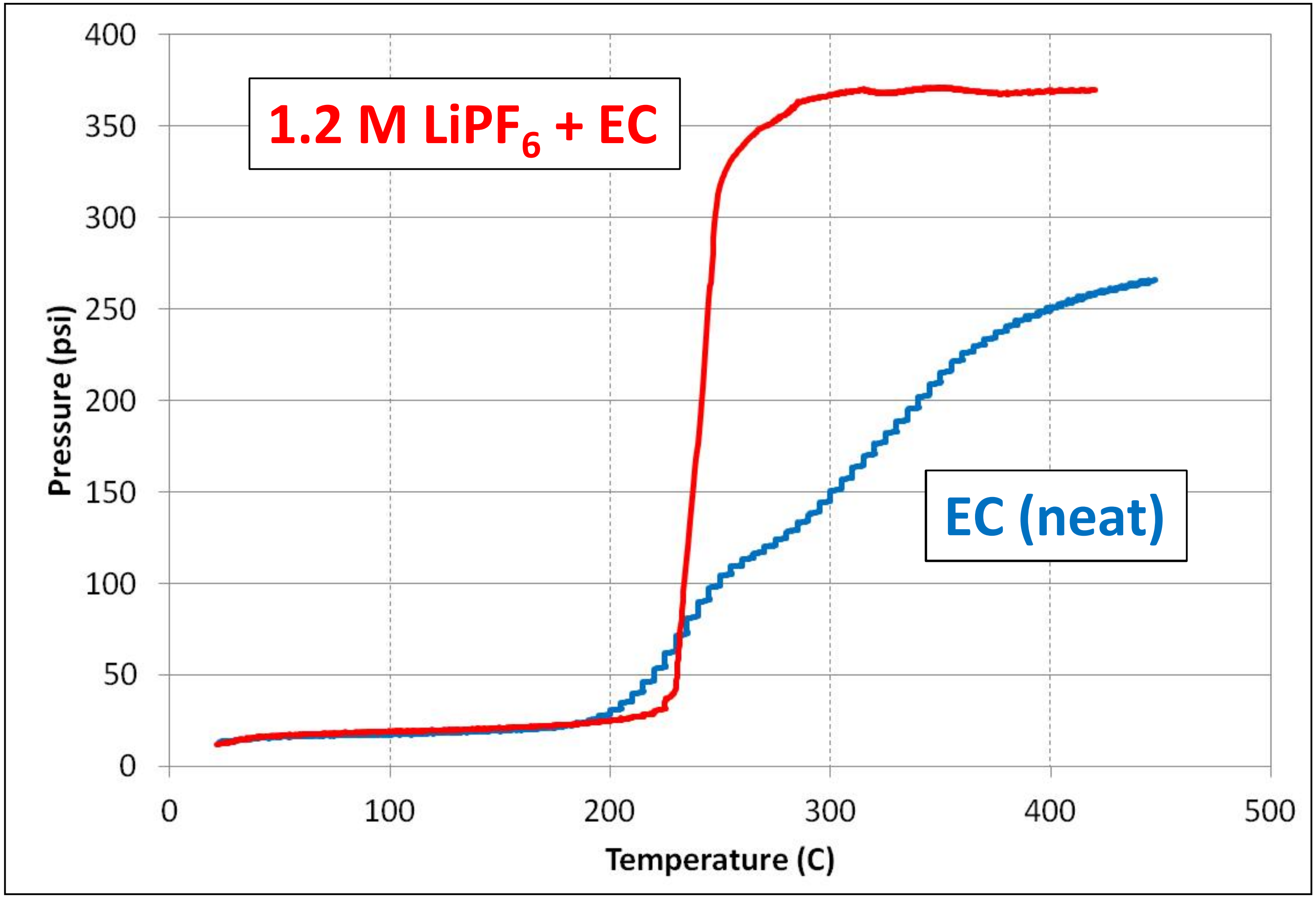
Alternative salts:

$LiN(CF_3SO_2)$ (LiTFSI)
$LiN(C_2F_5SO_2)$ (LiBETI)

Electrolytes are 30-50% HFE cosolvent

G. Nagasubramanian et al. J. Power Sources 196 (2011) 8604-8609

Electrolyte Decomposition

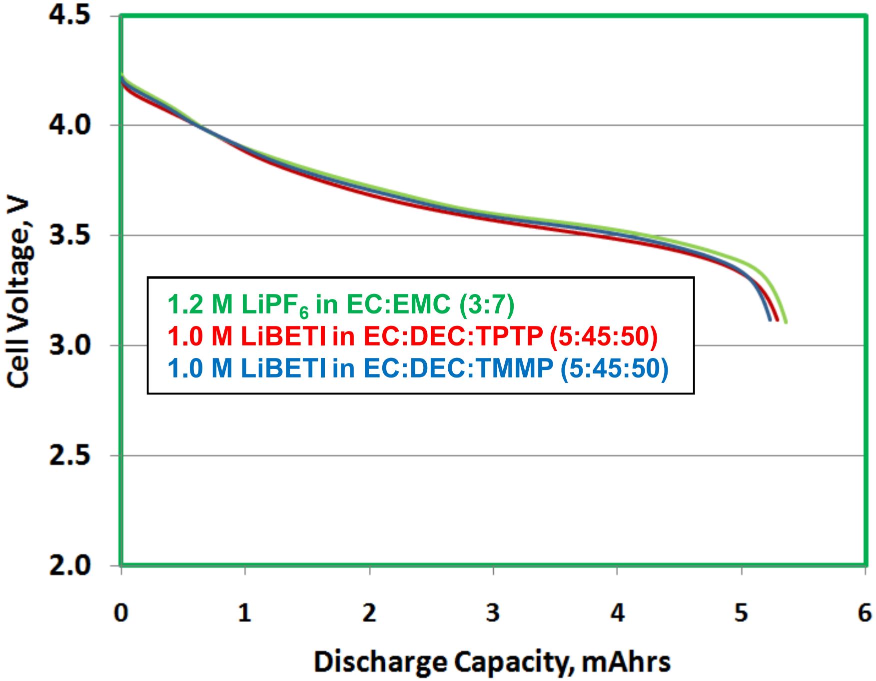


$LiPF_6$ catalyzes electrolyte solvent decomposition at elevated temperature

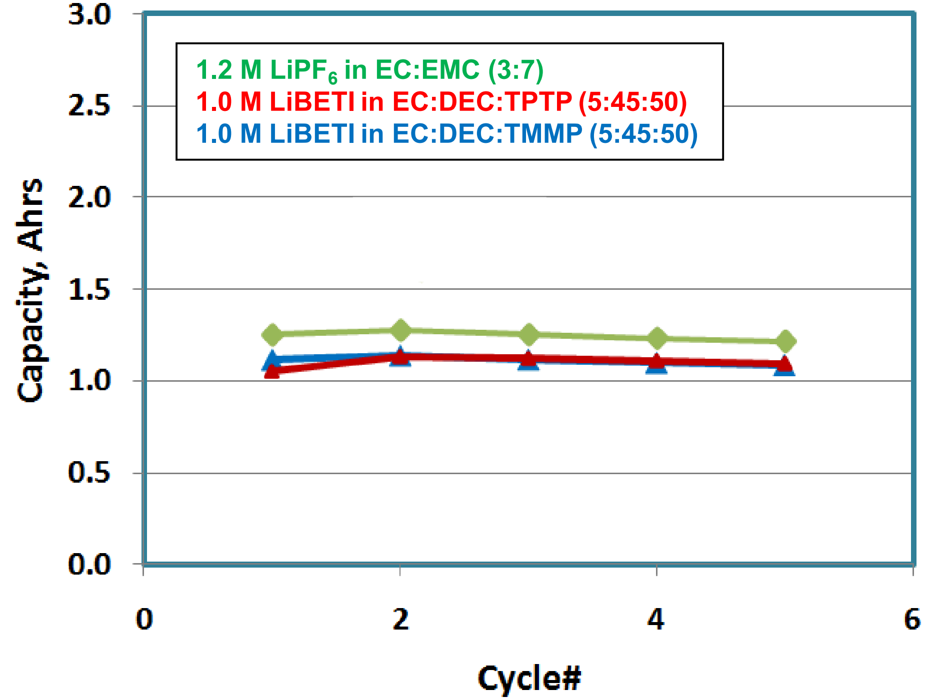
Nonflammable Electrolytes

Performance of NMC cells with HFE electrolytes

Discharge capacity in 2032 coin cells



Discharge capacity in 18650 cells



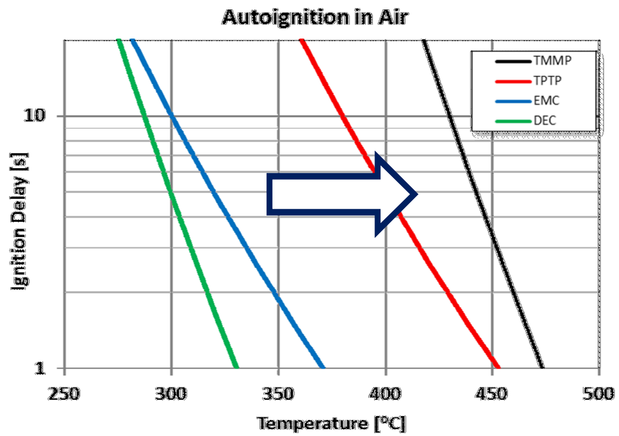
< 10% diminished capacity of the LiBETI/HFE electrolyte cell compared to the $LiPF_6$/EC:EMC cell

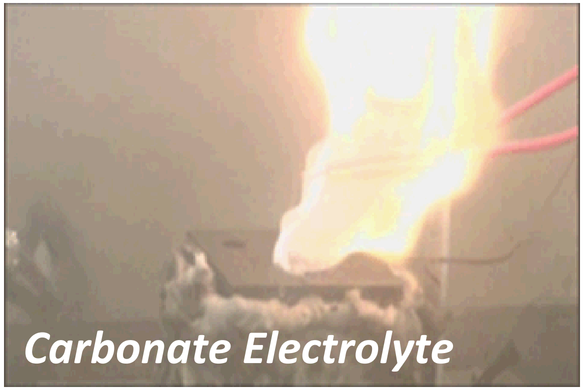
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

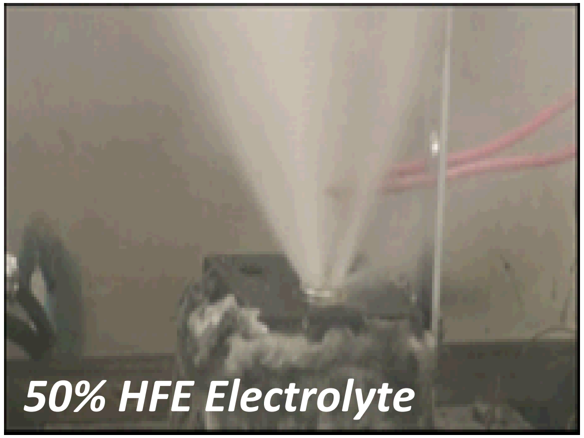
Electrolyte Flammability

Flammability of Hydrofluoro ether (HFE) Electrolytes

Electrolyte	Ignition (Y/N)	ΔTime (vent-ignition) (s)	Burn time (s)
EC:DEC (5:95 v%)	Y	<1	36
EC:DEC (5:95 v%)	Y	1	63
EC:EMC (3:7 wt%)	Y	5	6
EC:EMC (3:7 wt%)	Y	3	12
30% TMMP	Y	3	14
30% TMMP	N	NA	NA
30% TMMP	Y	1	27
30% TMMP	N	NA	NA
50% TPTP	N	NA	NA
50% TPTP	N	NA	NA
50% TPTP	N	NA	NA
50% TPTP	N	NA	NA
50% TMMP	N	NA	NA
50% TMMP	N	NA	NA
50% TMMP	N	NA	NA







HFEs show higher autoignition temps in air compared to carbonates

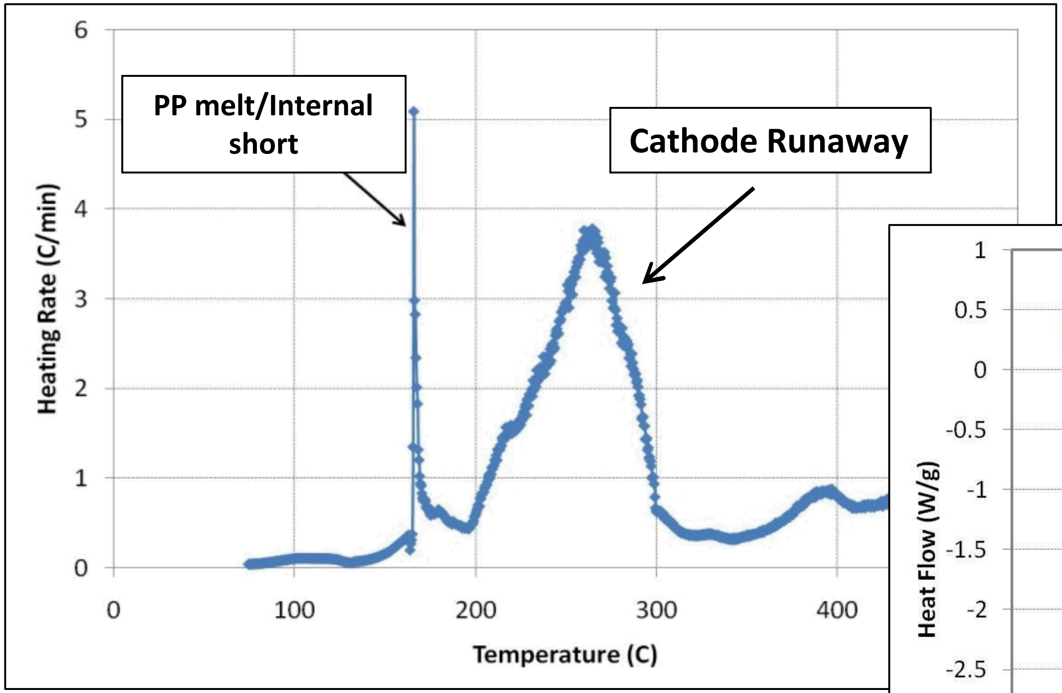
50% HFE electrolytes show no ignition/flammability

Thermal Stability of Materials

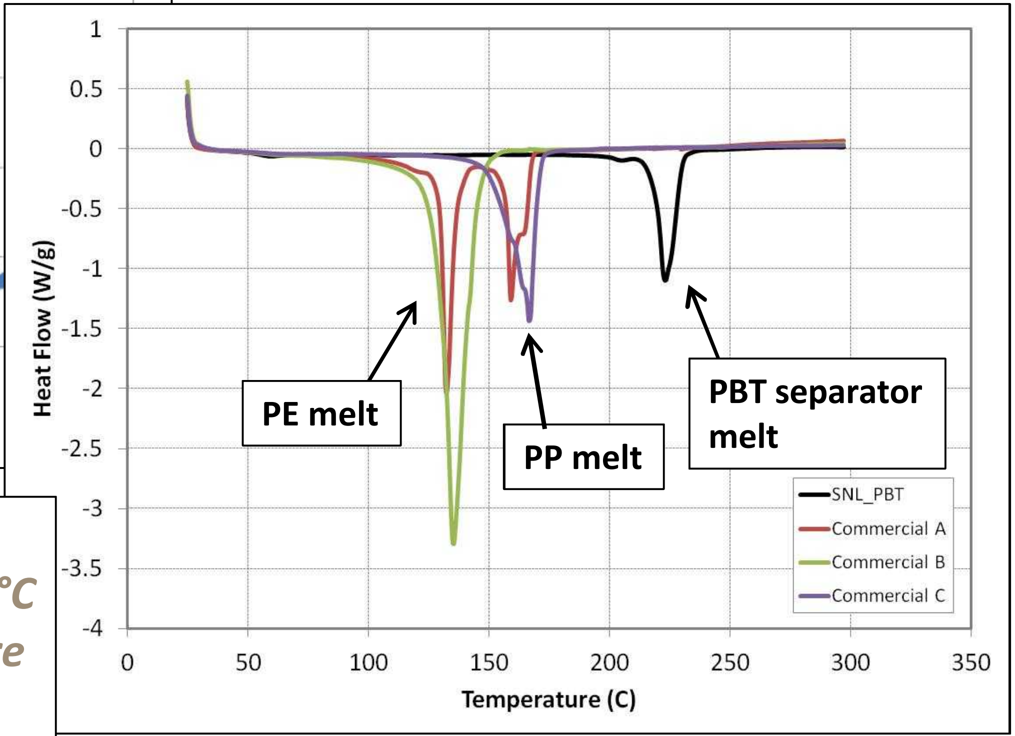
Advanced Separator Materials

Closing the gap between separator phase transition and cathode runaway temperature

Cell ARC



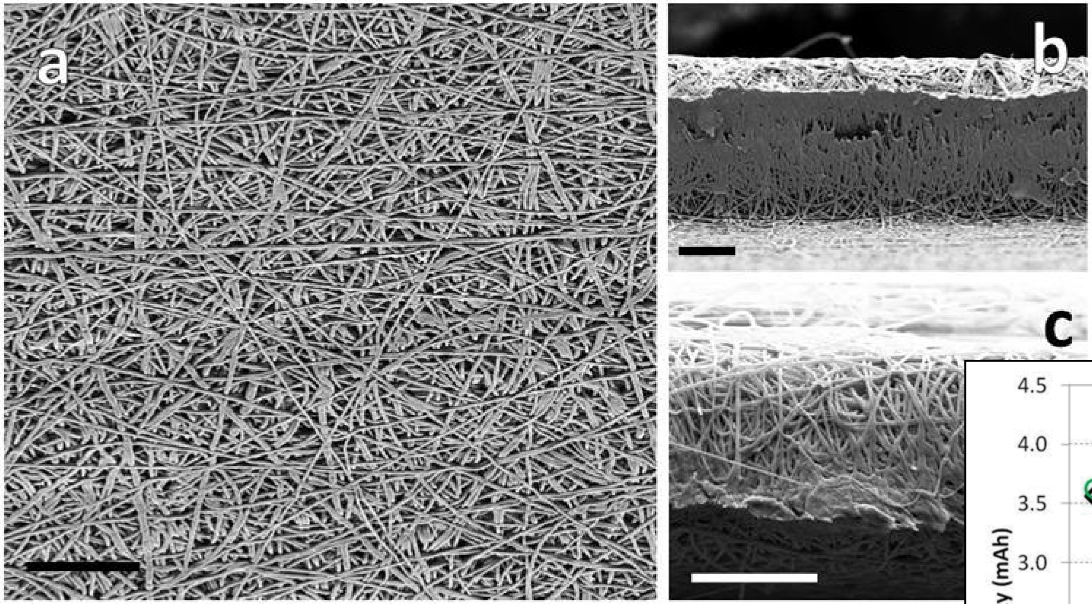
Separator DSC



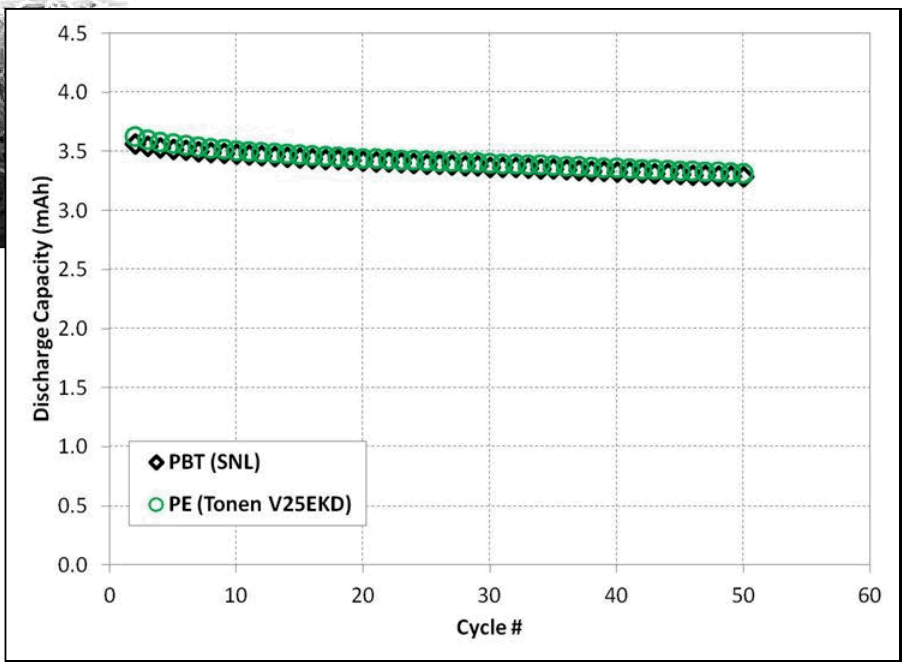
- *PE and PP melt between 135 and 160 °C*
- *Cathode runaway between 190 and 240 °C*
- *Should target higher melting temperature separators to improve cell stability*

C. J. Orendorff et al. Adv. Energy Mater (2013) DOI: 10.1002/aenm.201200292

Advanced Separator Materials



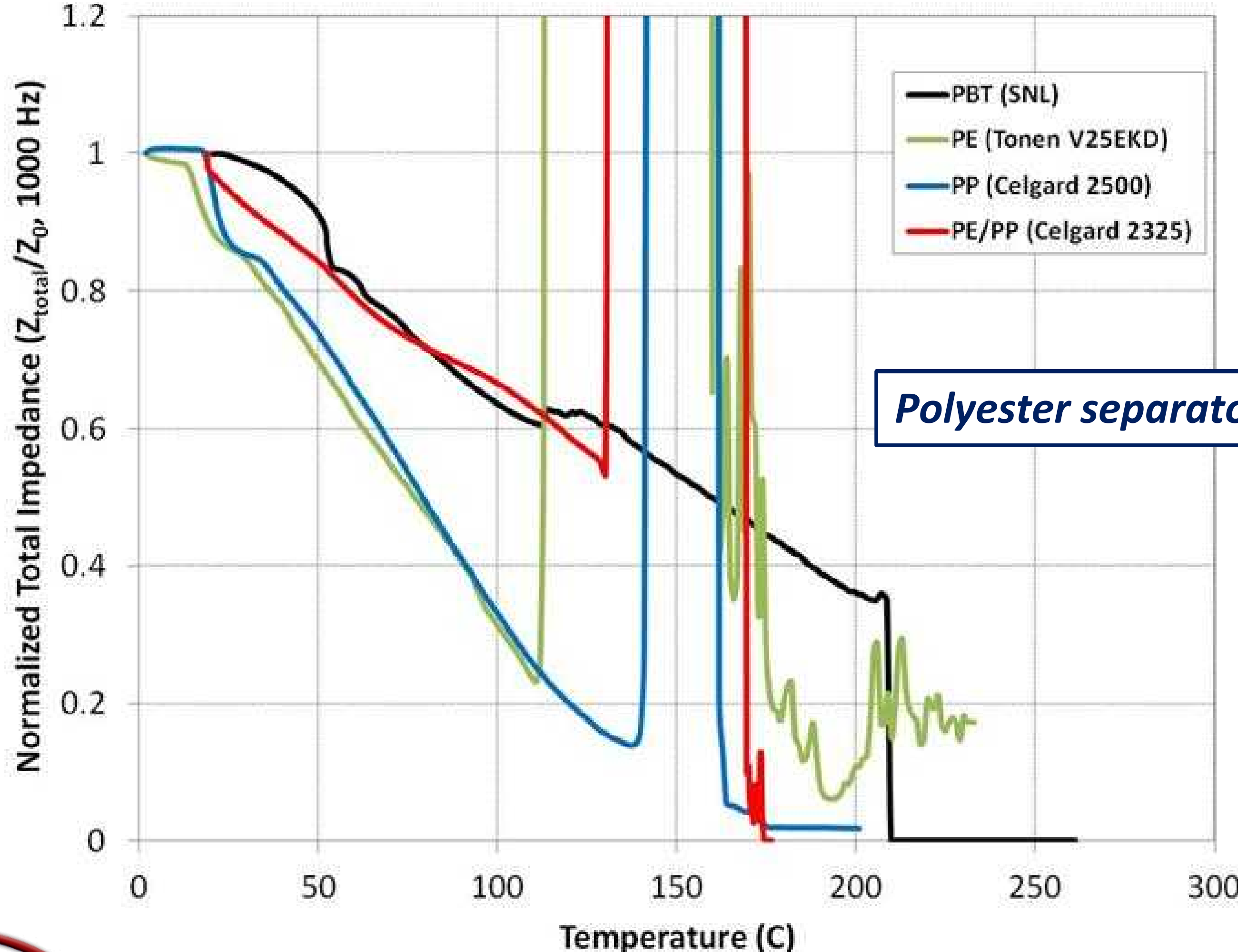
Spun fiber mat processing is scalable and low cost



Performance is comparable to commercial separators in cells

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Thermal Stability of Polyester Separators



Polyester separators stable to > 210 C

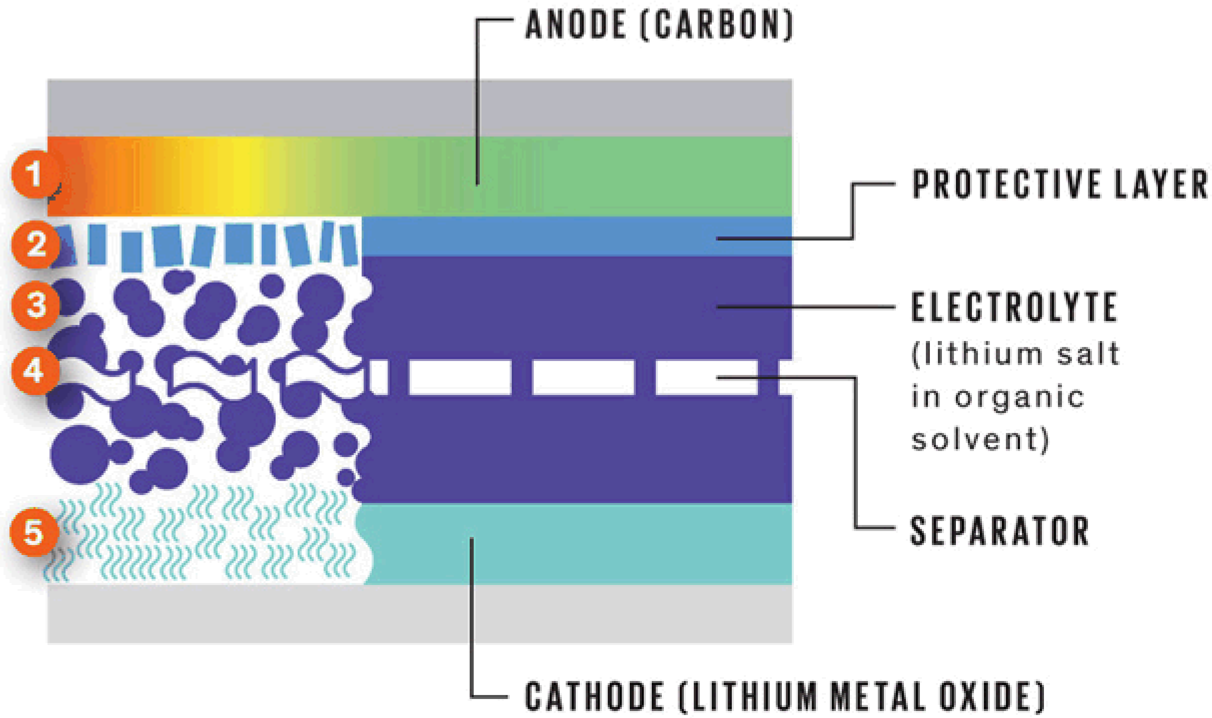
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

C. J. Orendorff et al. Adv. Energy Mater (2013) DOI: 10.1002/aenm.201200292

Cell materials are responsible for thermal runaway behaviors

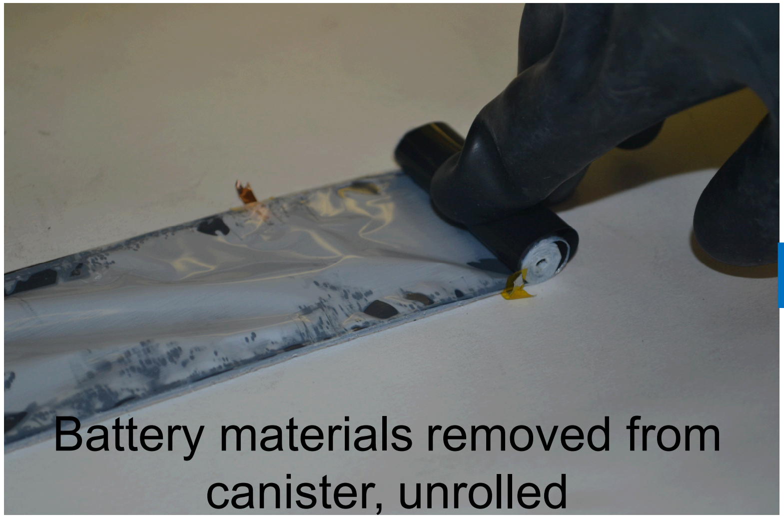
Thermal Runaway in a Lithium-Ion Battery

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.

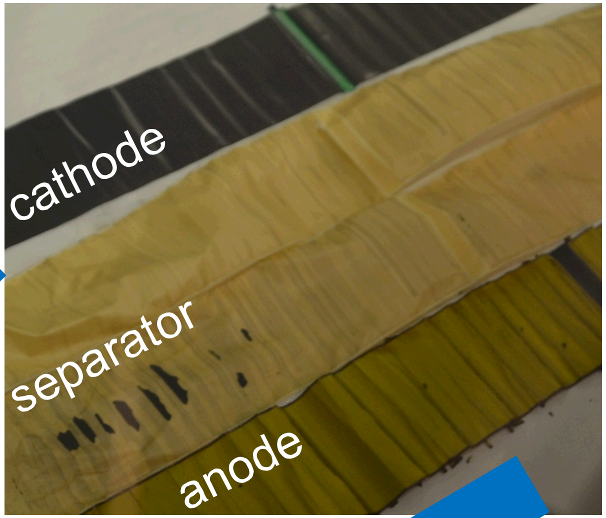


https://www.extremetech.com/extreme/208888-doping-lithium-ion-batteries-could-prevent-overheating-and-explosion

Batteries are disassembled to reveal steps of failure

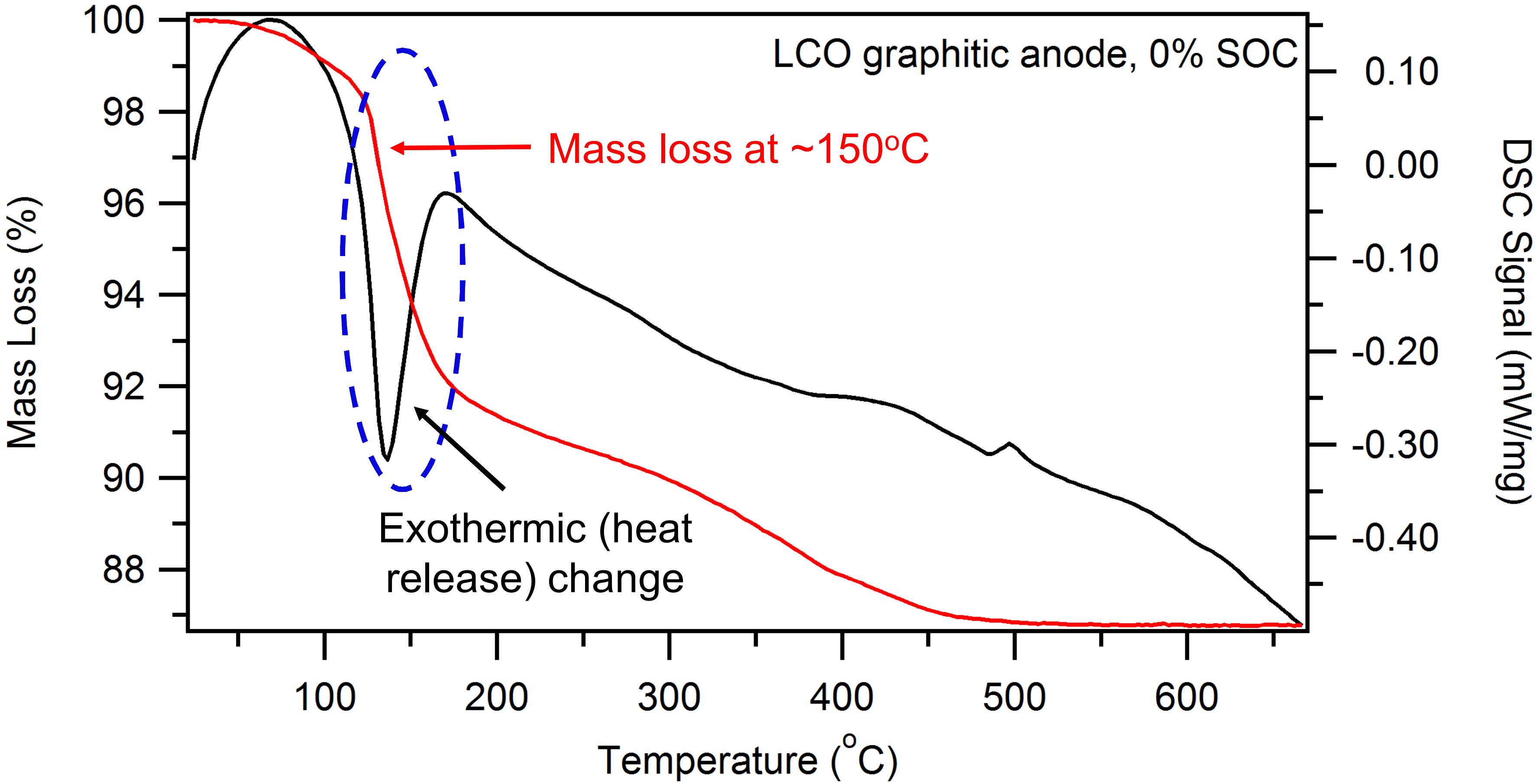


Disassembly



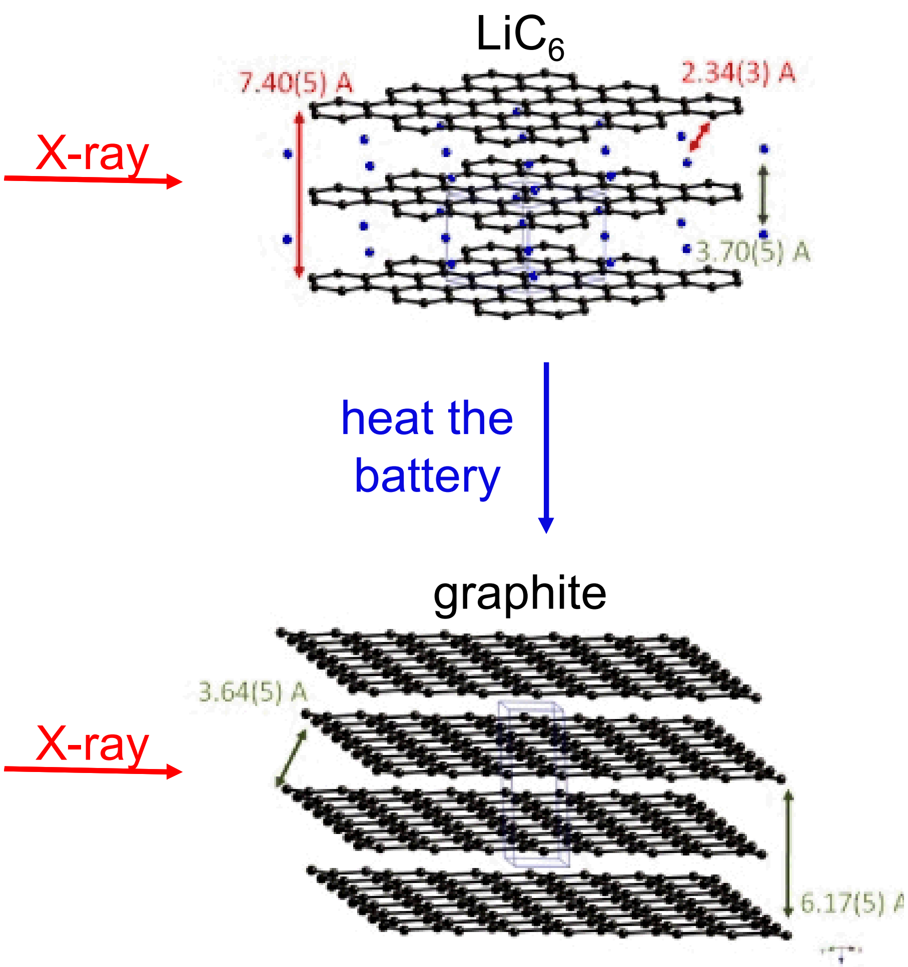
Temperature-resolved XRD shows how the material changes with temperature

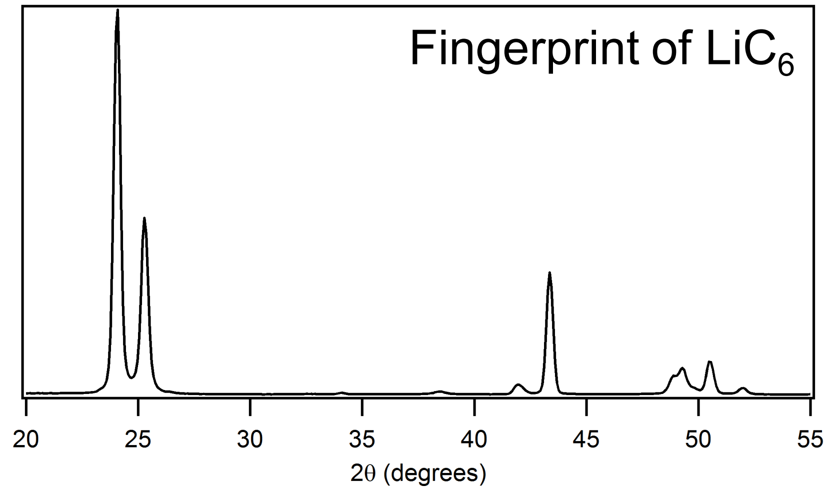
TGA/DSC reveals thermal stability

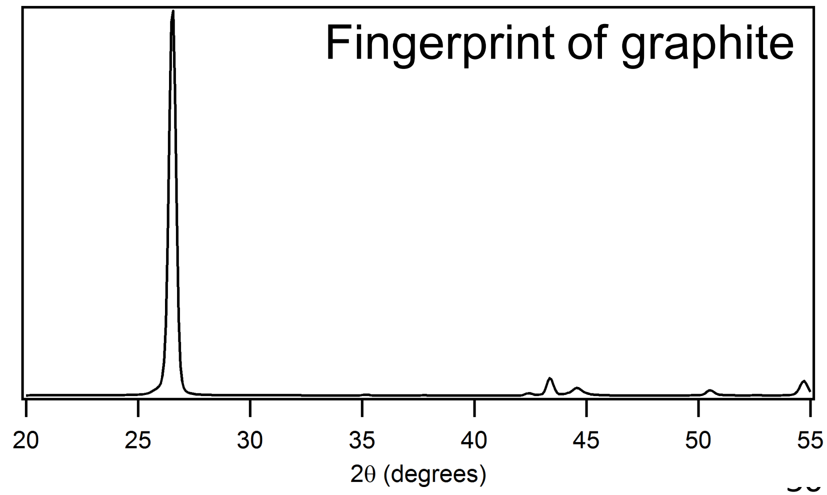


We have learned that the anode loses mass at 150°C and this also releases heat

Temperature-resolved XRD exposes decomposing structure

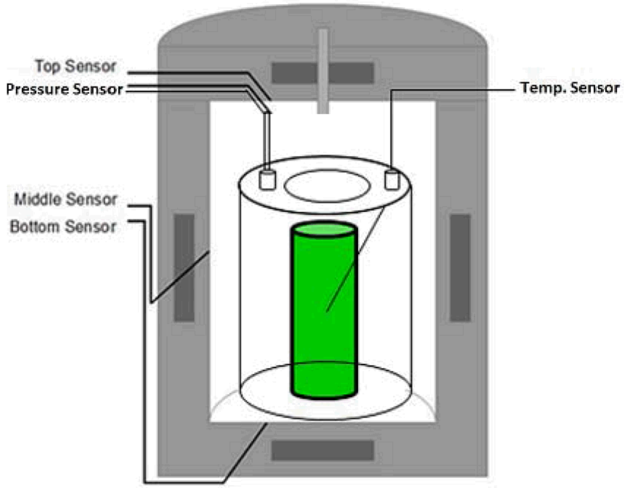


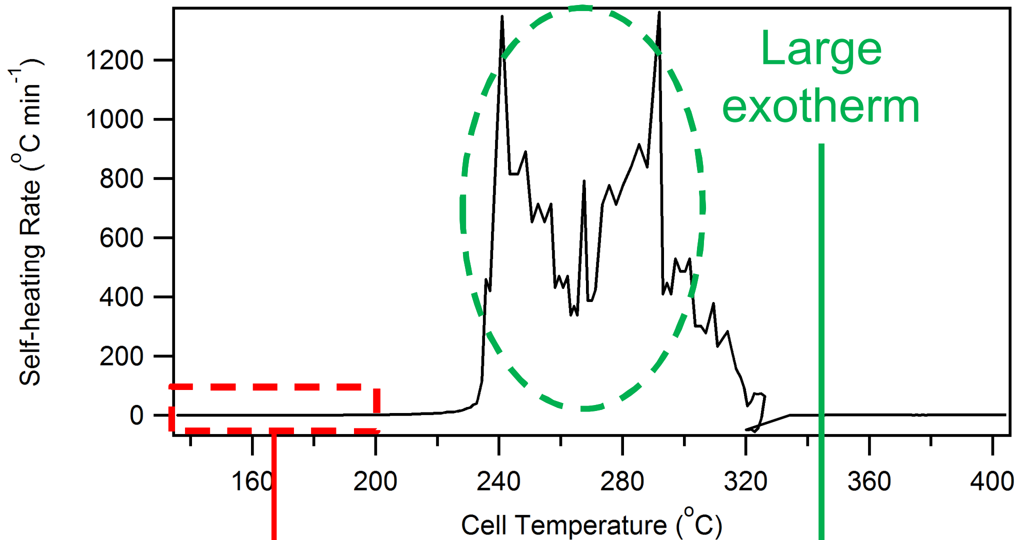


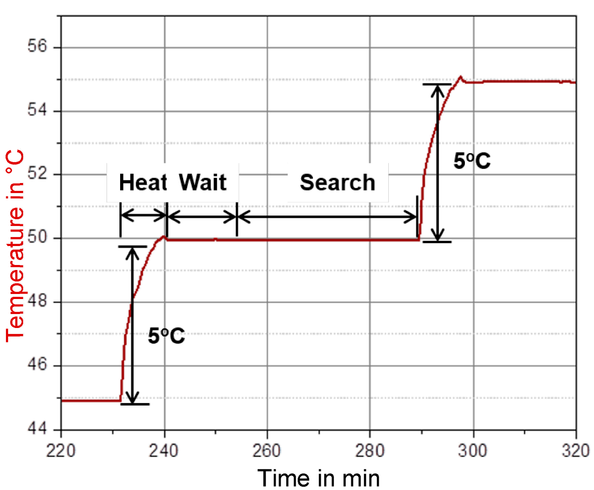


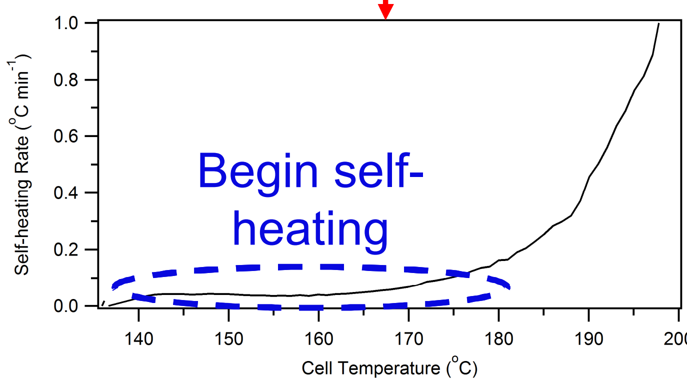
Schematic of LiC_6 and graphite: V. Petkov, A. Timmons, J. Camardese "Li insertion in ball-milled graphitic carbon studied by total x-ray diffraction" *Journal of Physics: Condensed Matter* **2011**, 23, 435003.

Accelerating Rate Calorimetry (ARC) demonstrates thermal runaway





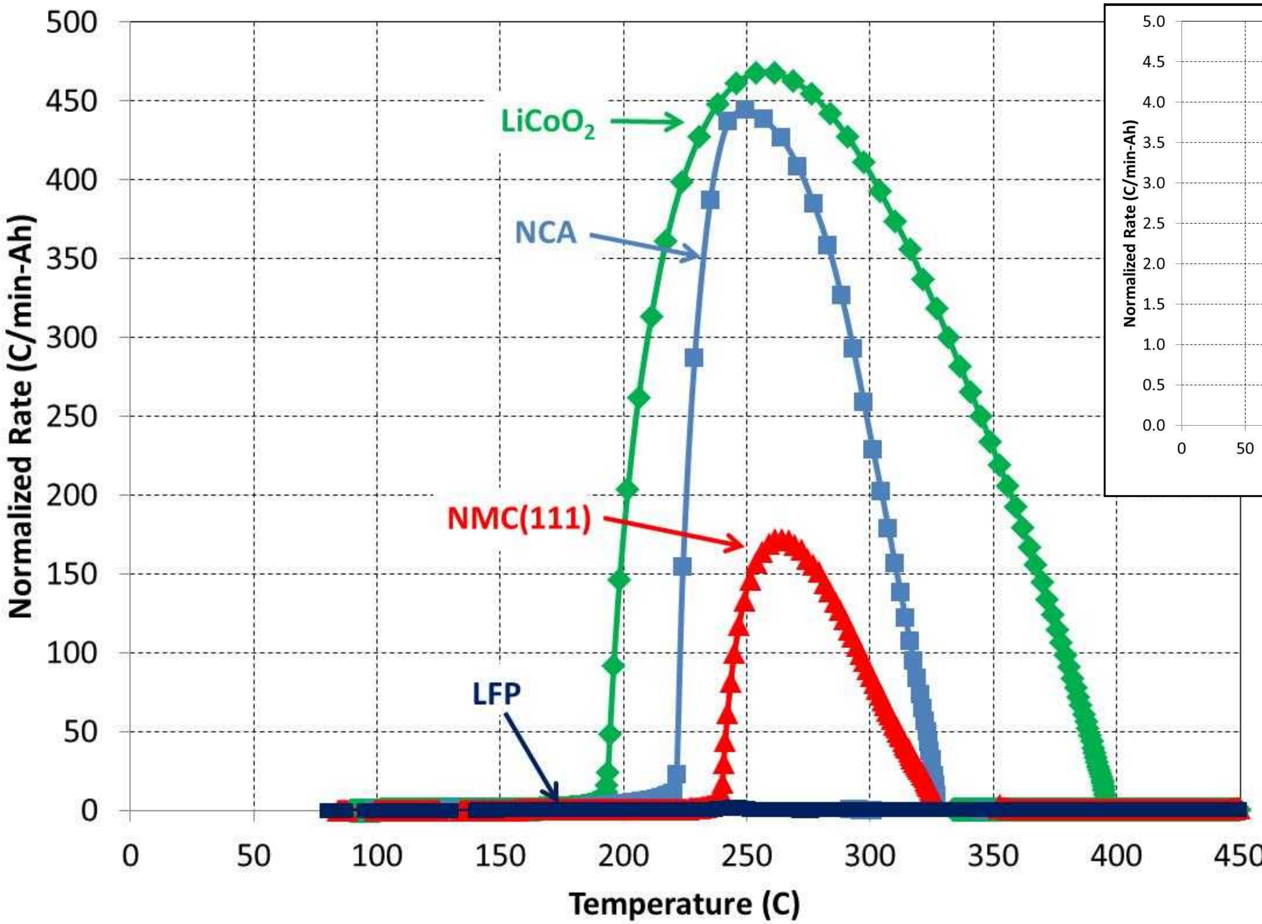


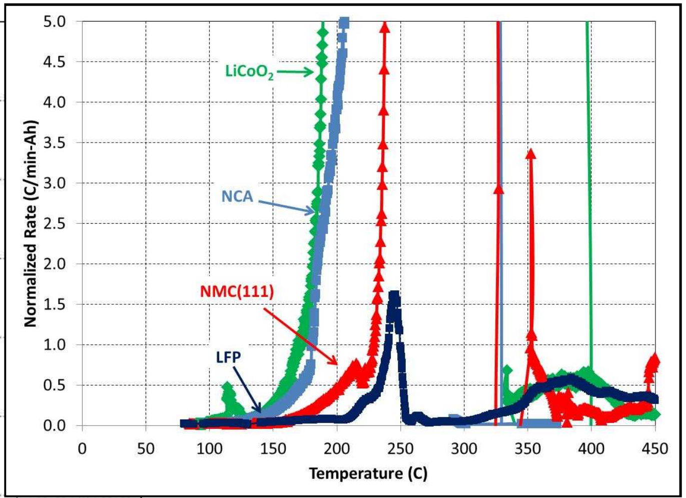


Schematic of ARC and heat-wait-seek: B. Lei, W. Zhao, C. Siebert, N. Uhlmann, M Rohde, H. J. Seifert "Experimental analysis of thermal runaway in 18650 cylindrical Li-ion cells using an accelerating rate calorimeter" *Batteries* **2017**, 3, 14.

Cell chemistry matters

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

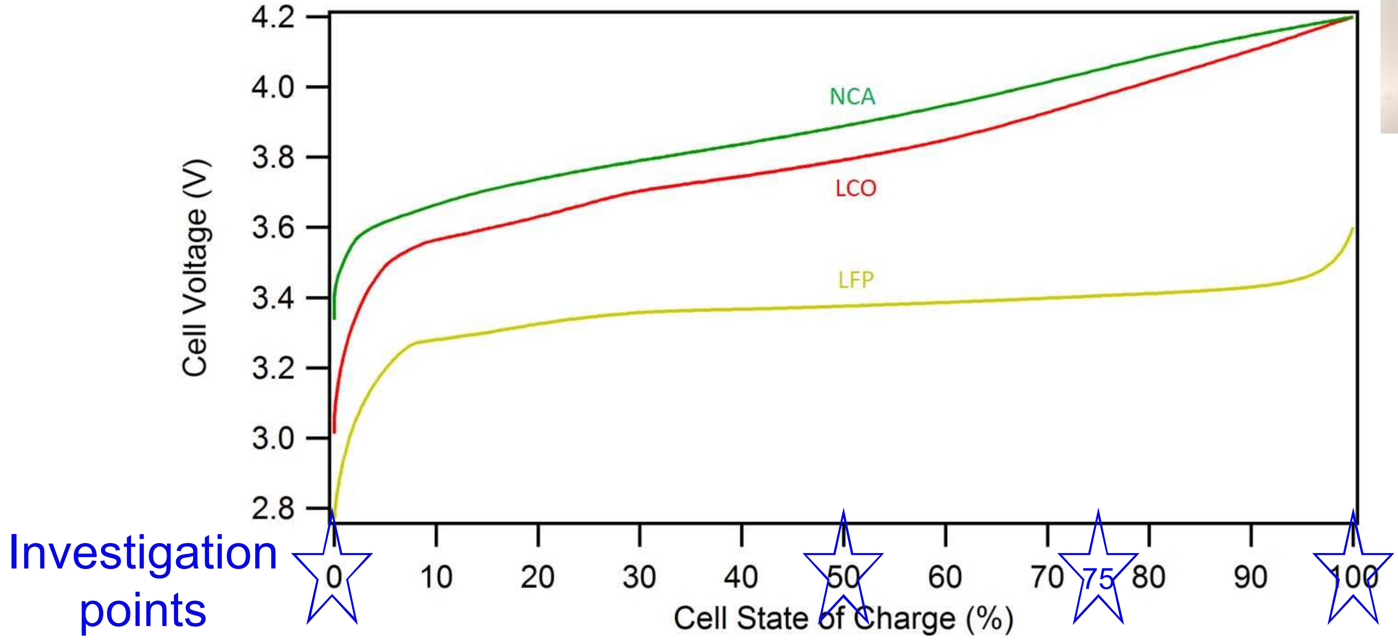




High Rate Runaway	
Cathode	$\Delta H_{runaway}$ (kJ/Ah)
$LiCoO_2$	15.9
NCA	9.8
NMC111	8.3
LFP	2.4

- **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?**

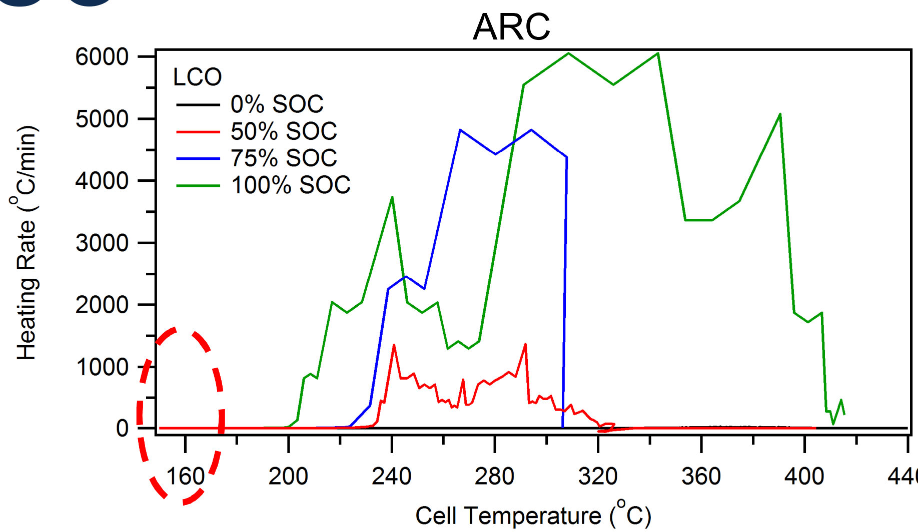
State of charge (SOC) matters

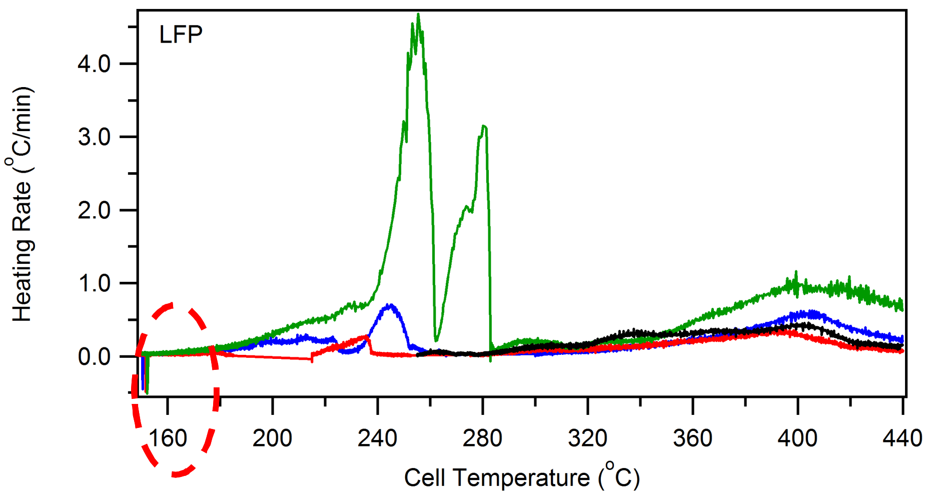


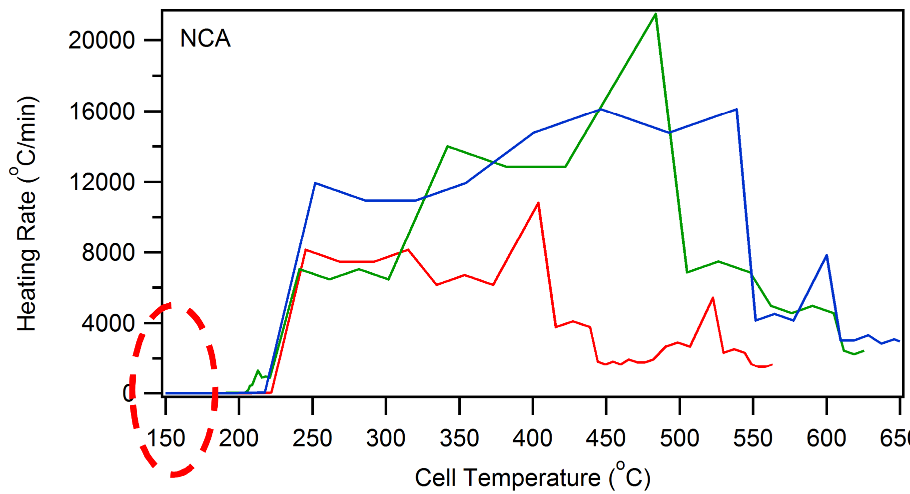
Think of state of charge (SOC) as the battery's "fuel gauge"
100%=full, 0%=empty

A full tank is more dangerous than an empty tank

Thermal runaway behavior changes with chemistry and SOC



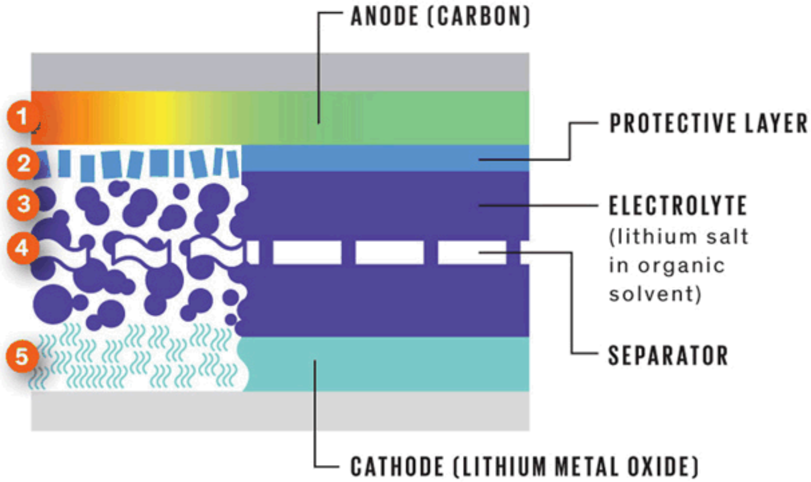




Onset temperature is ~150°C for all chemistries

Thermal runaway begins with anode decomposition

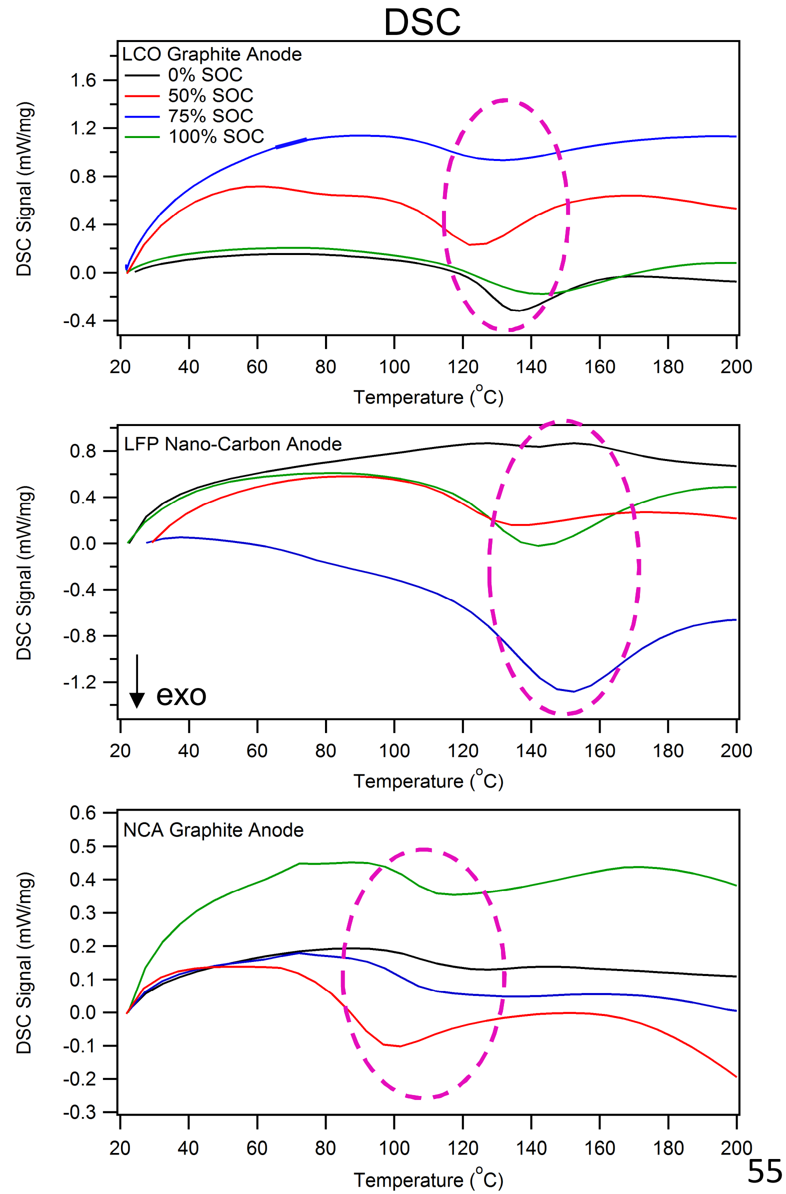
Sandia National Laboratories



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

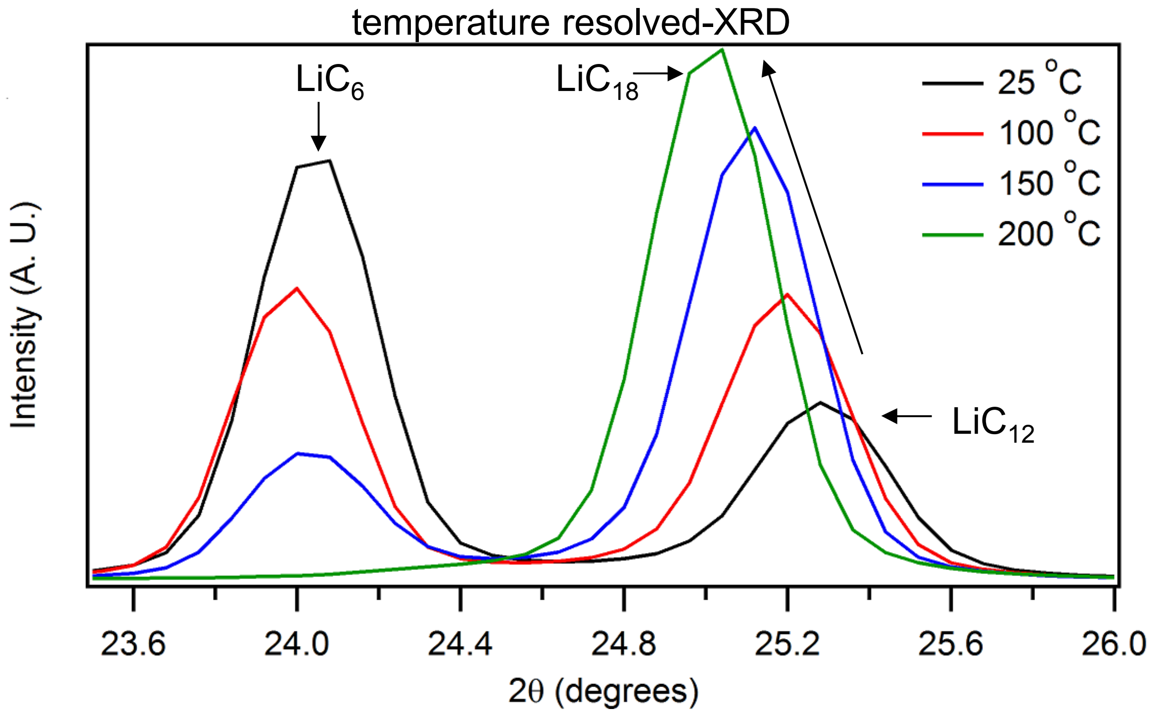
Underlying anode (1) is no longer protected, and reacts with the electrolyte (3) also releasing heat (exotherm).

This is the onset of thermal runaway detected in the ARC



Schematic of electrodes: https://www.extremetech.com/extreme/208888-doping-lithium-ion-batteries-could-prevent-overheating-and-explosion

Charged anodes decompose with temperature



As temperature increases, lithium reacts and is pulled out of the anode (recall lithium in the anode is like gas in a tank).

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

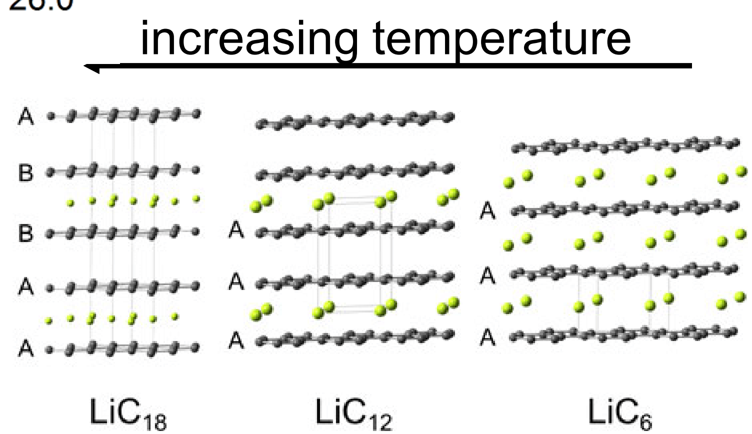
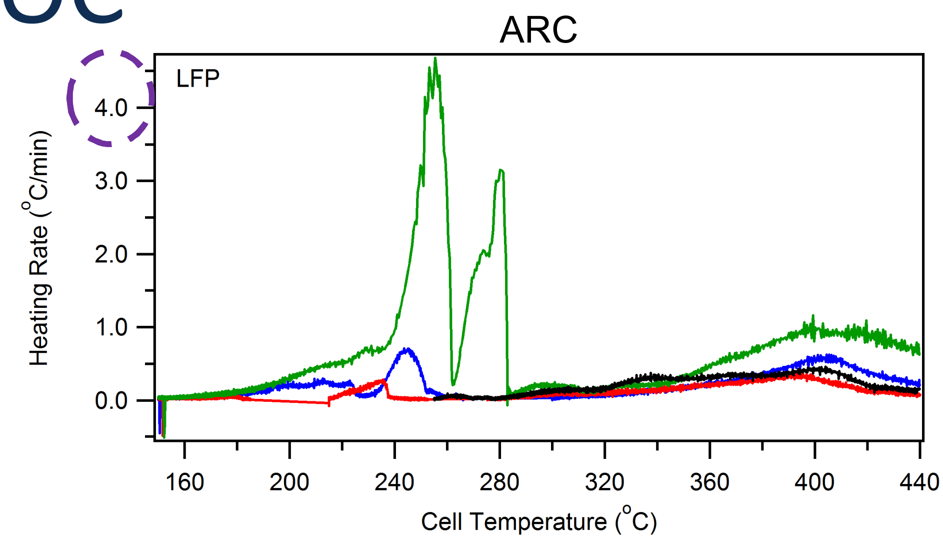
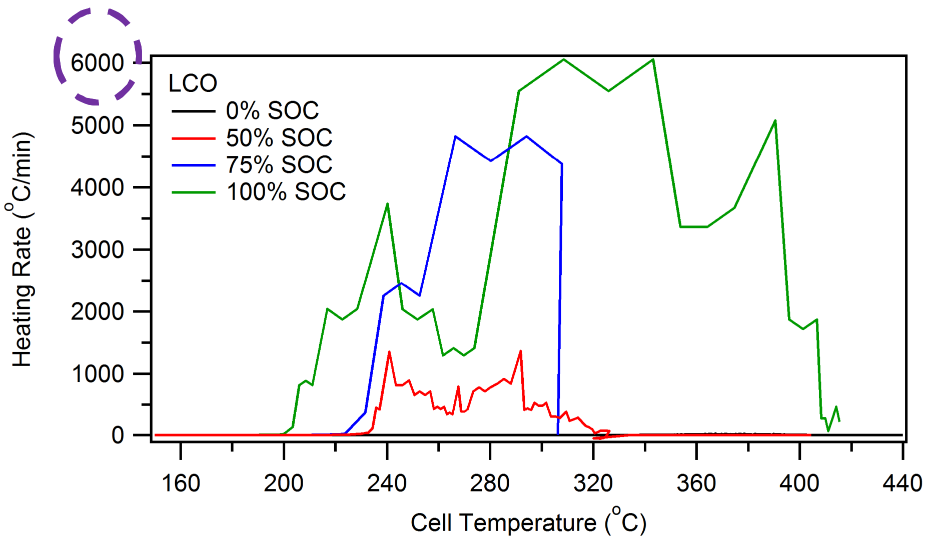
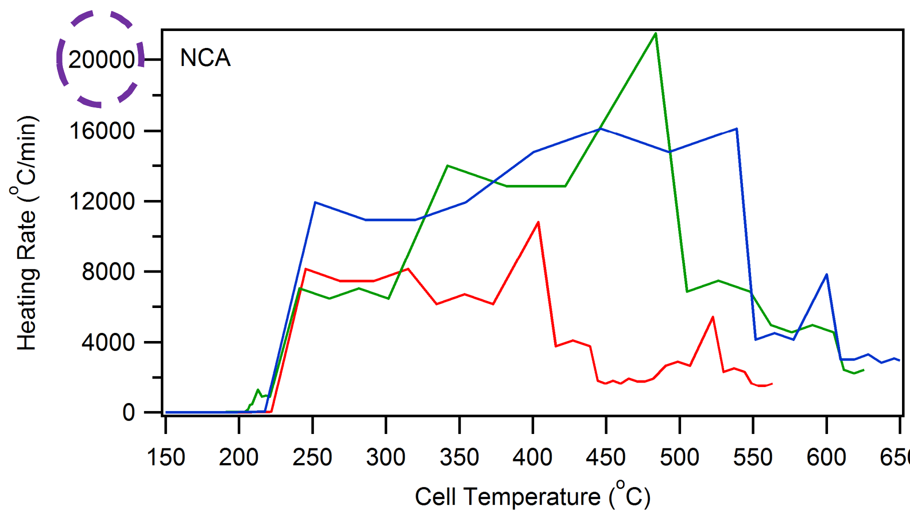


Image of LiC_6, LiC_{12}, and LiC_{18}: A. Missyul, I. Bolshakov, R. Shpanchenko "XRD study of phase transformations in lithiated graphite anodes by Rietveld method" *Powder Diffraction* **2017**, 1-7.

Thermal runaway behavior changes with chemistry and SOC

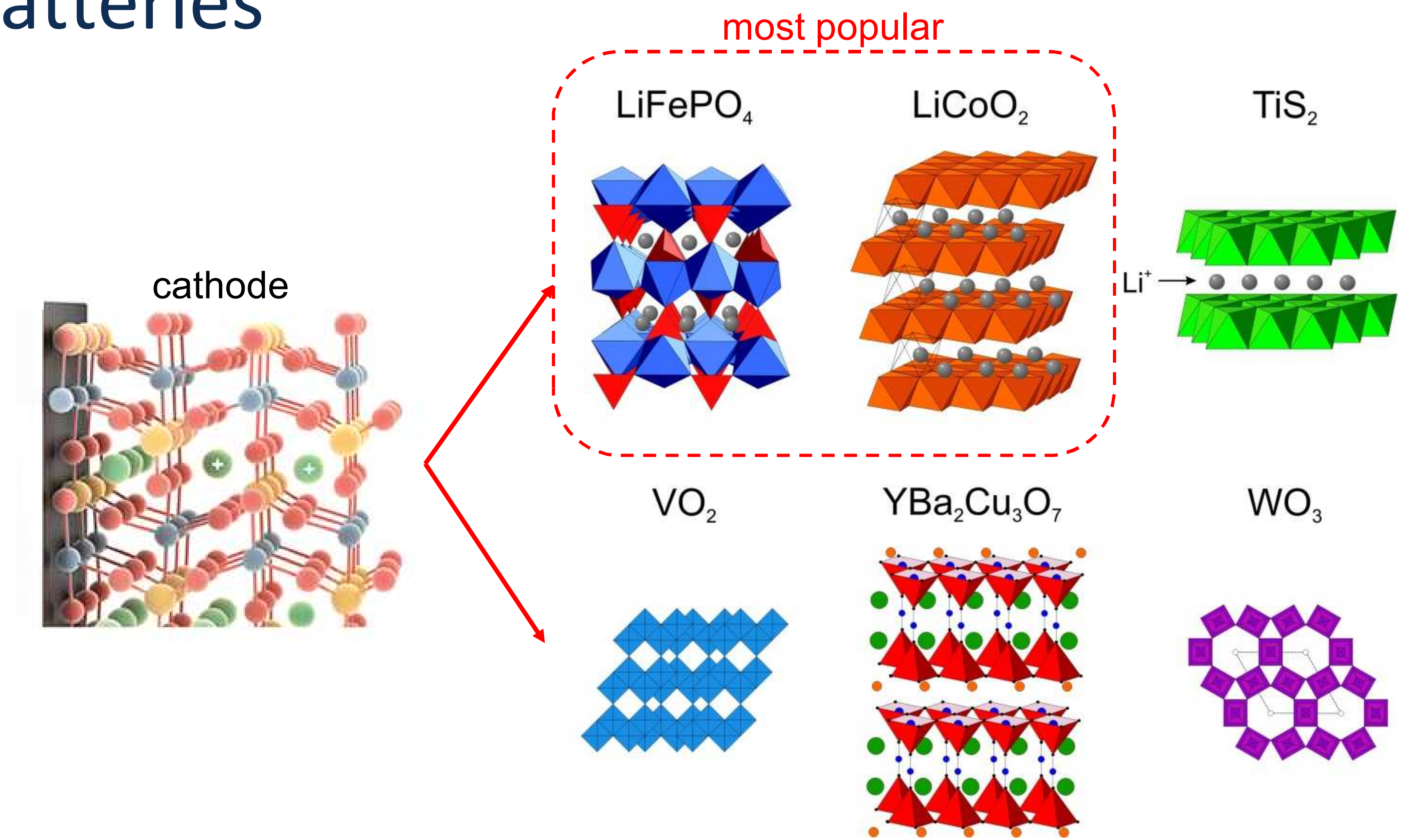






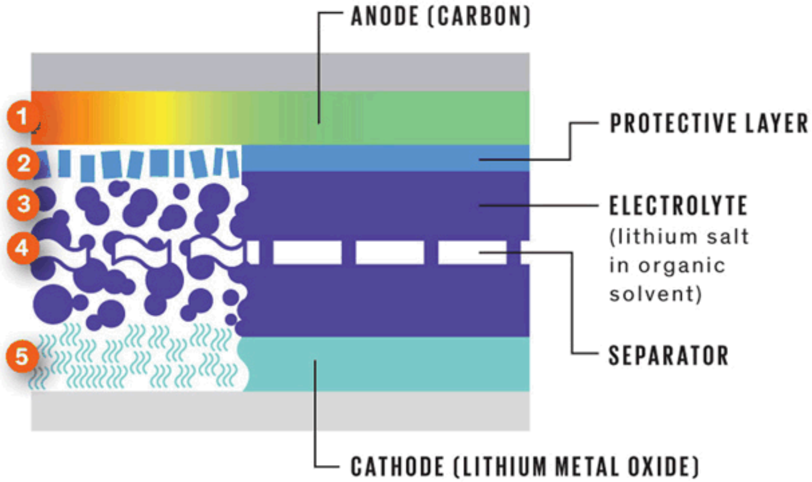
Maximum heating rate is chemistry dependent

There are many types of lithium-ion batteries



Cathode: http://visual-science.com/projects/lithium-ion-accumulators/infographics; different cathode structures: J. Molenda, M. Molenda "Composite Cathode Materials for Li-ion batteries based on LiFePO4 system" *Meetal, Ceramic and Polymeric Composites for Various Uses* 2011 DOI: 10.5772/21635

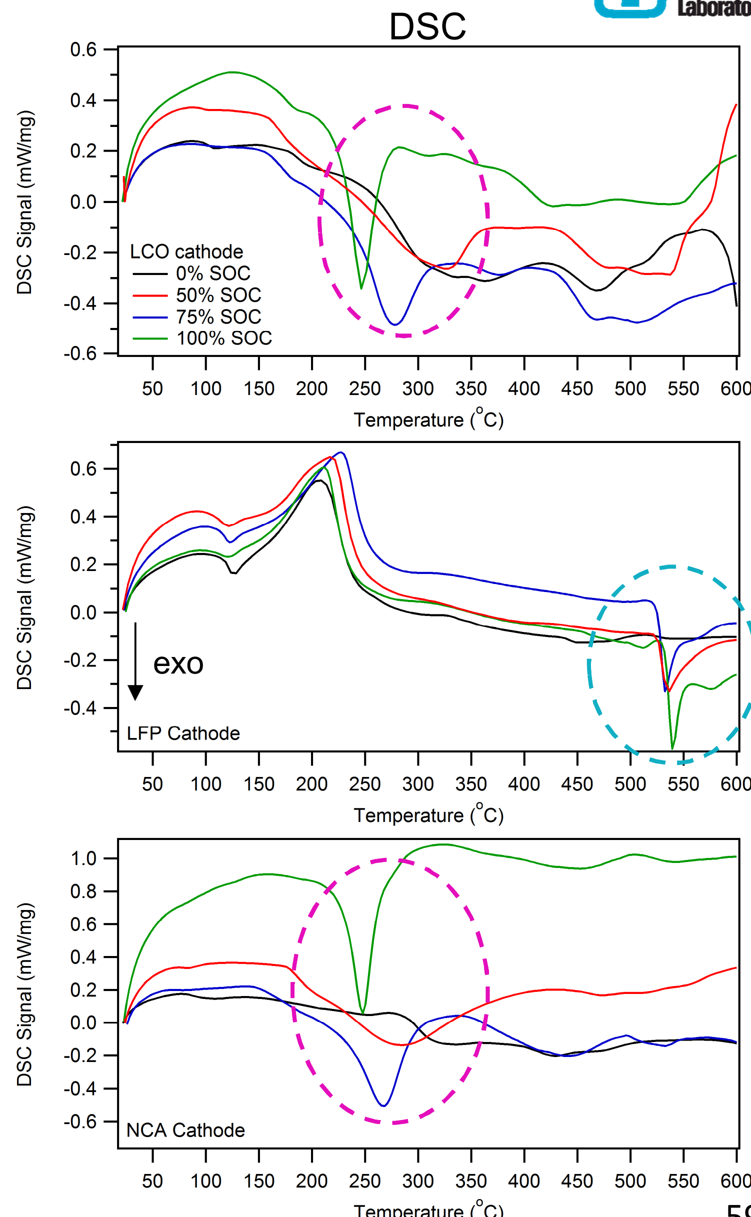
Cathode decomposition releases a lot of heat



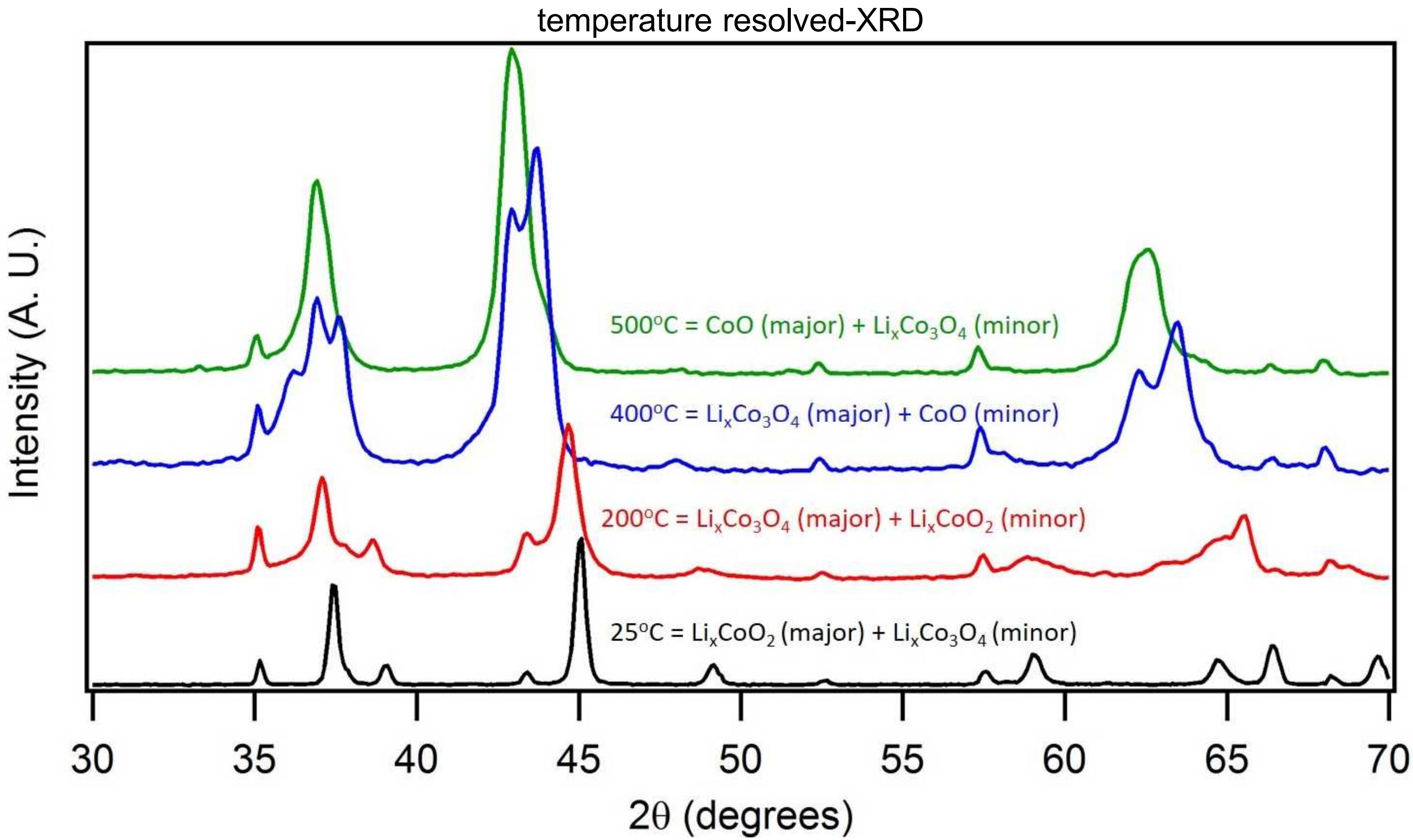
At higher temperatures, the LCO and NCA cathodes (5) break down, releasing a lot of heat (exotherm).

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).

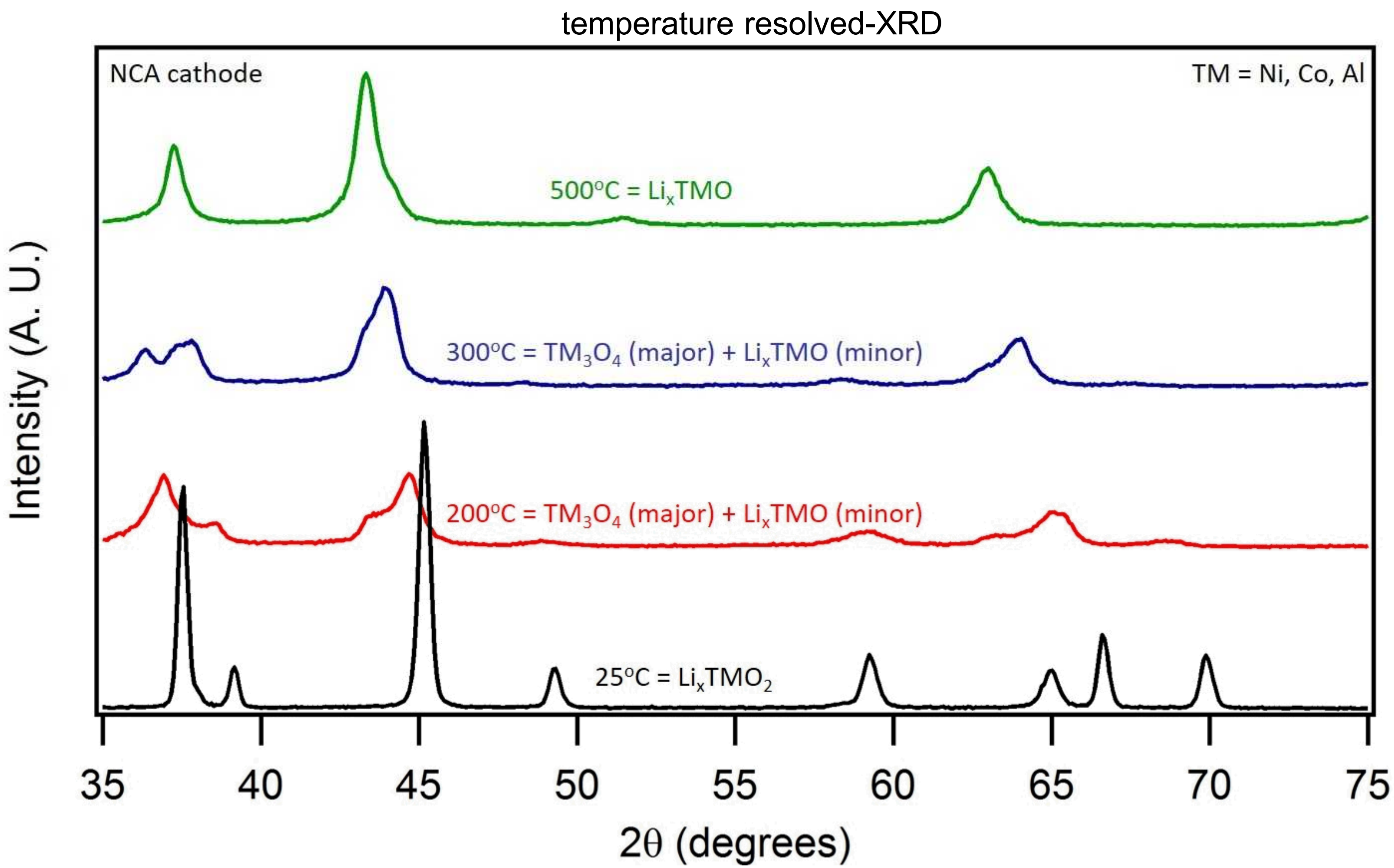


LCO cathode decomposes slowly



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

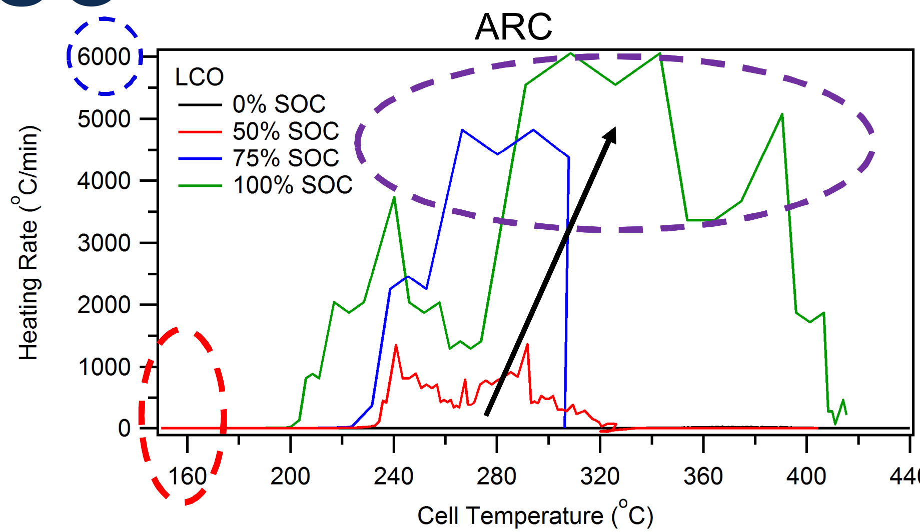
NCA cathode decomposes rapidly

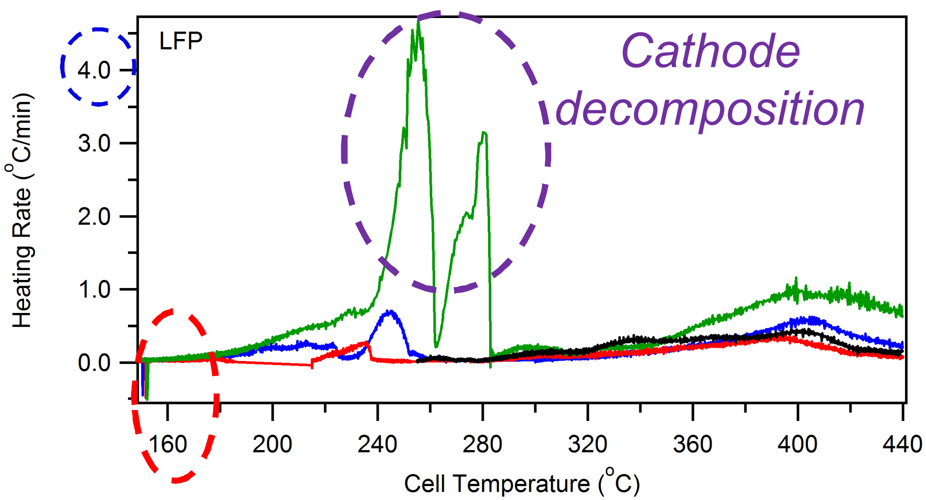


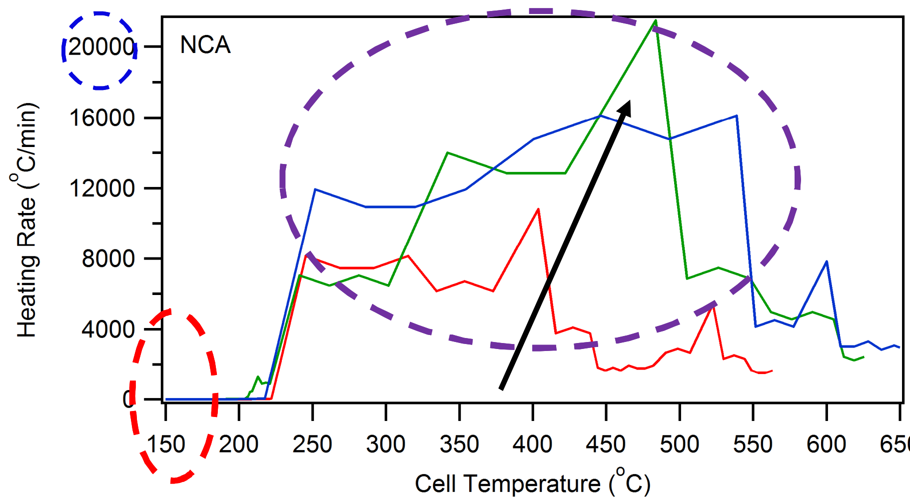
Cathode decomposition releases oxygen and heat.

Faster NCA decomposition results in higher heating rates in ARC.

Thermal runaway behavior changes with chemistry and SOC







Anode decomposition

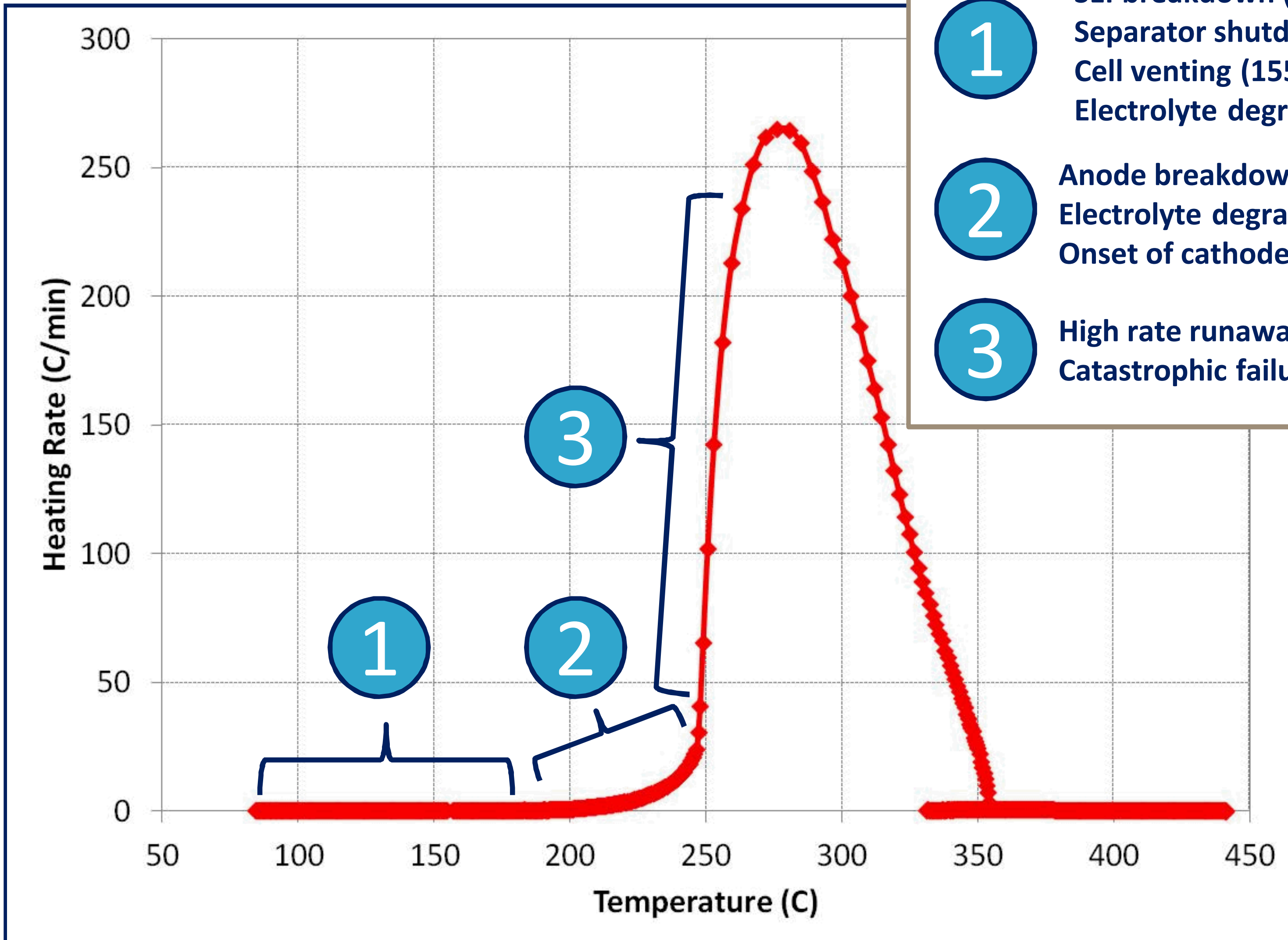
Cathode chemistry effects heat release rates

SOC effects heat release rates

Energetic Decomposition

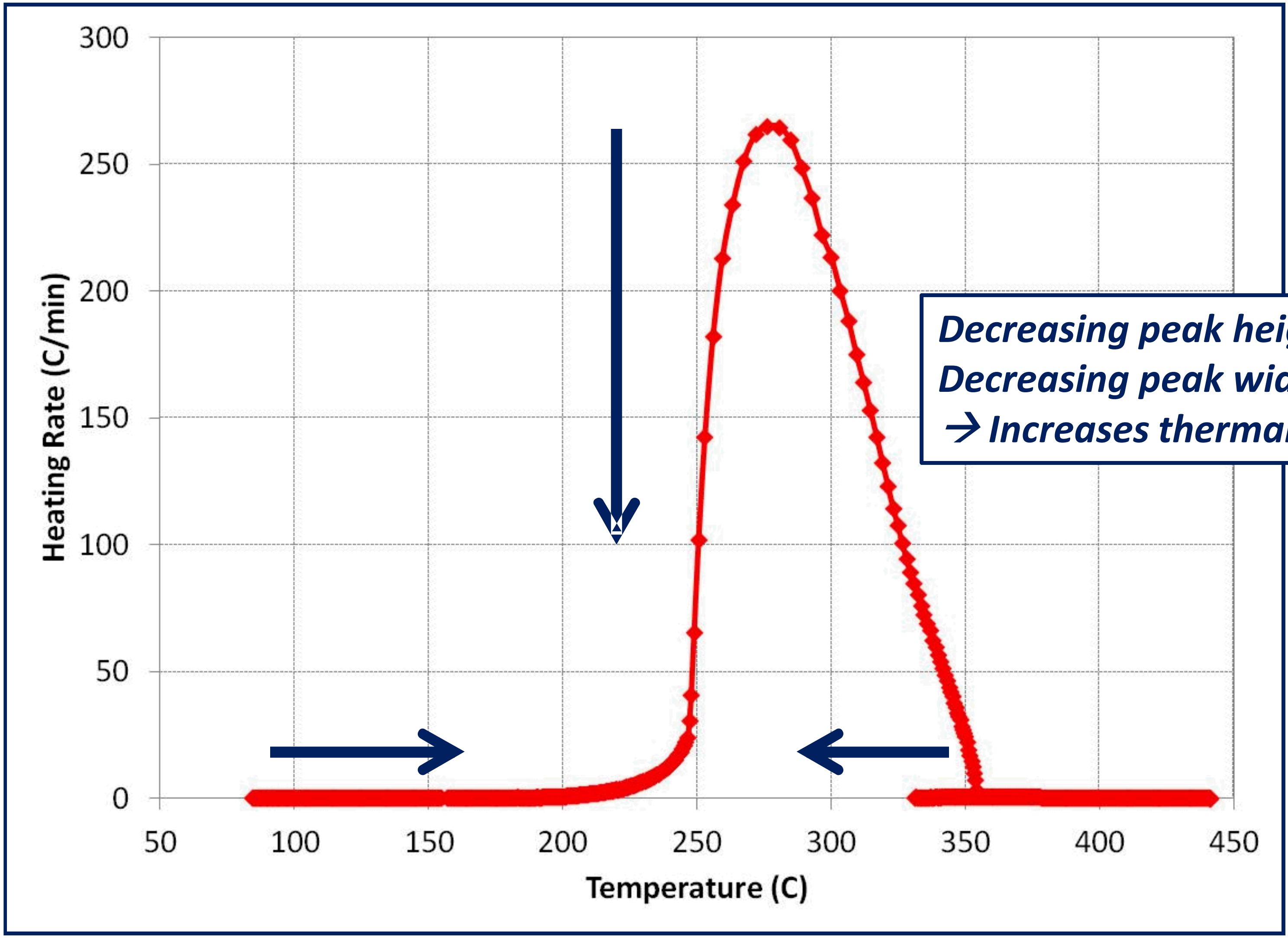
Stages of lithium-ion cell runaway

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



1. SEI breakdown (70-90 C)
   Separator shutdown
   Cell venting (155-165 C)
   Electrolyte degradation
2. Anode breakdown
   Electrolyte degradation
   Onset of cathode decomposition
3. High rate runaway
   Catastrophic failure

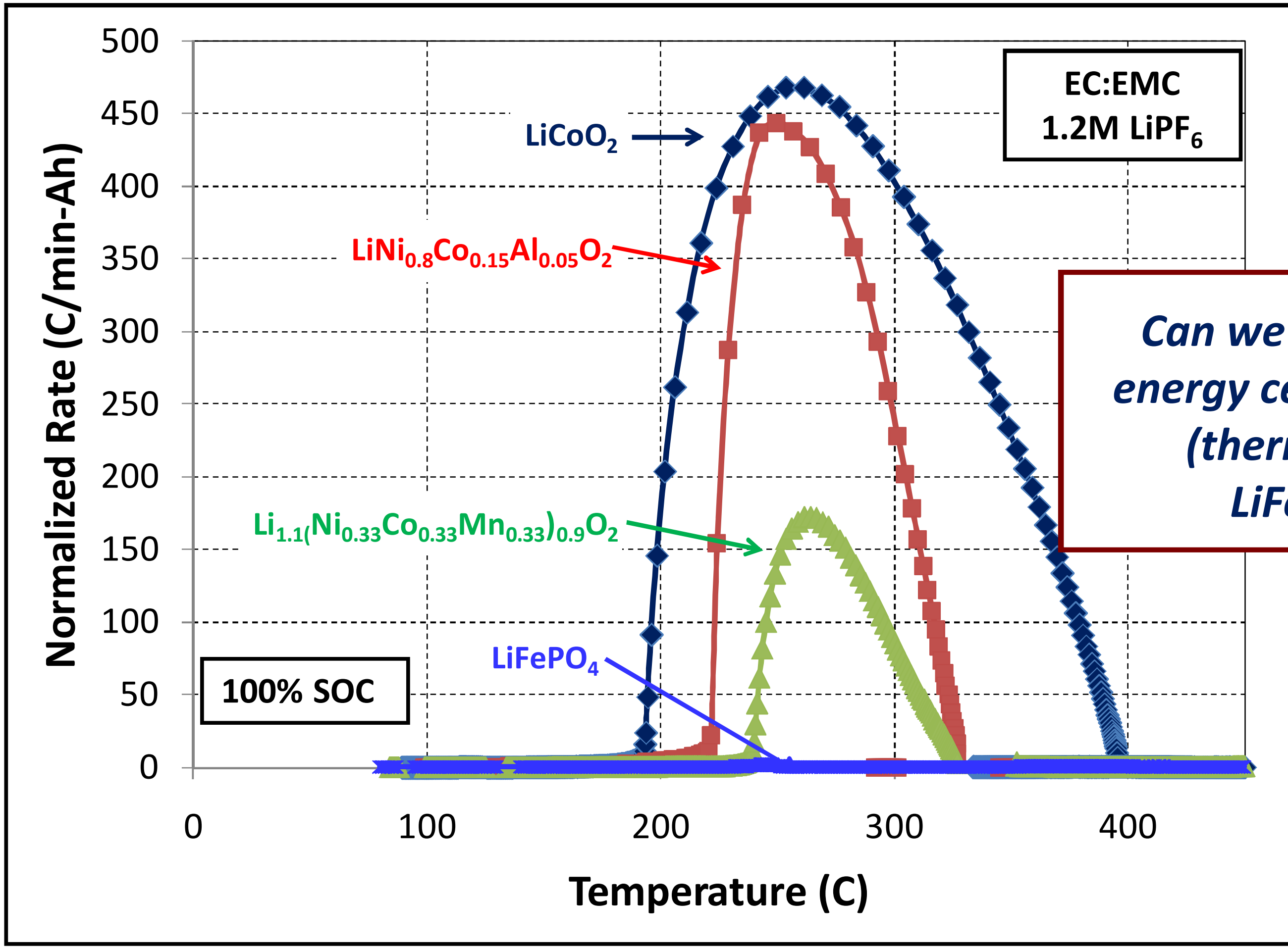
Stages of lithium-ion cell runaway



Decreasing peak height
Decreasing peak width
→ Increases thermal stability

Changing cathode chemistry

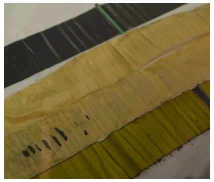
ARC of cells with different cathode chemistries

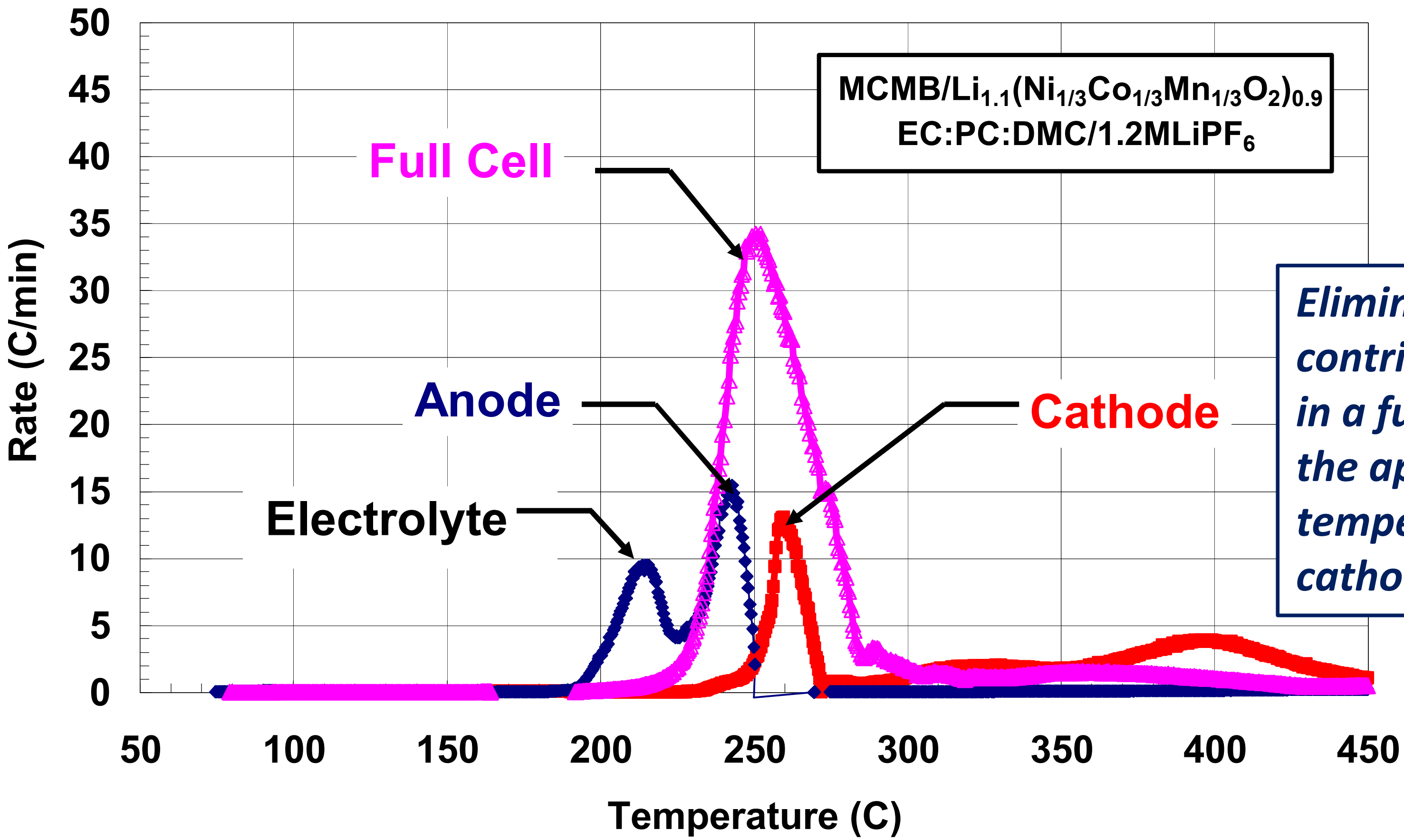


Can we have a higher energy cell that behaves (thermally) like a $LiFePO_4$ cell?

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

Anode and cathode runaway





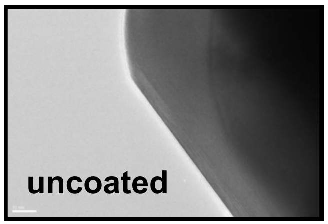
Eliminating the anode contribution to runaway in a full cell increases the apparent onset temperature for cathode runaway

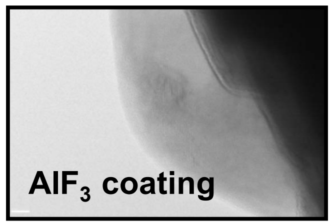
Results are consistent with stabilized anode response to thermal runaway when alumina coated by ALD

Coating active materials

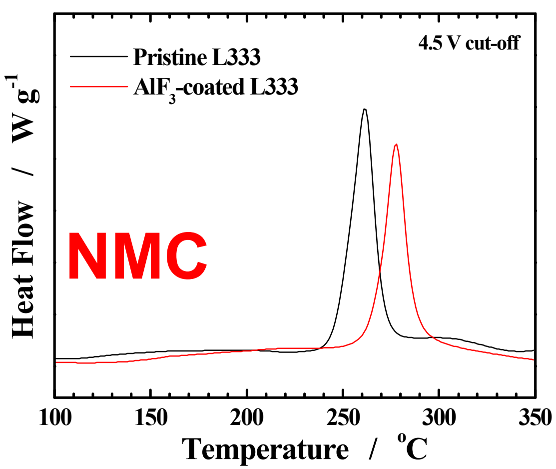
Collaboration with Khalil Amine and Zonghai Chen (ANL)

Inert coatings are used to stabilize the surface of active materials

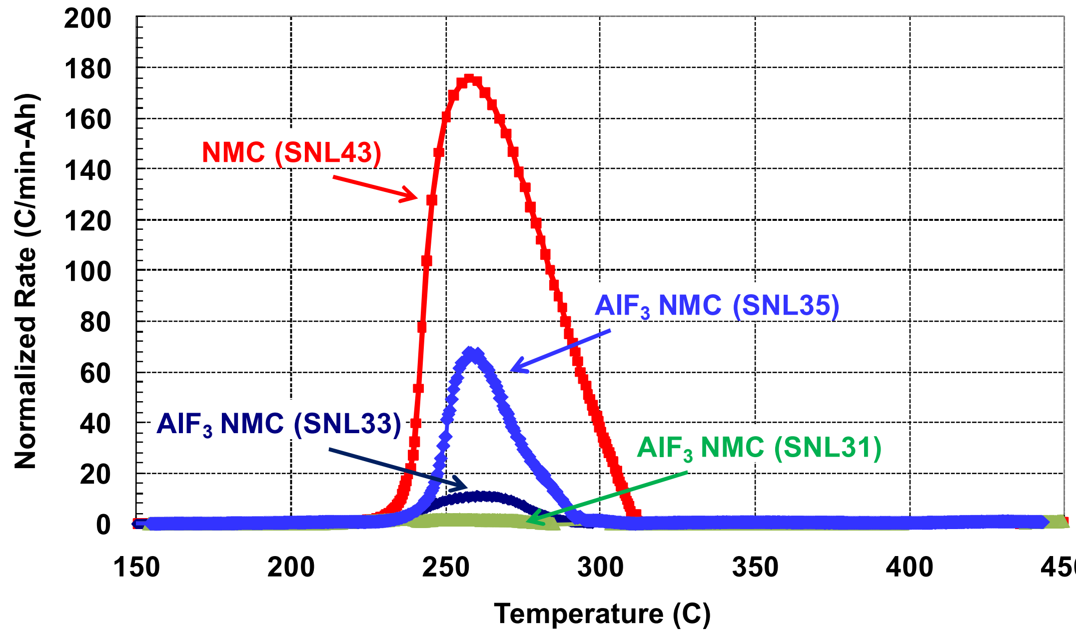




Cathode DSC



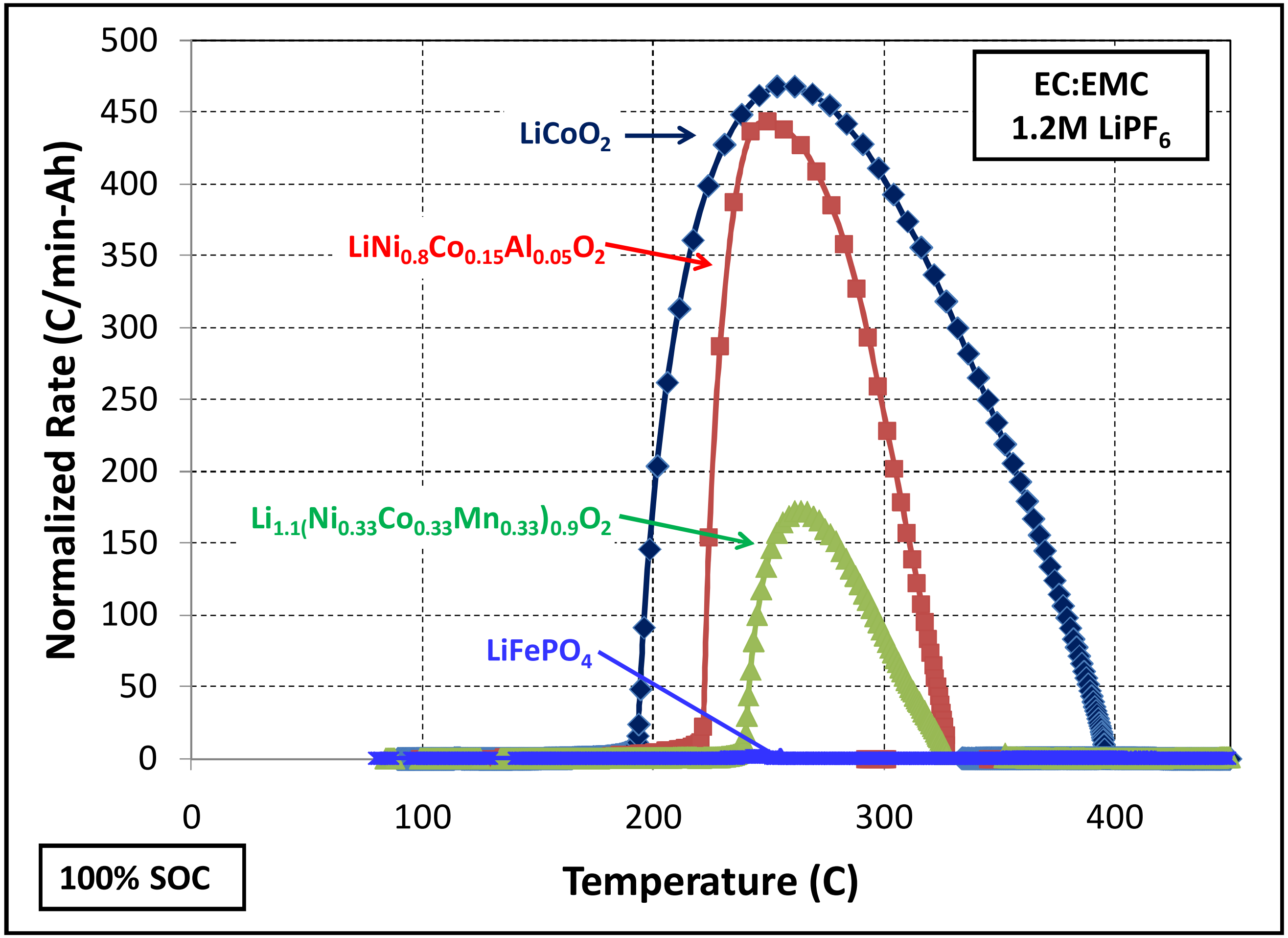
Cell ARC



Reduction in NMC cell runaway kinetics with 2% (wt) AlF_3 coatings

Focus is on commercial designs

ARC of cells with different cathode chemistries



Analyze commercial cell behavior to understand failure and enable improved mitigation of off-normal events

Al_2O_3-Coated Electrodes (ALD)

Collaboration with Steve George (CU Boulder)

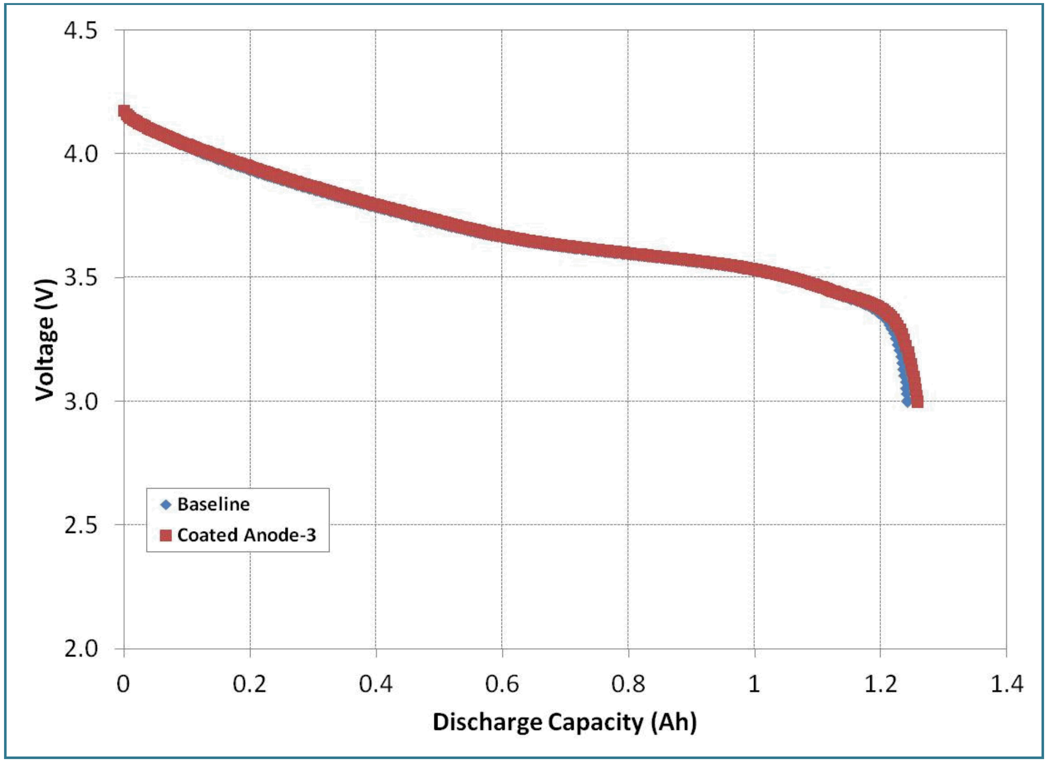
Cell builds

- Toda Li ($Ni_{1/3}Mn_{1/3}Co_{1/3}$)O_2 (NMC111) + Conoco Philips A10 graphite in 1.2 M $LiPF_6$ in EC:EMC (3:7)
- Electrodes coated at CU with Al_2O_3 by ALD
- Coated cathodes + uncoated anodes (C1-C3)
- Coated anodes + uncoated cathodes (A1-A3)

Performance measurements in 18650 cells

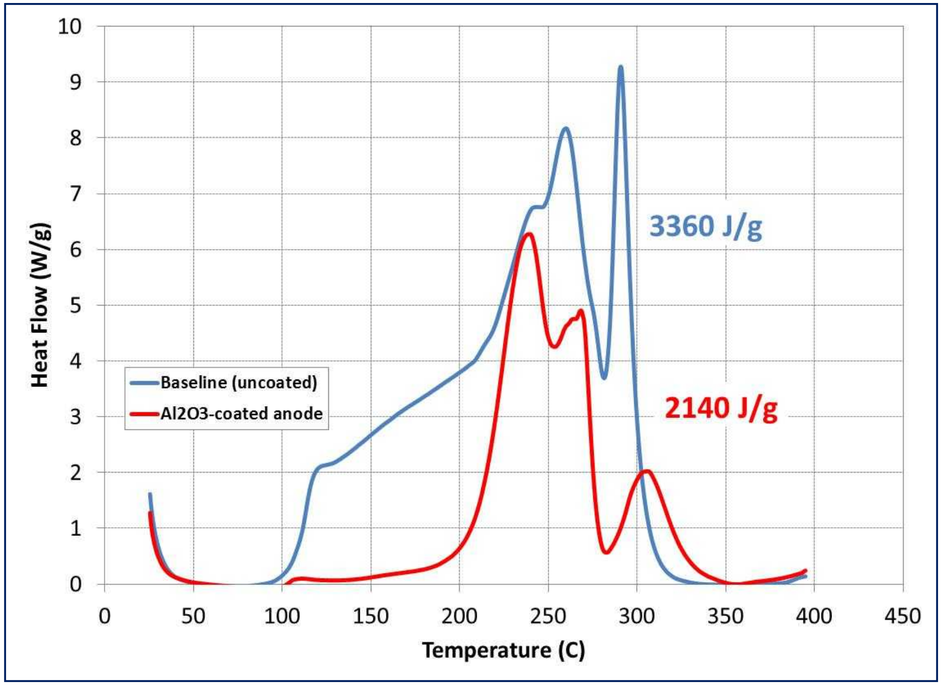
Calorimetry (DSC, ARC) to determine the effects of the coatings on the thermal runaway response of the

Discharge capacity at C/5 of 18650 cells

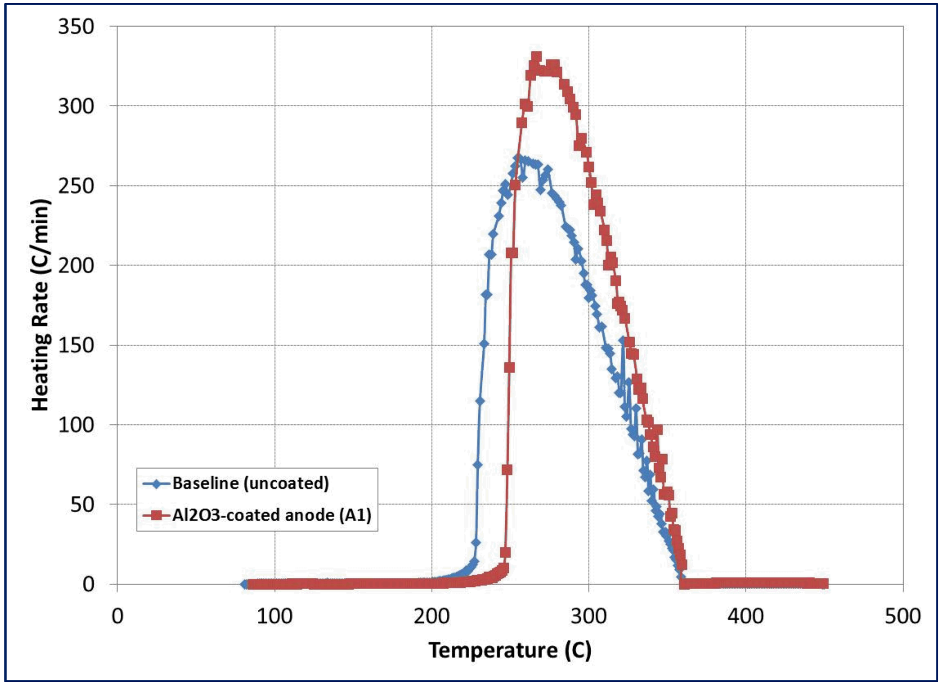


Al_2O_3-Coated Anodes (ALD)

Anode DSC

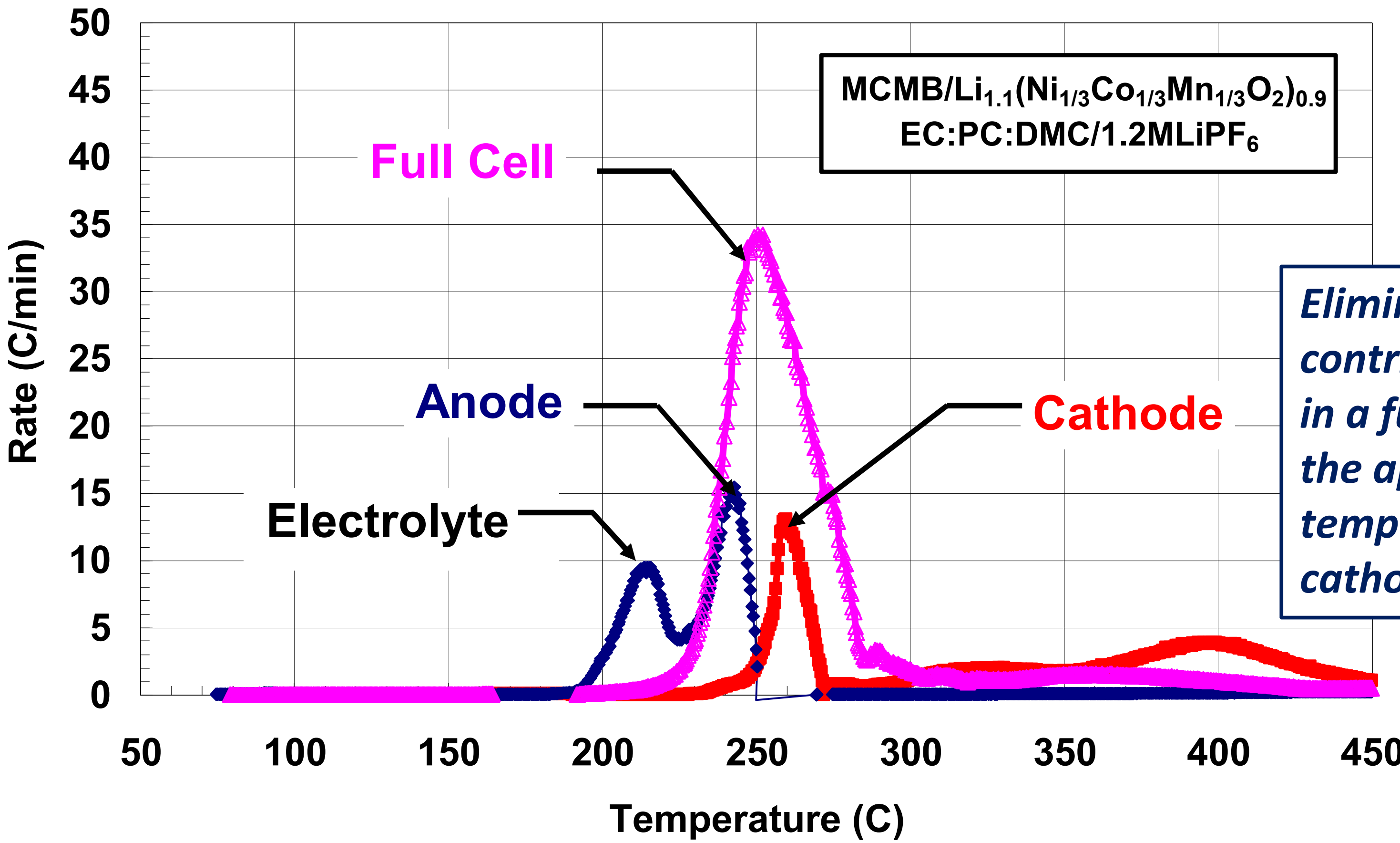


Cell ARC



- ***Stabilization of the anode interface (SEI) with Al_2O_3 coating***
- ***Increased high rate runaway onset temperature by 20 C***
- ***Suggests stabilization of the anode to high temperature decomposition by Al_2O_3 coating***

Anode and Cathode Runaway



Eliminating the anode contribution to runaway in a full cell increases the apparent onset temperature for cathode runaway

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

Agenda Overview

- Part II Modeling of Thermal Characteristics and Safety

- *Modeling of Materials and Thermal Kinetics*
  - Limitations of experimentalists
  - Modeling solution
    - Extend life
    - Improve reliability
    - Predict failure (propagation)
    - Scaling

Agenda Overview

Part II: Modeling of Thermal Characteristics and Safety

1. Thermal Abuse Behavior
    - Overview
    - Identifying Thermally-activated Reactions
    - Thermal Abuse Model
    - Results and Discussion
2. Electrode Microstructure and Thermal Interplay
    - Electrochemical-Thermal Model
    - Sources of Heat Generation
    - Active Material and Electrolyte Properties
    - Results and Discussion
    - Cold Start and Thermal Cross-talk
3. Thermo-electrochemical Analytics
    - Inverse Problem Definition
    - Analysis of DSC Measurements – Thermal Safety
    - Analysis of ARC Measurements – Heat Generation
4. Strategies for LIB Thermal Management

Agenda Overview

Part II: Modeling of Thermal Characteristics and Safety

1. Thermal Abuse Behavior
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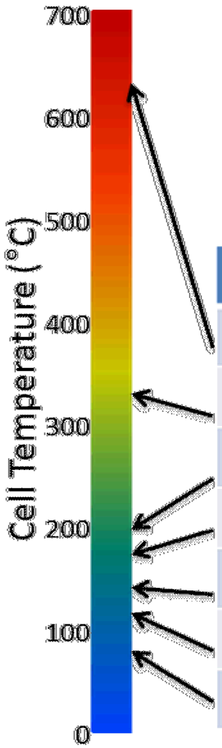
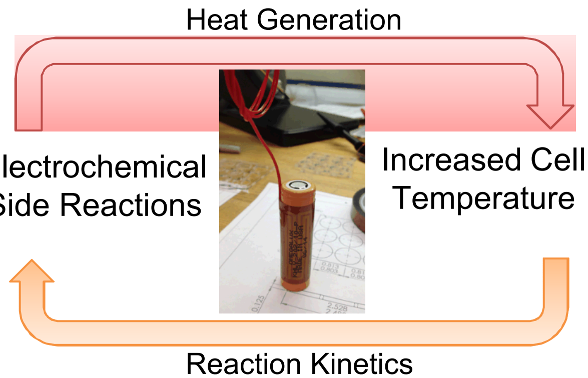
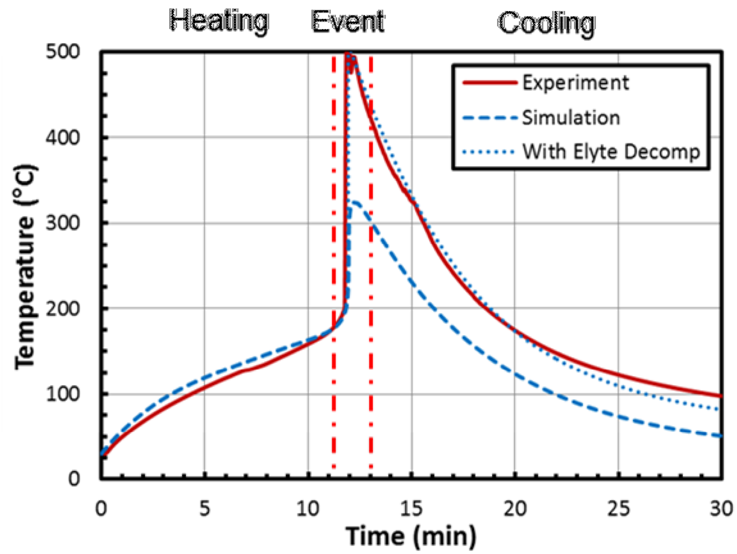
Lithium-ion Battery Thermal Safety





Onset T (°C)	Side Reaction
660	Aluminum melts
330	Anode collapse
160-225	Electrolyte vaporization and combustion
130-180	Separator melts, internal short
140	Cathode decomposition and electrolyte reaction
110-140	Secondary SEI formation and decomposition
85-105	Primary anode SEI decomposition



It is observed that beyond a certain cell temperature, thermally activated exothermic reactions take place, which rapidly raises the cell temperatures and the cells becomes inoperable upon cooling down.

*C. Lopez, J. A. Jeevarajan and P. P. Mukherjee (2015) *J. Electrochem. Soc.*, **162** (9), A1905
*C. Lopez, J. A. Jeevarajan and P. P. Mukherjee (2015) *J. Electrochem. Soc.*, **162** (10), A2163

Modeling Thermal Abuse Response

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cylindrical Li-ion cell

Evolution of cell temperature:

$$mC_p \frac{dT}{dt} = \dot{Q} - hA\left(T - T_\infty\right)$$

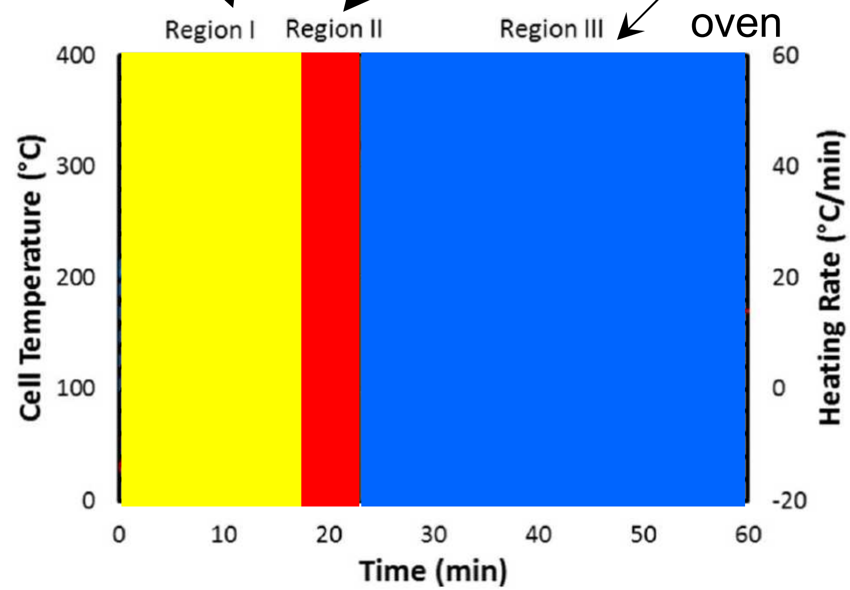
$$\dot{Q} = \dot{Q}_{anode} + \dot{Q}_{cathode} + \dot{Q}_{SEI} + \dot{Q}_{electrolyte}$$

At start $T_{oven} > T_{cell}$

Heat flows from oven to cell

Temperature rise due to abuse reaction heat

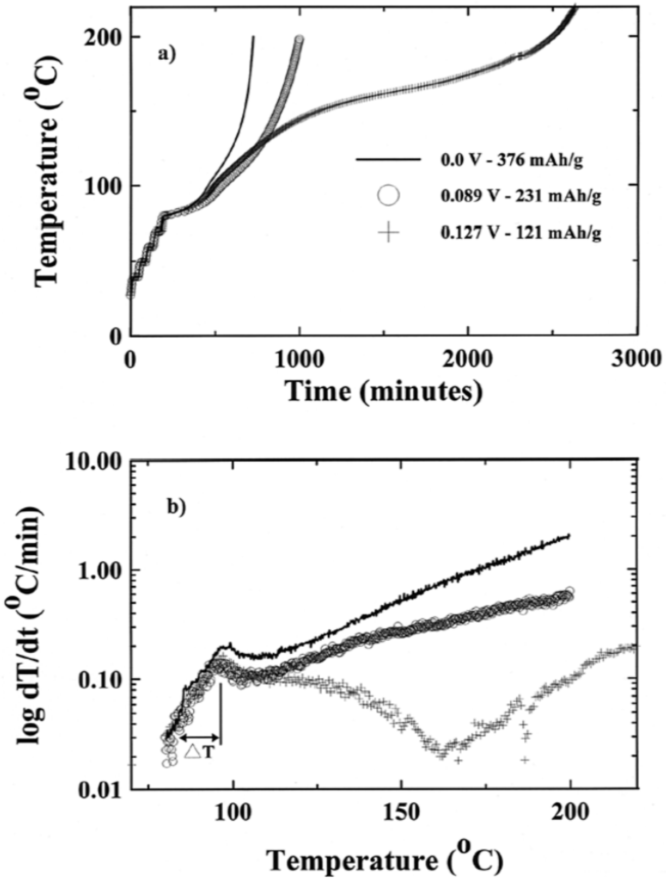
Heat rejection from cell to oven



cell temperature rise when placed in an oven

- Energy balanced performed on the cell reveals that there is internal heat generation which results in temperature rise.
- Since this temperature rise is observed beyond certain temperature, it is a result of thermally activated reactions.
- Electrode and electrolyte materials are quite reactive and in turn lead to self-sustained spontaneous reactions at elevated temperatures.

Identifying Thermally-activated Reactions



Accelerated Rate Calorimetry (ARC) profiles for graphite electrodes with different degrees of lithiation (ref: M. N. Richard and J. R. Dahn (1999) *J. Electrochem. Soc.* **146** (6) 2068)

ARC results for graphite electrodes at different lithiation states (0.0V is fully lithiated) reveal the existence of two distinct heat signature (dT/dt plots are more revealing):

1. Initial peak around 100°C which is independent of lithiation
2. Temperature rise which is a function of lithiation

The initial peak refers to reaction of metastable Li in SEI formed during formation cycles at electrode-electrolyte interface.

Temperature rise after all the metastable SEI Li is consumed is related to reaction of intercalated Li with electrolyte.

Thermally-activated Reactions at Anode

Reaction of metastable Li in SEI:

- Independent of the state of lithiation
- Relates to SEI film formed during the formation cycles
- k_s reaction frequency factor
- E_s activation energy
- ΔH_s reaction enthalpy

Rate of consumption of metastable Li, x_s:

$$\frac{dx_s}{dt} = -k_s \cdot \exp\left(-\frac{E_s}{k_b T}\right) \cdot x_s$$

Corresponding heat generation:

$$Q_s = -\Delta H_s \frac{dx_s}{dt}$$

Reaction of intercalated Li with electrolyte:

- Strongly depends on amount of intercalated Li
- As intercalated Li reacts with electrolyte, the resulting solid products deposit at electrode surface and increase the thickness of passivation layer

Rate of consumption of intercalated Li, x_i:

$$\frac{dx_i}{dt} = -k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

Growth of passivation layer, z:

$$\frac{dz}{dt} = k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

Corresponding heat generation:

$$Q_i = -\Delta H_i \frac{dx_i}{dt}$$

Notes:

- All concentrations and thickness are dimensionless quantities
- Each of these reactions is identified by kinetic triplet (k, E, ΔH). They are deduced from calorimetry data, e.g., ARC and DSC

Thermal Behavior of LIBs in an Oven Abuse Test

Evolution of cell temperature:

$$mC_p \frac{dT}{dt} = \dot{Q} - hA(T - T_\infty)$$

Heat generation:

$$\dot{Q} = \dot{Q}_{anode} + \dot{Q}_{cathode} + \dot{Q}_{SEI} + \dot{Q}_{electrolyte}$$

Reaction of metastable Li in SEI

$$\dot{Q}_{SEI} = \Delta H_{SEI} \cdot k_{SEI} x_{SEI} \exp\left(-\frac{E_{SEI}}{k_b T}\right)$$

Intercalated Li reacting with electrolyte (at anode)

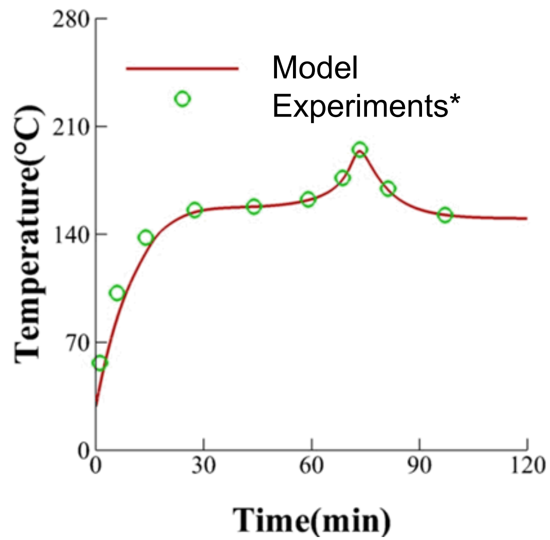
$$\dot{Q}_{anode} = \Delta H_{anode} \cdot k_{anode} x_{anode} \exp\left(-\frac{E_{anode}}{k_b T}\right) \exp\left(-{z}/{z_0}\right)$$

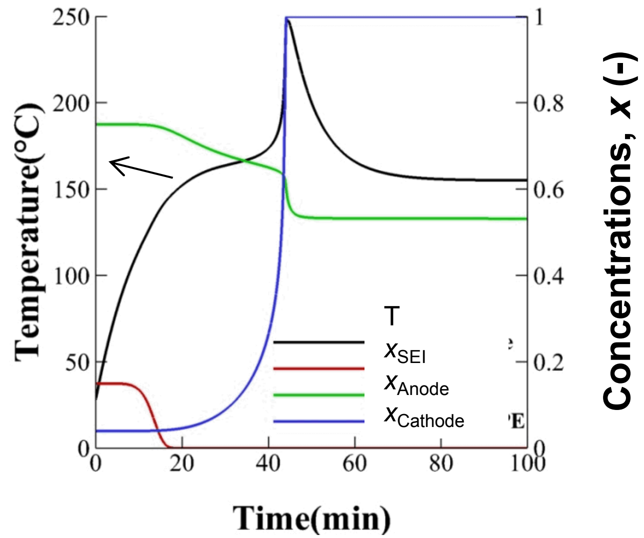
Intercalated Li reacting with electrolyte (at cathode)

$$\dot{Q}_{cathode} = \Delta H_{cathode} \cdot k_{cathode} x_{cathode} (1 - x_{cathode}) \exp\left(-\frac{E_{cathode}}{k_b T}\right)$$

Electrolyte decomposition at elevated temperatures

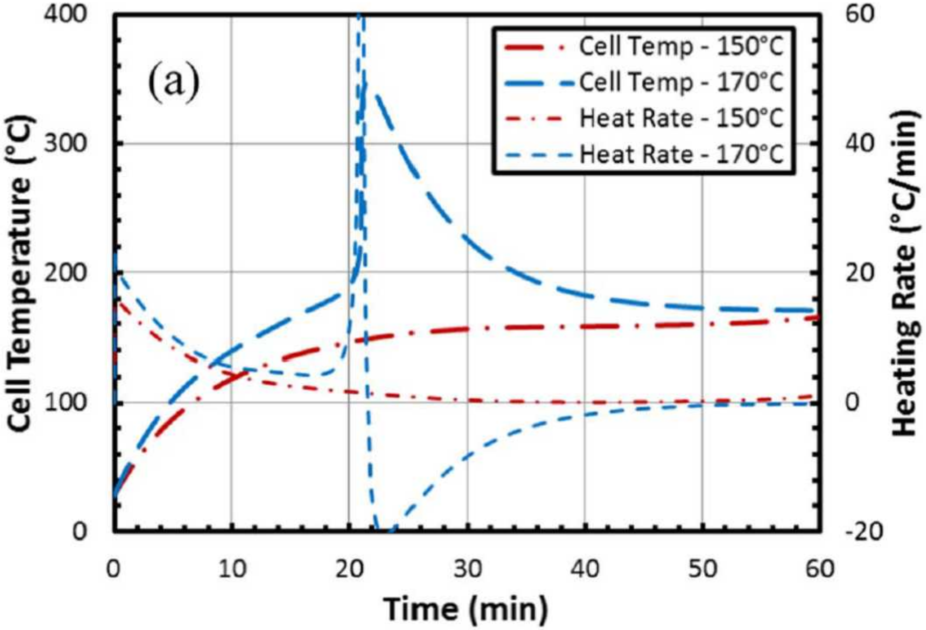
$$\dot{Q}_{electrolyte} = \Delta H_{electrolyte} \cdot k_{electrolyte} x_{electrolyte} \exp\left(-\frac{E_{electrolyte}}{k_b T}\right)$$





*M. N. Richard and J. R. Dahn (1999) *J. Electrochem. Soc.* **146**

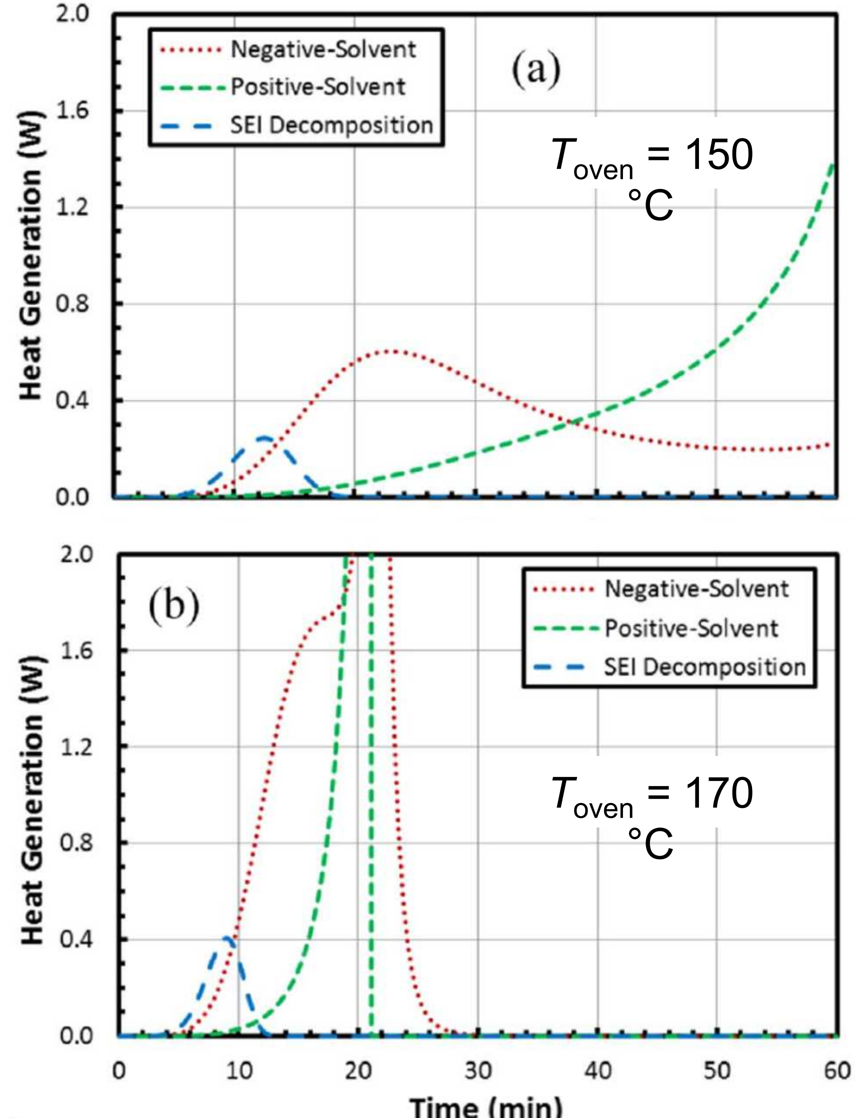
Results: Oven Temperature



Thermal runaway can be triggered by unfavorable ambient conditions.

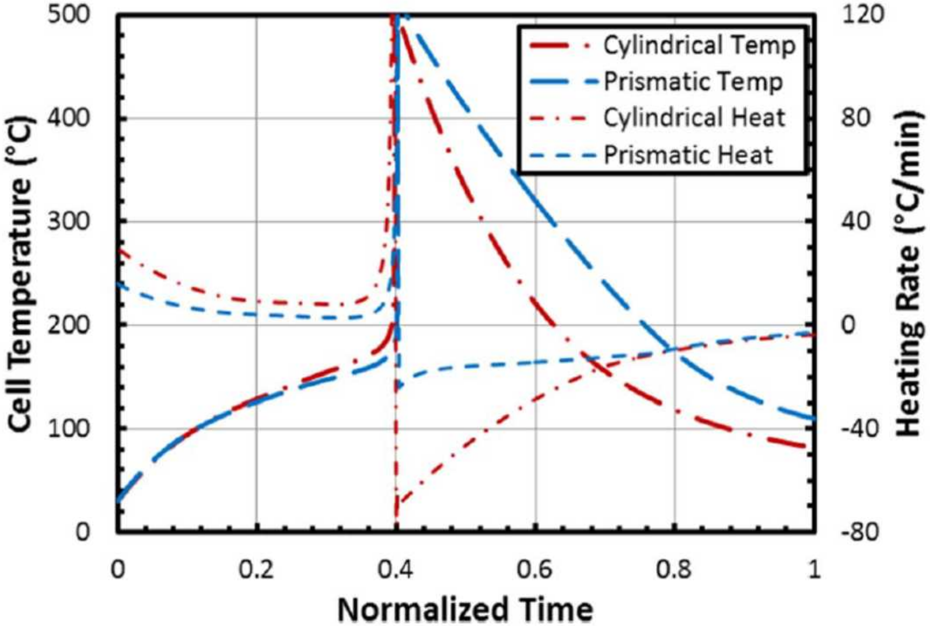
For high enough ambient conditions, the abuse reactions get activated and leads to thermal runaway.

Heat generation rates as a function of ambient conditions



* Lopez, Jeevarajan and Mukherjee (2015) *J. Electrochem. Soc.*, **162** (10) A2163

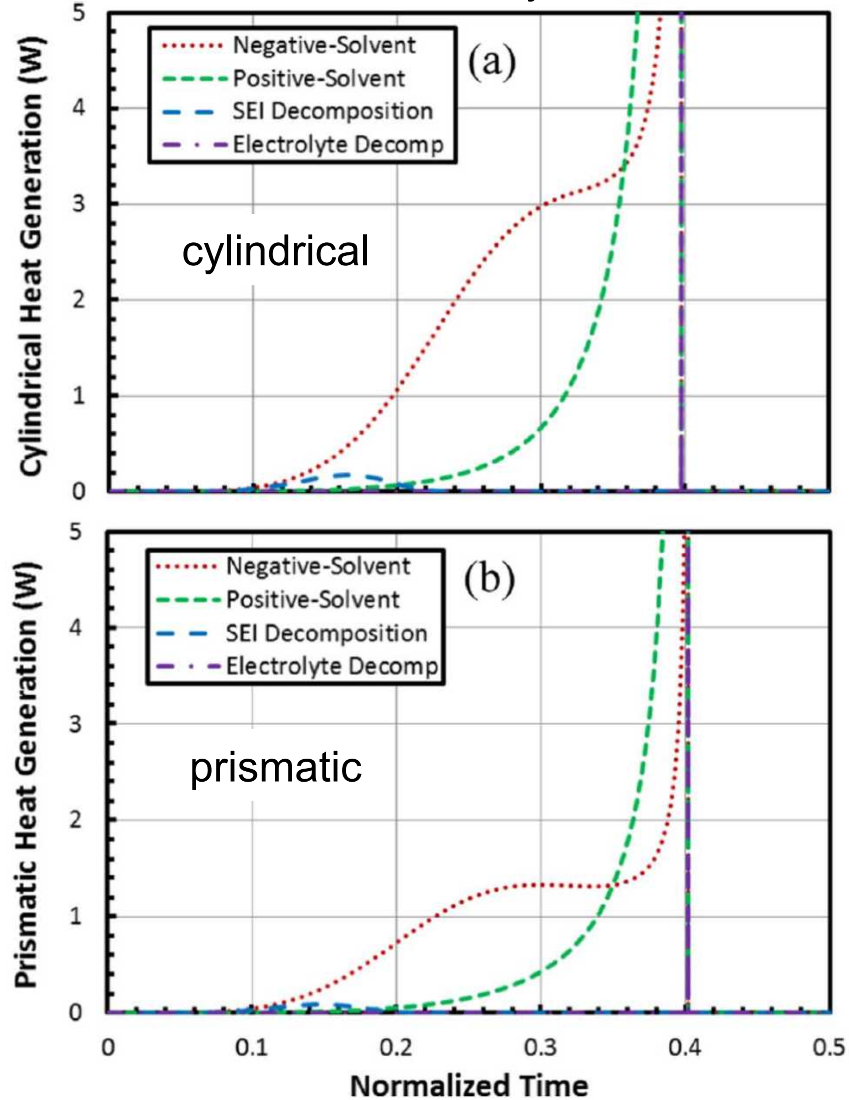
Correlating Cell Type with Abuse Response



Cell response to thermal trigger is a function of cell chemistry, capacity and geometry.

Heating rate is defined as $\frac{dT_{cell}}{dt}$

Heat generation rates as a function of cell chemistry



* Lopez, Jeevarajan and Mukherjee (2015) *J. Electrochem. Soc.*, **162** (10) A2163

Different Thermal Abuse Scenario

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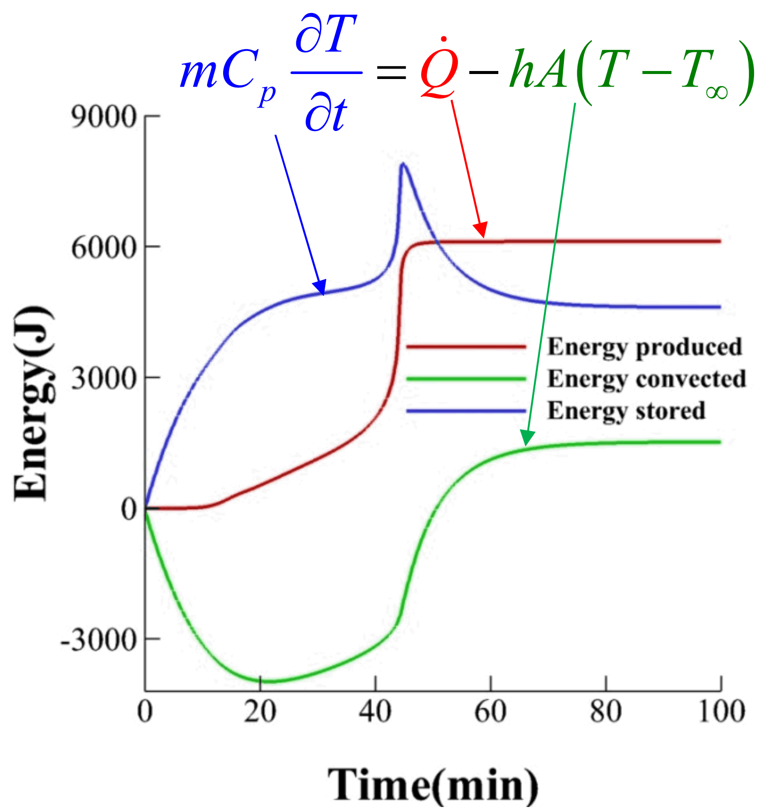
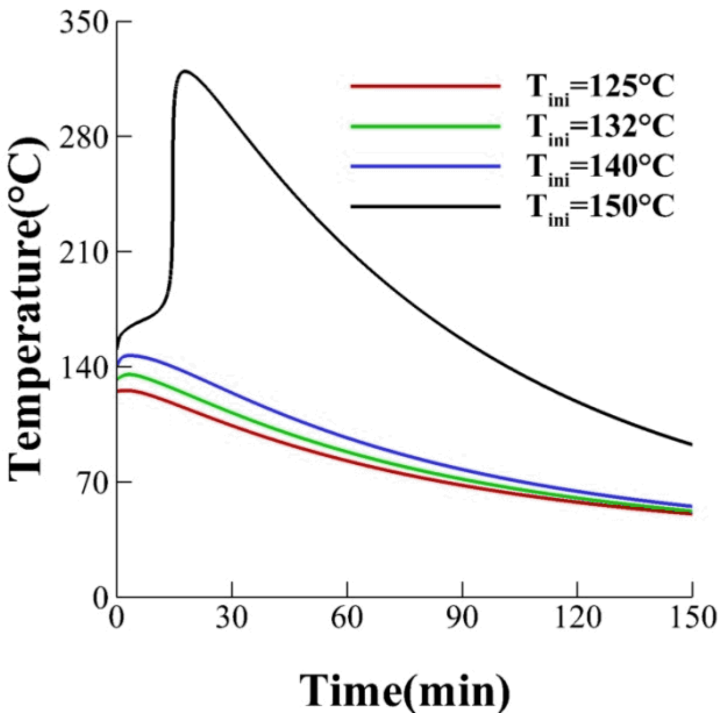
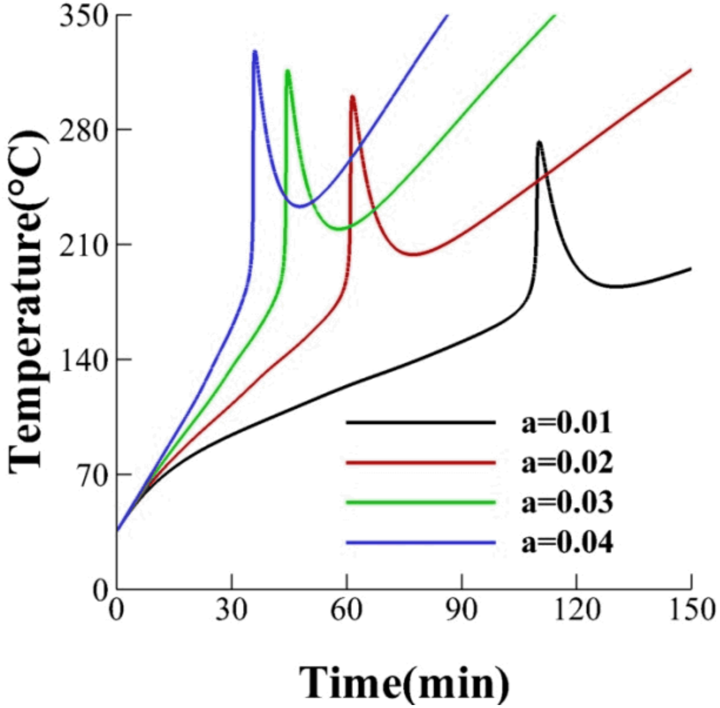




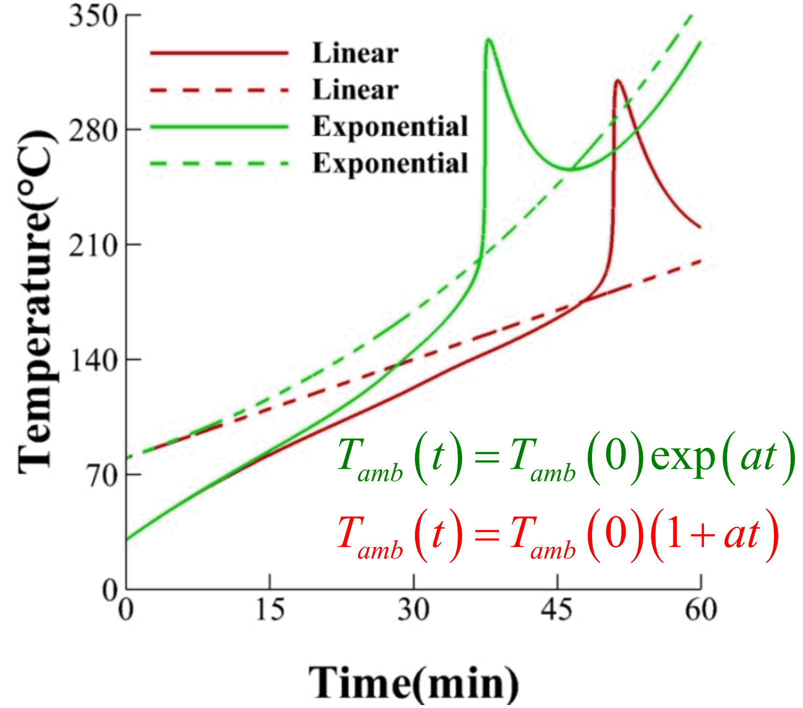
Energy budget for oven test at 155 °C ambient temperature (standard oven test).

Initial temperature cell temperature can rapidly rise and be well beyond 80 °C due to unexpected events such as overcharge, external or internal short. This can in turn trigger thermal abuse reactions.

Time Varying Ambient Temperature



Effect of rate of change of ambient temperature, a, on cell thermal response (ambient temperature increases linearly in time).



Effect of ambient temperature trends on thermal abuse (dashed line ambient T)

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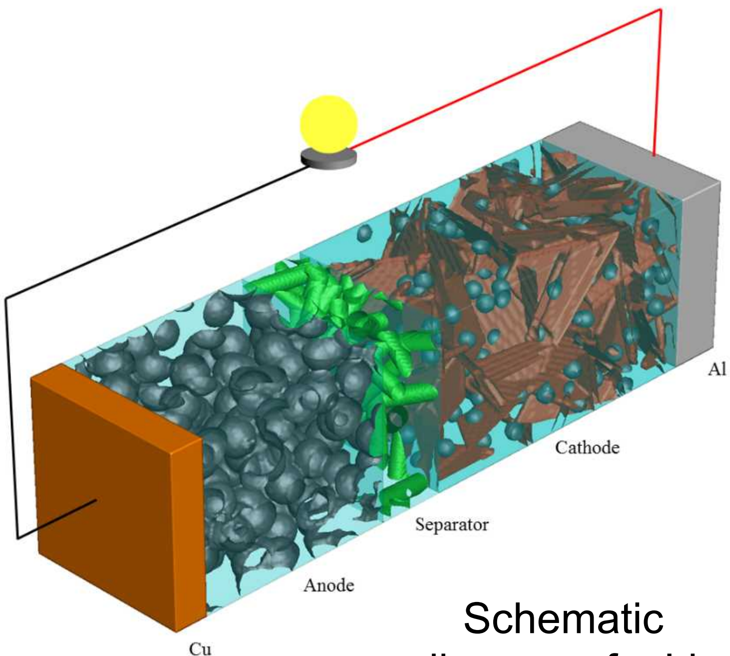
Electrochemical-Thermal Model



Schematic diagram of a Li-ion cell.

Operation of a Li-ion cell involves coupled transport processes:

- Li conservation in active material
- Li^+ conservation in electrolyte
- Charge transport in solid phase
- Charge transport in electrolyte phase
- Cell thermal transport

(1) Li balance in active material particles

$$\frac{\partial C_s}{\partial t} = \frac{\mathcal{D}_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_s}{\partial r}\right)$$

(2) Li^+ balance in electrolyte phase

$$\varepsilon \frac{\partial C_e}{\partial t} = \frac{\partial}{\partial x}\left(\mathcal{D}_e \frac{\varepsilon}{\tau}\frac{\partial C_e}{\partial x}\right) + \left(\frac{1-t_+}{F}\right)J$$

(3) Charge conservation in solid phase

$$\sigma^{eff}\frac{\partial^2 \phi_s}{\partial x^2} = J$$

(4) Charge conservation in electrolyte phase

$$\frac{\partial}{\partial x}\left(\kappa \frac{\varepsilon}{\tau}\frac{\partial \phi_e}{\partial x}\right) + \frac{\partial}{\partial x}\left(\kappa_D \frac{\varepsilon}{\tau}\frac{\partial \ln C_e}{\partial x}\right) + J = 0$$

(5) Cell thermal transport

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k^{eff}\frac{\partial T}{\partial x}\right) + \dot{Q}$$

Sources of Heat Generation

- **Entropic/Reversible Heat**: Contribution from the entropy change associated with the intercalation reaction ($T\Delta S$)

$$\dot{Q}_{rev} = -J\left(T\frac{dE}{dT}\right)$$

- **Kinetic/Reaction Heat**: Contribution from the overpotential (η) penalty paid at the electrode-electrolyte interface required to drive the intercalation reaction

$$\dot{Q}_{rxn} = J\eta = J\left(\phi_s - \phi_e - E\right)$$

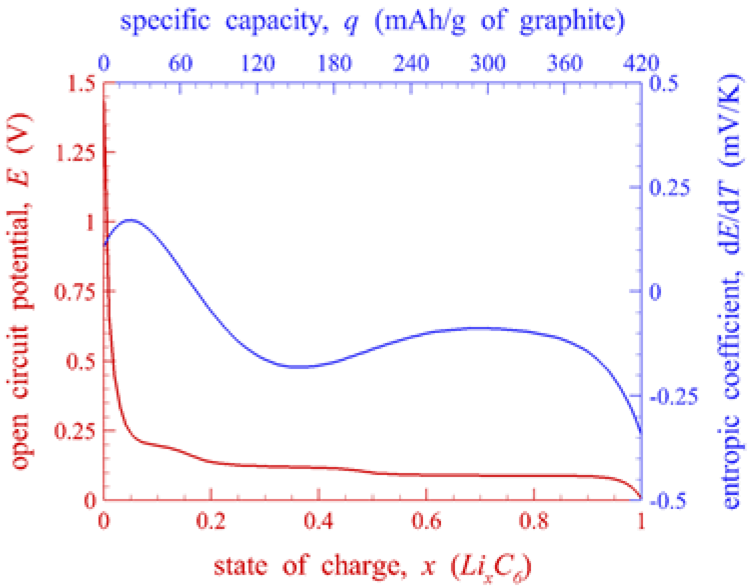
- **Joule/Ohmic Heat**: Contribution from the resistance to electron transport in the solid phase and ionic transport in the electrolyte phase.
  Solid phase: due to solid phase potential gradient
  Electrolyte phase: due to electrolyte phase potential gradient as well as concentration gradient

$$\dot{Q}^{s}_{ohmic} = \sigma^{eff}\nabla\phi_s.\nabla\phi_s$$

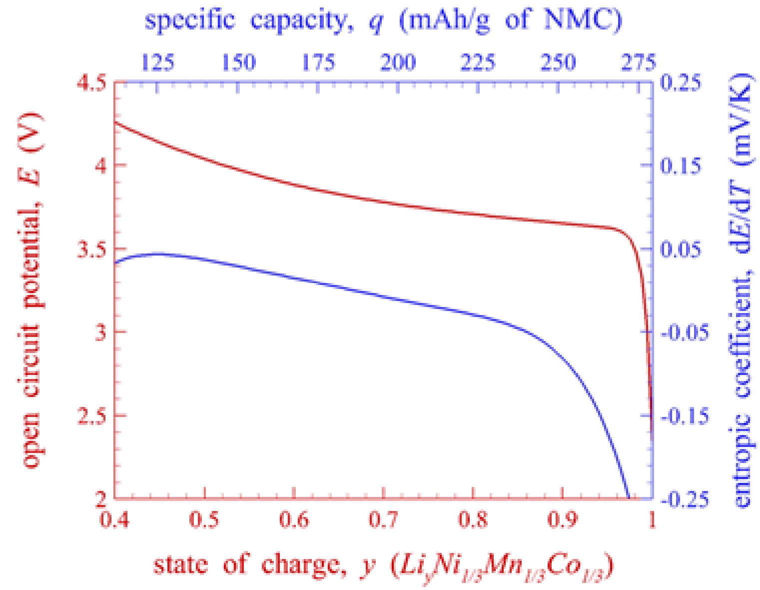
$$\dot{Q}^{e}_{ohmic} = \kappa\frac{\varepsilon}{\tau}\nabla\phi_e.\nabla\phi_e + \kappa_D\frac{\varepsilon}{\tau}\nabla\phi_e.\nabla\ln c_e$$

$$\dot{Q}_{total} = \underbrace{-J\left(T\frac{dE}{dT}\right)}_{\text{Entropic/Reversible Heat}} + \underbrace{J\left(\phi_s - \phi_e - E\right)}_{\text{Kinetic/Reaction Heat}} + \underbrace{\sigma^{eff}\nabla\phi_s.\nabla\phi_s + \kappa\frac{\varepsilon}{\tau}\nabla\phi_e.\nabla\phi_e + \kappa_D\frac{\varepsilon}{\tau}\nabla\phi_e.\nabla\ln c_e}_{\text{Ohmic Heat}}$$

Open Circuit Potential – (q, T) dependence



Open Circuit Potential and its temperature dependence for graphite



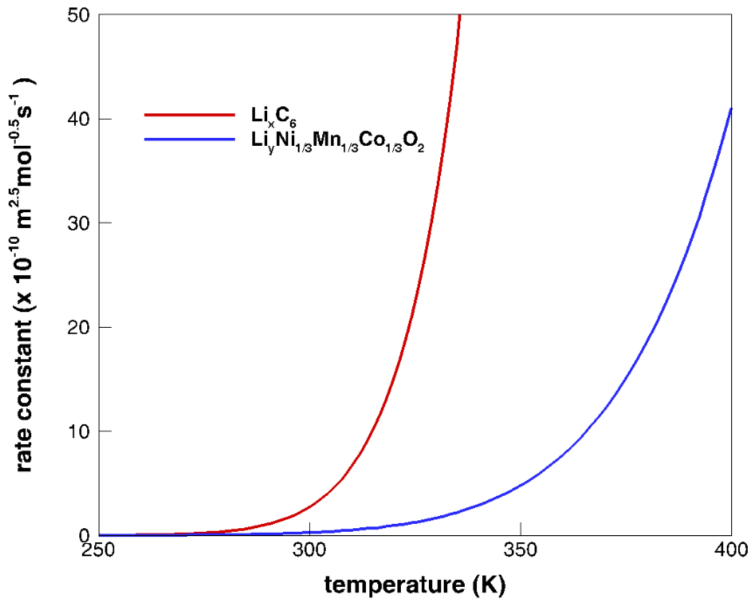
Open Circuit Potential and its temperature dependence for NMC333 cathode active material

$$E(q,T) = E(q,T_{ref}) + \frac{dE(q)}{dT}\left(T - T_{ref}\right)$$

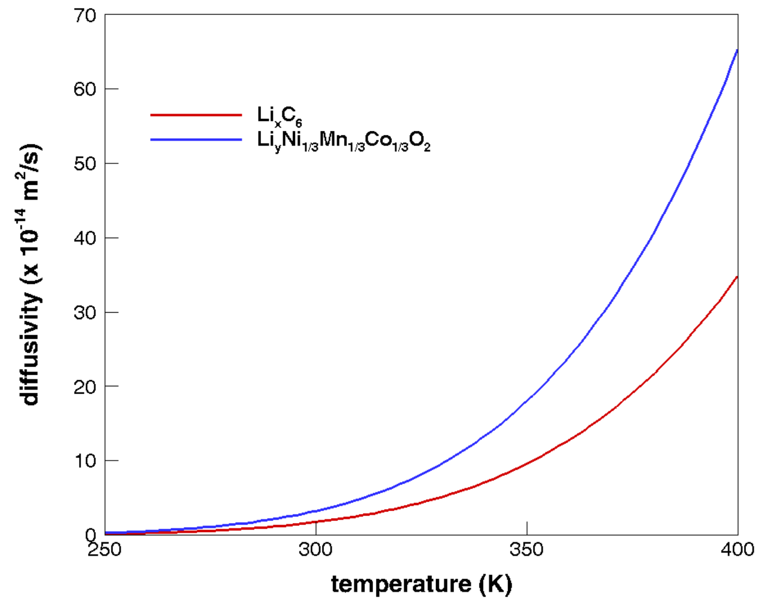
Reference OCP — Entropic Coefficient

- Open circuit potential (OCP) at any temperature is calculated using the reference OCP and the entropic coefficient contribution at the non-reference temperature.
- Entropic coefficient magnitude is of the order of milliVolts per Kelvin, hence corresponding reversible heat generation is small.

Transport and Kinetic Properties of Active Material



Temperature dependence of intercalation rate constant



Temperature dependence of solid phase diffusivity

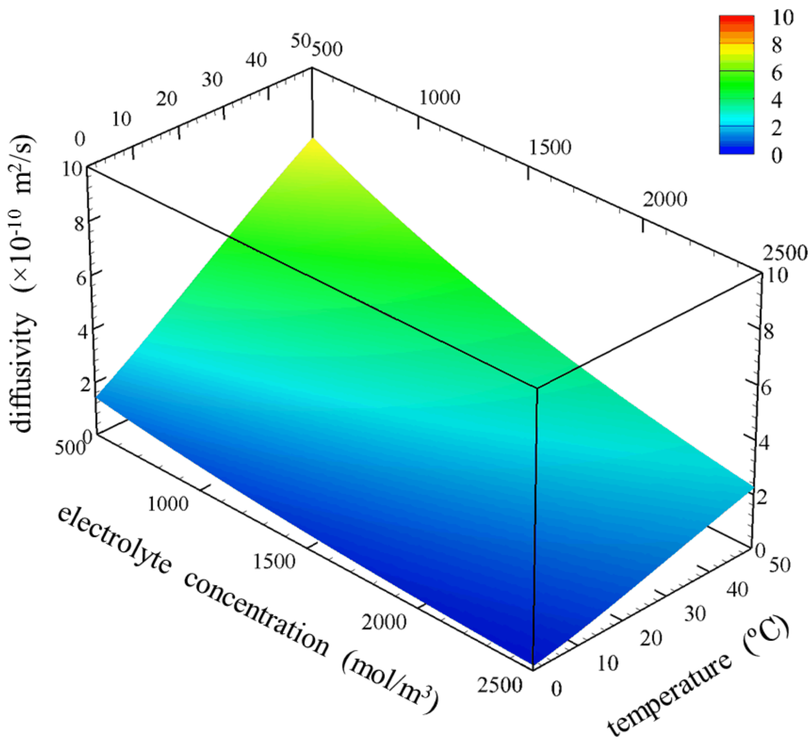
$$j_o(T) = k(T) C_s^{max} C_e^{0.5} \theta^{0.5} \left(1-\theta\right)^{0.5}$$

$$k\left(T\right) = k\left(T_{ref}\right) \exp\left[\frac{E_{a,k}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$

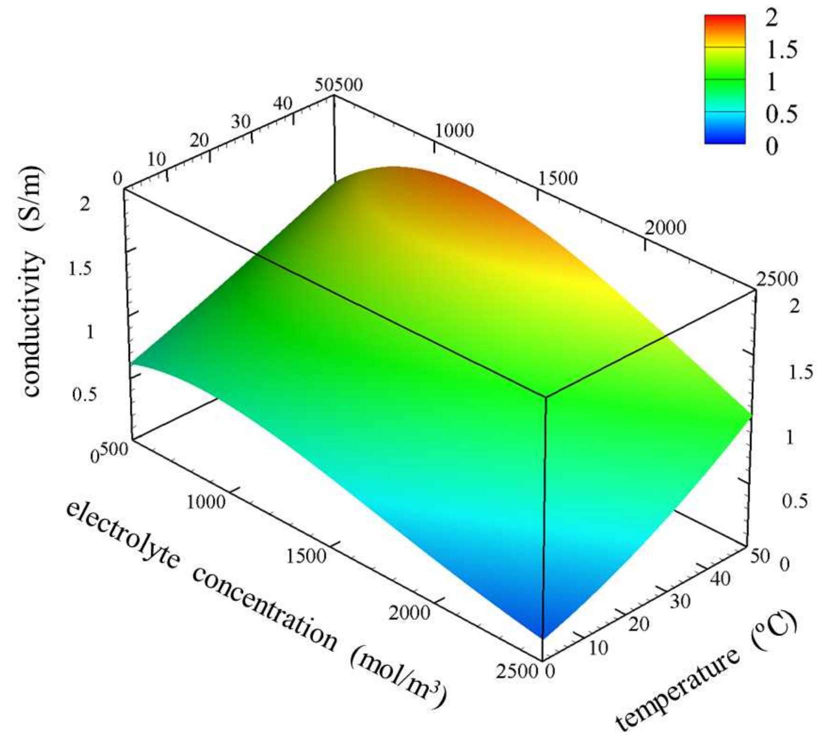
$$D_s\left(T\right) = D_s\left(T_{ref}\right) \exp\left[\frac{E_{a,D_s}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$

Both rate constant and solid phase diffusivity show Arrhenius dependence on temperature, correspondingly, exponential increase in magnitude is found with temperature.

Electrolyte Transport Properties



Diffusivity of Li^+ ions inside electrolyte, D_e, as a function of salt concentration and temperature

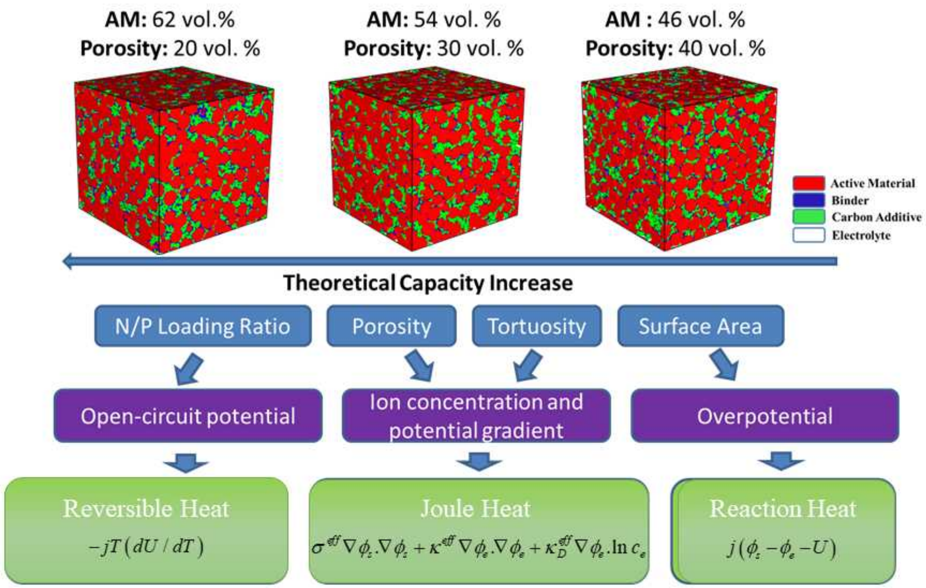


Ionic conductivity of Li^+ ions inside electrolyte, κ, as a function of salt concentration and temperature

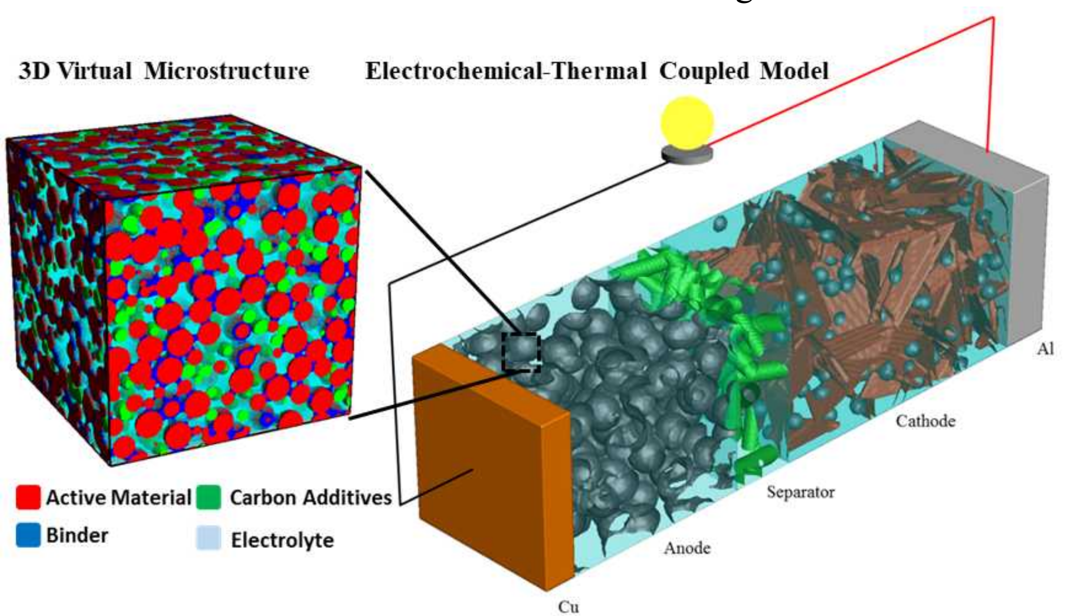
Both diffusivity and conductivity improve with temperature owing to increased kinetic energies of ions leading to more agile ions in the solution

* L.O. Valoen and J.N. Reimers, *J. Electrochem. Soc.*, **152** (5), A882 (2005)

Electrochemical – Thermal – Microstructure Interplay



Interaction between microstructure and heat generation



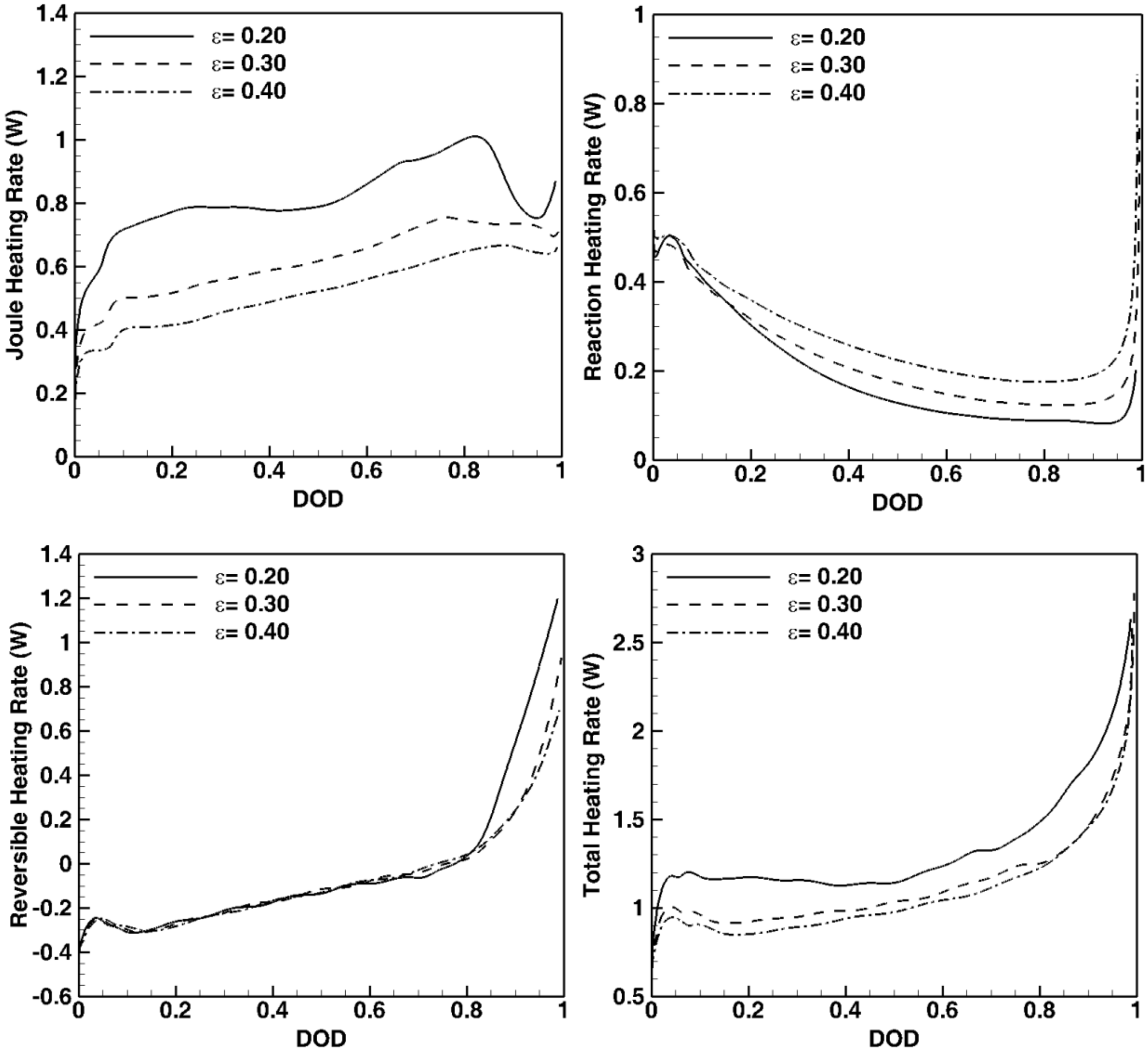
Generally, anode and cathode are composed of active material (electrochemical reaction site), conductive additive (enhances electronic conductivity of solid phase) and binder (gives mechanical rigidity to the electrode).

The arrangement of these phases affects the tortuosity of the pore phase, active area and effective electronic conductivity of the solid phase which have a considerable impact on the electrochemical-thermal performance of the cell.

Schematic diagram of electrochemical-thermal-microstructure model

*C.-F. Chen., A. Verma and P. P. Mukherjee (2017) *J. Electrochem. Soc.*, **164** (11), E3146

Microstructure Effects on Heating Rates



Low porosity increases transport resistance leading to higher Joule heat contribution.

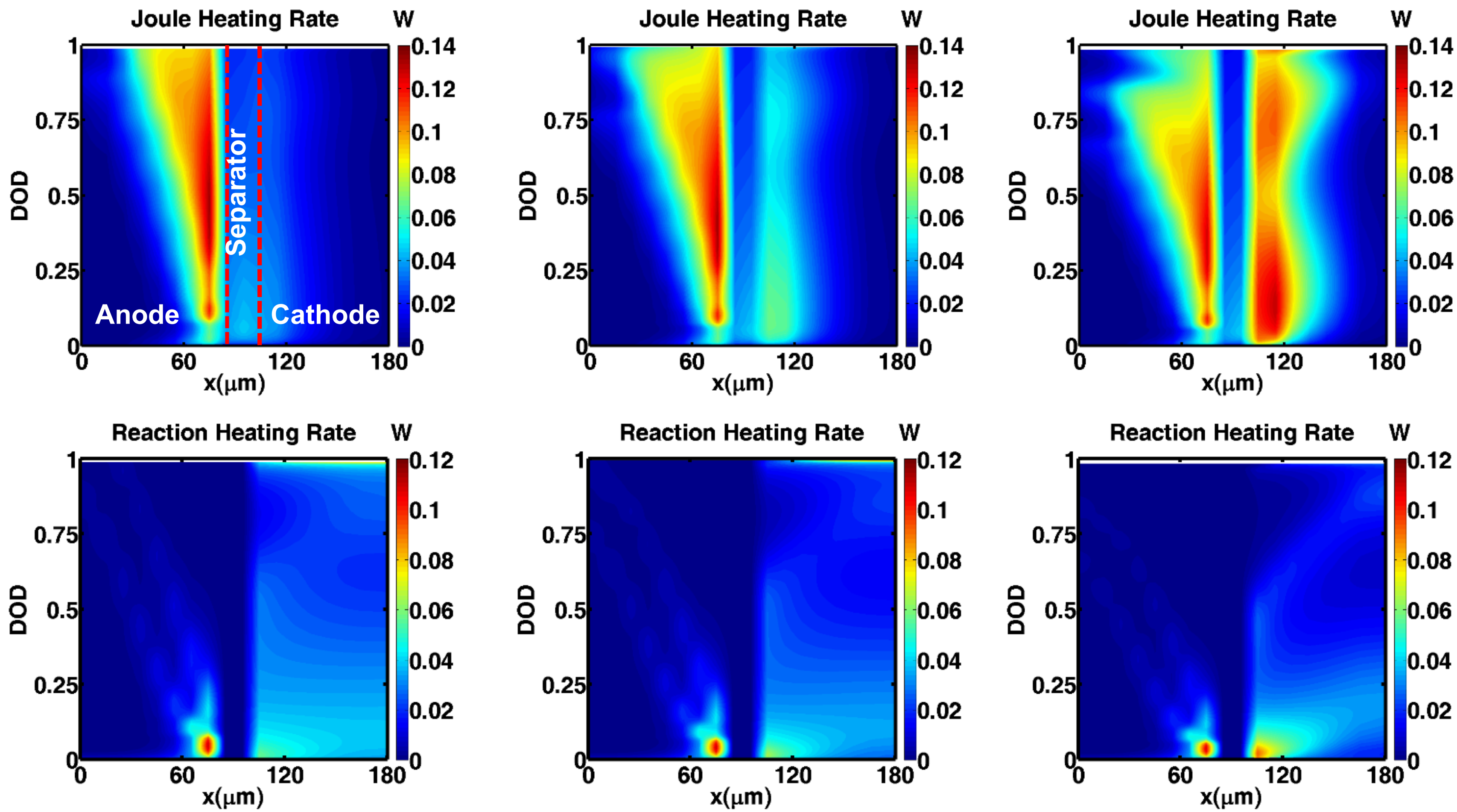
Reaction heat has opposite trend to Joule heat for most part of the DOD range because of higher interfacial area.

Reversible heat is similar for the three porosities investigated except at end of discharge.

Joule heat is the dominant contributor to the total heat generation rate

*C.-F. Chen., A. Verma and P. P. Mukherjee (2017) *J. Electrochem. Soc.*, **164** (11), E3146

Joule and Reaction Heating Rates



$\varepsilon = 0.4$ $\varepsilon = 0.3$ $\varepsilon = 0.2$

- As cathode porosity decreases, tortuosity and consequently pore phase resistance increases leading to high joule heating rate
- Interfacial area decrease with increase of porosity leads to enlargement of overpotential and consequently reaction heating rate increase.

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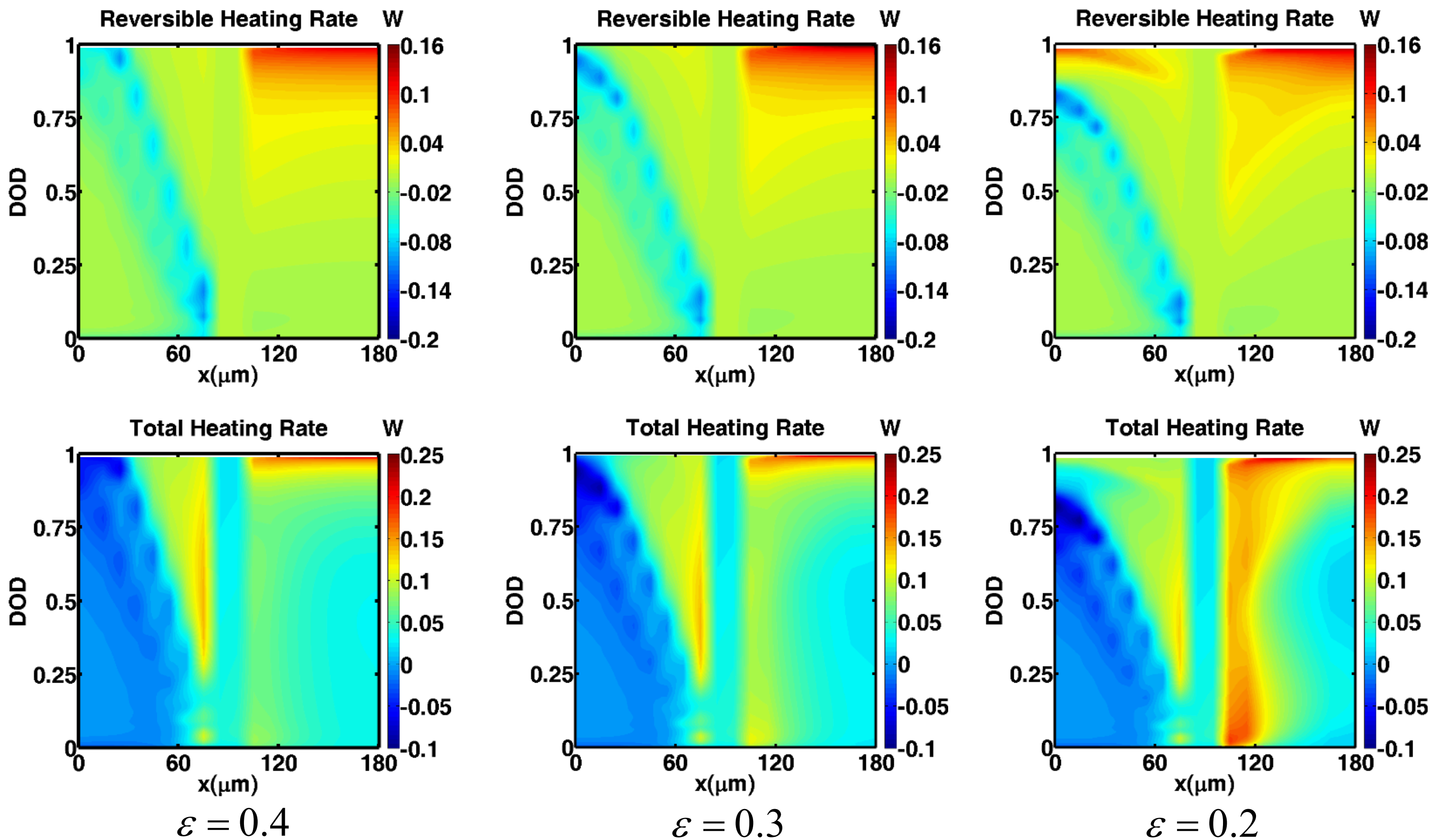
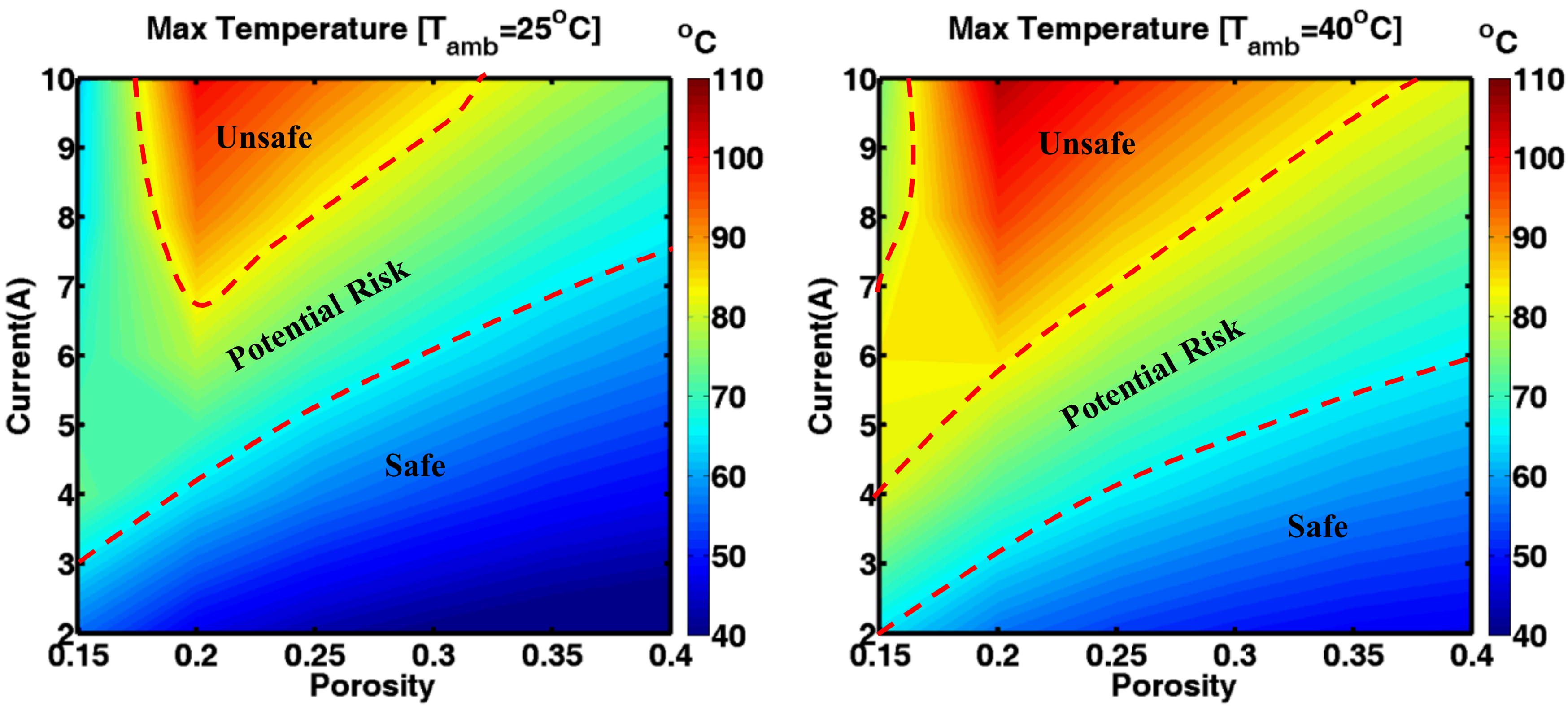
Reversible and Total Heating Rates



- Reversible heat can take negative values and is negligible for a major range of DOD owing to small magnitude of entropic coefficient ($dE/dT \sim 0.5$ mV/K).
- Total heat rate magnitude is dominated by the joule heat rate for most part of discharge.

*C.-F. Chen., A. Verma and P. P. Mukherjee (2017) *J. Electrochem. Soc.*, **164** (11), E3146

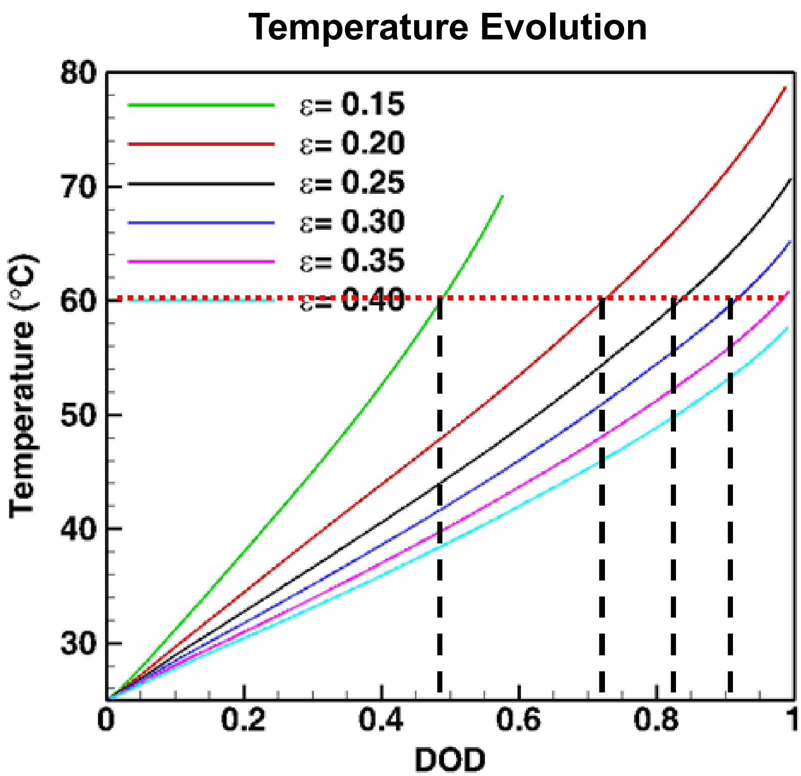
Microstructure Implications on Safety

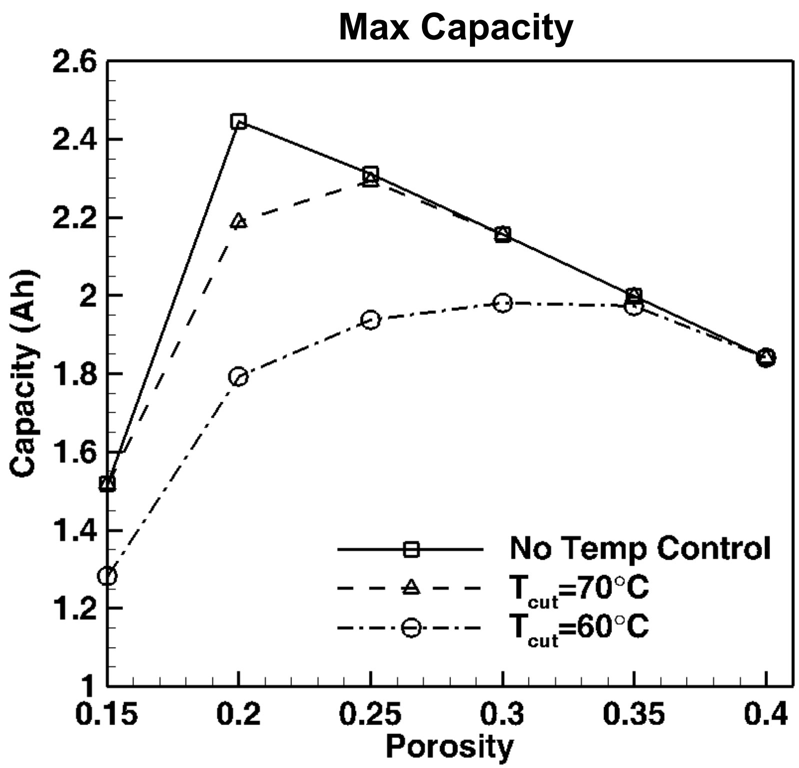


Safe region corresponds to T < 60 °C. *Potential Risk* region corresponds to 60 °C < T < 80 °C. *Unsafe region* corresponds to T > 80 °C. The *safe region* decreases when the ambient temperature is increased.

*C.-F. Chen., A. Verma and P. P. Mukherjee (2017) *J. Electrochem. Soc.*, **164** (11), E3146

Temperature Control using Microstructure





To limit the cell temperature at a certain temperature, discharge needs to be cut-off at different DOD, which comes at the cost of cell capacity (External shutdown)

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Low Temperature Operation of Lithium Ion Cell

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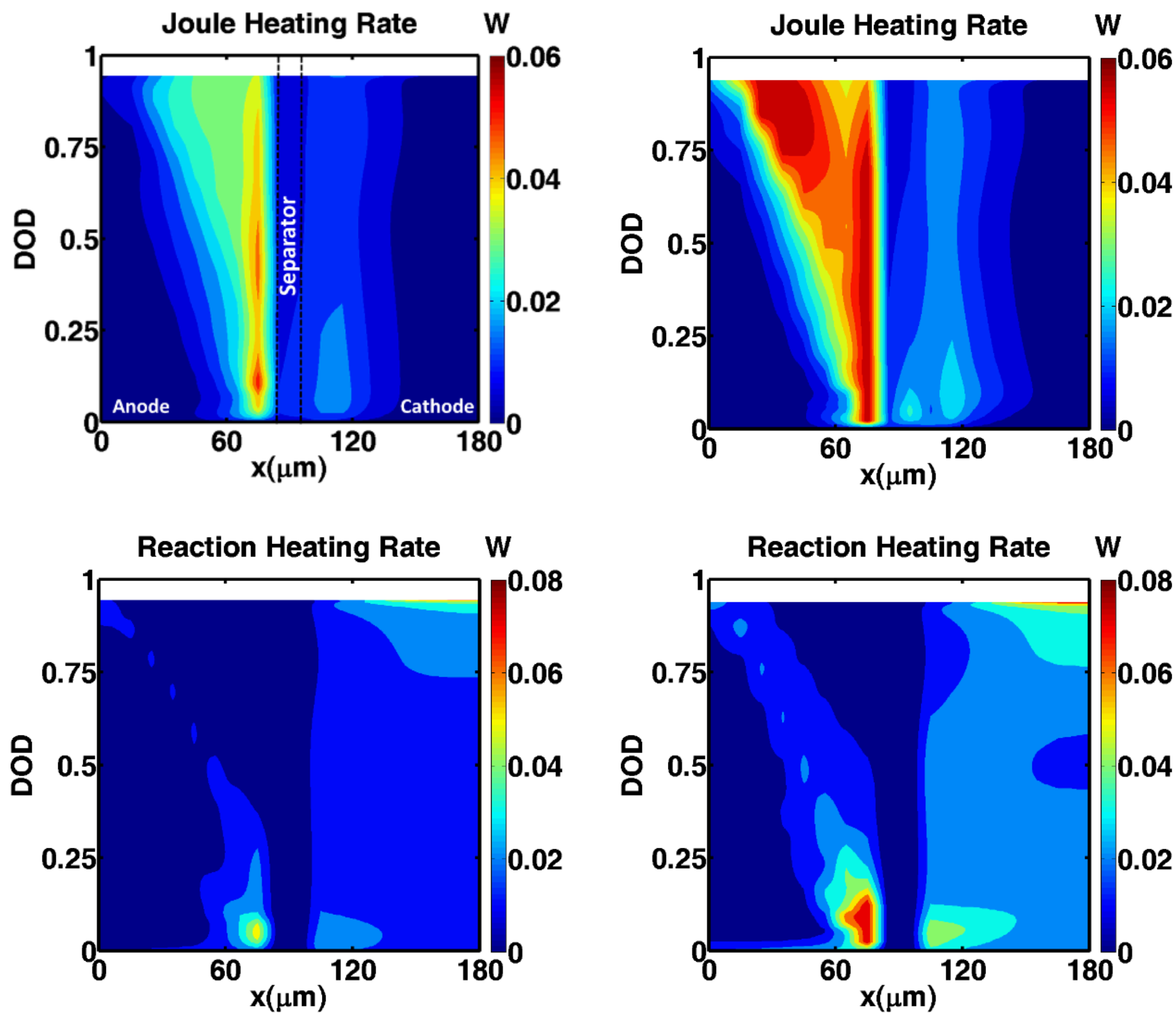
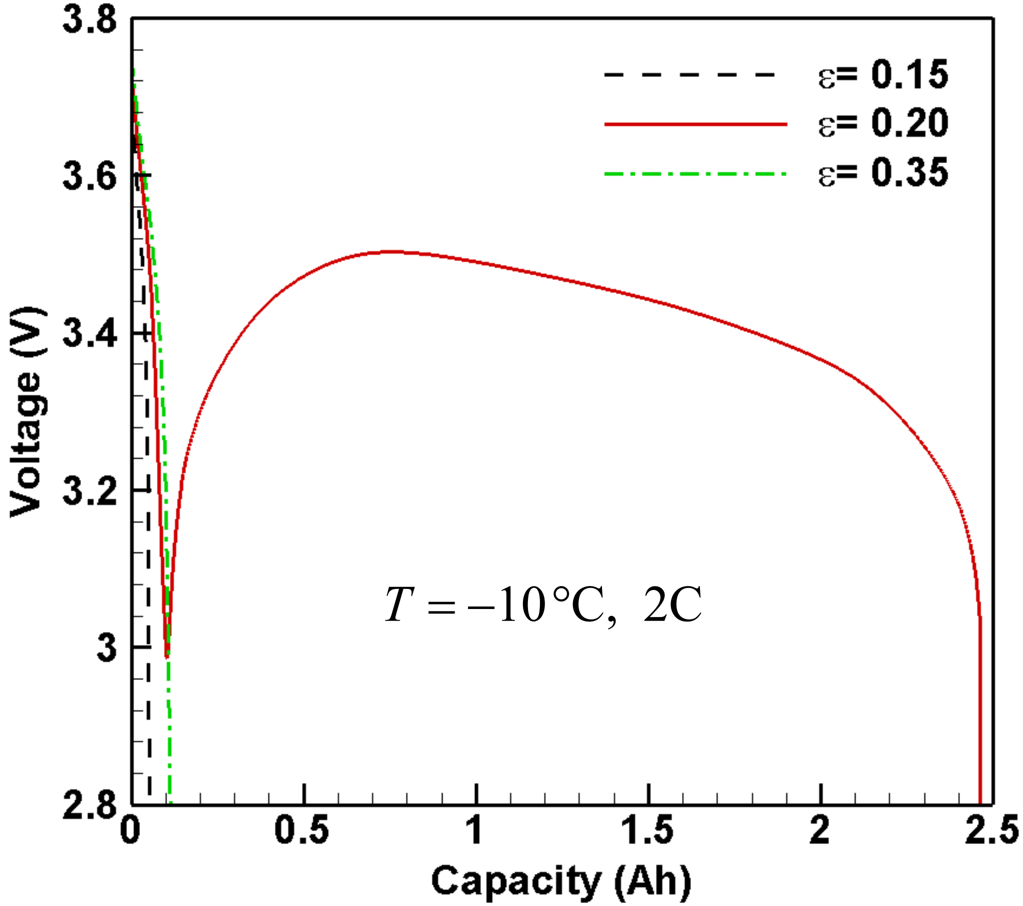


$T = 0\,°C$ $T = -10\,°C$

High heat generation rate due to increased ohmic transport resistance and kinetic resistance at low temperatures can be utilized for cold start of the cell.

Microstructure Implications on Cold Start

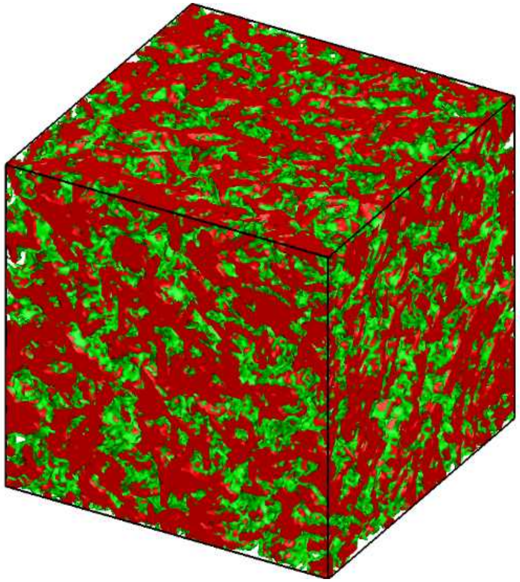


Operation at intermediate porosity can be used for cold start applications. Tradeoff between cell porosity and C-rate can be established to improve sub zero performance of the cell.

- 15% porosity electrode has very high transport resistance and the cell voltage drops below cutoff.
- 35% porosity electrode does not give rise to appreciable heat generation that would sustain cell operation and leads to cell shutdown.

Differences in Anode and Cathode Microstructures

Graphite anode

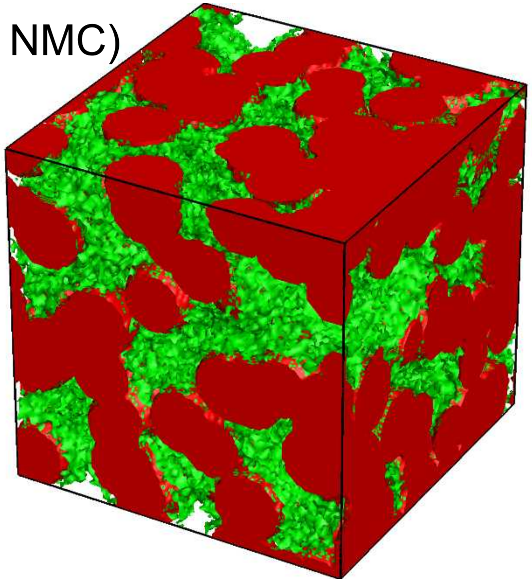


- graphite
- binder
- void (electrolyte)

Platelet particle

Composite cathode

- active material (e.g., NMC)
- carbon + binder
- void (electrolyte)

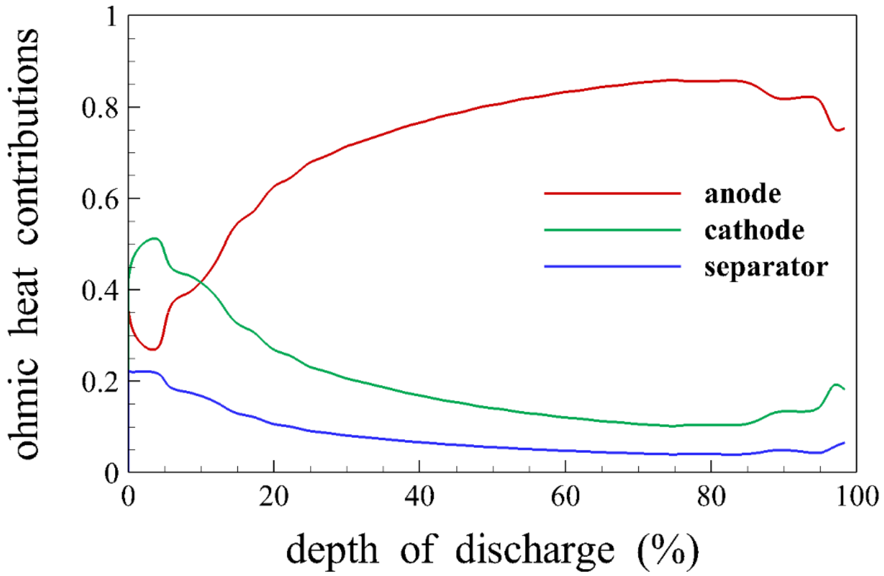


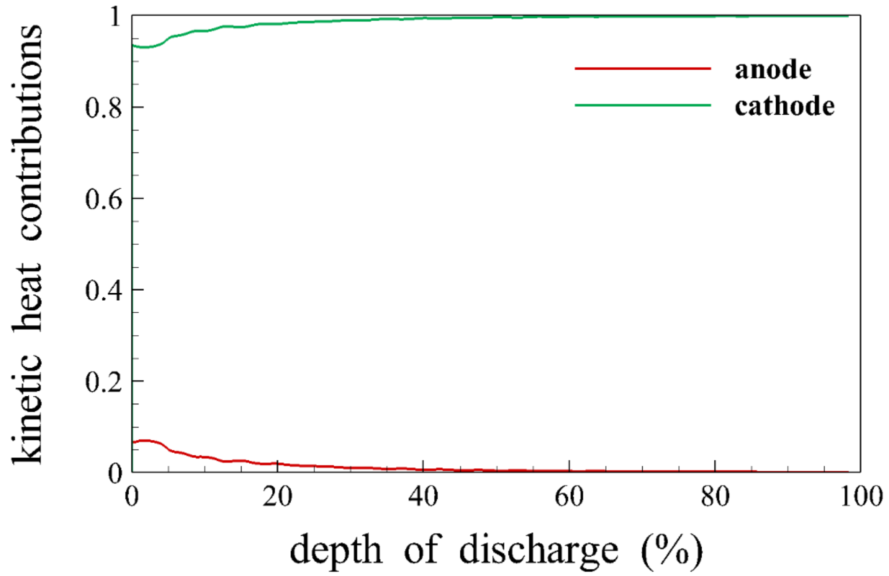
Spherical particle

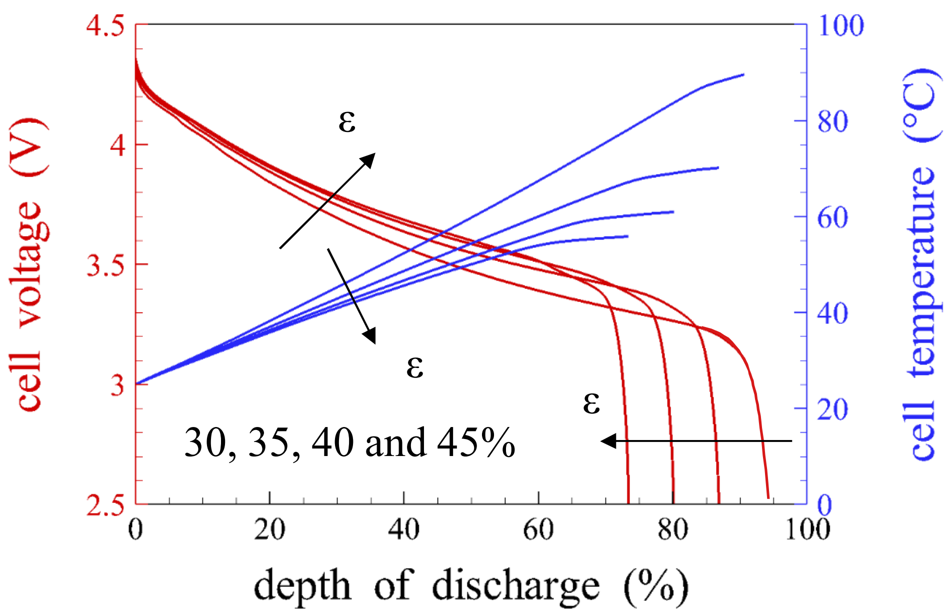
- The electrode microstructures for anode and cathode are quite different – both in terms of particle morphology as well as relative amounts of various phases.
- These structural differences leads to distinct microstructural properties, which in turn affects cell dynamics.

*Mistry and Mukherjee (2017) in preparation

Thermal Cross-talk between Electrodes







- Anode's contribution to heat generation is the most dominant, given significant transport resistance.
- Increasing anode porosity reduces ohmic heat and gives lower cell temperature, but also negatively affects cell capacity.

Agenda Overview

Part II: Modeling of Thermal Characteristics and Safety

1. Thermal Abuse Behavior
2. Electrode Microstructure and Thermal Interplay
3. Thermo-electrochemical Analytics
   - Inverse Problem Definition
   - Analysis of DSC Measurements – Thermal Safety
   - Analysis of ARC Measurements – Heat Generation
4. Strategies for LIB Thermal Management

Inverse Problem Definition and Analysis

Consider heat conduction in 1D: $\rho C_p \frac{dT}{dt} = k \frac{d^2T}{dx^2}$

Forward problem: given material properties and boundary conditions, find temperature field
Inverse problem: given temperature field and boundary conditions, find material properties

An important aspect of Inverse problems is that the solution of governing equation (analytical, semi-analytical, numerical) is employed to quantify desired properties. In other words, **analysis stage is important and quite more complex than usual experiments**. Essentially, complexities are transferred from experimental stage to analysis stage.

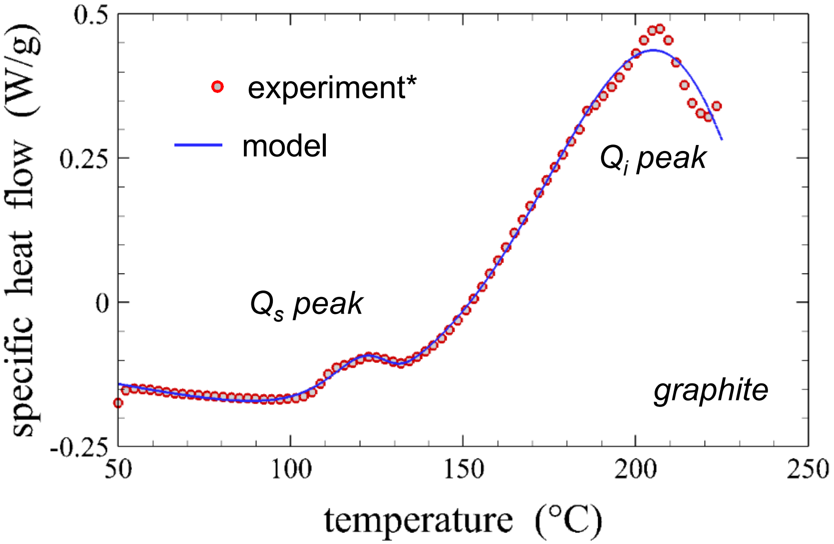
Inverse Problems in the context of LIBs:

1. Estimating thermophysical properties of LIBs (heat capacity and anisotropic thermal conductivities)
2. Quantify heat generation rate for LIBs without using a Calorimeter
3. Simultaneously characterize reversible and irreversible heat generation terms from calorimetry measurements

Salient features:

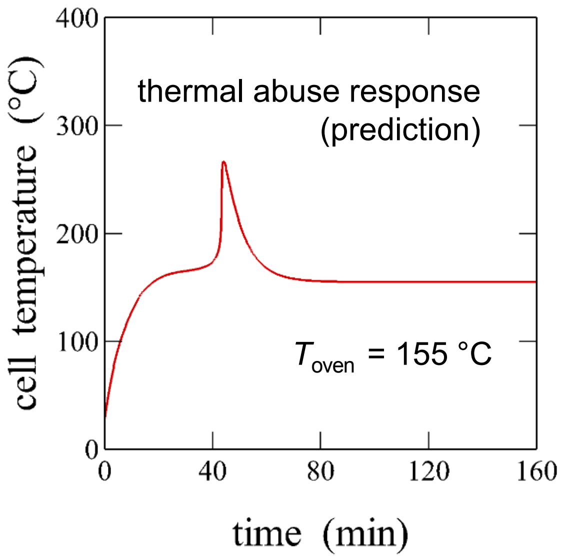
- Simpler experimental design, e.g., calorimeter-free
- Reduction in different type of experiments, e.g., internal resistance, heat capacity and heat generation can all be inferred from a single set of calorimetry measurements
- Shorter experiment duration, e.g., TIS experiments are performed within 5-7 minutes since transient response can be accurately interpreted – no need to wait for steady state

DSC adds Fidelity to Thermal Abuse Model



H, k, E

results for graphite



Consumption of metastable Li in SEI:

$$\frac{dx_s}{dt} = -k_s \cdot \exp\left(-\frac{E_s}{k_b T}\right) \cdot x_s$$

Consumption of intercalated Li:

$$\frac{dx_i}{dt} = -k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

Growth of SEI layer (upon reaction with electrolyte)

$$\frac{dz}{dt} = k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

DSC response:

$$q = -C\frac{dT}{dt} - H_s\frac{dx_s}{dt} - H_i\frac{dx_i}{dt}$$

The quantities shown in red are extracted from analysis of DSC measurements.

Thermal abuse response: $mC_p\frac{dT}{dt} = \dot{Q} - hA\left(T - T_\infty\right)$

Thermal mass for an 18650 cell

$$\dot{Q} = \dot{Q}_s + \dot{Q}_{ai} + \dot{Q}_{ci} + \dot{Q}_e$$

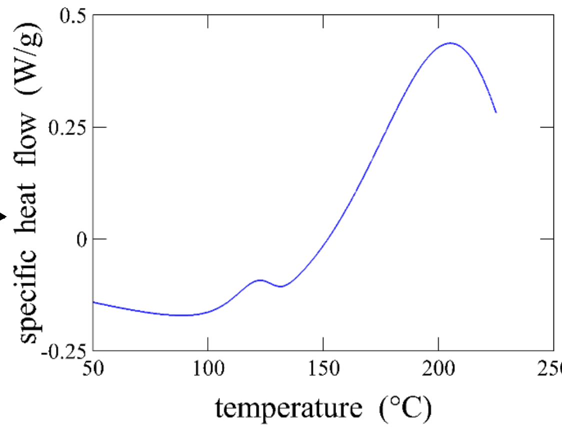
* Du Pasquier et al. (1998) *J. Electrochem. Soc.* **145** (2) 472

Extracting Reaction Kinetics from DSC Data

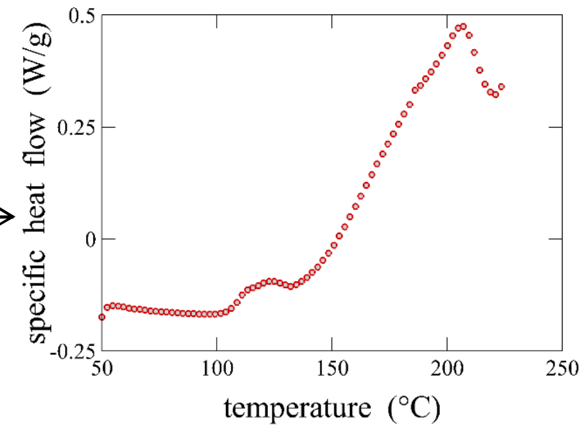
Model predictions

DSC measurements

assume reaction kinetics (k, E, ΔH)

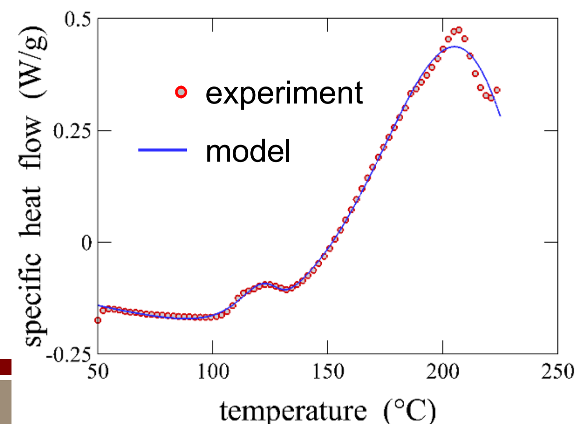


compare with DSC data



update kinetics till predicted and measured responses match

- DSC measurements are interpreted using mathematical description of DSC experiment.
- Such consistent analysis extracts all the relevant system information such as material heat capacity and thermally activated reactions.



converged solution gives kinetic details and material information

* A. Mistry *et al.* (2017) in preparation

Reaction Propagation during DSC Test

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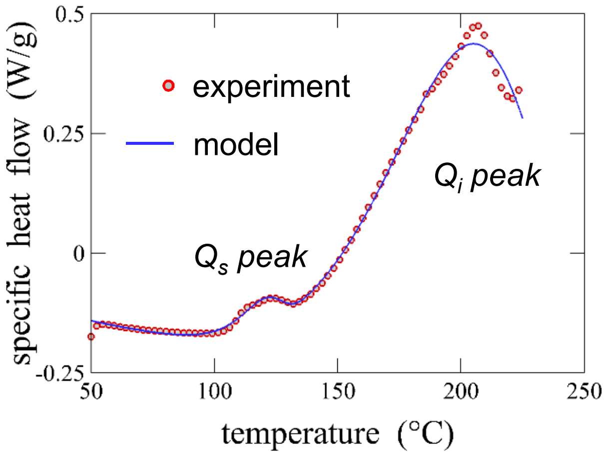
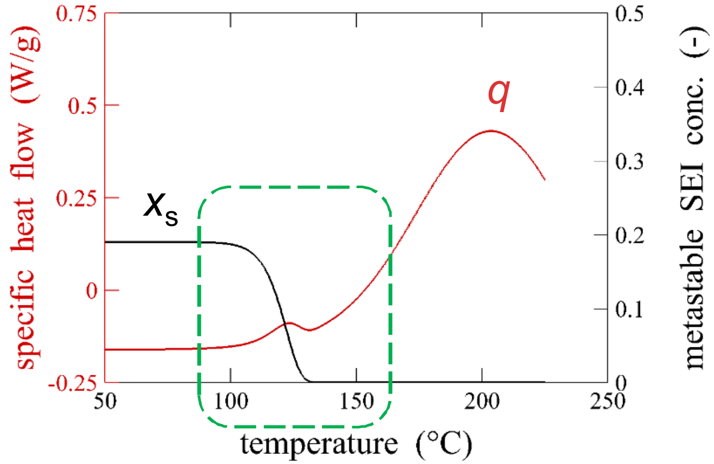
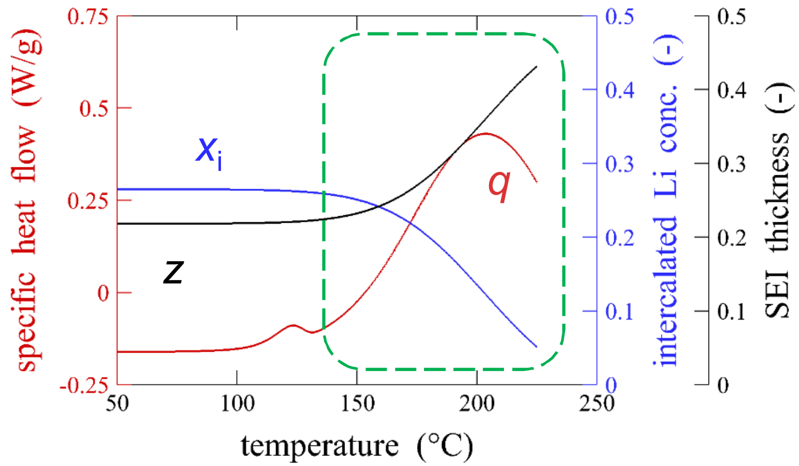




Reaction of metastable Li in SEI

$$\frac{dx_s}{dt} = -k_s \cdot \exp\left(-\frac{E_s}{k_b T}\right) \cdot x_s$$



- DSC profile for graphite has two distinct peaks
- Depending on the scanning rate (dT/dt ≡ °C/min), the reactions can overlap, which in turn makes the mathematical analysis complicated.
- On the other hand, in ARC measurements, the reactions are triggered successively, which makes the corresponding analysis relatively easier.

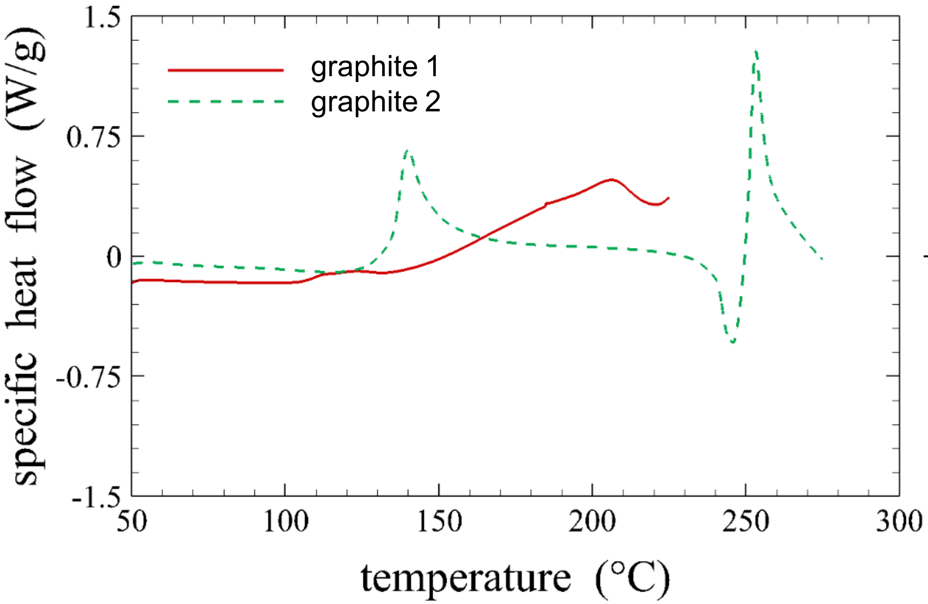
Reaction of intercalated Li with electrolyte

$$\frac{dx_i}{dt} = -k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

$$\frac{dz}{dt} = k_i \cdot \exp\left(-\frac{E_i}{k_b T}\right) \cdot x_i \cdot \exp\left(-z/z_0\right)$$

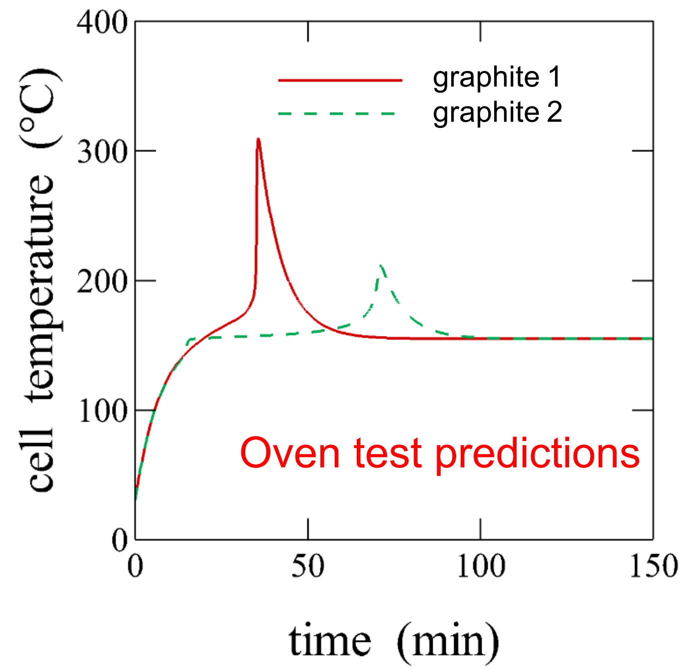
* A. Mistry *et al.* (2017) in preparation

Effect of Particle Morphology on Thermal Abuse



Roth et al. (2004) *J. Power Sources* **134**, 222
Profatilova et al. (2009) Electrochim. Acta **54**, 4445

H, *k*, *E*

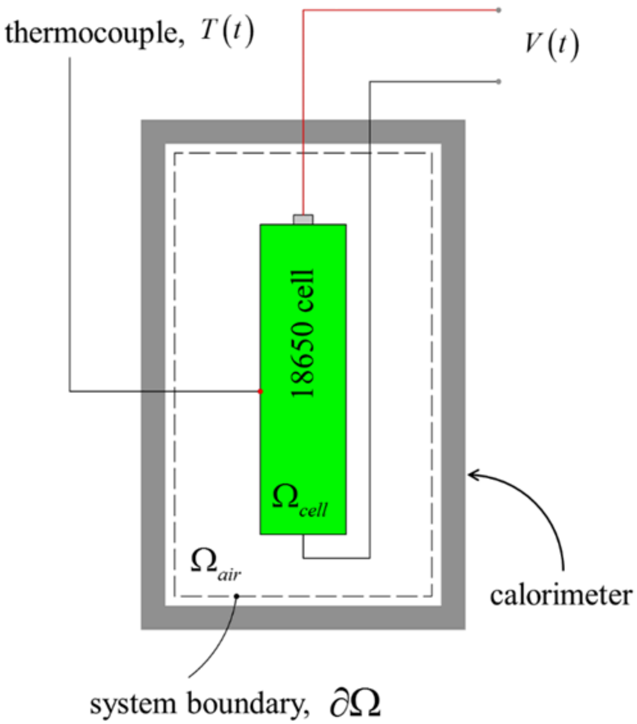


* A. Mistry *et al.* (2017) in preparation

Three different graphite materials with different particle morphology are studied here. Particle morphology changes the electrode-electrolyte interphase as well as intercalation behavior which translates to different DSC and thermal abuse profiles.

- Commenting on thermal safety based on DSC measurements is somewhat misleading. For example, the highest peak (graphite 2) does not necessarily mean unsafe material.
- One should appropriately analyze the data to extract reaction kinetics and then use oven test model.

Interpreting ARC to Characterize Heat Generation



Calorimeter testing of Li-ion cells to quantify heat generation.

*A. Mistry *et al.*, (2017) *ready for submission*

Consider a Li-ion cell for which the open circuit voltage is measured at different states of charge and temperatures.

Calorimeter testing is usually employed to quantify the amount heat generation during operation of such a cell. The generated heat has two components:

1. Reversible/ entropic heat
2. Irreversible/ joule heat

Calorimeter data cannot distinguish between the two contributions.

Q. Can a consistent experimental technique be developed to deconvolve the two heat generation measurements from single calorimetry data?

Note that the thermodynamic state of a Li-ion cell can be defined by two state variables:

1. Stored charge, q
2. Cell temperature, T

As Li-ion systems have Li^+ as responsible charge carrier, stored charge directly corresponds to Li^+ concentration.

Thermodynamic Analysis of Li-ion Cells

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The First law of Thermodynamics, helps quantify the internal energy changes taking place inside a system (here Li-ion cell) in terms of its interaction with universe across system boundaries:

$$dU = \delta Q - \delta W$$

The internal energy change *dU* accounts for change in system internal energy due to various different modes. For a Li-ion cell, energy changes are associated with temperature, pressure and charge (three intensive state variables)

$$dU = \left.\frac{\partial U}{\partial T}\right|_{p,q} dT + \left.\frac{\partial U}{\partial p}\right|_{T,q} dp + \left.\frac{\partial U}{\partial q}\right|_{T,p} dq$$

The first two terms are known from Thermodynamic treatment of simple closed systems as:

$$\left.\frac{\partial U}{\partial T}\right|_{p,q} = mC_v \quad \text{and} \quad \left.\frac{\partial U}{\partial p}\right|_{T,q} = -mv$$

specific heat at constant volume — specific volume at constant *T*

- Dependence of internal energy on stored charge is due to electrochemical reactions taking place inside the cell.
- Energy changes taking place due to electrochemical reactions are quantified in terms of thermodynamic (cell) voltage: $dG_{T,p}^{echem} = -E \cdot dq$

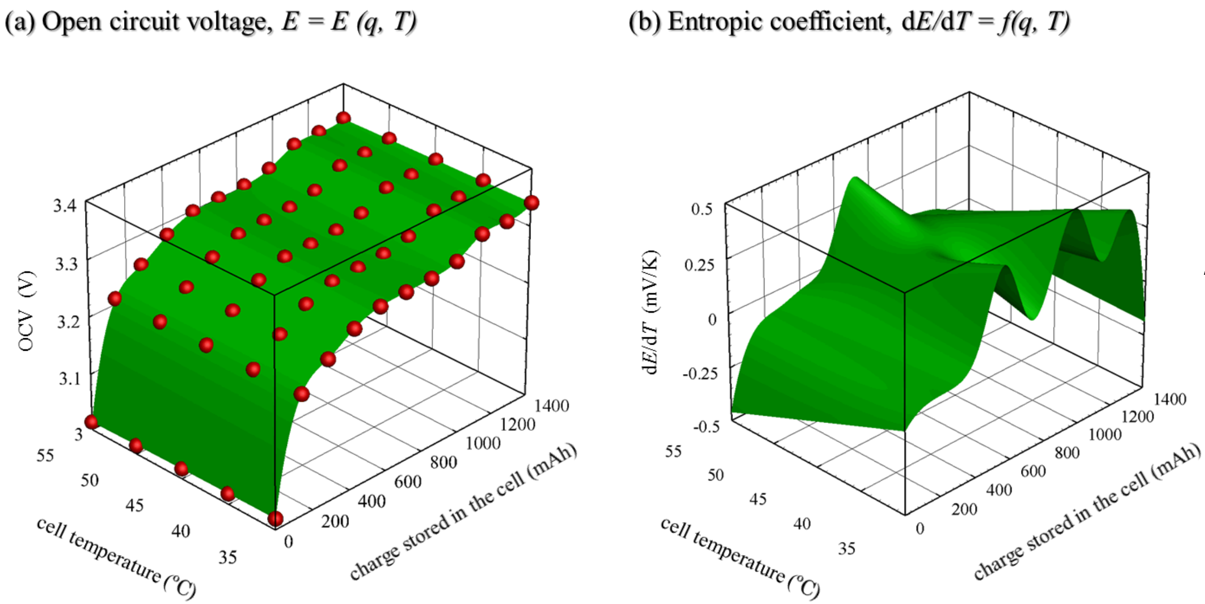
Using Thermodynamic relations, this energy change can be expressed as an internal energy change, and net internal energy change can be expressed as:

$$dU = mC \cdot dT - mv \cdot dp - \left(E - T\frac{\partial E}{\partial T} \right) \cdot dq$$

Pressure changes can be neglected inside calorimeter, and using sign convention for work interactions, the First law of Thermodynamics can be written for an 18650 cell inside a calorimeter:

$$mC \cdot dT - \left(E - T\frac{\partial E}{\partial T} \right) \cdot dq = -V \cdot dq$$

Thermodynamic Analysis of Li-ion Cells (2)



Generating OCV function based on experimental measurements of thermodynamic voltage at different states of charge and cell temperature. Red dots correspond to experimental data points.

*A. Mistry *et al.*, (2017) *ready for submission*

In terms of rate equation:

$$mC\frac{dT}{dt} = (E - V)I - \left(T\frac{\partial E}{\partial T}\right)I$$

The First law description for an 18650 cell being operated inside a calorimeter:

$$mC \cdot dT - \left(E - T\frac{\partial E}{\partial T}\right) \cdot dq = -V \cdot dq$$

Rearranging:

$$mC \cdot dT = \left(E - T\frac{\partial E}{\partial T}\right) \cdot dq - V \cdot dq$$

$$mC \cdot dT = (E - V)dq - \left(T\frac{\partial E}{\partial T}\right)dq$$

- Note that the mechanical energy changes are neglected as pressure variation during testing of a closed cylindrical cell are insignificant.
- Also, calorimeter is a system with adiabatic walls, hence no heat passes through the system boundaries.

Results: Electrochemical Operation in ARC

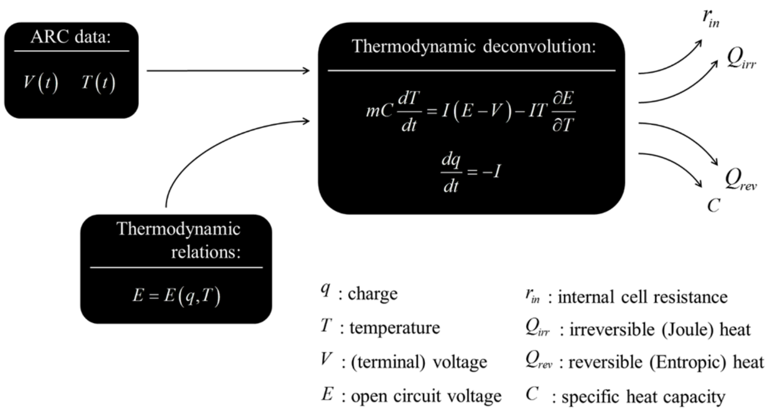
Substituting for various terms:

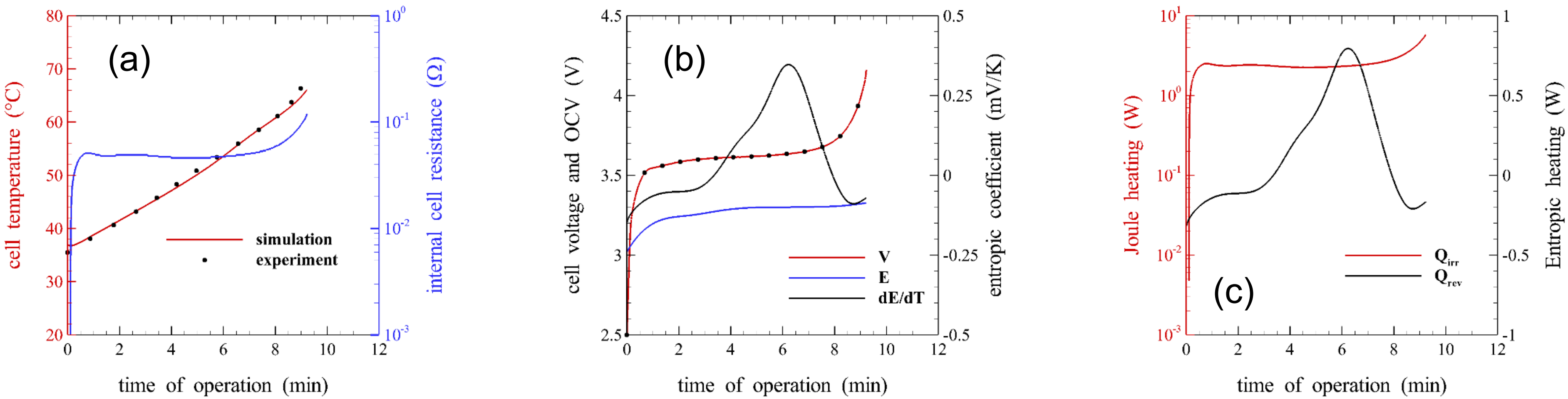
$$mC\frac{dT}{dt} = I(E-V) - IT\frac{\partial E}{\partial T} = \dot{Q}$$

Irreversible heat — $I(E-V)$

Reversible heat — $IT\frac{\partial E}{\partial T}$

Total heat recorded in a calorimeter — $\dot{Q}$

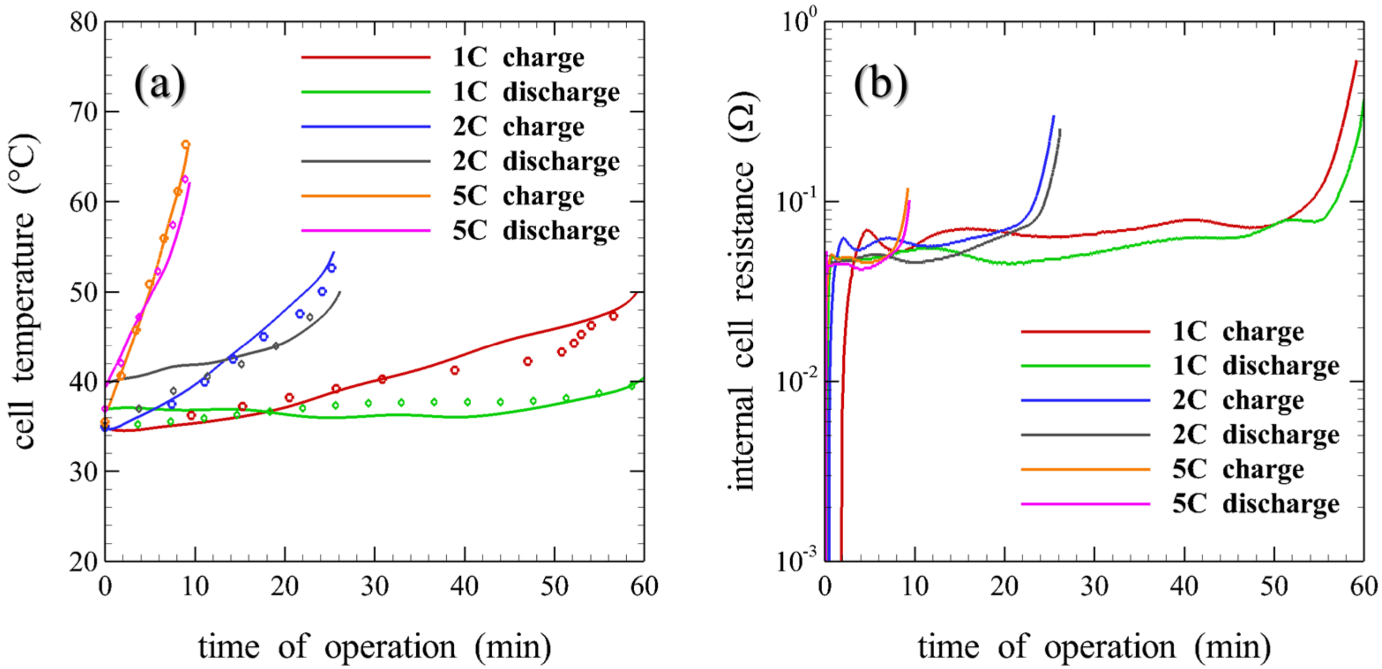




(a) Predicted temperature response based on cell voltage measurements and internal resistance build up (b) evolution of OCV and entropic coefficient (c) different heat generation components. These results are for charging at 7 A current.

*A. Mistry *et al.*, (2017) *ready for submission*

Consistent Interpretation of ARC Measurements



For a given cell, appropriate specific heat value gives consistent predictions at different rates of operation and for both charging and as well as discharging operation. (a) cell temperature predictions along with measurements (dots) (b) internal resistance build up. Average internal resistance decreases as C-rate increases. This can be attributed to higher average temperature and subsequently better transport efficiency.

*A. Mistry *et al.*, (2017) *ready for submission*

Calorimeter-free Characterization of Heat Generation

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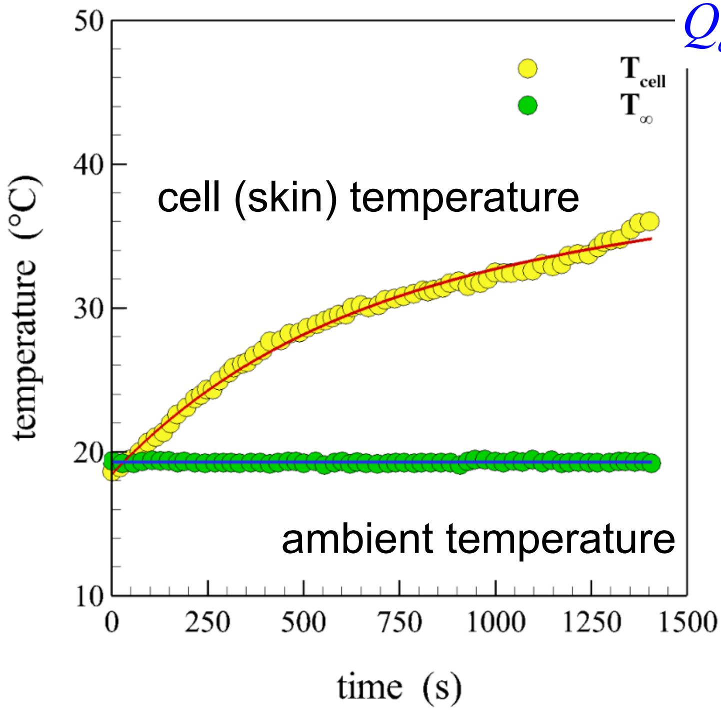
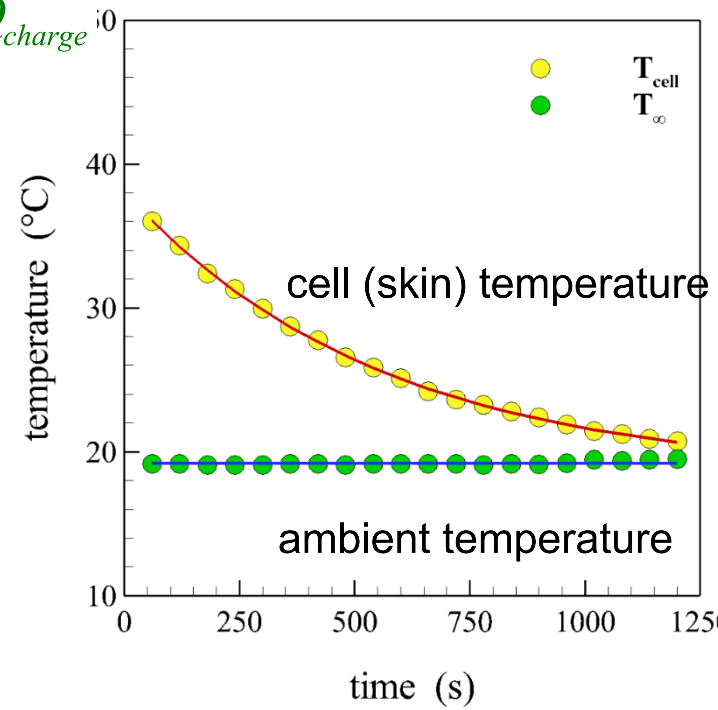
The procedure outlined before can be extended to quantify heat generation rates without using an ARC

Test sequence: rest – discharge – rest – charge sequence

h $\dot{Q}_{discharge}$ $\dot{Q}_{charge}$





2C cell discharge

$$mC\frac{dT}{dt} = \dot{Q} - hA\left(T - T_{\infty}\right)$$

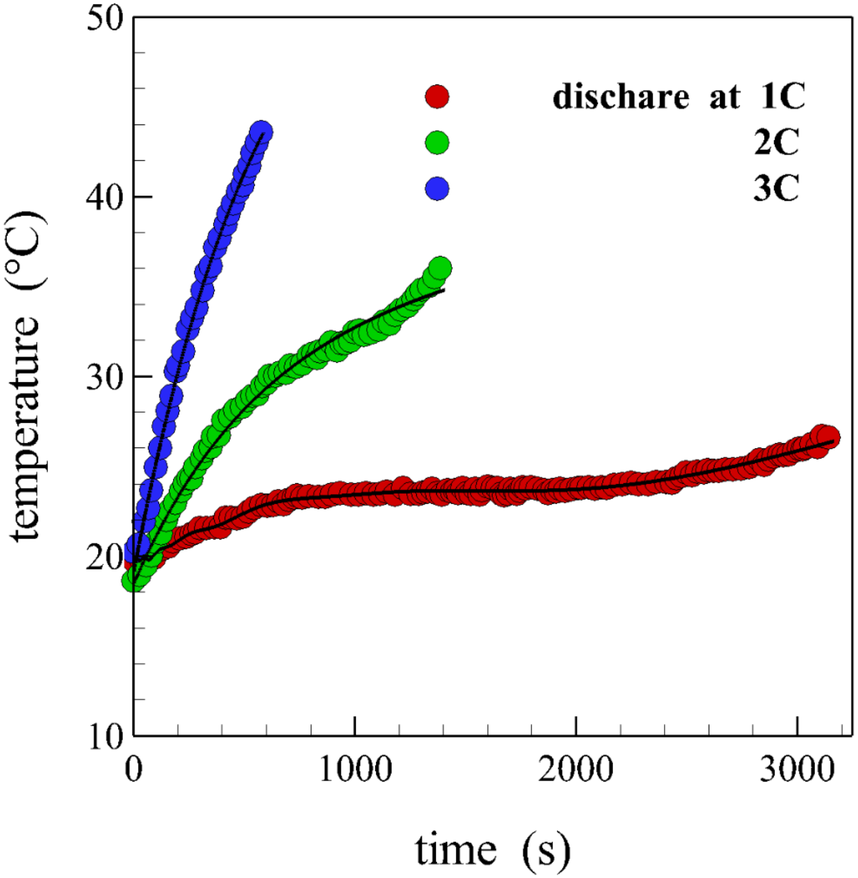
Rest after discharge

$$mC\frac{dT}{dt} = -hA\left(T - T_{\infty}\right)$$

*Mistry *et al.* (2017) in preparation

Red quantities are

Effect of Operation Rate on Heat Generation



Temperature measurements at different discharge rates (from a fully charged state).

Heat generation and internal resistance estimates from measurements

C-rate	avg(Q) [W]	avg(r_{in}) [mΩ]
1C	0.2556	52.8008
2C	1.0993	56.7803
3C	2.6657	61.1963

- This calorimeter-free method quantifies heat generation accurately.
- Internal resistance derived from analysis is close to that measured explicitly.

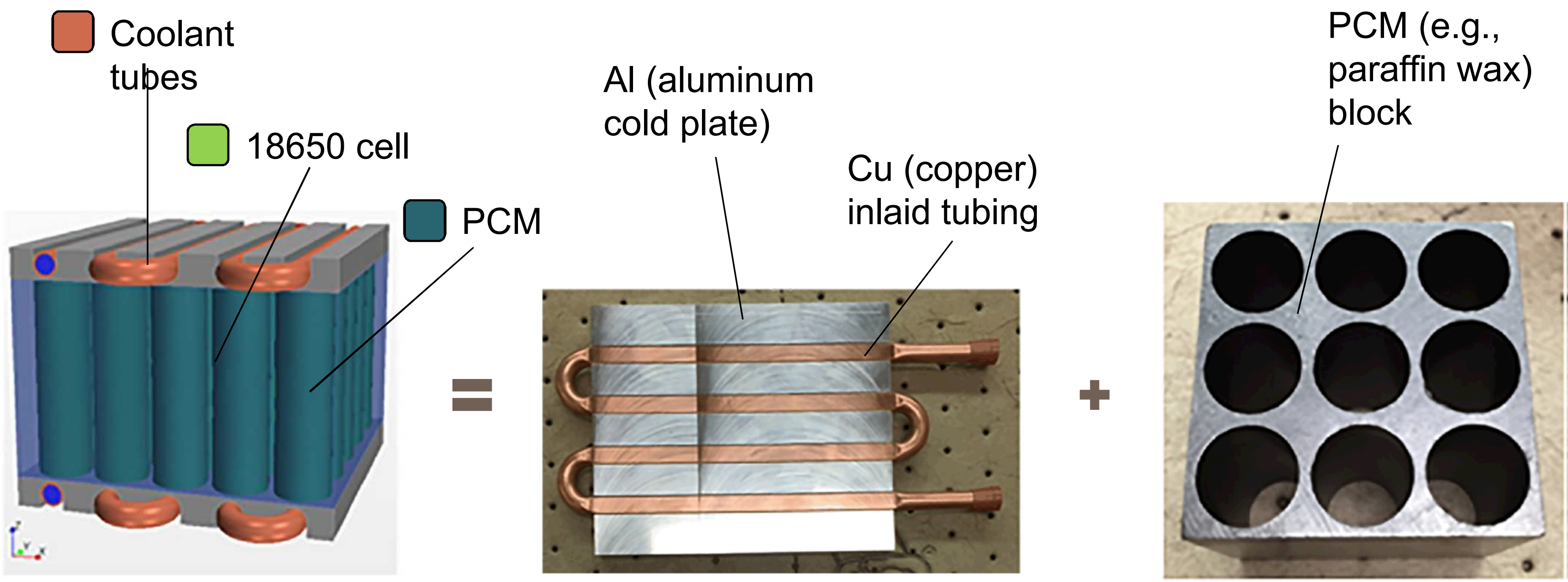
*Mistry *et al.* (2017) in preparation

Agenda Overview

Part II: Modeling of Thermal Characteristics and Safety

1. Thermal Abuse Behavior
2. Electrode Microstructure and Thermal Interplay
3. Thermo-electrochemical Analytics
4. Strategies for LIB Thermal Management

Hybrid Cooling System for LIB Pack



Cooling system for a pack of 18650 cells

Active thermal management (heat exchanger)

Passive thermal management (phase change material)

Objectives:

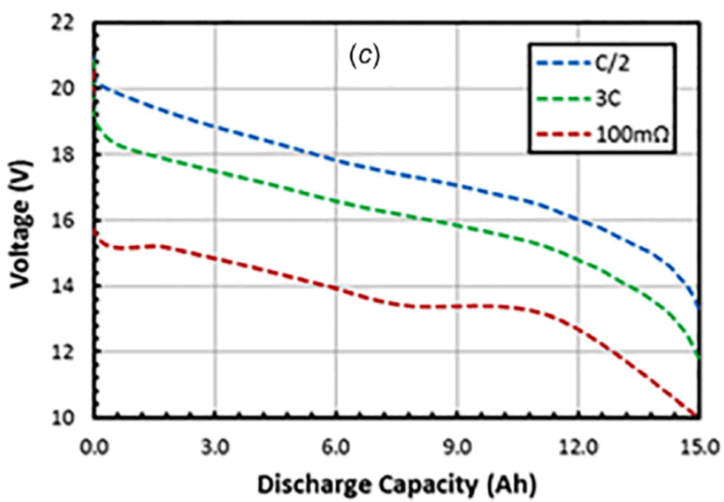
- Assess relative importance of active and passive cooling strategies on thermal management of medium size Lithium-ion battery packs
- Study interplay among cooling system and cell's electrochemical-thermal response for different conditions
- Estimate influence of cooling system modifications (for both active and passive components)

*C. Lopez, J. A. Jeevarajan and P. P. Mukherjee (2017) *J. Electrochem. En. Conv. Stor.*, **13** (3), 031007

Electrochemical – Thermal Responses

Sandia National Laboratories

Cell: **LG18650C2** Li-ion **2.8 Ah** cells
Anode: Graphite
Cathode: $LiCoO_2$
Electrolyte: $LiPF_6$ in EC/EMC/DMC

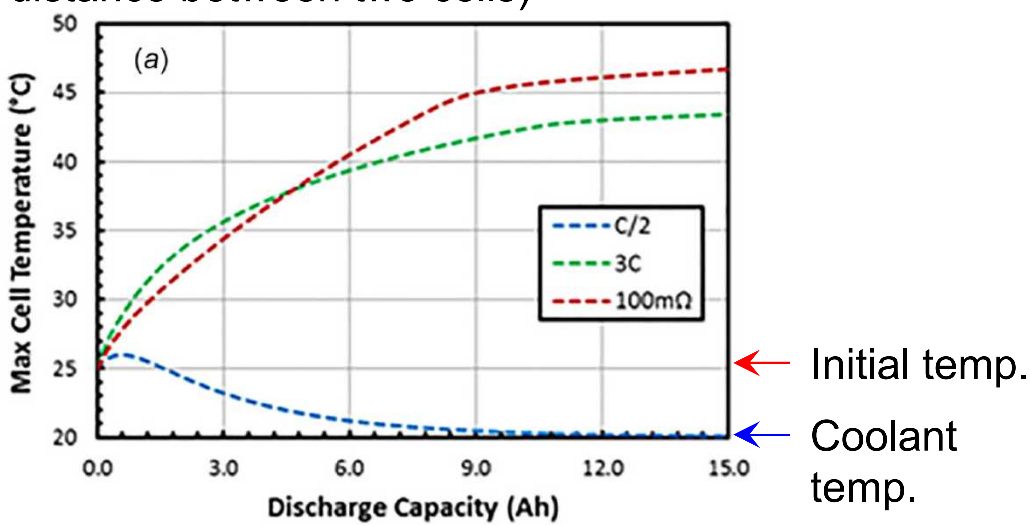


Discharge response of a 5S5P battery pack

Results:
C/2: nominal discharge
3C: fast discharge
100 mΩ: external short (abuse)

Cell response is simulated using NTG (Newman, Tiedeman and Gu) model

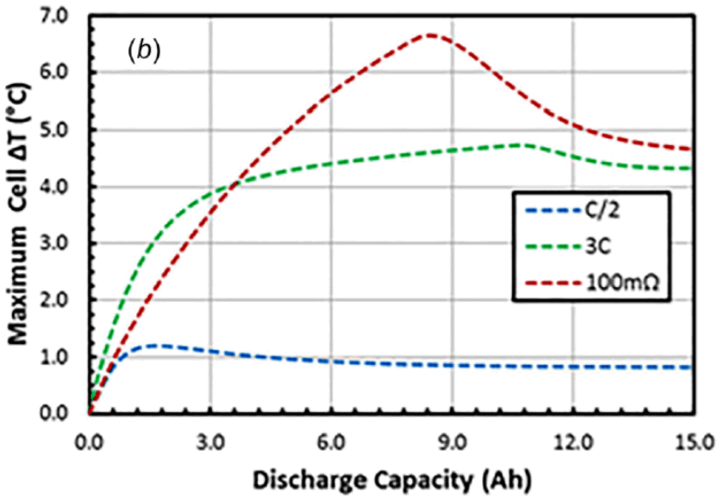
Thermal management:
Active: Water flow at Re = 1125 (laminar flow)
Passive: Paraffin wax 2mm spacing (min distance between two cells)



1. At C/2, heat generation is small and active cooling dissipates heat sufficiently
2. At 3C and external short, heat generation is large enough such that coolant cannot dissipate heat and cell temperature rises rapidly. Passive cooling kick in in 42-45°C (melting range for Paraffin Wax)

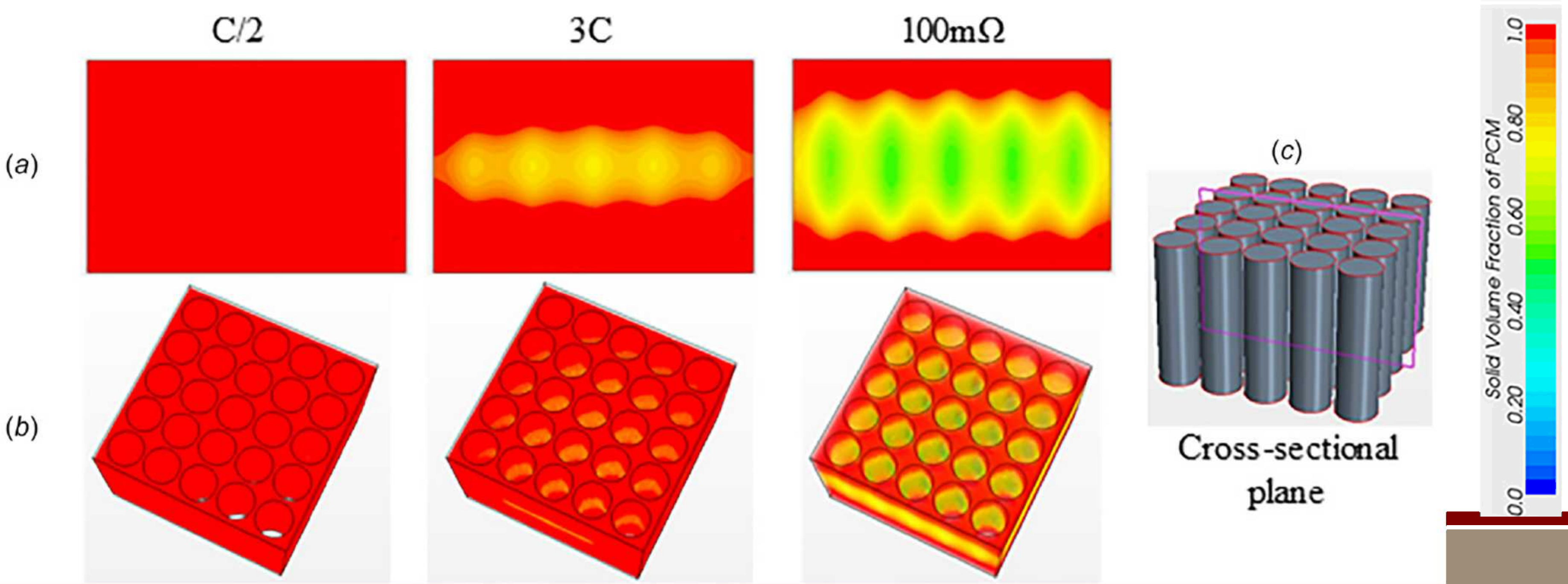
*C. Lopez, J. A. Jeevarajan and P. P. Mukherjee (2017) *J. Electrochem. En. Conv. Stor.*, **13** (3), 031007

Temperature Field and State of PCM

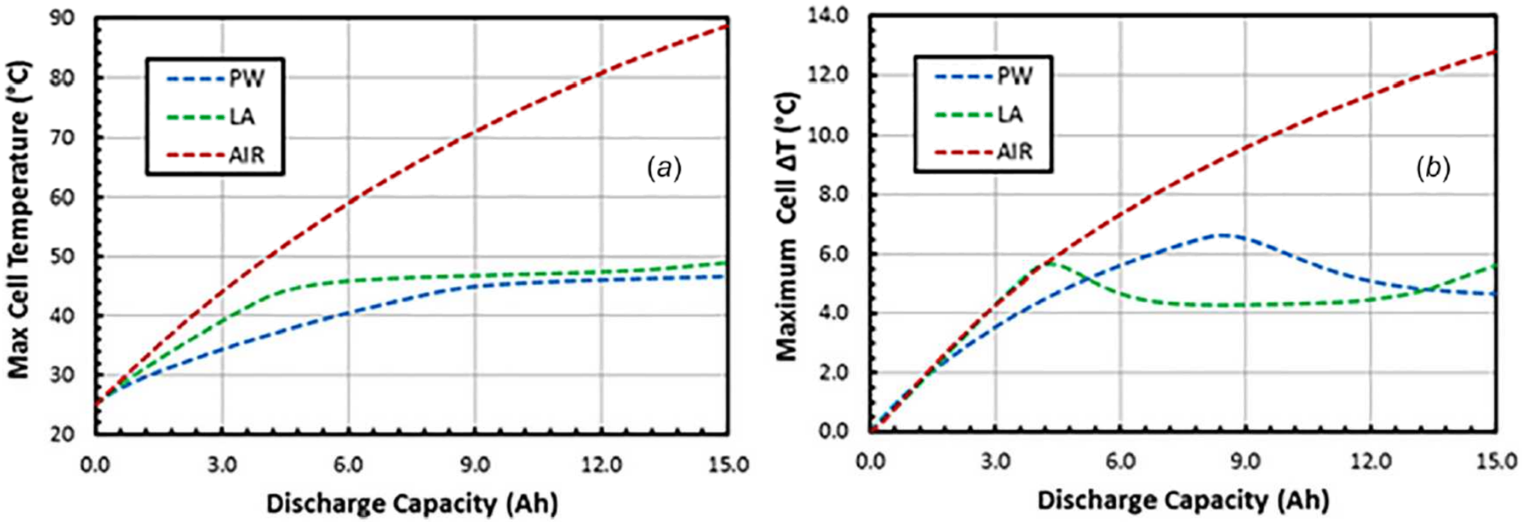


$\Delta T = |T_{core} - T_{surf}|$ reflects the poor thermal conduction inside Li-ion cells

- During external short, heat generation rate rises rapidly (even more than a high rage, e.g., 3C, discharge).
- This reflects in greater melting of PCM block.
- Plots represent situation at the end of operation.



Variations in Cooling System



- Lauric acid (LA) and Paraffin Wax (PW) has similar meting temperature range.
- LA has higher melting heat but lower conductivity, compared to PW.
- For PCM to work, heat should be transported to PCM, which in turn depends on PCM's conductivity. Since, LA has an order of magnitude smaller conductivity, corresponding cell block exhibits faster temperature rise and higher thermal gradients.
- Thus, passive cooling system is not just about choosing a material with higher latent heat. A careful adjustment of thermophysical properties is required that sufficiently facilitates limiting heat transport modes.

Material	Melting range	Latent heat	Thermal conductivity
Lauric acid	41 – 43 °C	211.6 kJ/kg	1.6 W/m-K
Paraffin wax	42 – 45 °C	123.0 kJ/kg	16.6 W/m-K

Acknowledgements

Sandia National Laboratories

Graduate student contributors: Aashutosh Mistry, Ankit Verma

U.S. DEPARTMENT OF ENERGY

National Aeronautics and Space Administration

Underwriters Laboratories

Texas Instruments

National Science Foundation
WHERE DISCOVERIES BEGIN

That’s all for now …

Thank You!

Agenda Overview

- Part III Systems and Engineering Aspects including Safety and Reliability

- *Systems and Engineering Aspects of Safety and Reliability*
  - Cell to system – defined
    - Battery management system
    - Auxiliary components
  - Improvements in materials for:
    - Thermal management
    - Control electronics
    - Power electronics
  - Impacts on large-scale energy storage systems
    - Safety
    - Performance
    - Reliability
    - Cost

Improving battery safety

Development of Inherently Safe Cells

- Safer cell chemistries
- Non-flammable electrolytes
- Shutdown separators
- Non-toxic battery materials
- Inherent overcharge protection

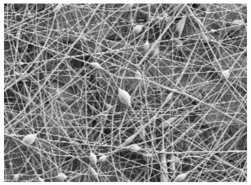
Safety Devices and Systems

- Cell-based safety devices
  - current interrupt devices
  - positive T coefficient
  - Protection circuit module
- Battery management system
- System design

Effective Response to off-normal Events

- Modelling
- Suppressants
- Containment
- Advanced monitoring and controls

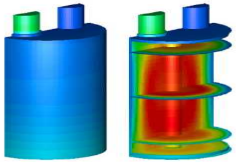
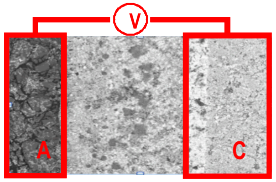
Battery safety – stationary storage




Materials R&D to date:
- Non-flammable electrolytes
- Electrolyte salts
- Coated active materials
- Thermally stable materials

Materials R&D needs:
- Viable flow batteries
- Aqueous electrolyte batteries
- High specific heat suppressants
- Vent gas composition


Testing
- Electrical, thermal, mechanical abuse testing
- Failure propagation
- Suppressants and delivery
- Large scale thermal and fire testing (TTC)

Simulations and Modeling
- Multi-scale thermal models
- Validating failure propagation models
- Fire Dynamic Simulations (FDS)

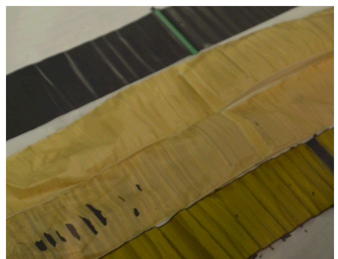
Procedures, Policy, and Regulation
- Overarching
- Installations
- Complete systems
- Components
- International

Improving battery failure mitigation

Collaboration: codes, standards, and regulations

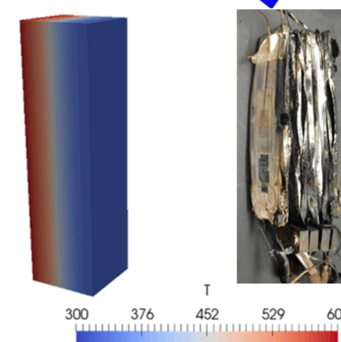
Collaboration: incident response

Baseline electrochemical performance analysis



Materials characterization and thermal stability testing

Electrochemical and whole-cell and string abuse response analysis



Modeling of thermal propagation

Collaboration: vent plume composition (NM Tech)

System selection fraught with uncertainty

Problem:

- Cells have application-specific operation and performance
- Chemistry Selection for an ESS installation must consider
  - Cost
  - Size
  - Safety
  - Application
  - Reliability
  - Performance
  - Manufacturer reputation
  - Battery management
- Comparable information on cells from different manufacturers is difficult to ascertain

"Energy Storage Safety Strategic Plan" https://energy.gov/oe/downloads/energy-storage-safety-strategic-plan-december-2014

System selection fraught with uncertainty

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LG Chem

PRODUCT SPECIFICATION

Description	Document No.	Date	Rev
Lithium Ion LG 18650 HG2 3000mAh	PS-HG2-Rev0	2015-01-28	0

Contents

3/11

11 page document with testing details

Panasonic — Lithium Ion **NCR18650A**

Features & Benefits

- High energy density
- Long stable power and long run time
- Ideal for notebook PCs, boosters, portable devices, etc.

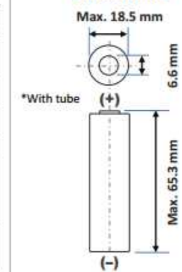
* At temperatures below 10°C, charge at a 0.25C rate.

Specifications

Rated capacity(1)	Min. 2900mAh
Capacity(2)	Min. 2950mAh Typ. 3070mAh
Nominal voltage	3.6V
Charging	CC-CV, Std. 1475mA, 4.20V, 4.0 hrs
Weight (max.)	47.5 g
Temperature	Charge*: 0 to +45°C Discharge: -20 to +60°C Storage: -20 to +50°C
Energy density(3)	Volumetric: 620 Wh/l Gravimetric: 225 Wh/kg

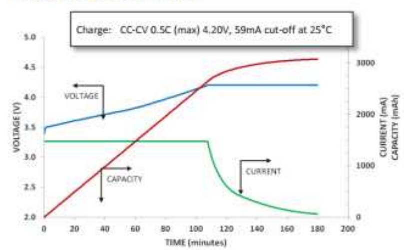
(1) At 20°C (2) At 25°C (3) Energy density based on bare cell dimensions

Dimensions

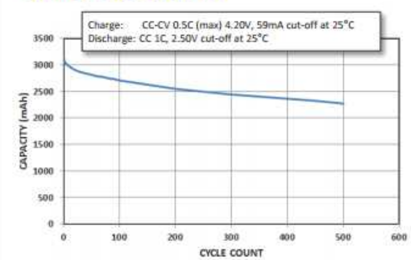


For Reference Only

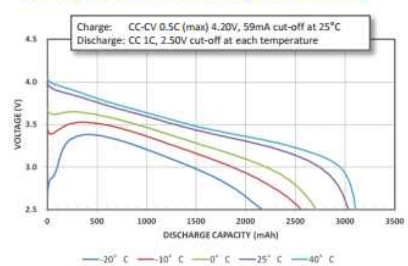
Charge Characteristics



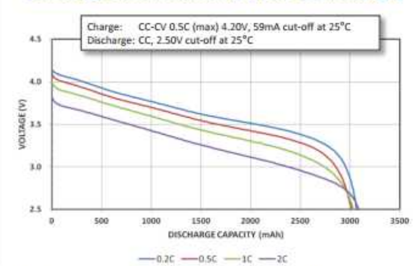
Cycle Life Characteristics



Discharge Characteristics (by temperature)



Discharge Characteristics (by rate of discharge)



The data in this document is for descriptive purposes only and is not intended to make or imply any guarantee or warranty.

Operating ranges and some data

(1) http://www.batteryspace.com/prod-specs/8427_specification.pdf (2) http://www.batteryspace.com/prod-specs/9989.specs.pdf

System selection fraught with uncertainty

Sandia National Laboratories

Problem:

- Cells have application-specific operation and performance
- Chemistry Selection for an ESS installation must consider
  - Cost
  - Size
  - Safety
  - Application
  - Reliability
  - Oversizing
  - Manufacturer reputation
  - Performance
  - Pack management
- Comparable information on cells from different manufacturers is difficult to ascertain

Approach:

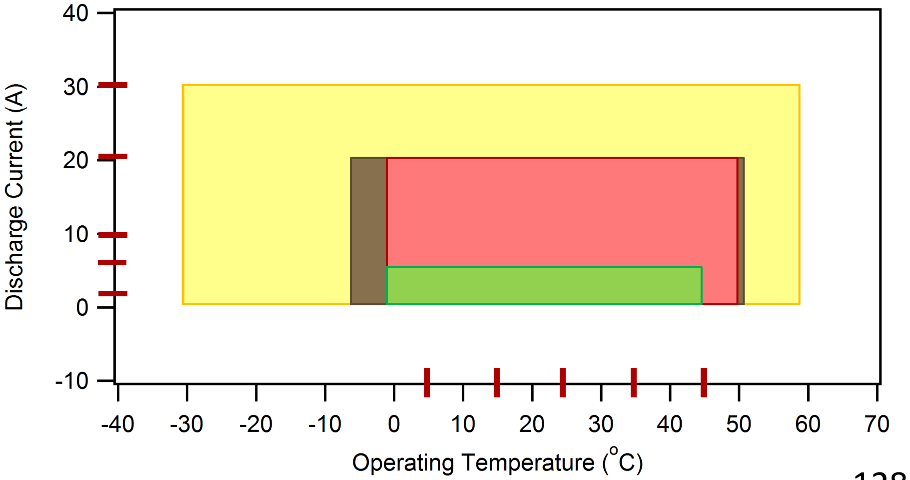
- Quantify performance with uniform methodology
- Find effects of compounding operation conditions
- Identify unintended abuse or aging conditions
- Extrapolate results to long-term cell safety and reliability

"Energy Storage Safety Strategic Plan" https://energy.gov/oe/downloads/energy-storage-safety-strategic-plan-december-2014

Cell operation constraints

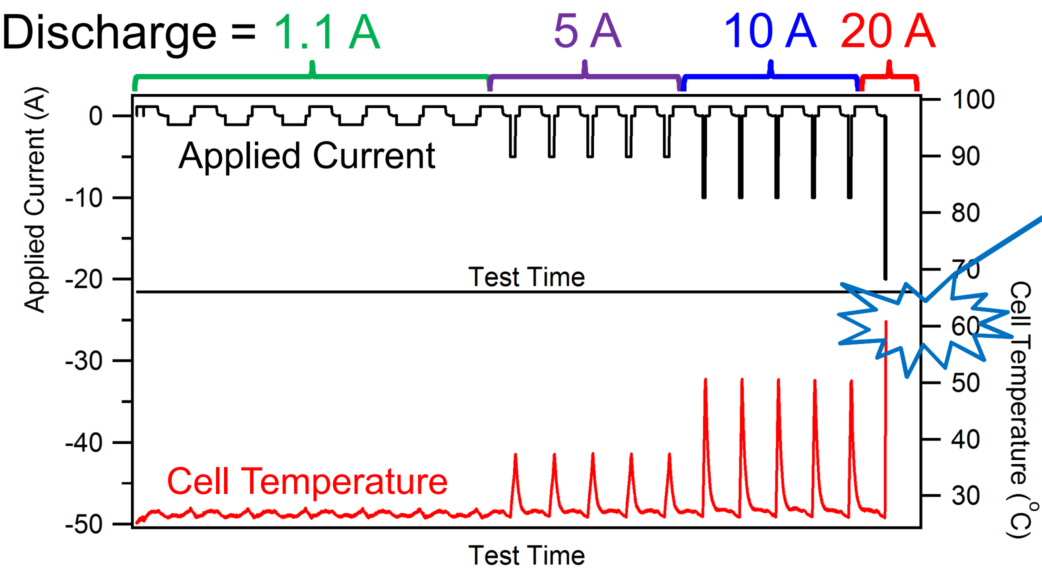
Cathode Chemistry	AKA	Specific Capacity (Ah)	Average Potential (V vs Li°/Li+)	Max Discharge Current	Acceptable Temperature (°C)
[redacted]					
$LiFePO_4$	LFP	1.1	3.3	30	-30 to 60
[redacted]					
$LiNi_{0.80}Mn_{0.15}Co_{0.05}O_2$	NMC	3.0	3.6	20	-5 to 50

LCO LFP NCA NMC



Avoiding accelerated aging or abuse

LFP, 25 °C environment



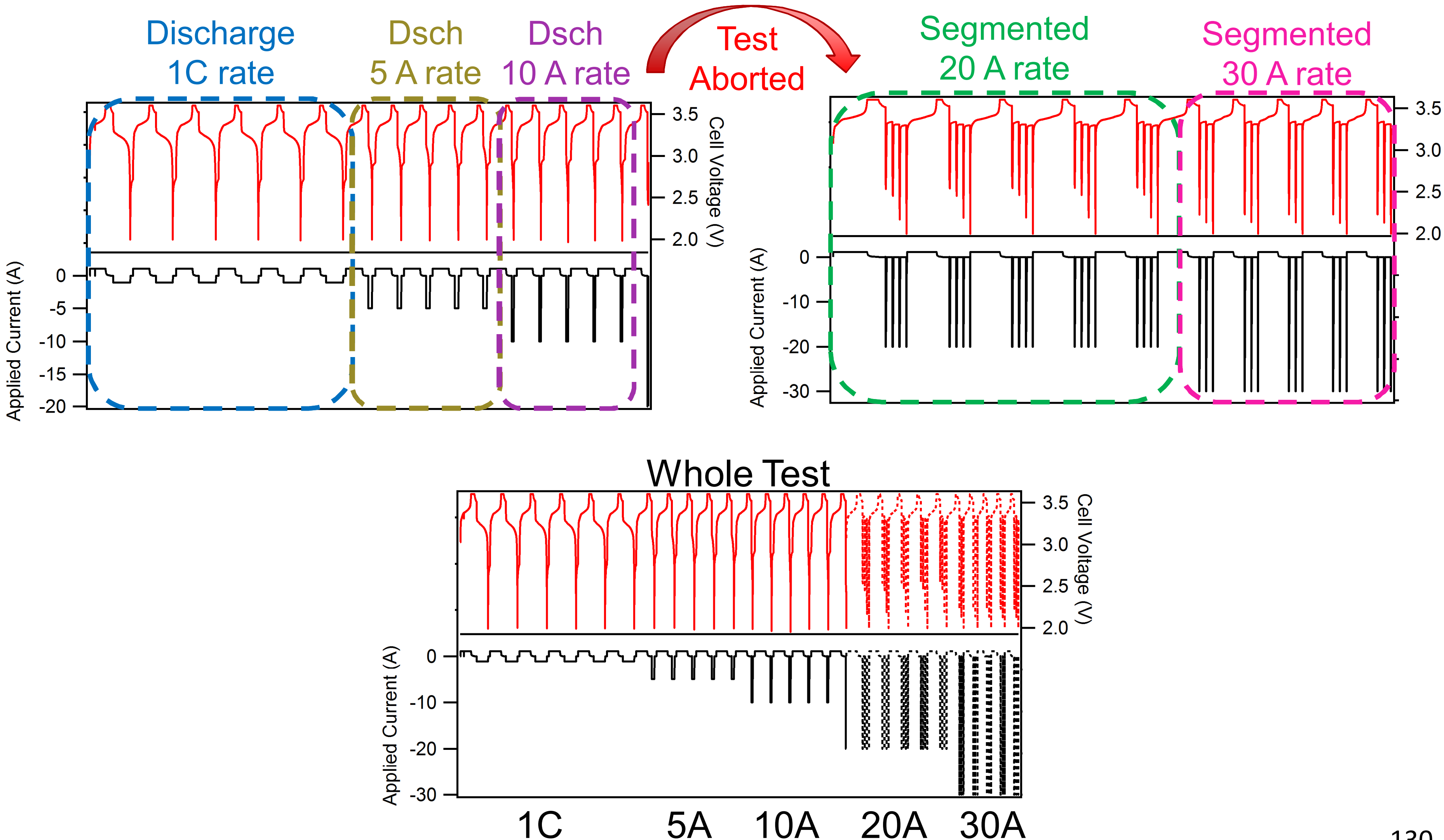
Current = 20 A (max = 30 A)
Environment = 25 °C
Cell skin Temp = 60 °C!!!

Most packs don't monitor individual cell skin temperatures.
Unintended abuse condition under 'normal' operation.

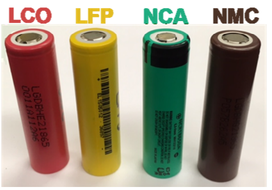
Pristine Cell

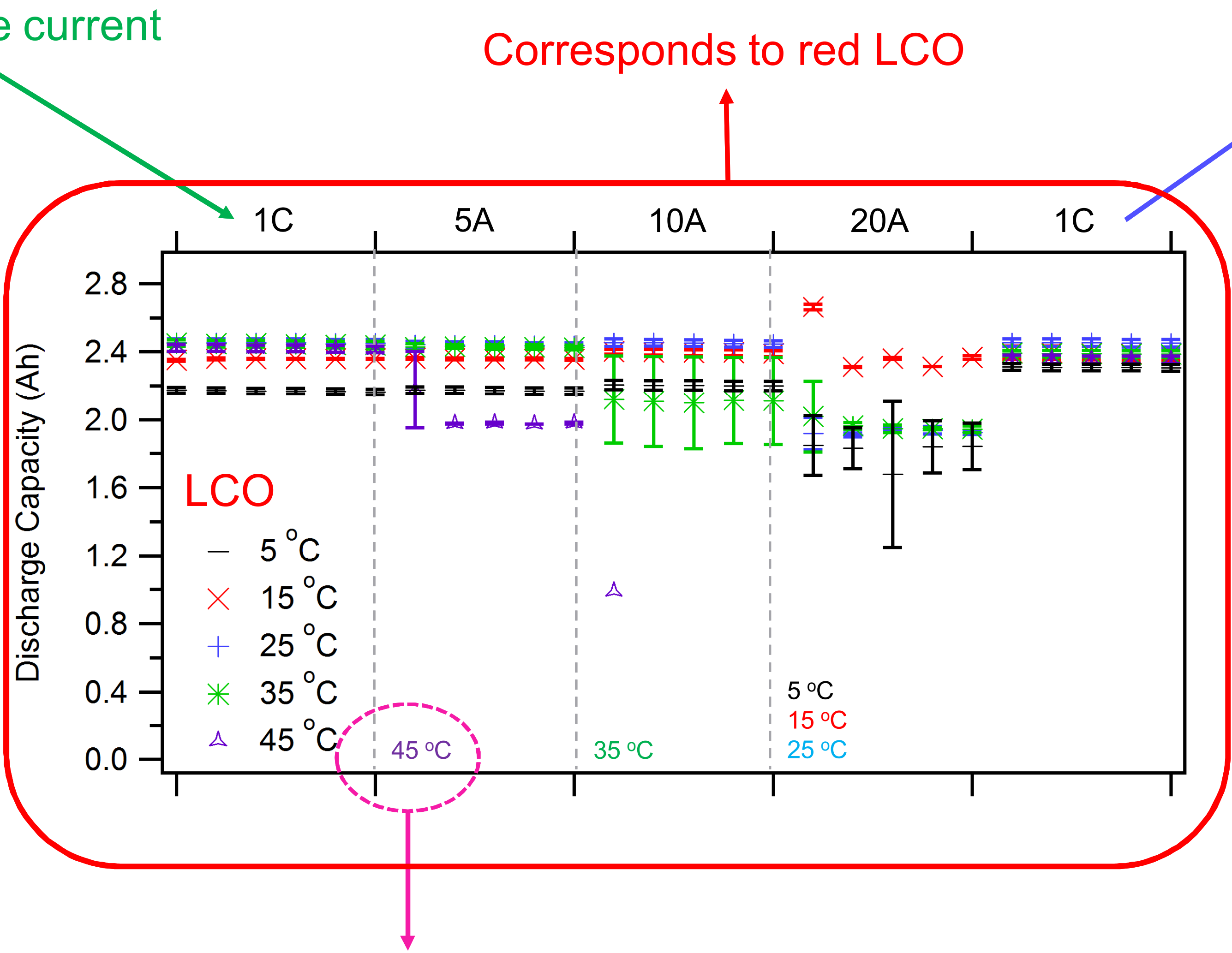
Abused Cell

Evaluating cell chemistries uniformly



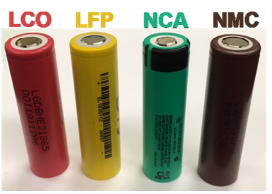
Cycling data for each chemistry is coalesced on one plot

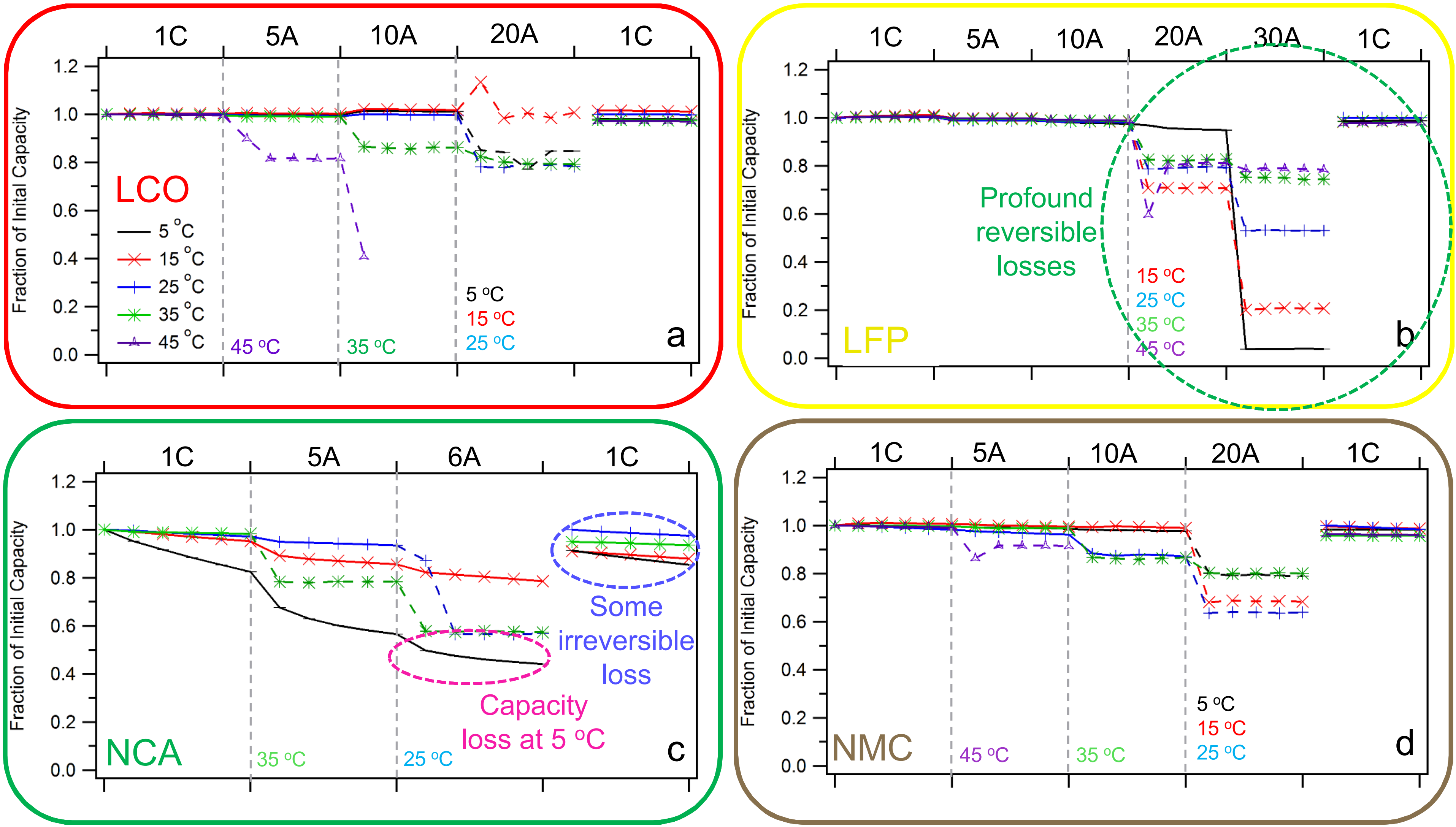




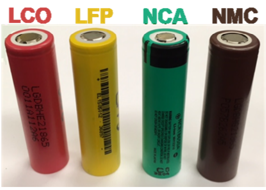
Segmented discharging began at 45 °C

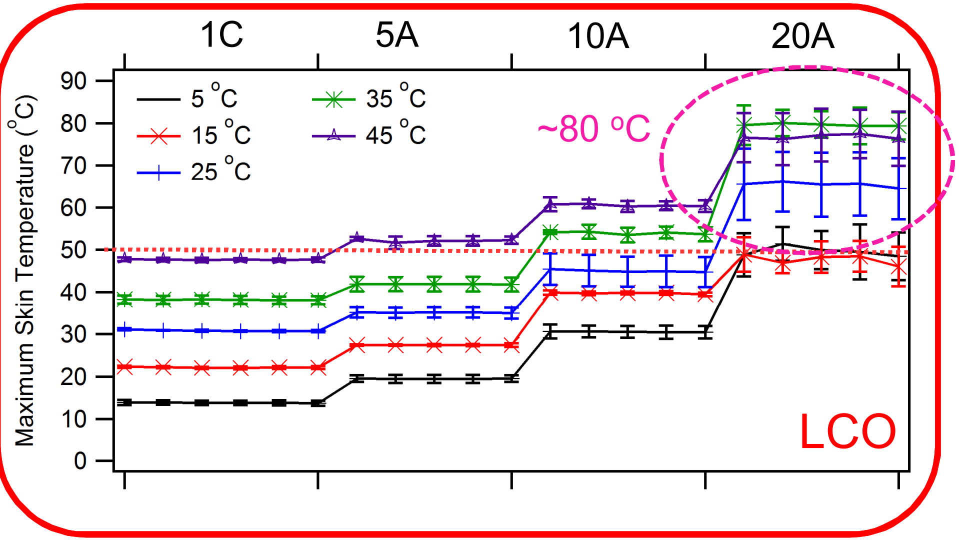
NCA experiences lasting capacity losses after cycling

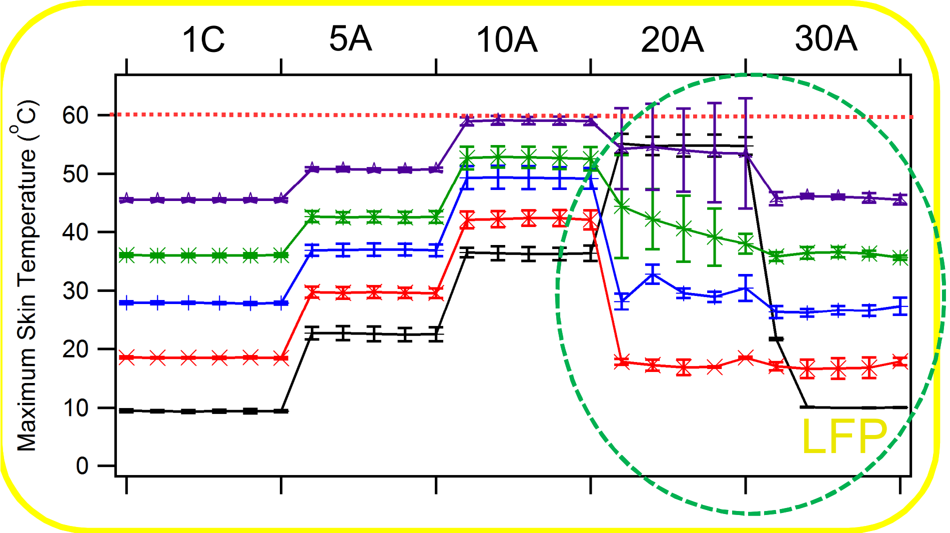


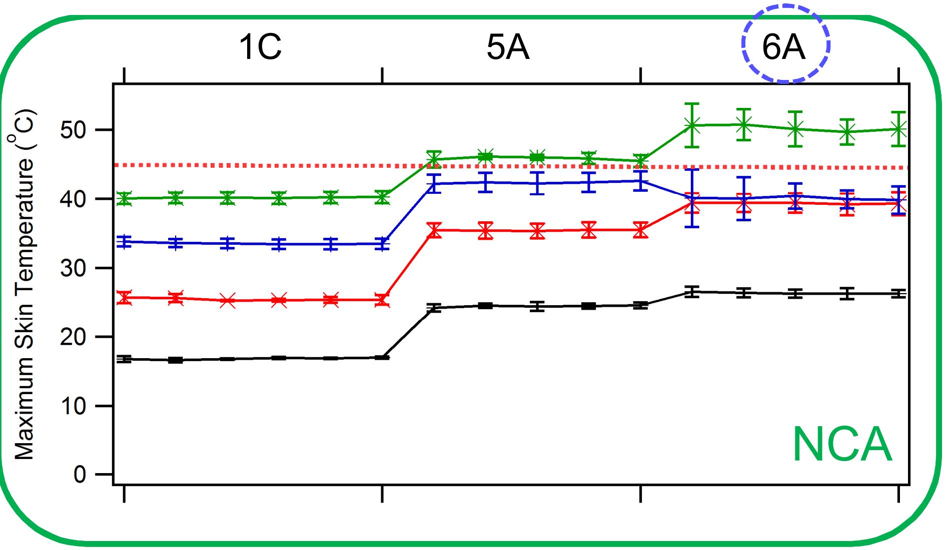


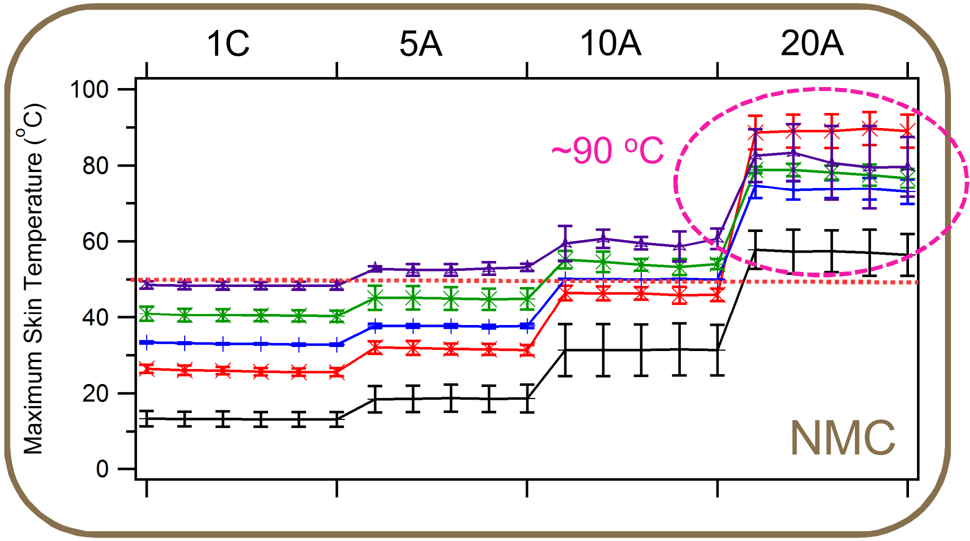
Significant self-heating can occur if cells are unmonitored





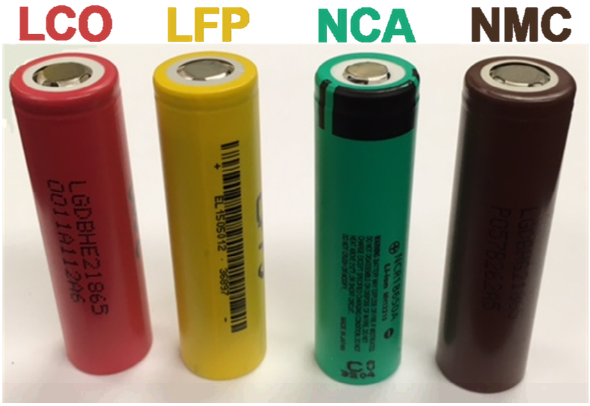




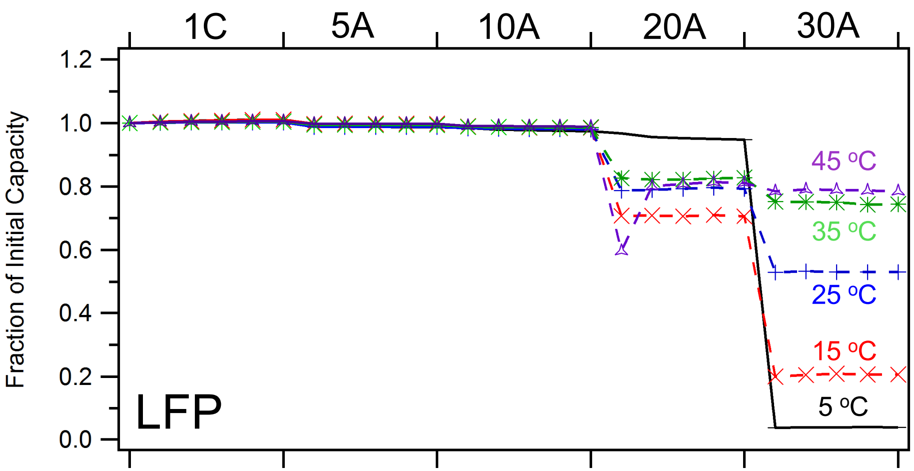


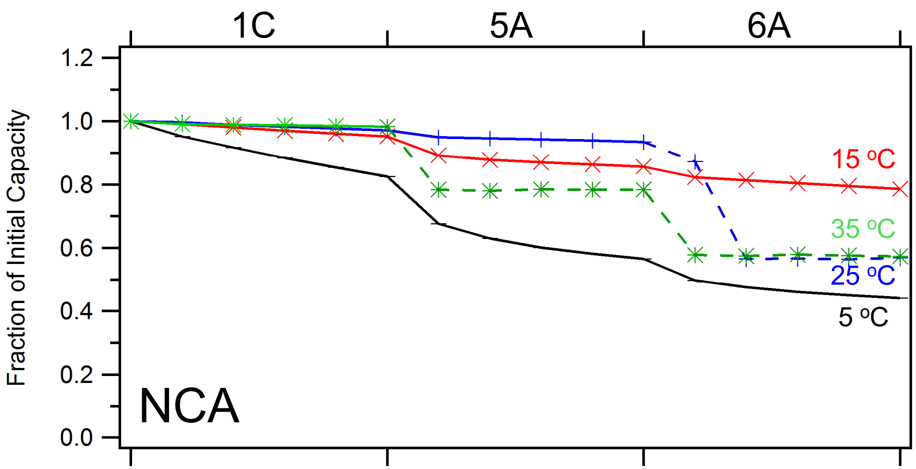
Cells are highly application-specific

- Parameters such as energy density and cost per capacity can not solely be used to choose a cell
- Operating conditions combine to produce unintended abuse and accelerated aging
- NCA experiences aging, likely from Li plating at low temperatures
- Small losses quantified here can be extrapolated to rapid cell death
- This work should be continued to include other relevant chemistries and cell formats



Reliability varies by cell and conditions





- No temperature effects at currents ≤ 10 A
- higher temperature = less capacity loss

- Capacity loss with higher currents, higher/lower temperatures
- 15 °C immune to most losses

Reliability of a battery impacts risk and varies with chemistry, conditions, and history

Battery System Safety

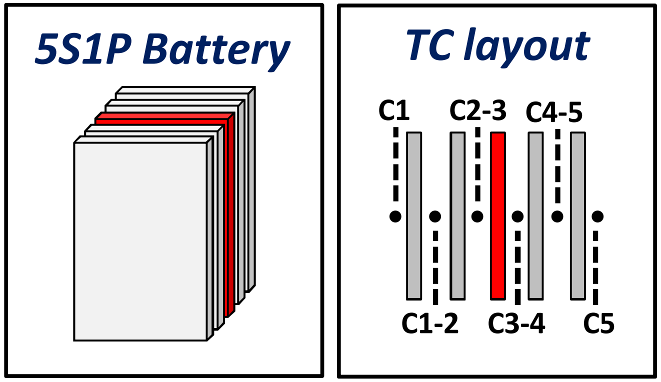
Battery System Field Failures

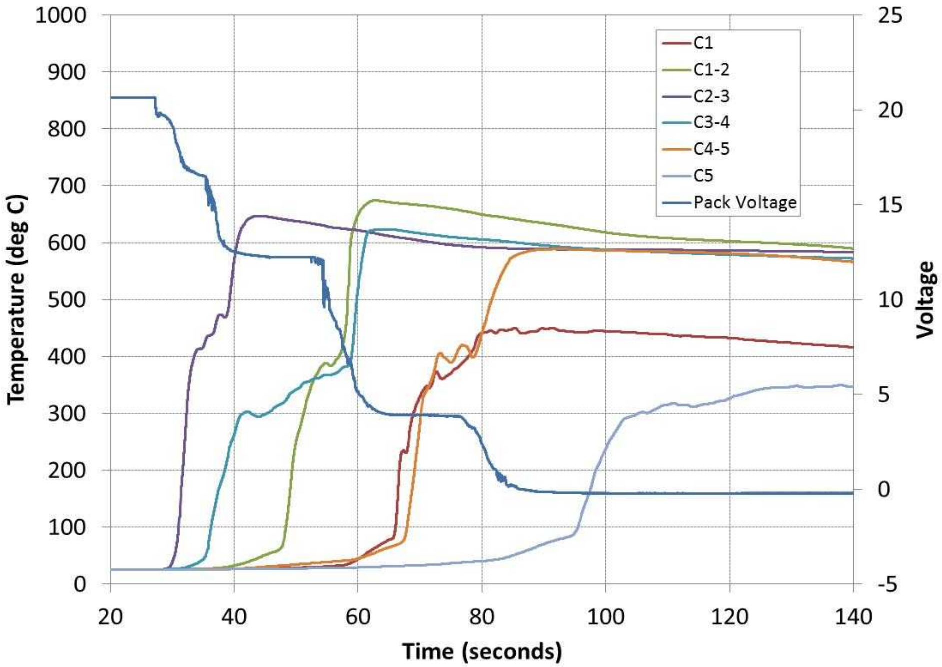
- Single point (or multi-point) failures within the battery or outside the battery that lead to catastrophic failure
  - Internal short circuits (latent defect)
  - Use conditions
  - Abuse conditions (forseen or unforseen)
  - Control electronics failure (connectors, power electronics, boards, low voltage short)
- Internal short circuits have garnered considerable attention from consumer electronics field failures
- Other failure modes will likely gain more attention for large scale applications because the use conditions are considerably different
- Allowing single point failures to propagate through a battery is an unacceptable scenario to ensure battery safety

Summary

- Fielding the most inherently safe chemistries and designs can help address the challenges in scaling up lithium-ion
- Material choices can be made to improve the inherent safety of lithium-ion cells
- Testing single cell failure propagation throughout a battery system is critical for understanding the potential vulnerabilities and safety margin for a battery
- A comprehensive evaluation of all lithium-ion cell components is essential to ensure safety and reliability for these cell in large battery systems – great impact on public adoption
- No single inherently safe chemistry or mitigation strategy exists, solution in the form of numerous strategies – impact on electrochemical performance

Propagation testing (5S1P)





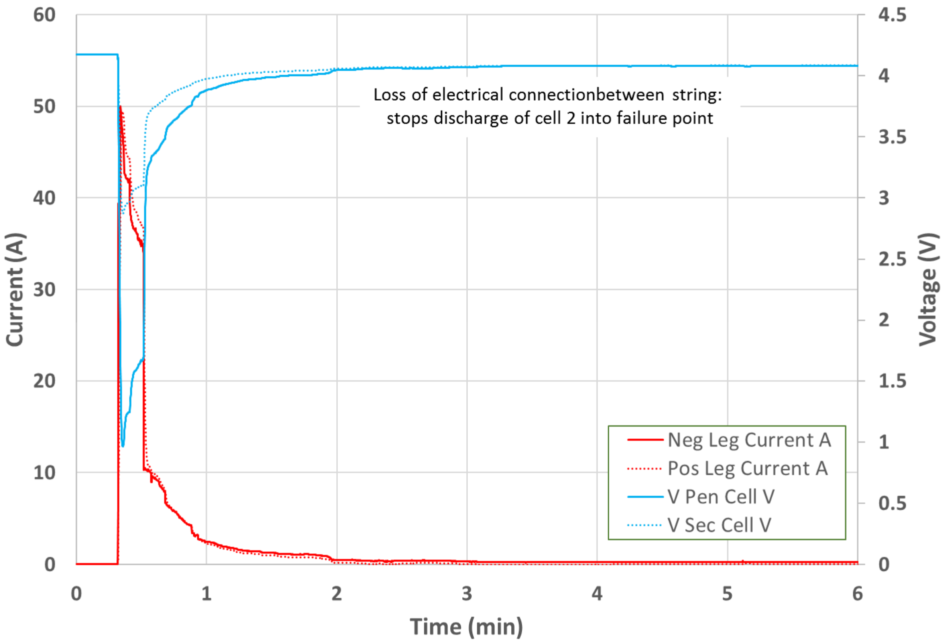
Key Challenges:

- *Scale – What test setup size becomes representative of real conditions*
- *Statistical significance – Abuse consequences can be highly stocastic*
- *Modeling at high confidence – Robust models need complementary data*

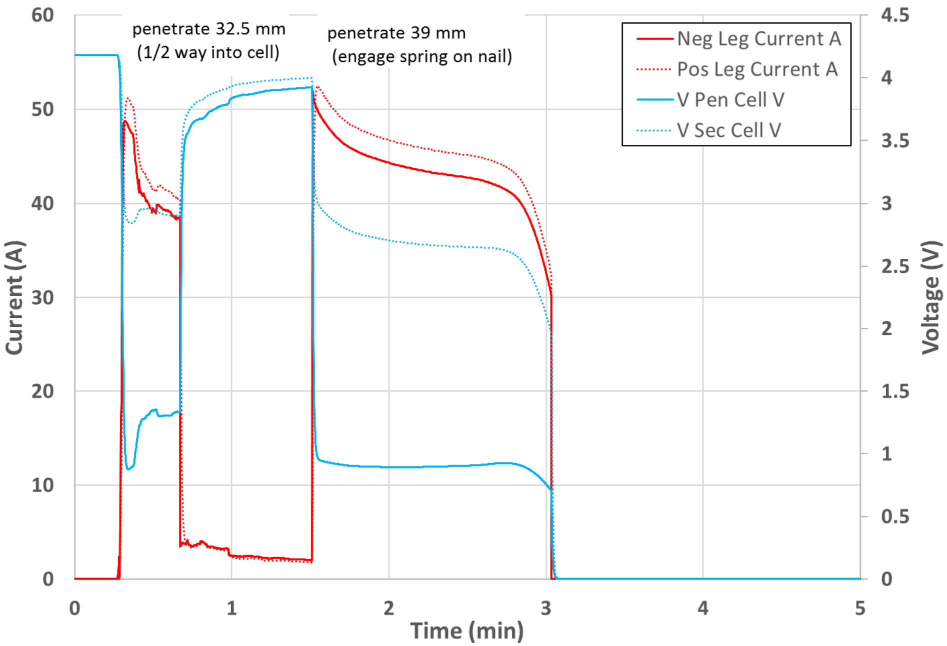
Short circuit current during failure propagation:NMC

Failures initiated by mechanical insult to cell 1 which is connected to cell 2 through constantan bridge wire

18650 NMC 3Ah cells – 1s2p



18650 NMC 3Ah cells – 1s2p
Improved mechanical contact



- ***Peak currents across constantan bridge during failure propagation consistent between setups: ~50A***
- ***Total energy discharged into cell 1 varies based on robustness on electrical connection allowing cell 2 to discharge into failure point longer: without spring 0.027 kJ (lost battery connection) and with spring 5.3 kJ***

Agenda Overview

- Part IV Research and Development Priorities for a More Resilient Energy Storage System

- *Research and Development Priorities for Energy Storage System Resilience*
  - State of ESS safety research
  - ESS design gap areas
    - Materials understanding
    - System engineering
    - Propagation prevention (phase change materials? Incident preparedness?)
  - Incident preparedness
    - Water additives
    - Gaseous extinguishers
    - Phase change materials

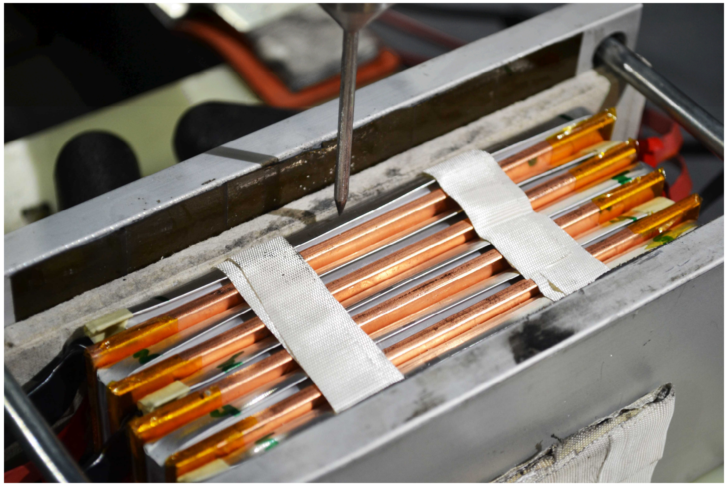
Failure propagation testing: Inclusion of thermal management

Methodology:

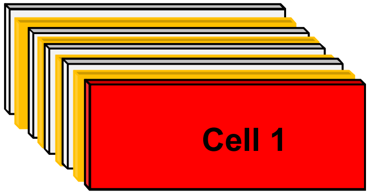
- Experimentally determine a reproducible thermal runaway initiator for each cell type
- Use this initiator to trigger a single cell thermal runaway failure in a battery
- Evaluate the propagation of that failure event

Experiment

- COTS $LiCoO_2$ 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

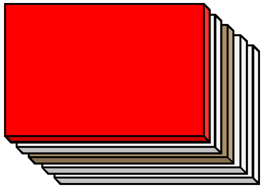


J. Lamb et al. J. Power Sources 283 (2015), 517-523 and C. J. Orendorff et al. SAND2014-17053

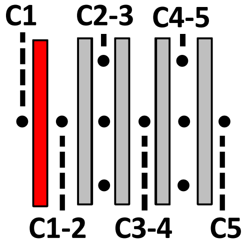
Failure propagation: No thermal management

Failures initiated by mechanical insult to edge cell of COTS $LiCoO_2$ (3Ah cells)

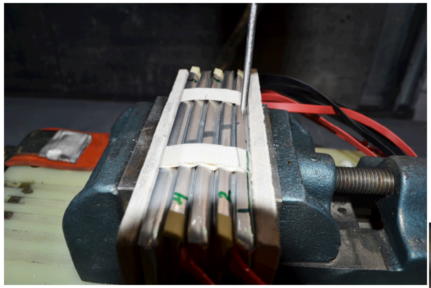
5 cell Battery

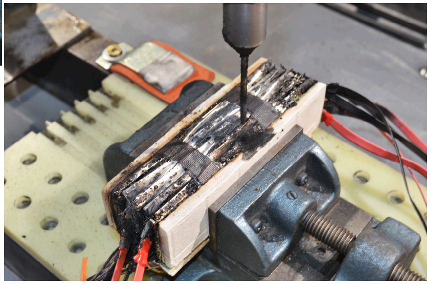


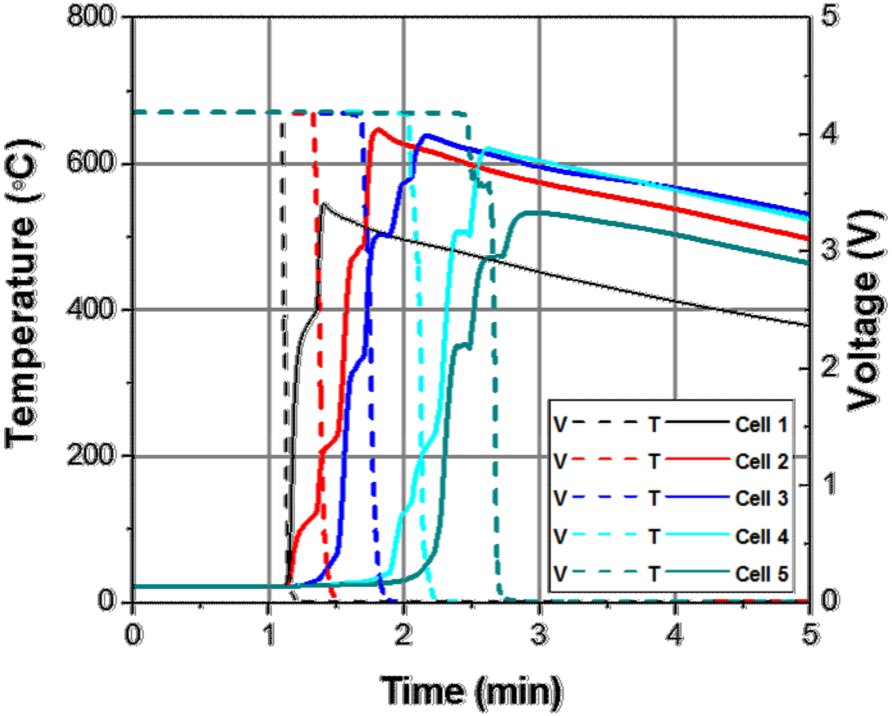
TC layout



- Successful initiation at Cell #1
- Propagation to adjacent cells
- Cascading failure to entire battery over 60 s





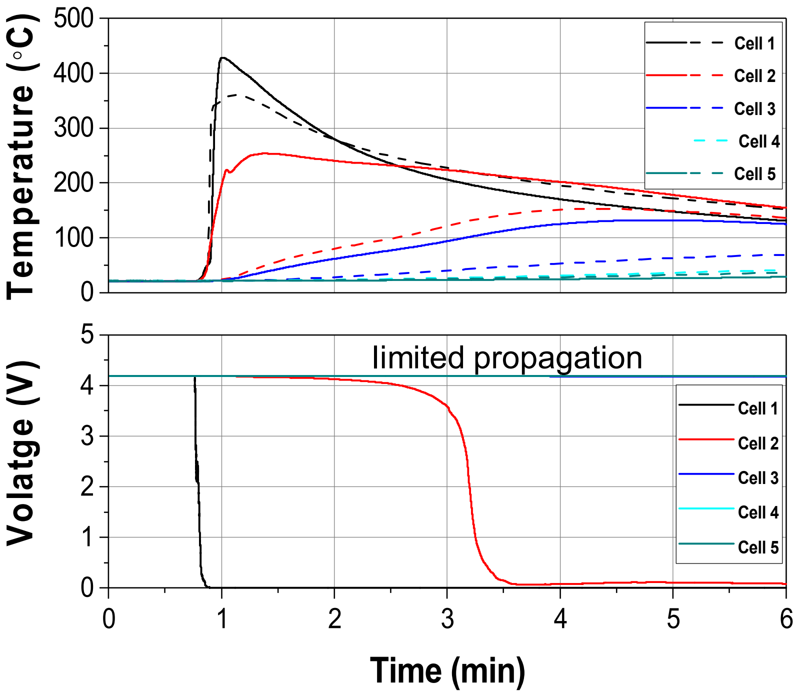


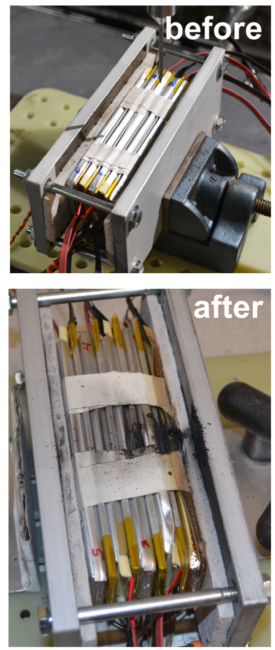
- ***Observed complete propagation when cell are close packed with no thermal management***

Failure propagation: Aluminum spacer

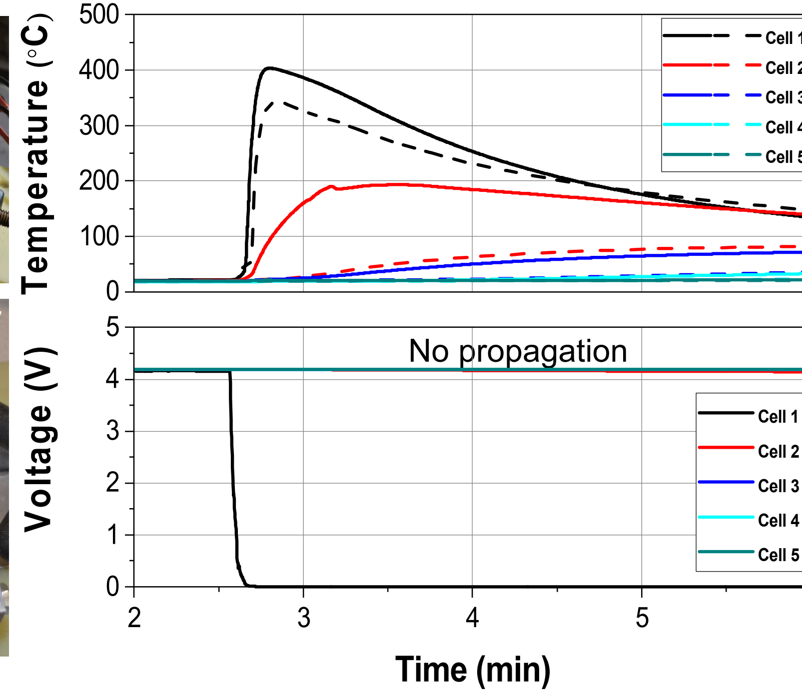
Failures initiated by mechanical insult to edge cell of COTS $LiCoO_2$ packs

$LiCoO_2$ – 1/16" thick spacers





$LiCoO_2$ – 1/8" thick spacers

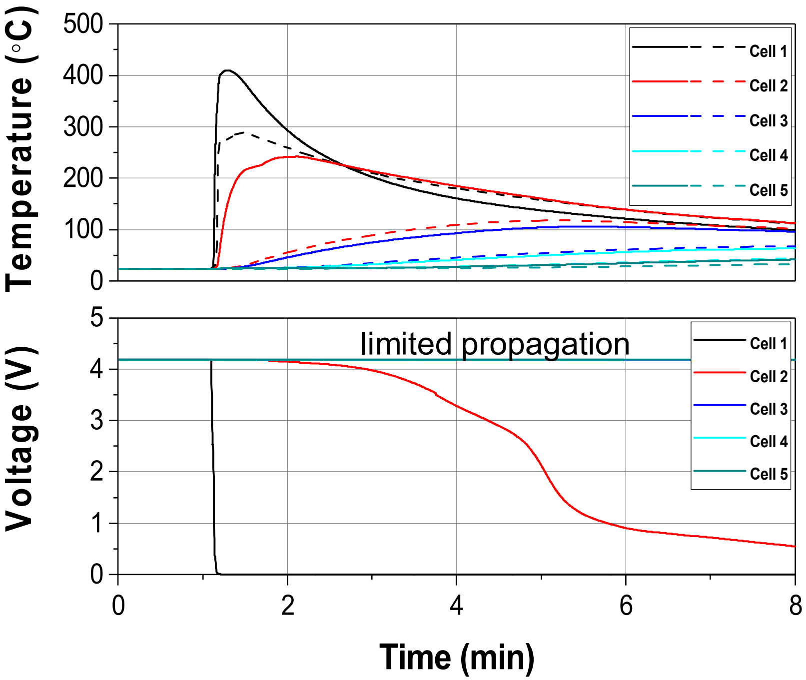


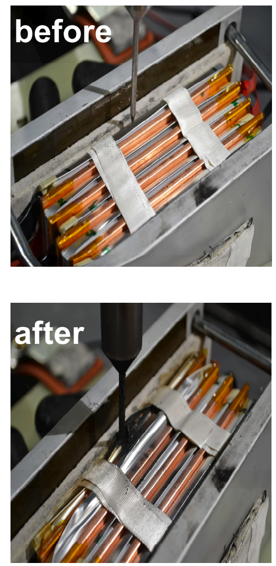
- ***Addition of aluminum spacers cut to the size of 3 Ah COTS cells was achieved***
- ***Failure of cell 1 in both cases were consistent and peak temperatures reached ~400 °C***
- ***Limited propagation (from cell 1 to 2) occurred with the thinner material (1/16")***
- ***No propagation was realized when space thickness was increased to 1/8"***

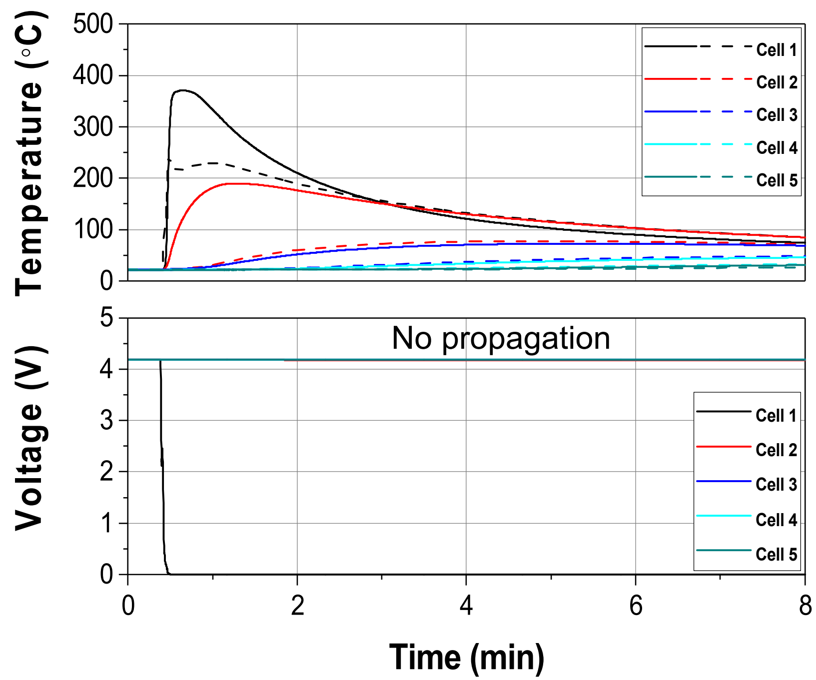
Failure Propagation: Copper spacer

Failures initiated by mechanical insult to edge cell of COTS $LiCoO_2$ packs

$LiCoO_2$ – 1/16" thick spacers	***$LiCoO_2$ – 1/8" thick spacers***

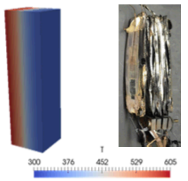




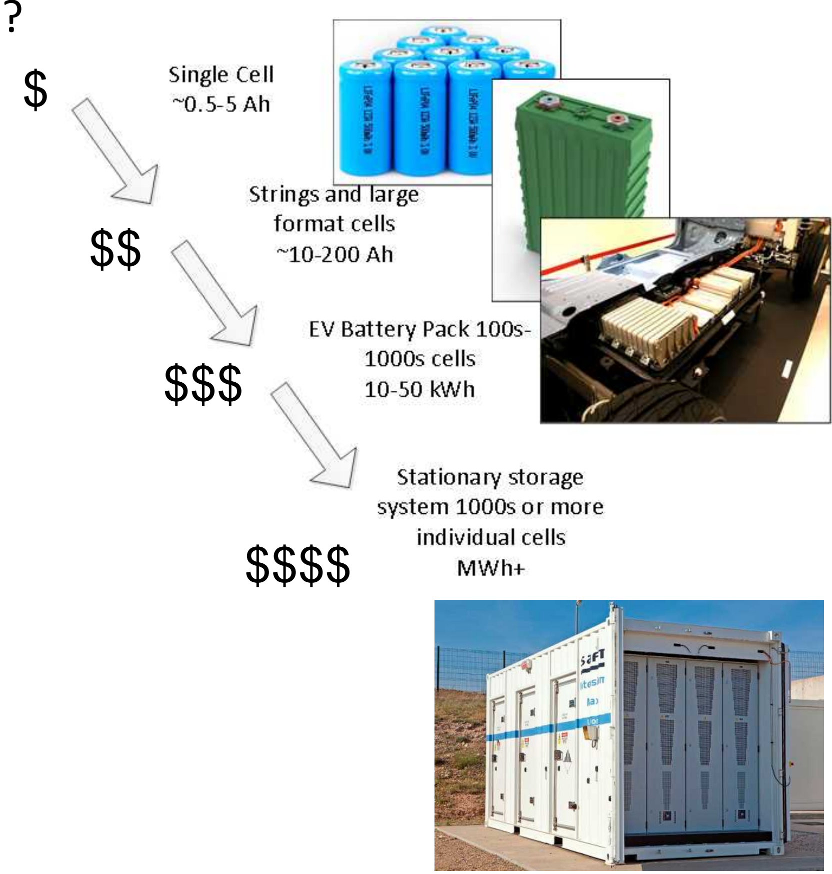


- *Addition of copper spacers cut to the size of 3 Ah COTS cells was achieved for comparisons of spacer size and material (Al vs Cu)*
- *Failure of cell 1 in all cases were consistent and peak temperatures reached ~400 °C*
- *Limited propagation (from cell 1 to 2) occurred with the thinner material (1/16")*
- *No propagation was realized when space thickness was increased to 1/8"*

Models with testing mitigate safety risks

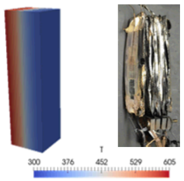


- How bad can a Li-Ion battery fire be at grid storage scale?
- Will a single cell in runaway cause cascading failure?
- Cost of safety testing increases with scale
- Models complement test programs

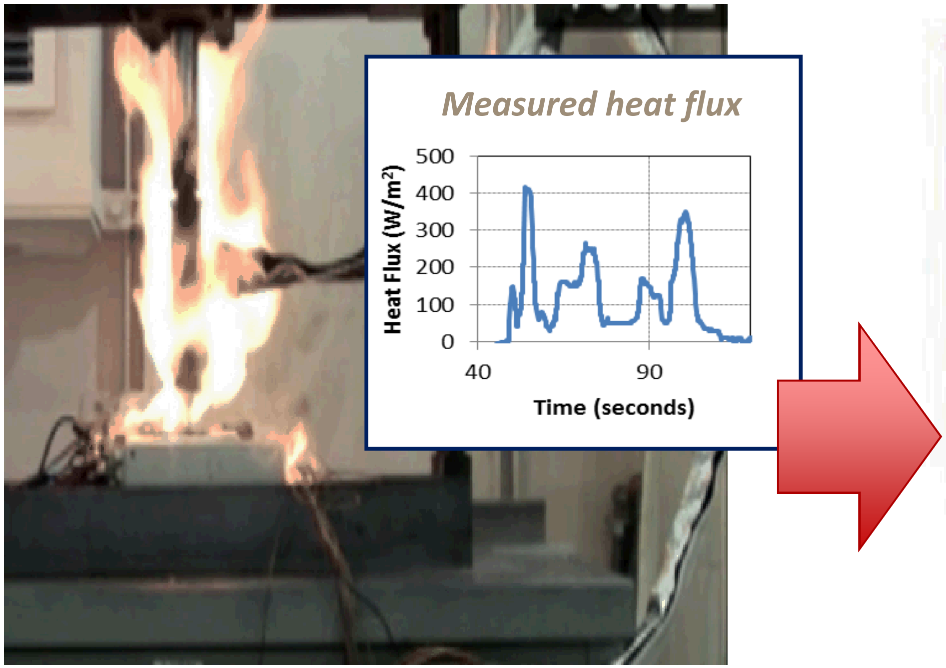


www.cnn.com www.nissan.com
www.samsung.com www.saft.com
www.internationalbattery.com

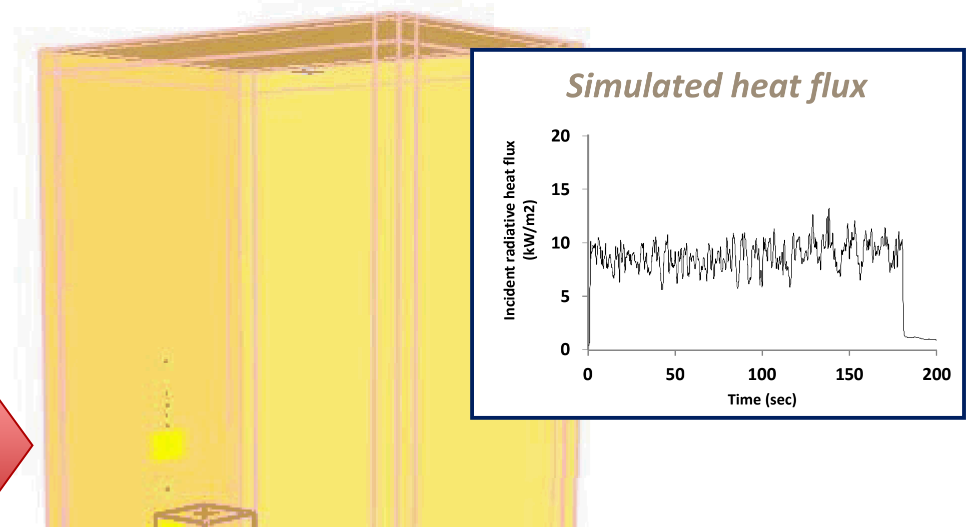
Quantifying battery fires

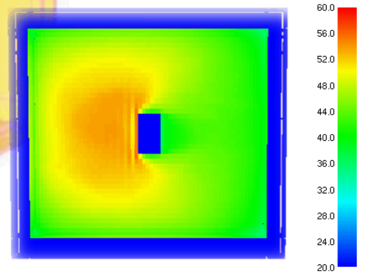


Experimental Data from Battery Fires



Fire Dynamic Simulations (FDS) of Battery Fires

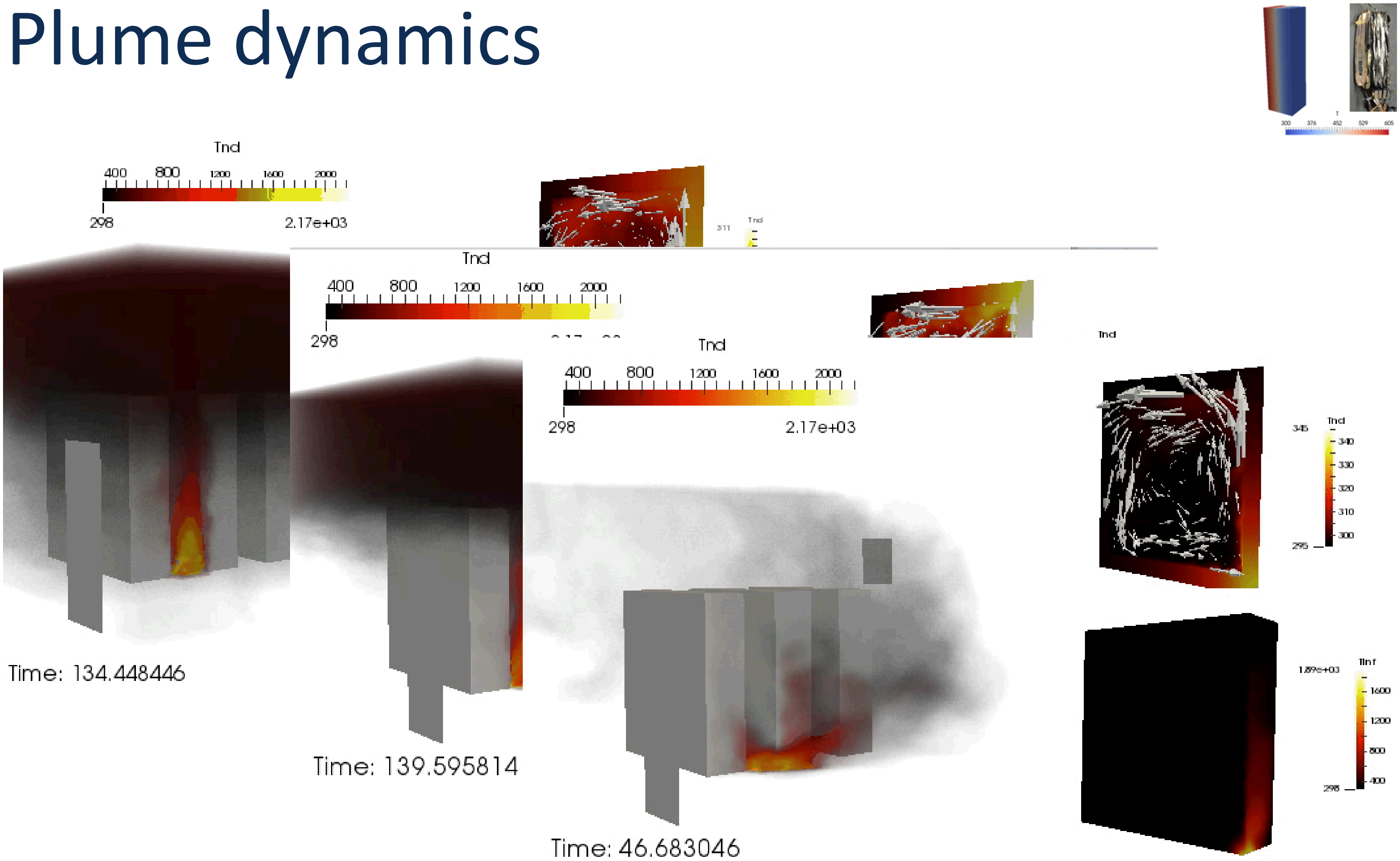




Test bay ceiling temperature

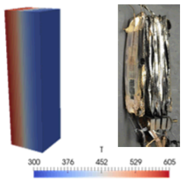
- Scale up experiments to **validate FDS models** (Wh → kWh → MWh)
  - Feedback to **design** storage systems
  - Inform **fire suppression** system design

Plume dynamics



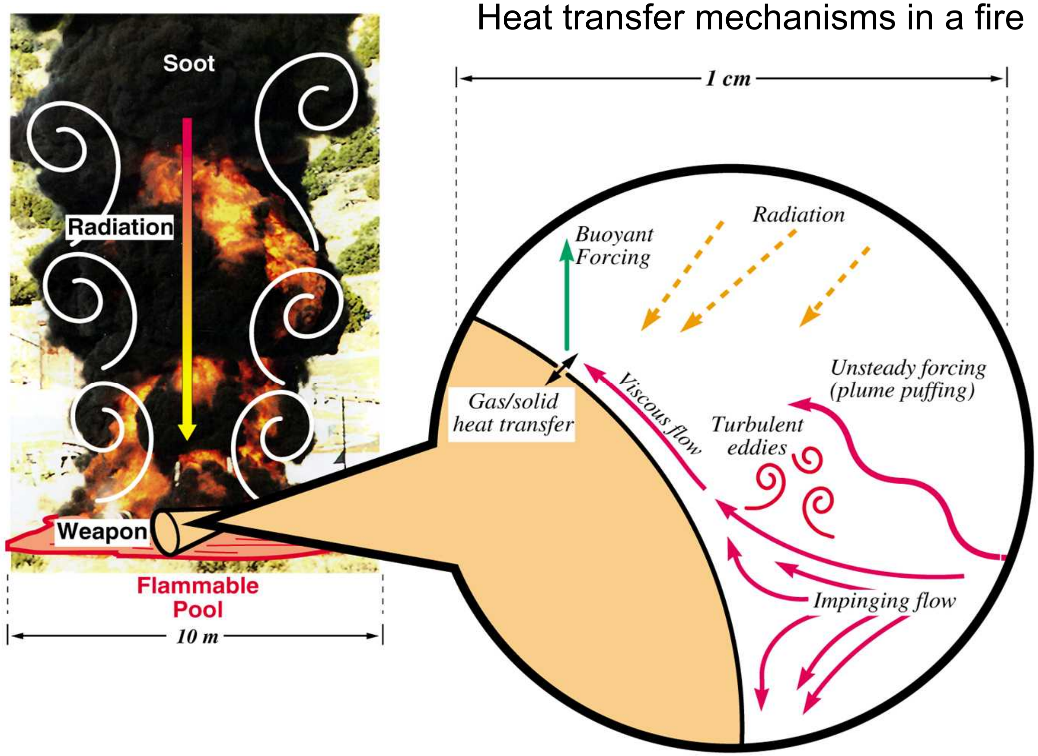
Three ventilation comparison still shot

Sandia tools suitable for battery safety analysis

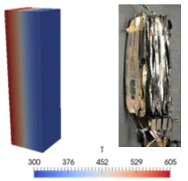


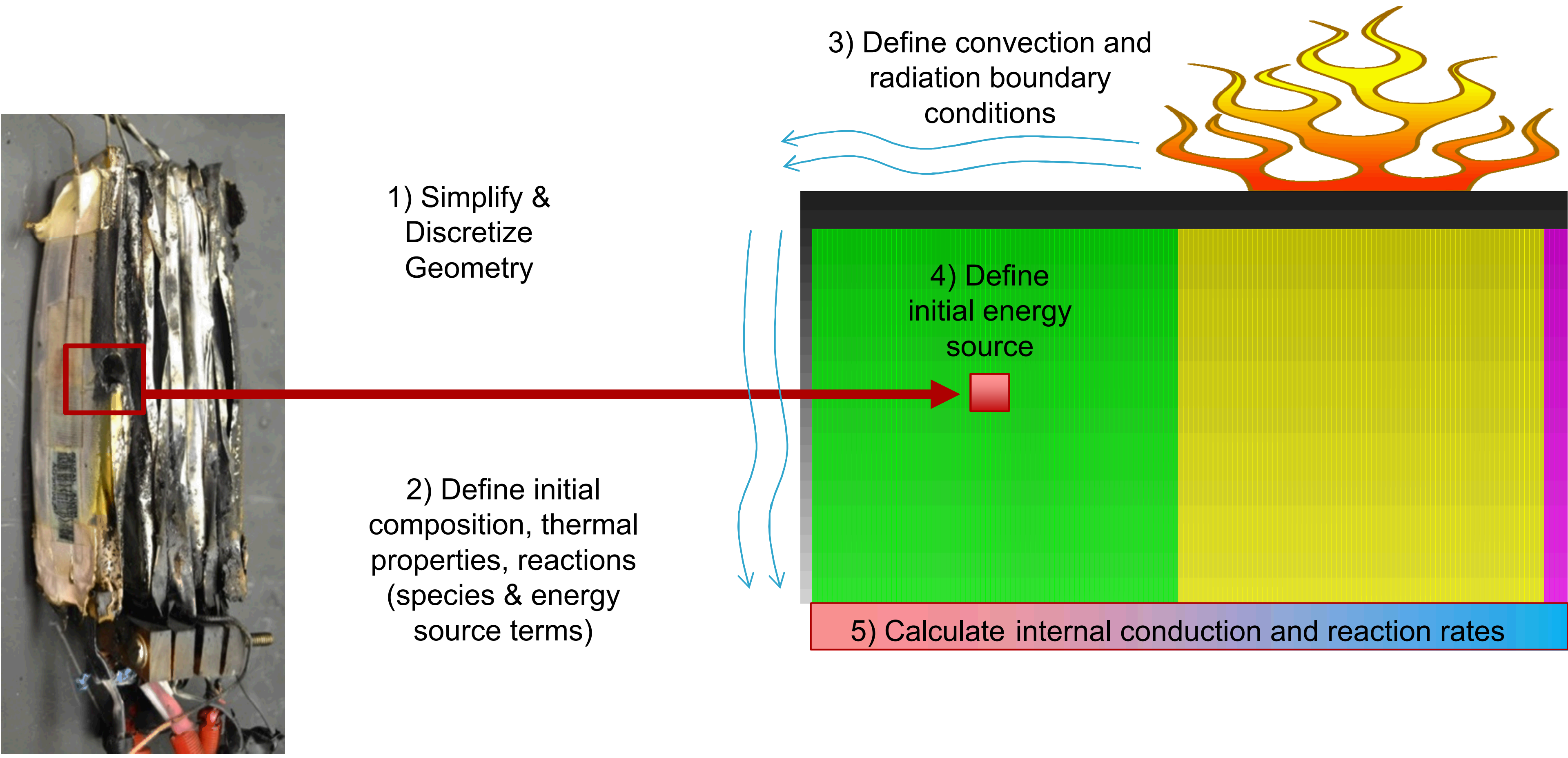
- Sierra-Mechanics integrated simulation tools developed at Sandia
  - Original purposes included safety analysis of weapons in fire scenarios
  - Product of DOE-NNSA investments via Advanced Scientific Computing (ASC) program
- Charged batteries include both ‘fuel’ and ‘oxidizer’ internally
  - Similar to energetic materials such as rocket propellants

Heat transfer mechanisms in a fire

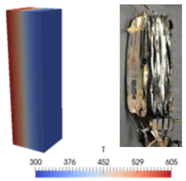


Thermal runaway model design



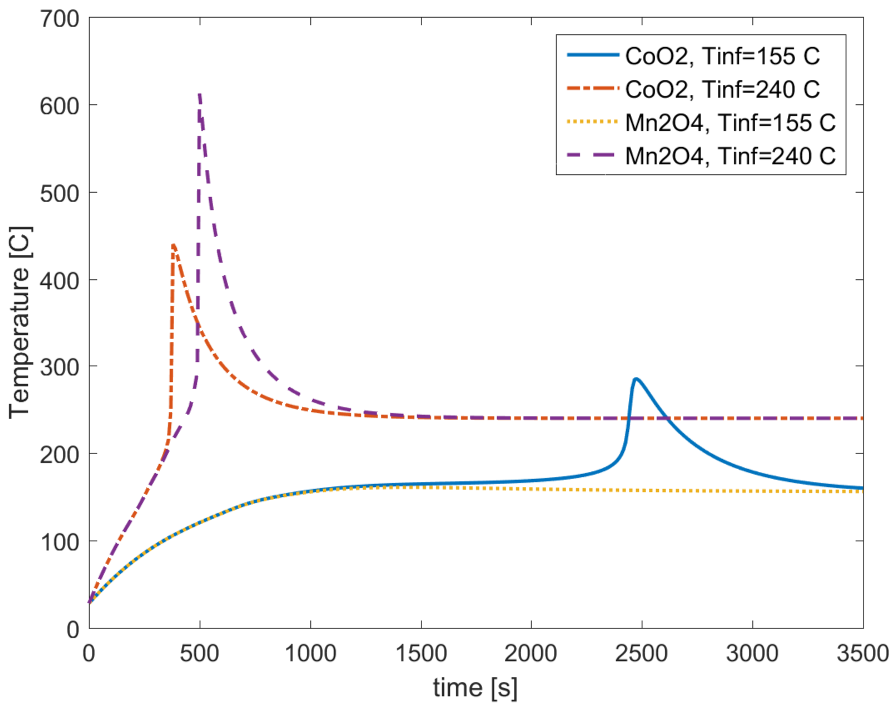


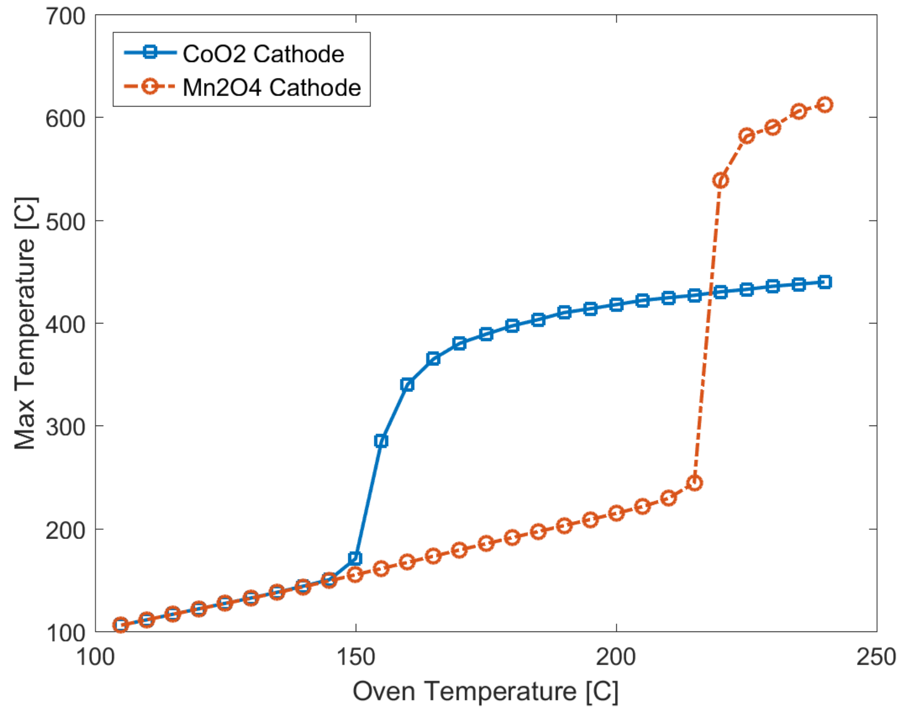
Cathode chemistry drives cell failure



Simulated oven tests for 18650 cells

2 cathode materials, 2 temperatures

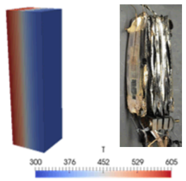


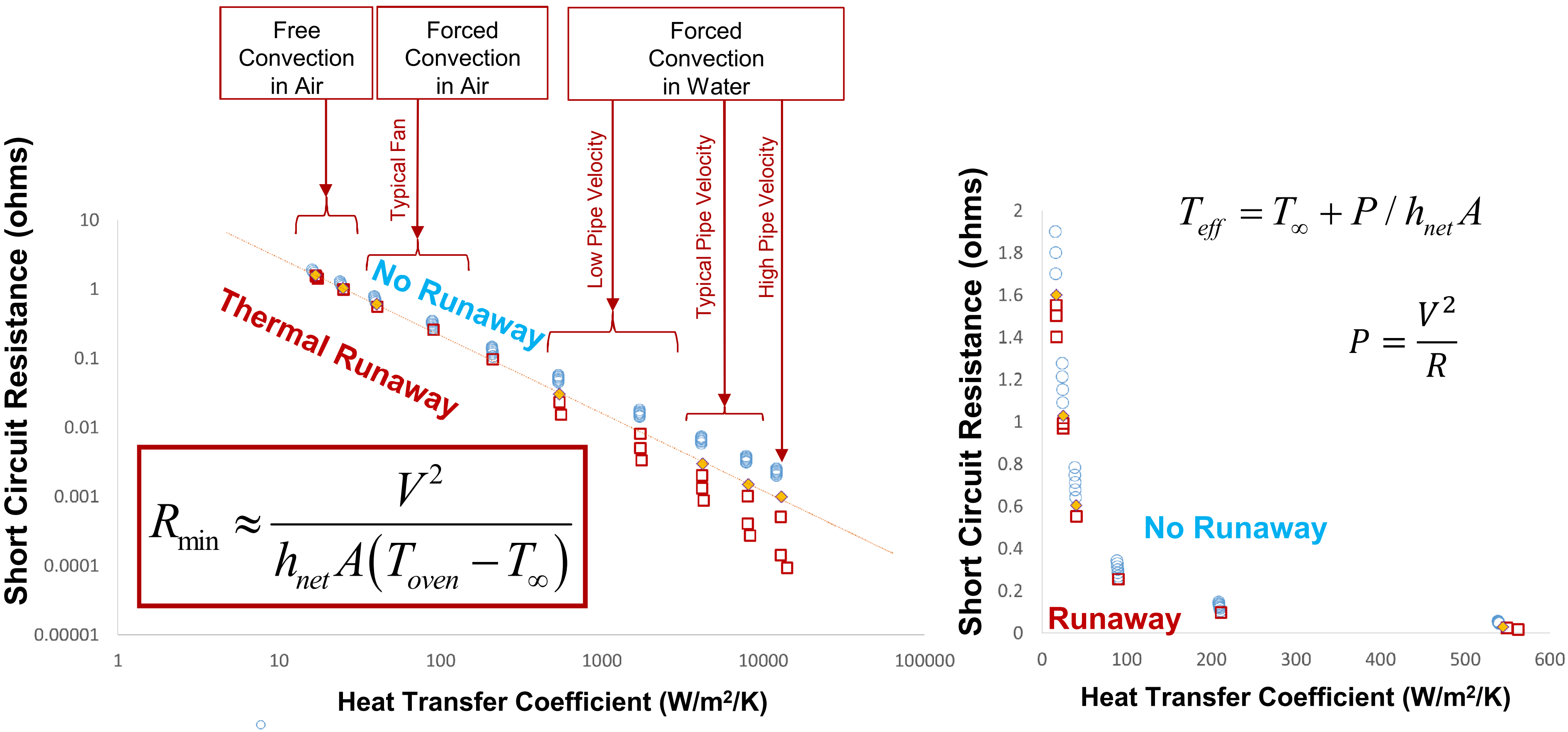


- Differences in cathode chemistry must be understood and quantified to predict thermal runaway of single cells

$LiCoO_2$ model from Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society 148(7): A755-A761.
$LiMn_2O_4$ model from Spotnitz, R. and J. Franklin (2003). Journal of Power Sources **113**(1): 81-100.

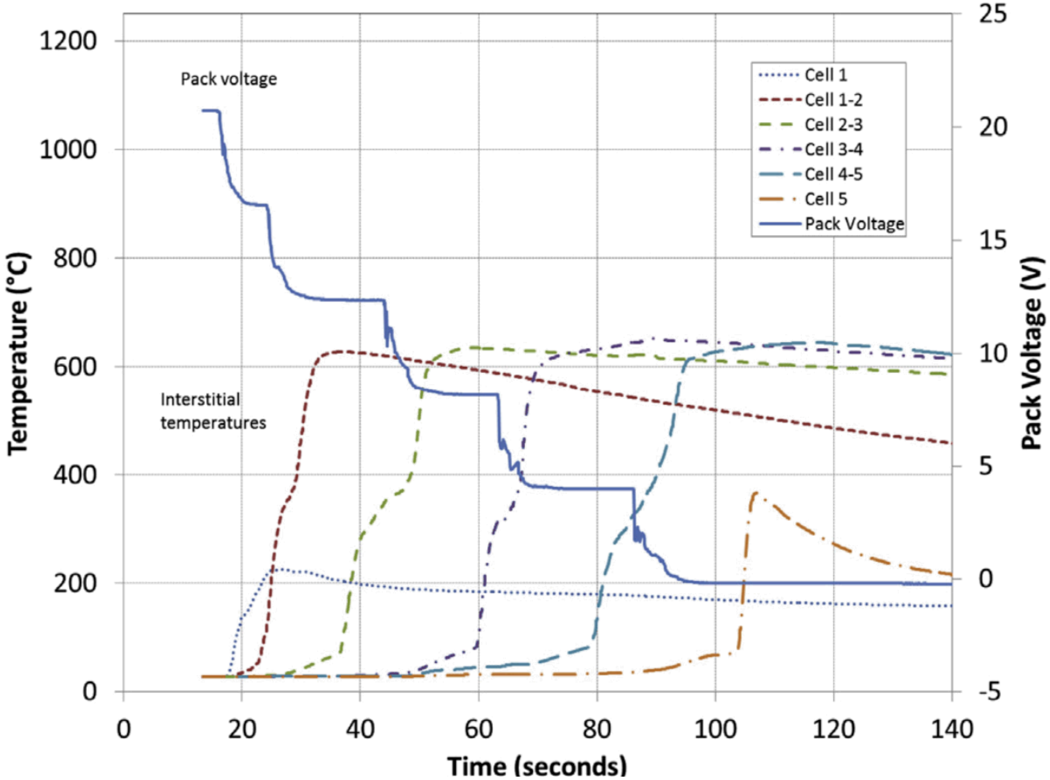
Cooling needed to suppress runaway

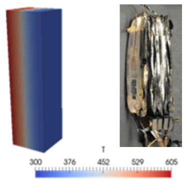


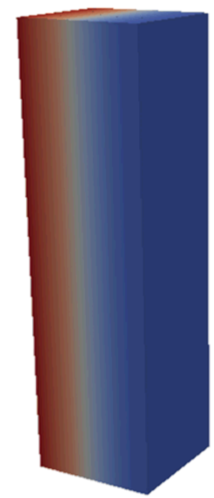


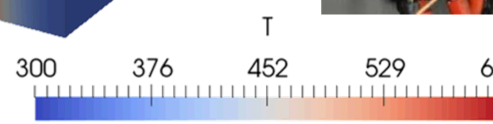
- Models can be used to estimate cooling requirements
  - Simulation shows homogeneous heating of 18650 cells (varying short resistance and cooling)
  - Internal temperature variation will be worse for large format systems and localized shorts

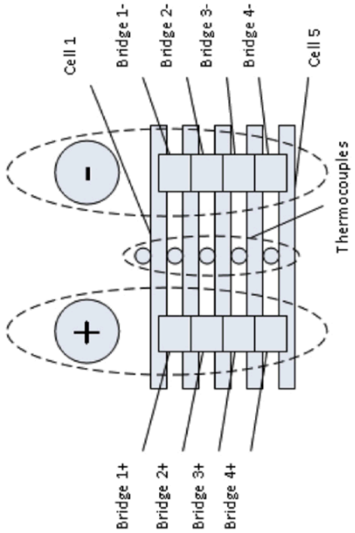
Cascading Propagation Observed in Li-Ion Packs





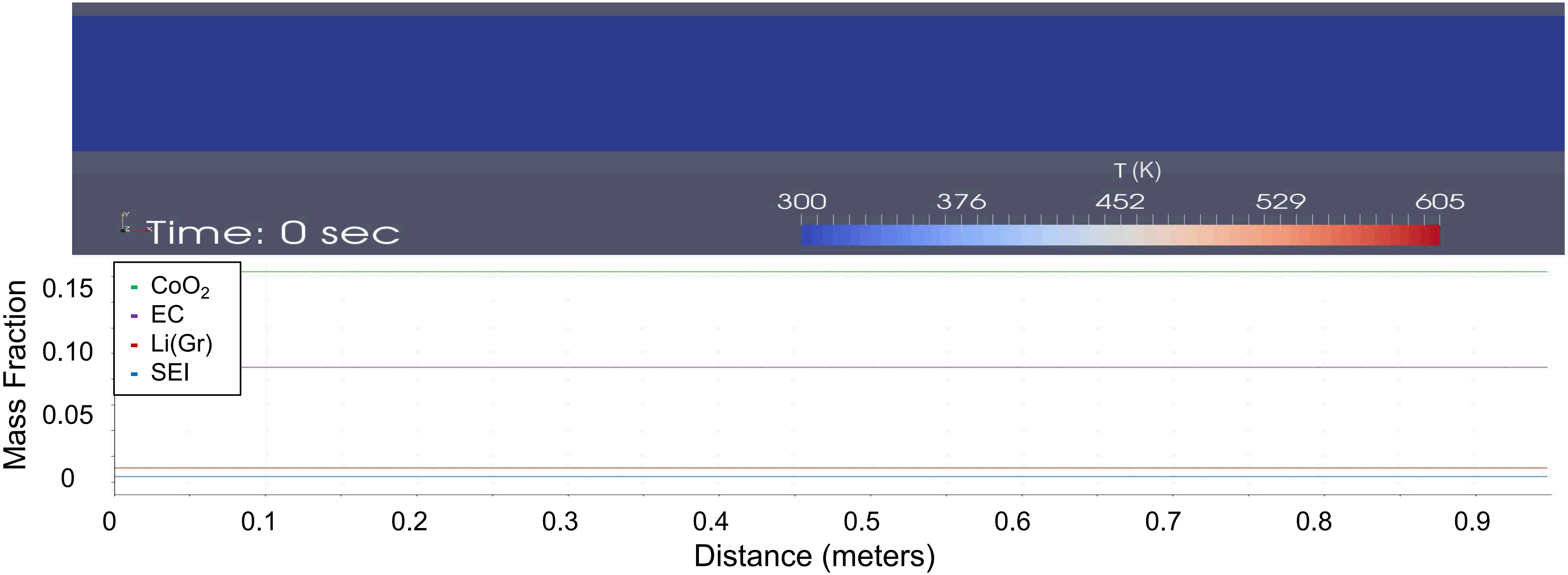




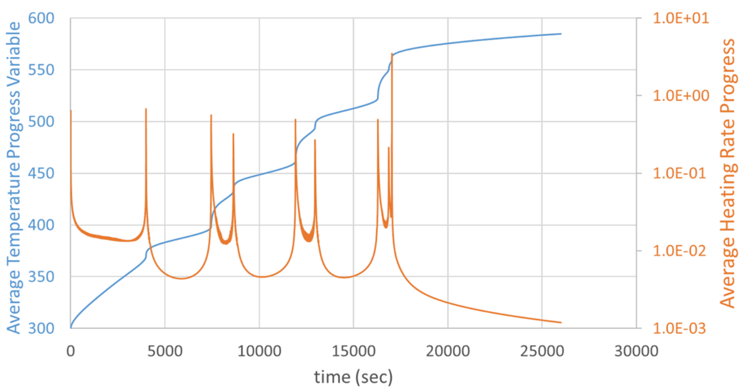


- Experimental propagation in 5 stacked pouch cells at Sandia
- Investigating effects of
  - State of charge
  - Intermediate layers
  - Cell geometry
- Good pack-scale model validation cases

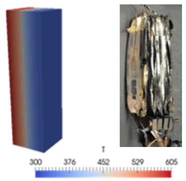
Pulsation at Large Scales Can Obscure Continuing Propagation



- 1st responders may incorrectly assume battery fire is extinguished during slow periods
  - Heating rate varies by 100x (note log scale)
  - Simulation shown requires 5+ hours to propagate
    - Model extended to large scales (128 cells, ~1 meter) at small cost relative to measurements
- Slow periods are best opportunity for cooling

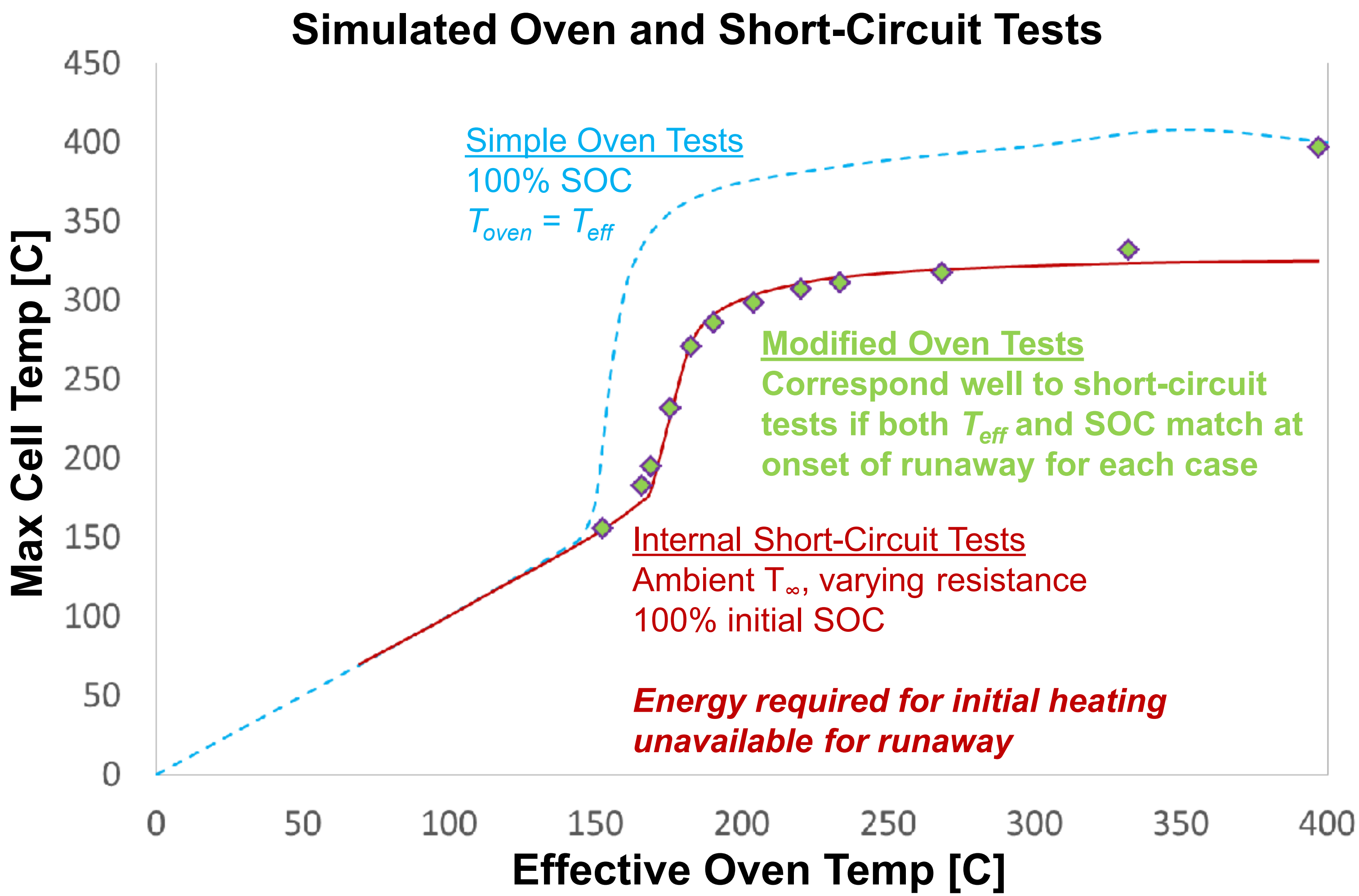


Are different heat sources analogous?

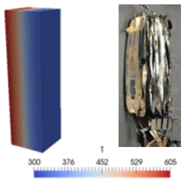


Energy balance on a cell yields:

$$T_{eff} = T_\infty + P / h_{net} A \qquad P = \frac{V^2}{R} \qquad h_{net} = h + h_{rad} = h + \varepsilon\sigma\left(T_w^2 + T_\infty^2\right)\left(T_w + T_\infty\right)$$



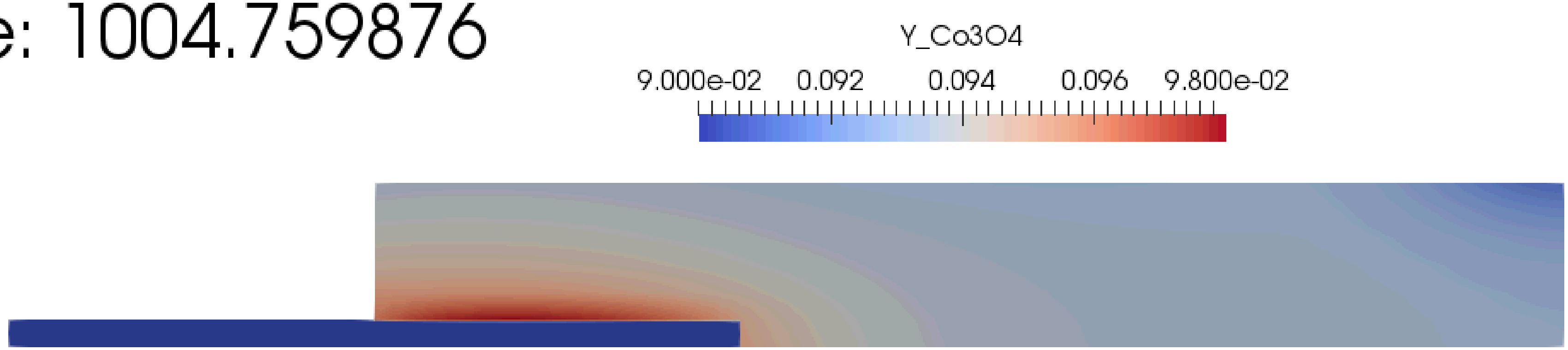
Heat Transfer Limits Thermal Reactions



R = 1.4 ohm, h = 7 W/m^2/K, Meshed 18650 with 50% heat release in nail

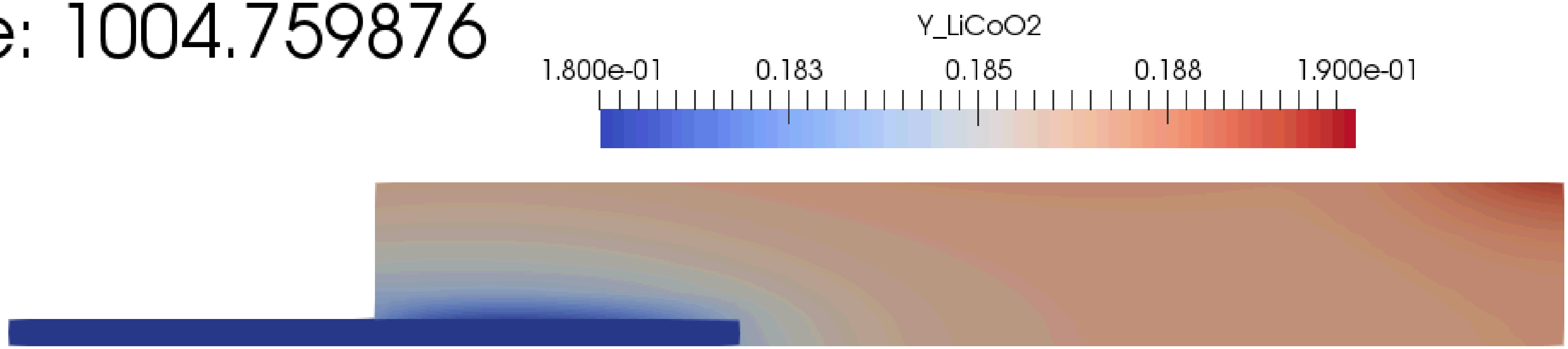
Time: 1004.759876

Thermal Reaction Cathode Product

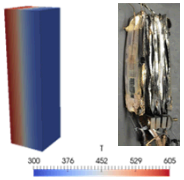


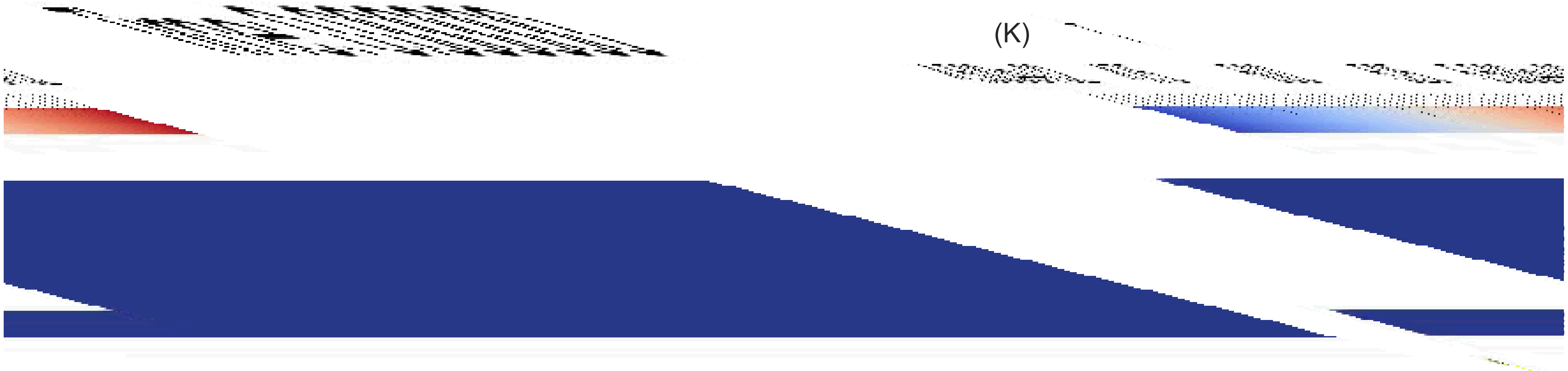
Short Circuit Cathode Product

Time: 1004.759876



Runaway in Meshed 18650 with Nail Less Pronounced than Lumped 18650





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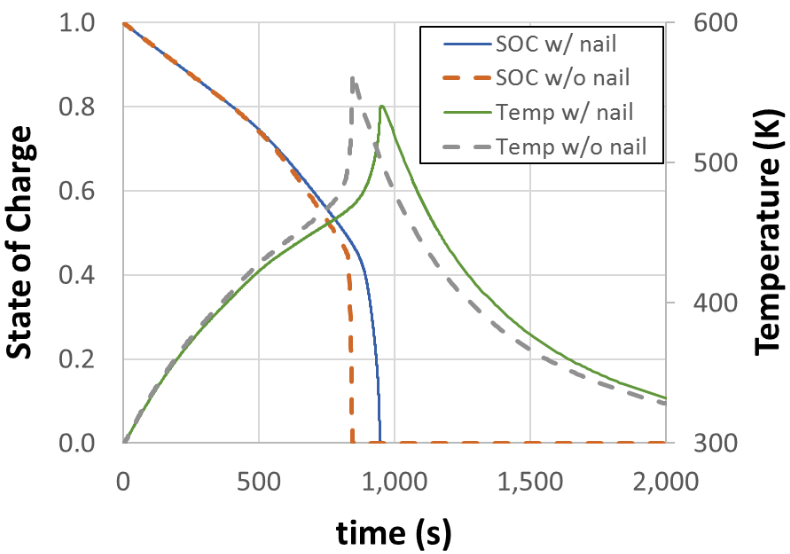
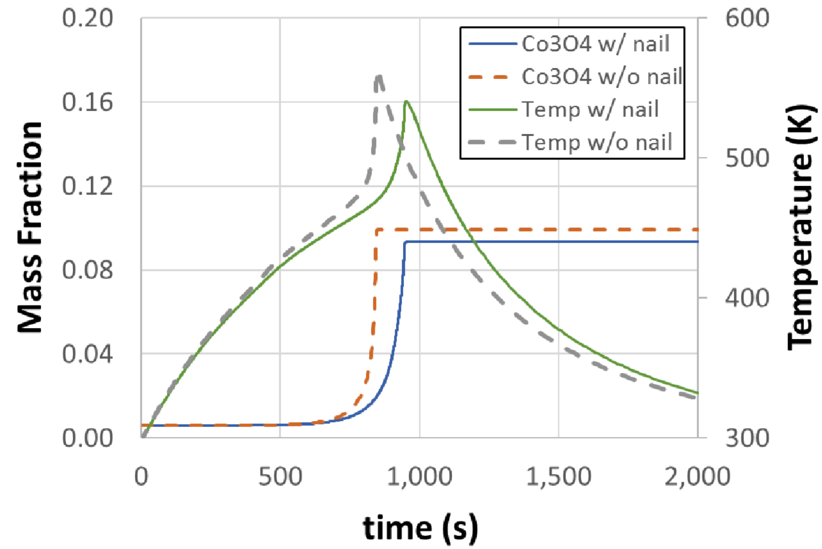
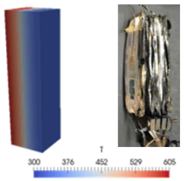
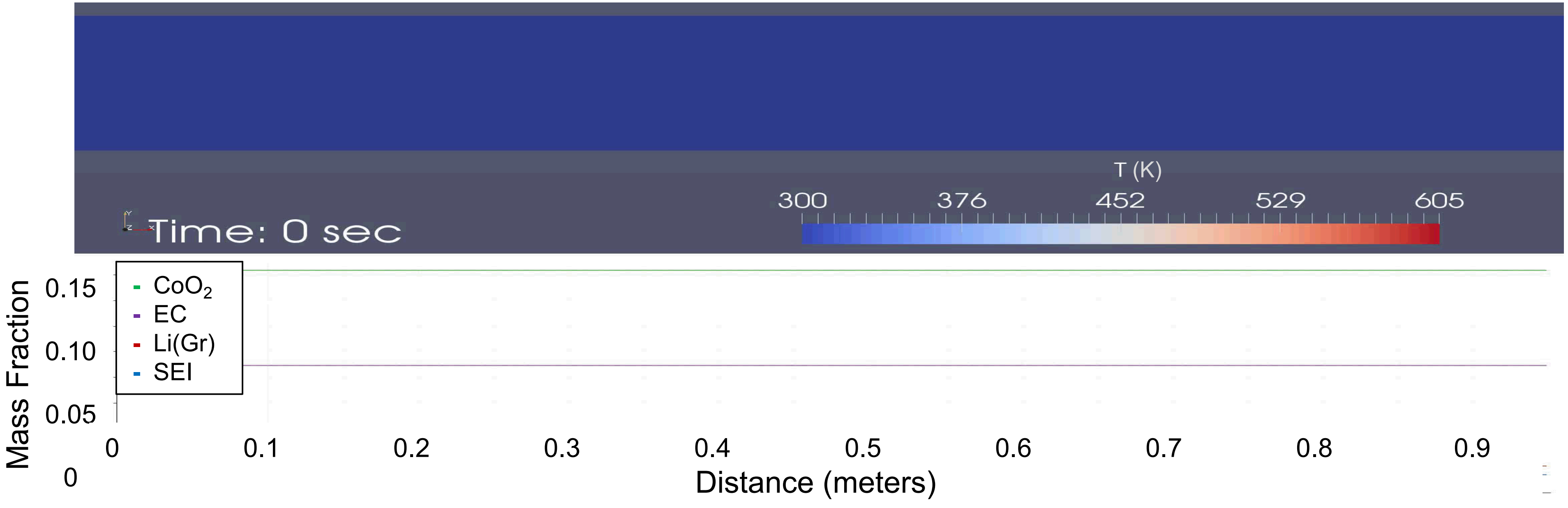




- Effects of inhomogeneity increase as scale increases beyond the lumped-capacitance regime

Pulsation at Large Scales Can Obscure Continuing Propagation





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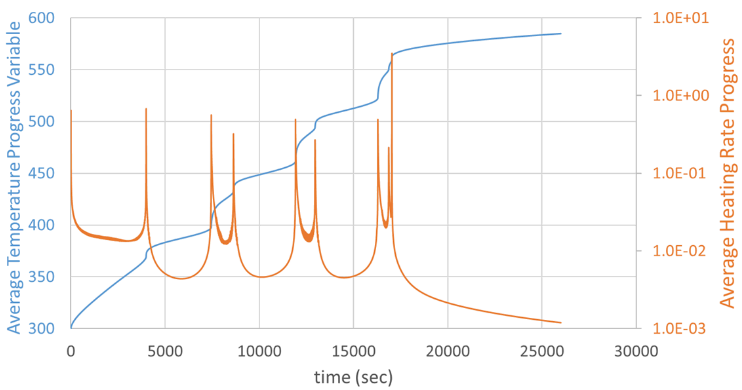
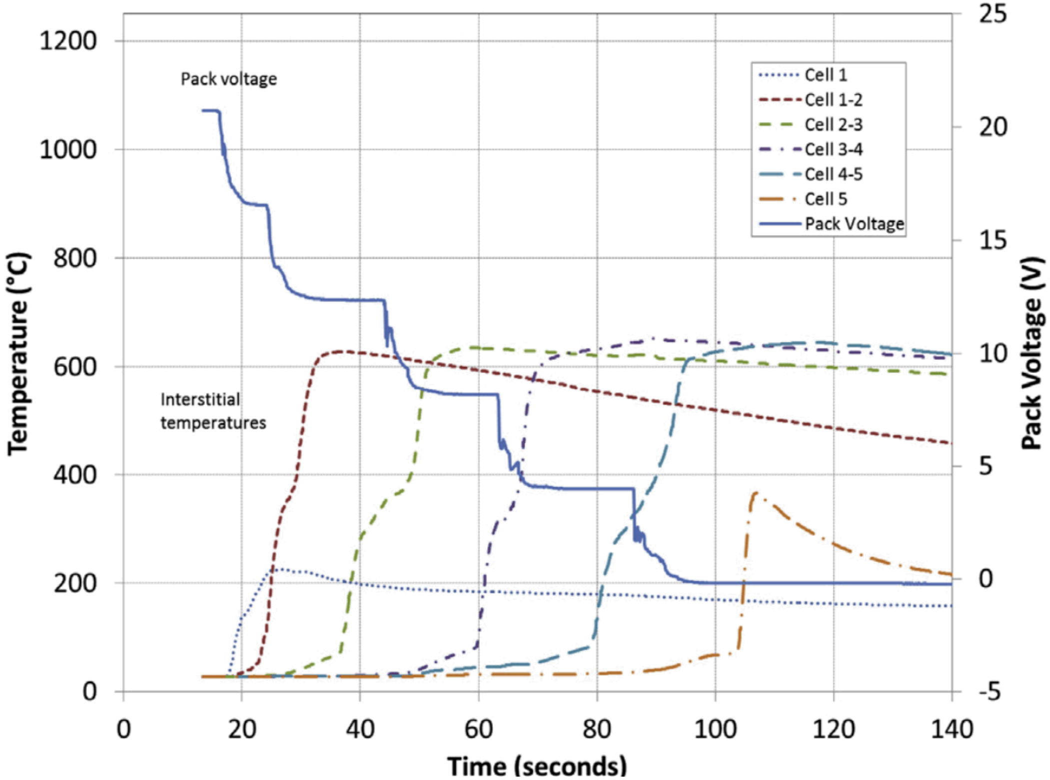
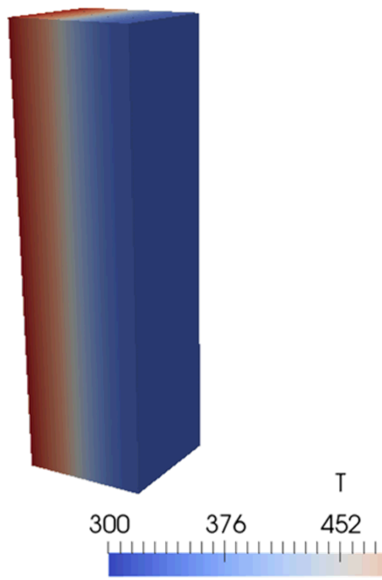
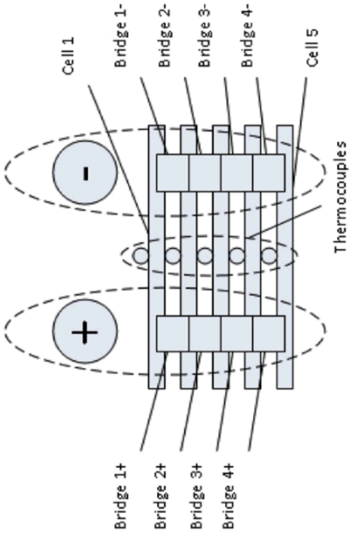


Cascading Propagation Observed in Li-Ion Packs

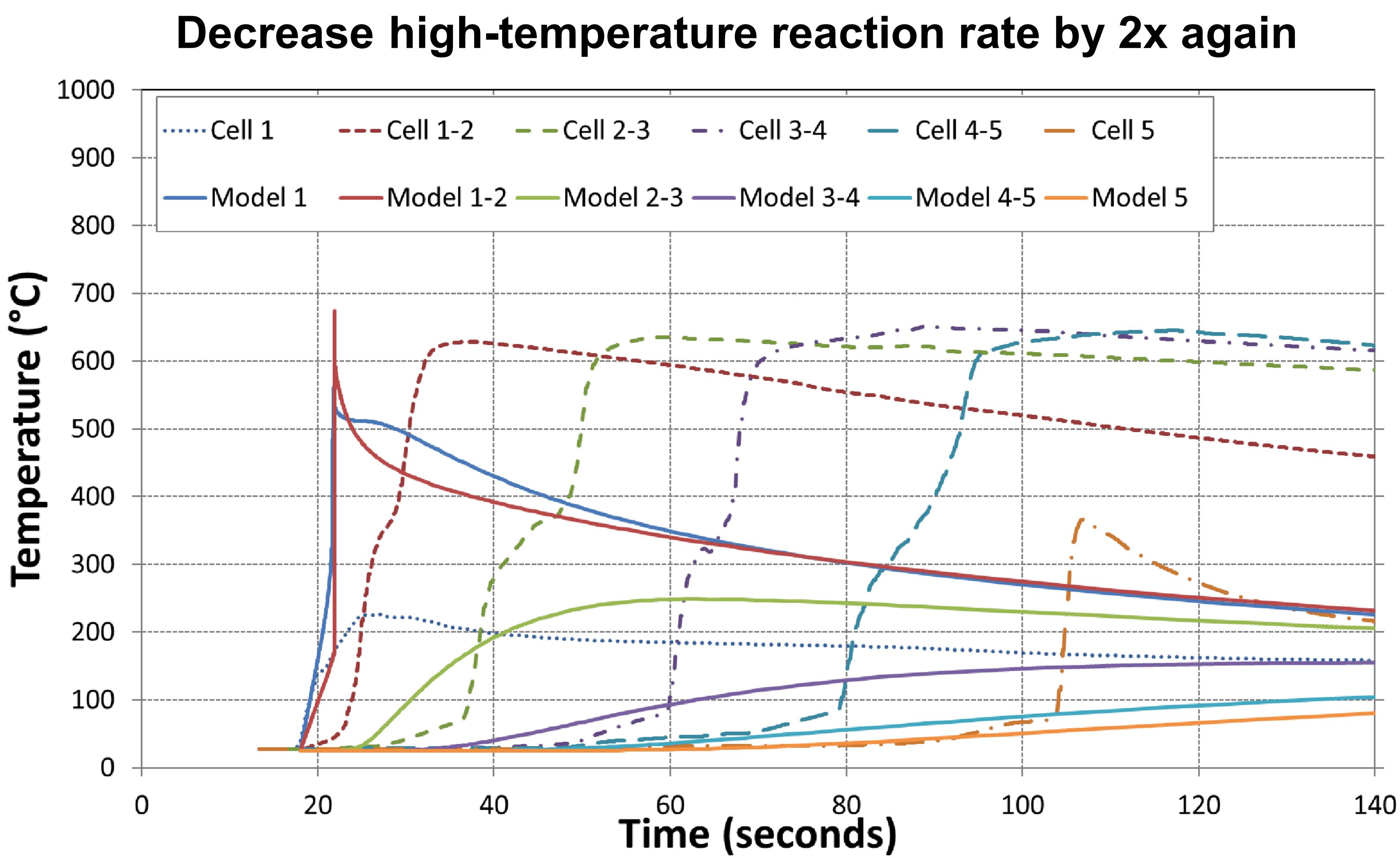






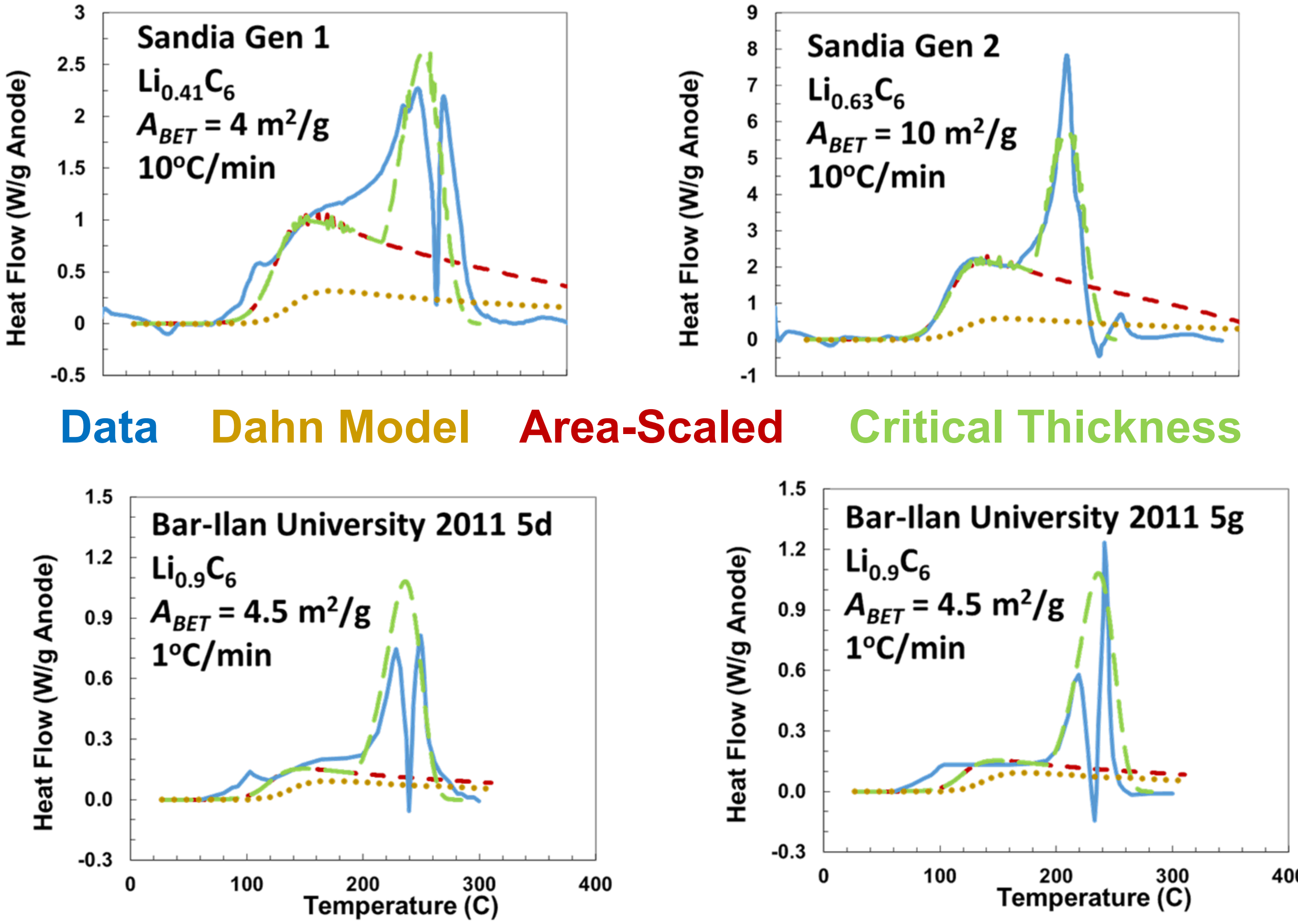
- Experimental propagation in 5 stacked pouch cells at Sandia
- Investigating effects of
  - State of charge
  - Intermediate layers
  - Cell geometry
- Good pack-scale model validation cases

High-Fidelity Models Required for Cascading Failure



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

Prior models had incomplete accounting of heat release



Data from Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

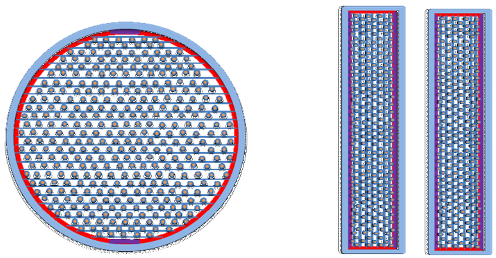
Key anode model improvements

Area-Scaled Model

- SEI Passivation layer inhibits lithium reduction of electrolyte, exp(-z).
- H_{rxn} thermodynamically consistent with $2LiC_6 + EC \rightarrow 2C_6 + C_2H_4 + Li_2CO_3$

$$\frac{dz}{dt} \propto \frac{A_{rxn,ref}}{A_{rxn}} \approx \left(\frac{A_{BET,ref}}{A_{BET}}\right)^{n_1}, n_1 < 1$$

- Reaction scales with effective surface area.



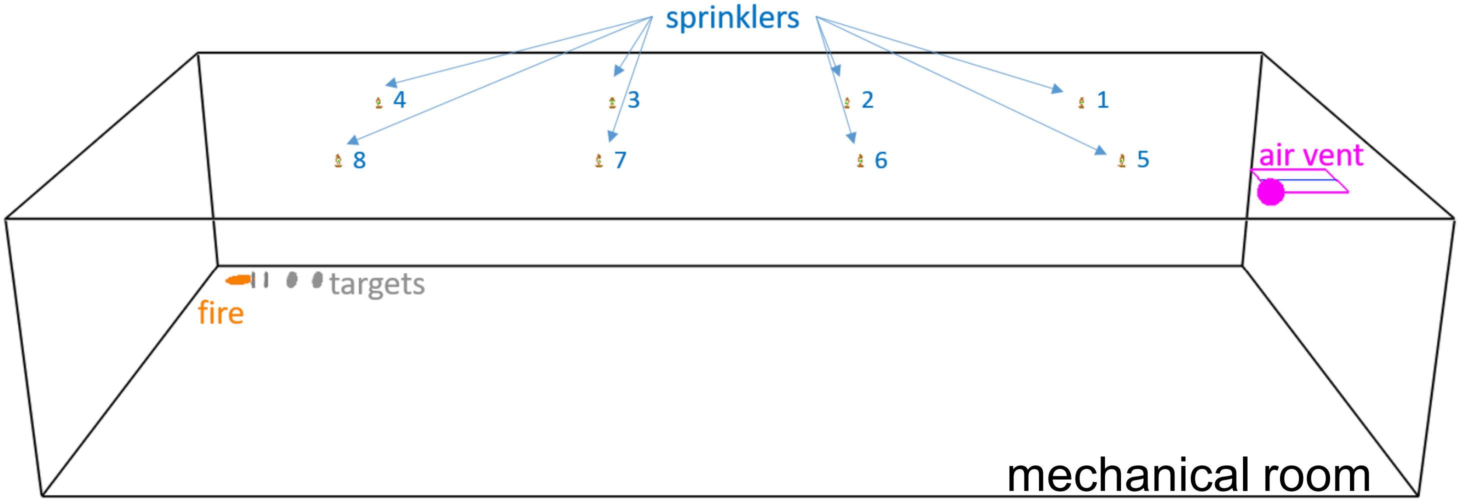
= Graphite Basal Planes (smooth)
= Graphite Edges (rough)
= SEI Layer

$$z = min(z, z_{crit}) \quad \text{where} \quad z_{crit} \propto x_{sei,crit}\left[\frac{A_{BET}}{A_{BET,ref}}\right]^{n_2}$$

Critical Effective Layer Thickness

- Limit to passivation layer growth with heating.
  - Endothermic defoliation (or other process) observed. Fracture, cracking?
  - Defects in SEI more likely on on edges.

Batteries in buildings need to be controlled by sprinkler systems

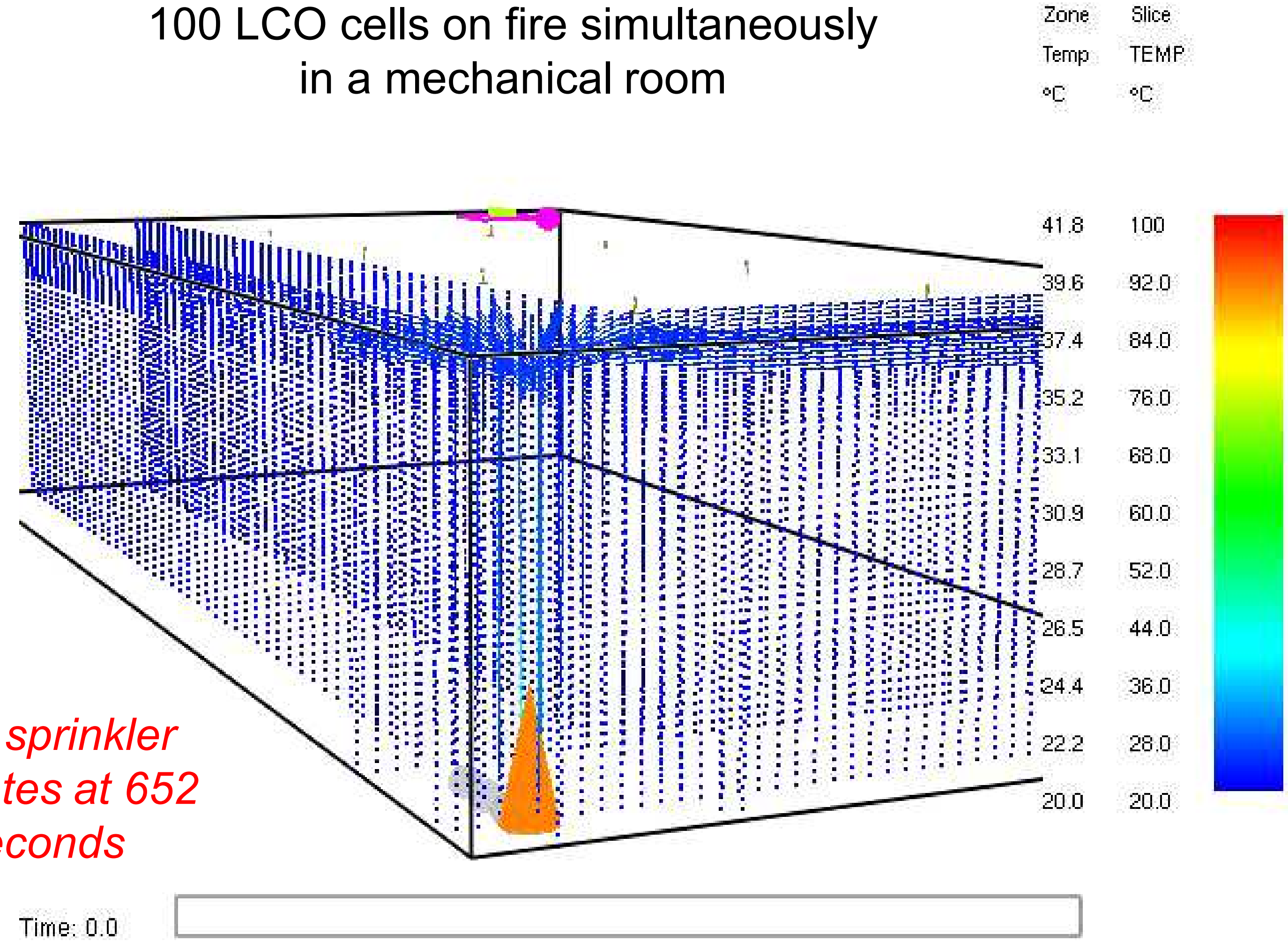


Sprinkler systems are designed to control the fire until firefighters can arrive.

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

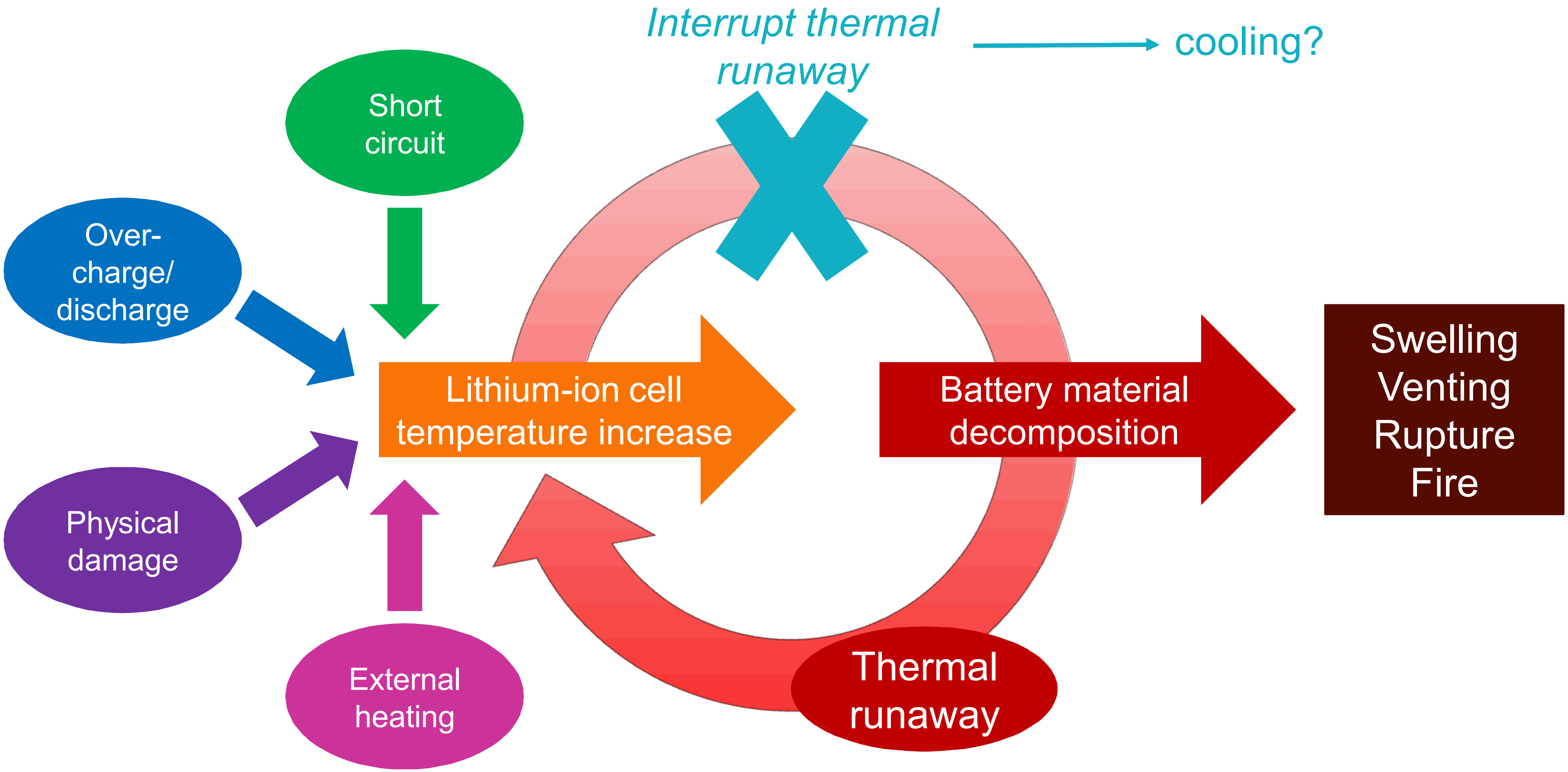
Rapid sprinkler response can control small battery fires

100 LCO cells on fire simultaneously in a mechanical room

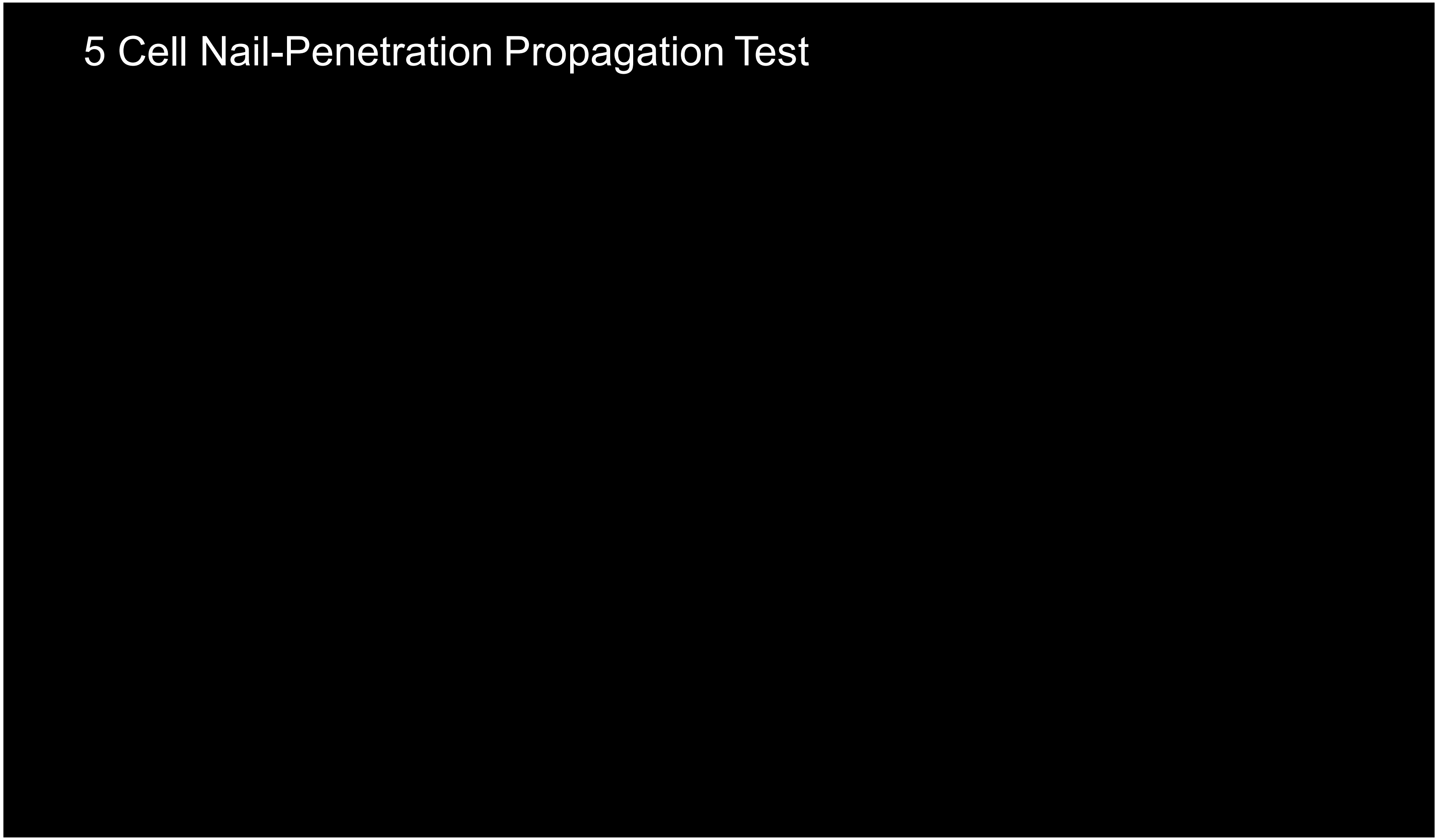


One sprinkler activates at 652 seconds

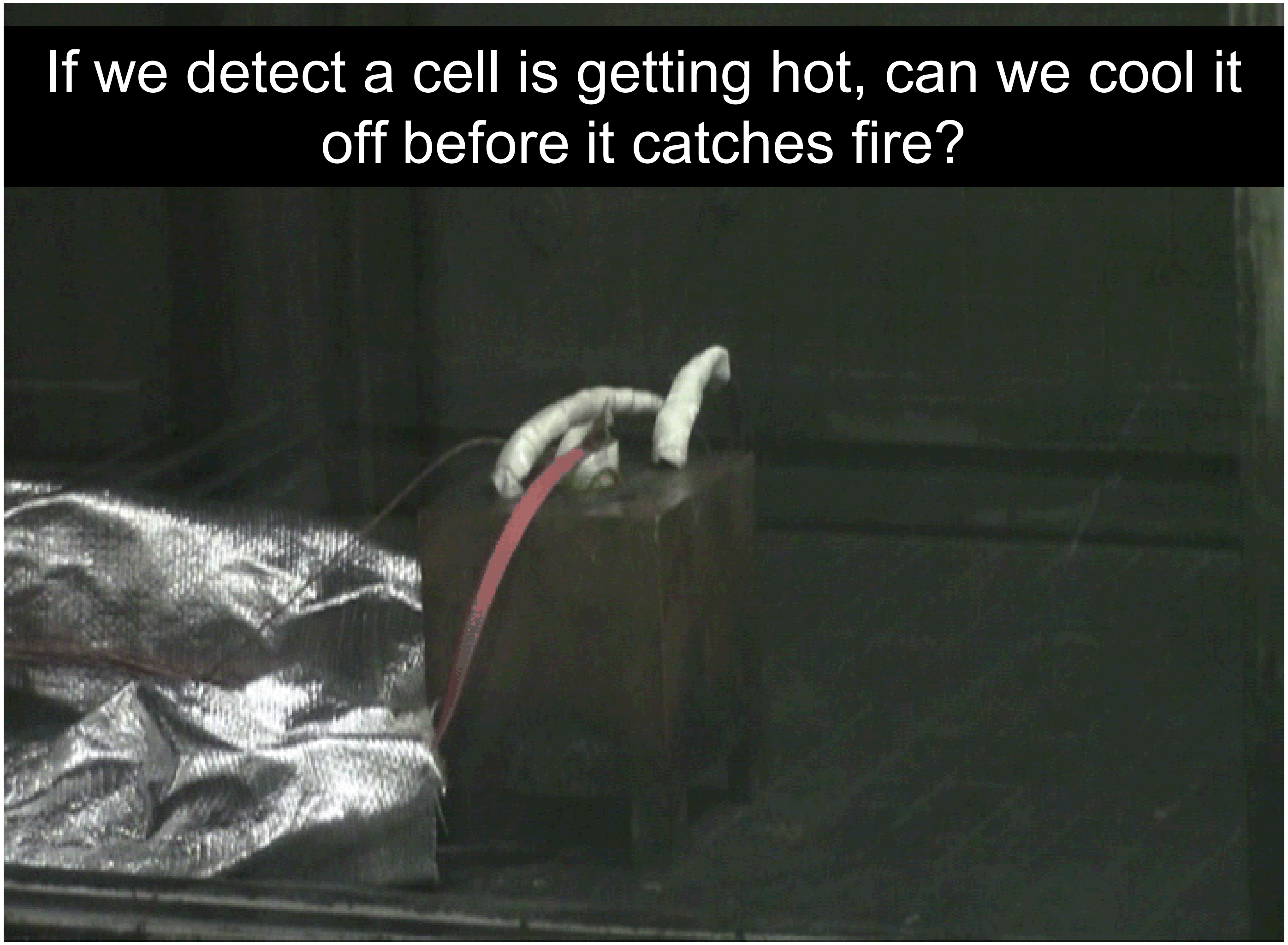
Can we prevent a battery fire?



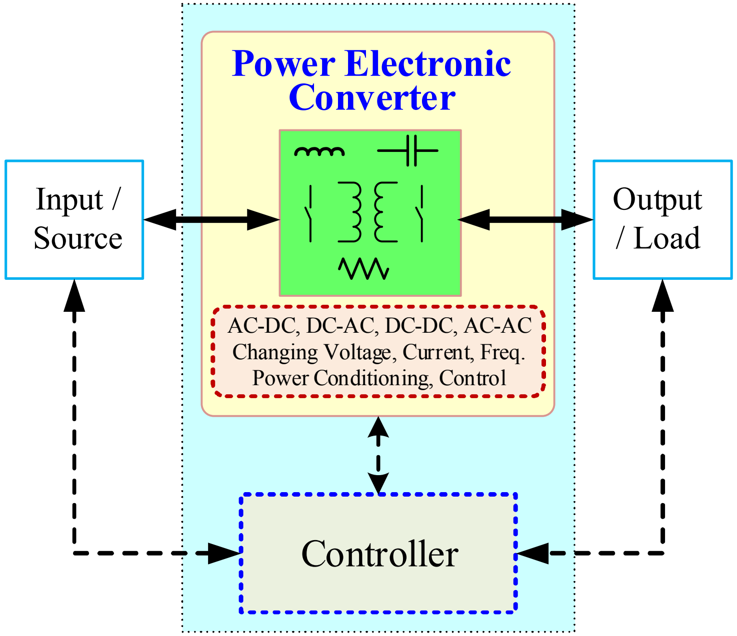
Failure in one battery can take out a whole pack/system

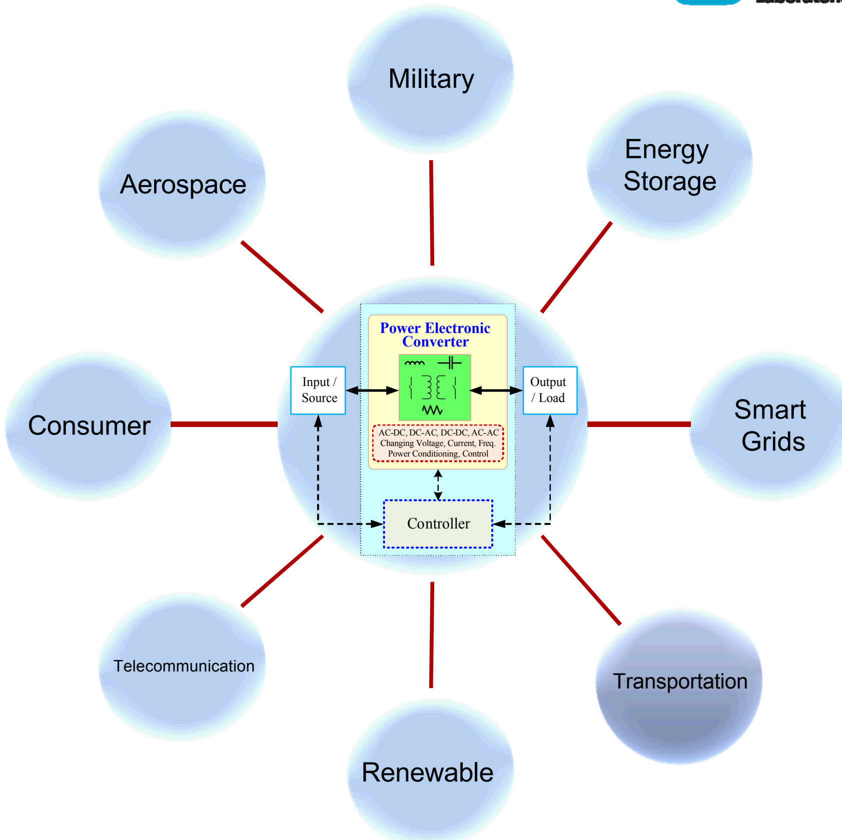


LCO thermal runaway critical point



Power Electronics





- Power Electronics is an enabling technology;
- It synthesizes, processes, converts, conditions and controls the power flow;
- Approximately 30% of all electric power currently generated uses PE somewhere between the point of generation and distribution. By 2030, it is expected that 80% of all electric power will flow through PE.

OE Power Electronics Program

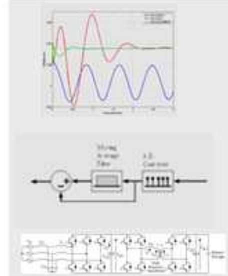
Materials R&D	Devices	Power Modules	Power Conversion System	Applications

Materials R&D
- Gate Oxide R&D
- Advanced Magnetics

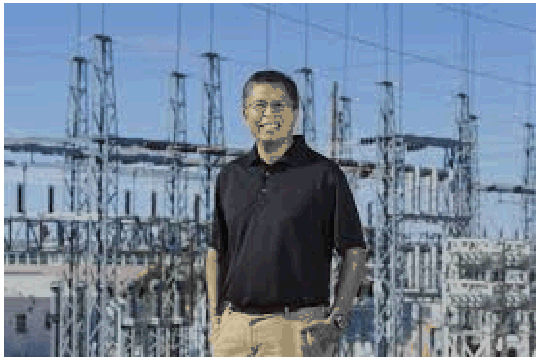
Devices
- ETO
- SiC Thyristors
- Monolithically integrated SiC transistors
- WBG Characterization & Reliability
- High energy dielectric capacitors

Power Modules
- SiC High Temp/density Power Module
- HV SiC JFET Module
- HV, HT Reworkable SiC half-bridge modules

Power Conversion System
- Dstatcom plus energy storage for wind energy
- Optically isolated MW Inverter
- High density inverter with integrated thermal management
- High temp power inverter



Applications
- FACTS and Energy Storage
- Power smoothing and control for renewables
- Dual active bridge for advanced energy storage system designs



- Led by Stan Atcitty
- Started 1998
- Five R&D 100 Awards
- Five US Patents, three pending
- Over 50 technical publications
- Power Electronics for Renewable & Distributed Energy Systems book

@ SNL Energy Storage PE Lab:

- High performance computing lab;
- Simulation Software (Matlab®/Simulink®, PLECS®, PSIM®;
- Hardware in the loop (HIL) forthcoming.

Grid Energy Storage Challenges

- Cost competitive storage technology - Life-cycle cost, efficiency, ED, cycle life, capacity fade etc.
  - Lack of understanding in ES cell performance in grid-level system,
  - Optimization and efficient coupling between electro-chemistry of storage medium and power electronics for grid interface,
- Validated reliability and **safety** – essential for user confidence;
- Equitable regulatory environment – reducing institutional and regulatory hurdles;
- Industry acceptance – industry should have confidence that storage will deploy as expected, and deliver as predicted and promised.

Source: Grid Energy Storage – U.S.DOE, December 2013

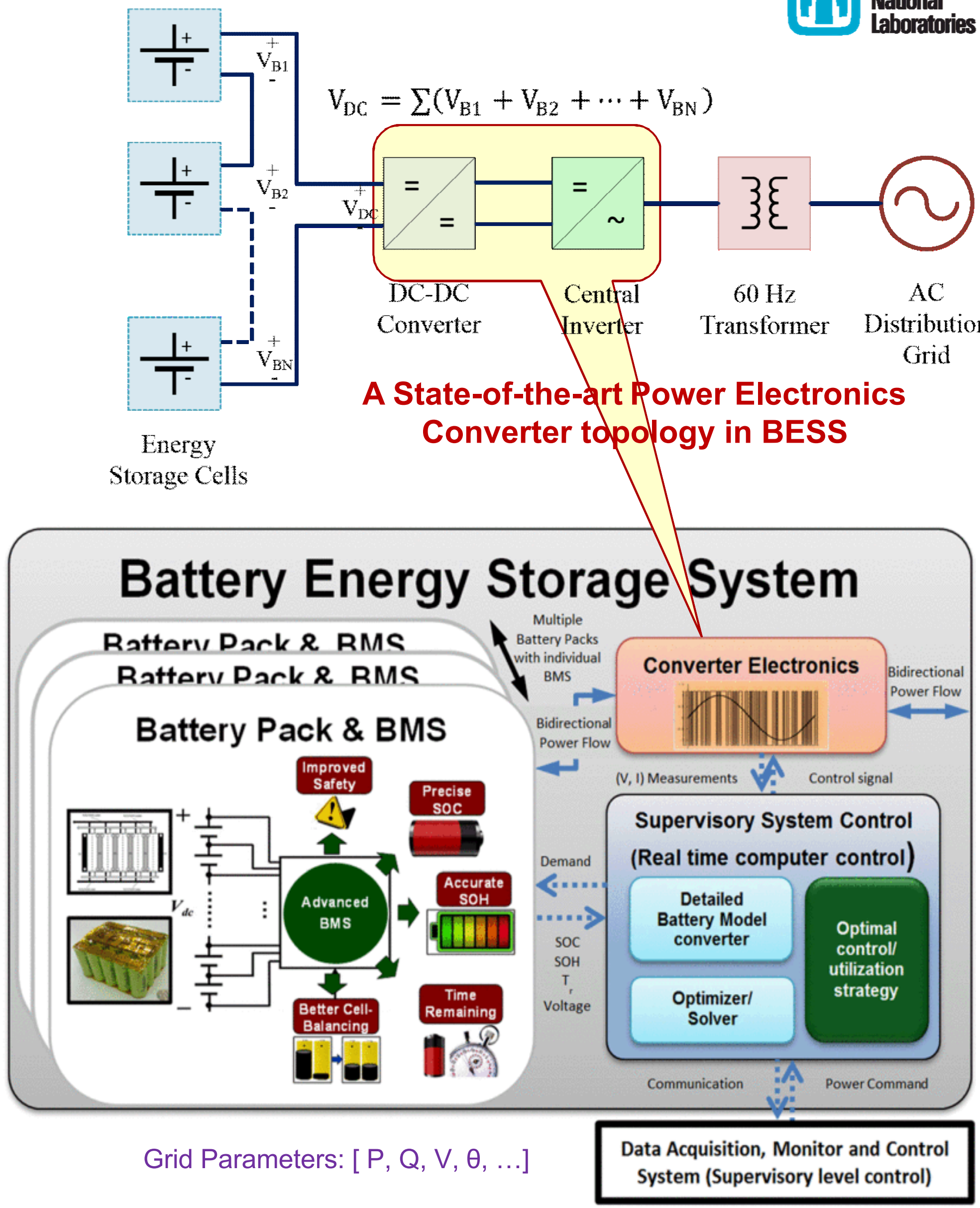
State-of-the-art PE Converters in ESS

▪

▪

▪

▪



BMS Image reproduced with permission from M.T.Lawder et al.

PE Research for ESS @ SNL (Org. 8811)

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Li-CoO_2 Batteries under testing condition
Photo Courtesy: Heather Barkholtz, SNL

What is Control?

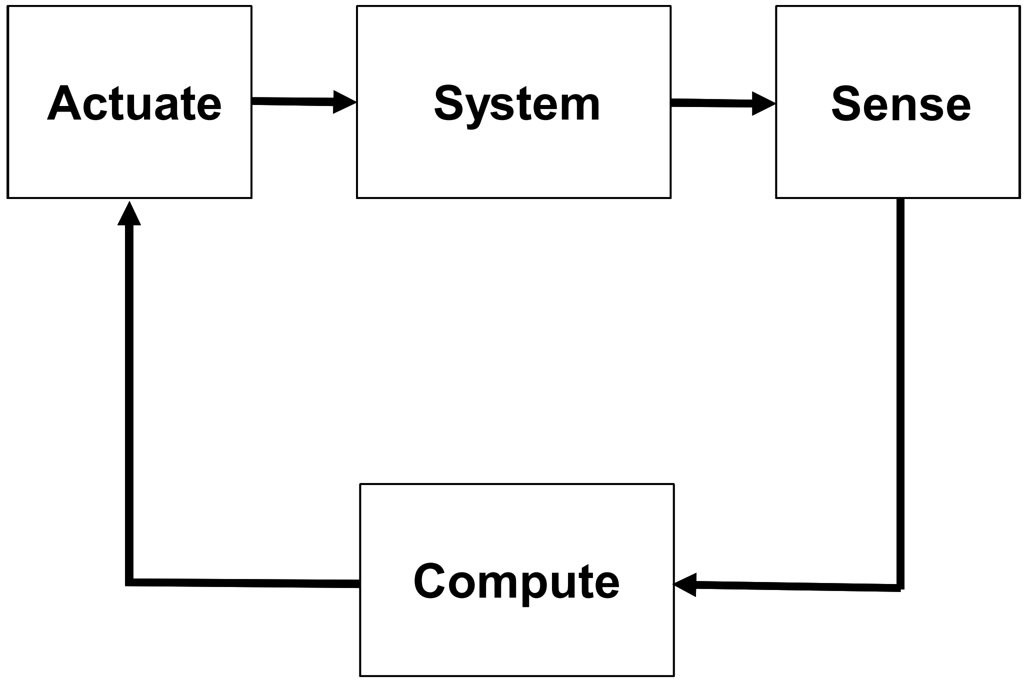
The design of an action that affects a system in a desired way.

- System – Something that changes over time (has dynamics).
- Control – Influence how the system changes.

What do you think of when someone says ***control system***?

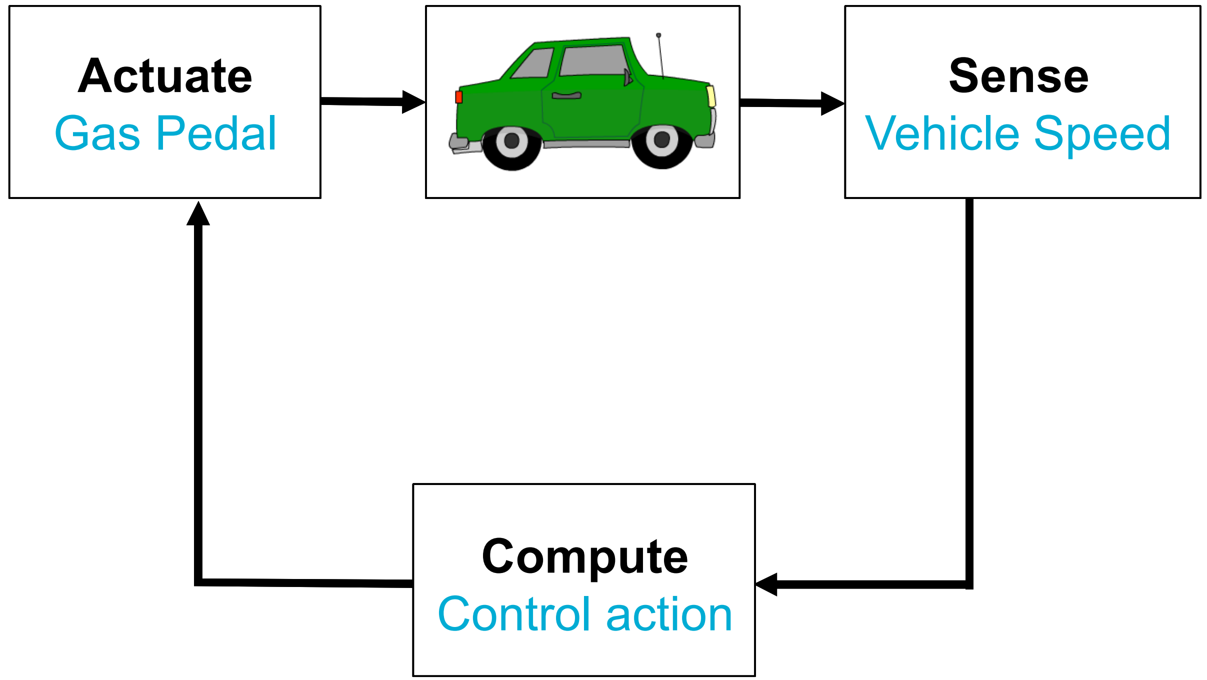
(Feedback) Control System

The design of an action that affects a system in a desired way.

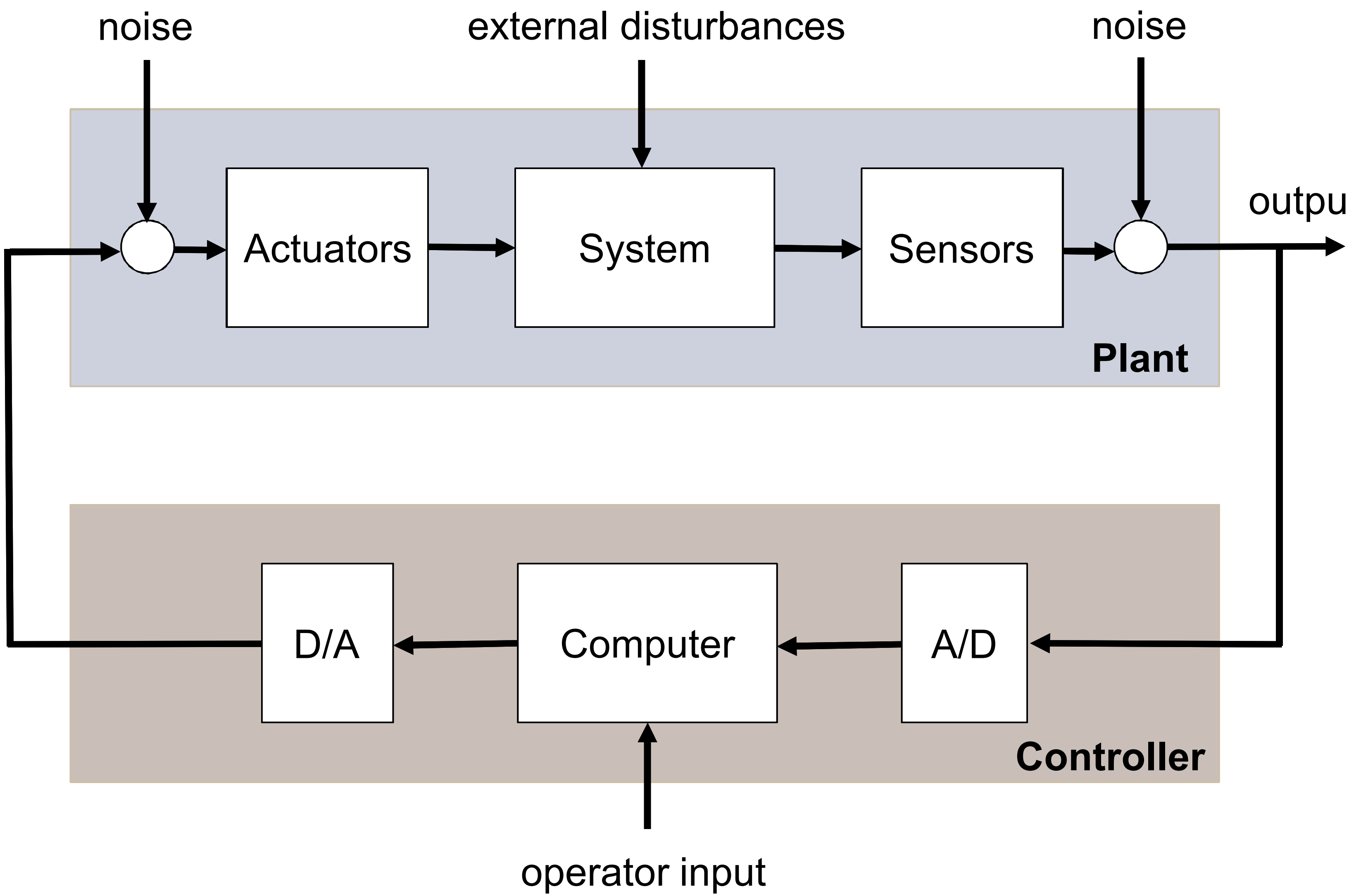


- System – Something that changes over time (has dynamics).
- Control – Influence how the system changes.

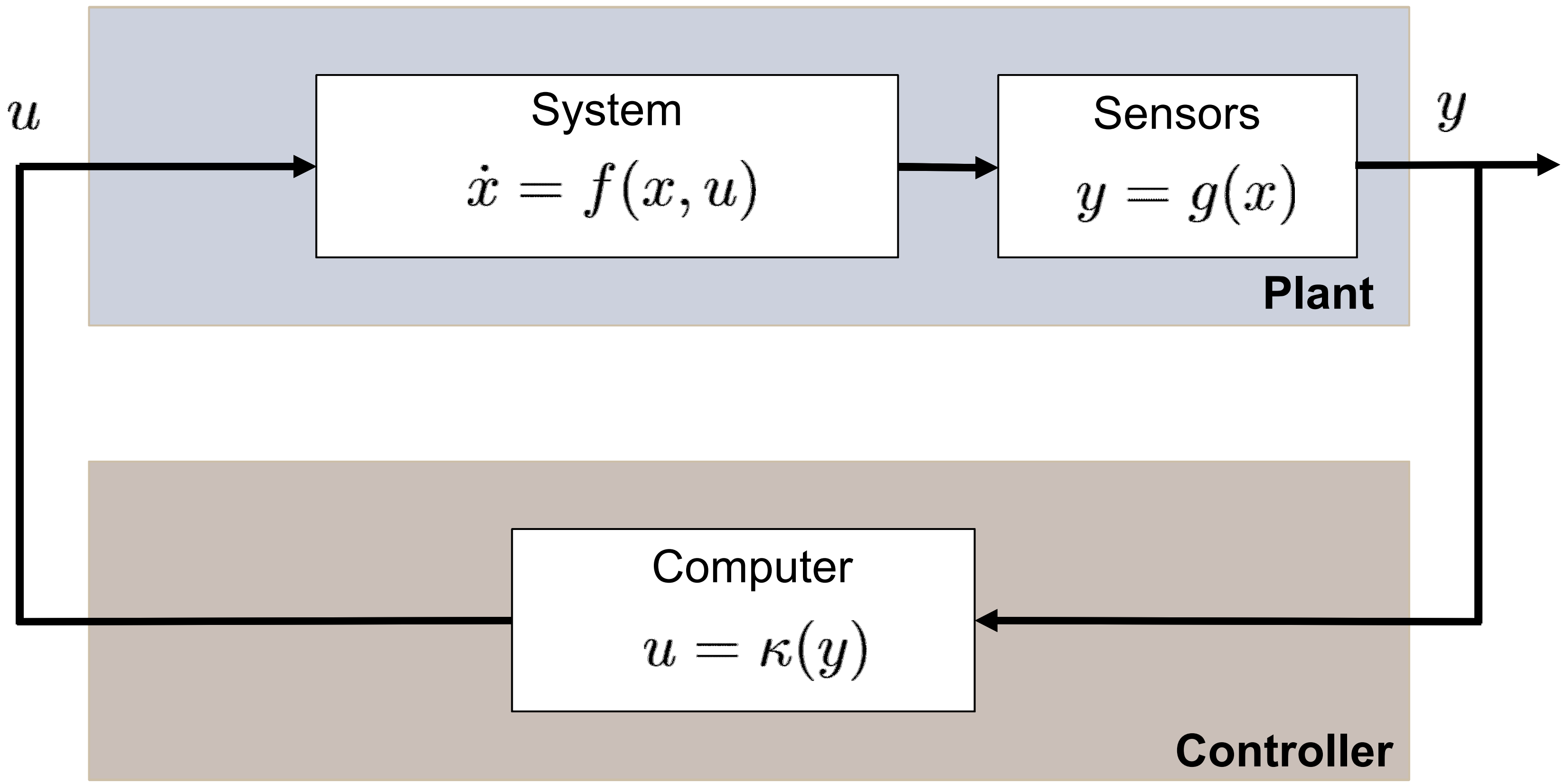
Example: Cruise Control



Modern Control System



Mathematical Formulation



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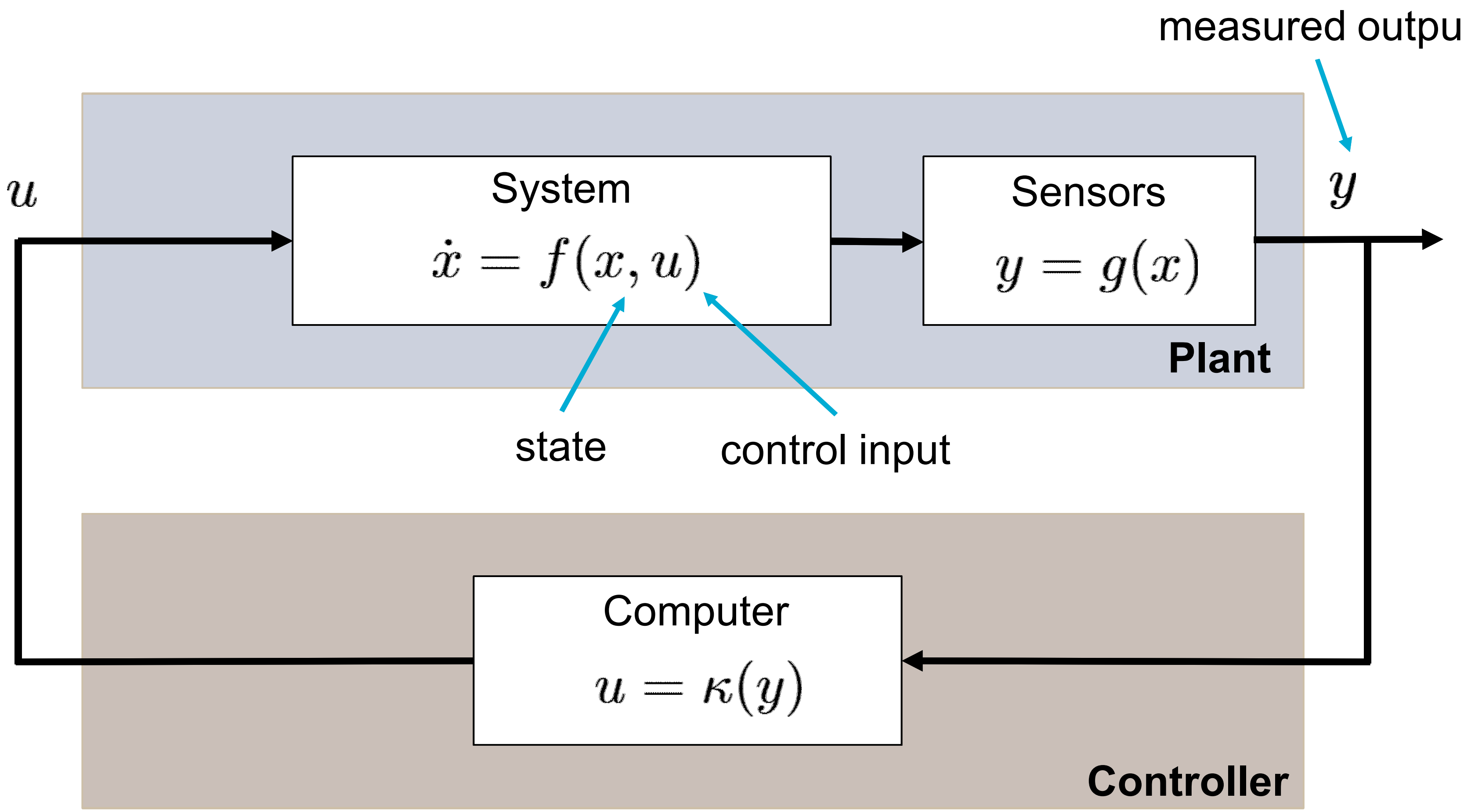
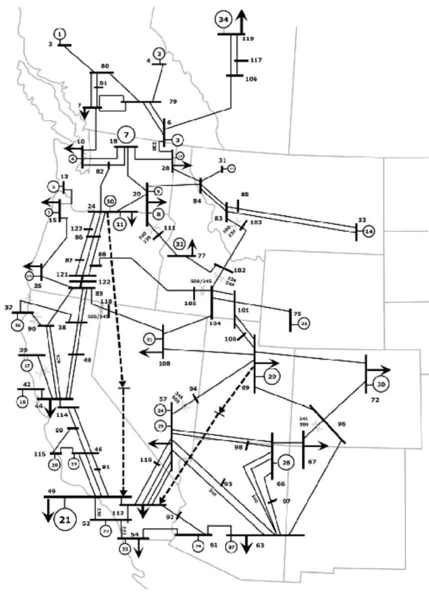


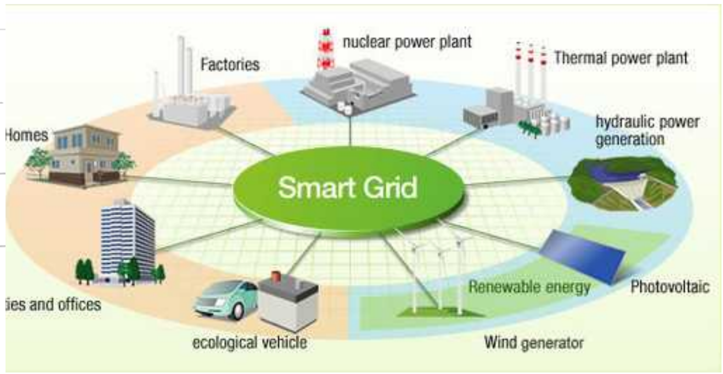
Control of Energy Storage

The design of an action that affects a system in a desired way.

- Control action – charge/discharge
- Constraints:
  - State of Charge (SOC)
  - Ramp rate (how fast charge/discharge)
  - Response time (how fast power electronics)
  - Cycle life
  - ...

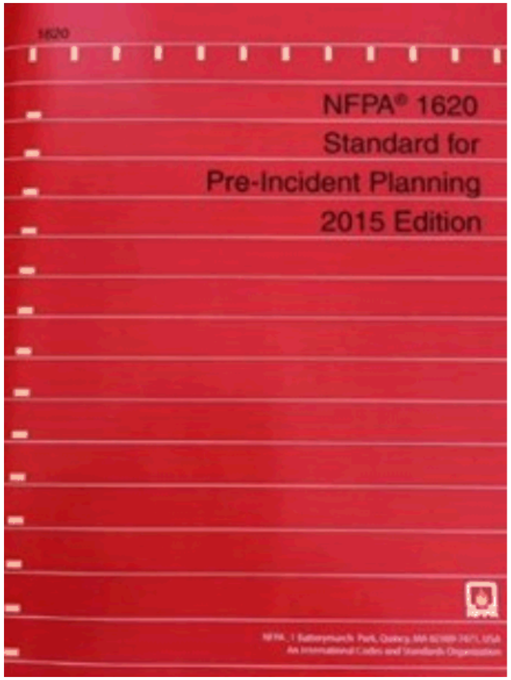
- Applications:
  - Power Systems
  - Energy Management





Incident Preparedness

- Safety Data Sheet locations
- Markings and signage
- ESS location, size and battery chemistry
  - Open racks or closed cabinets
- Gas detection
- Ventilation
- Main battery disconnect
- Fixed suppression systems
  - Type, location of standpipe, sprinkler and nearest hydrant
- Exposures



Safety Data Sheets- Key Information

- Battery Chemistry
- Health Hazards
- Firefighting Measures
- Emergency contact or building representative

DOE ESS Database
http://www.energystorageexchange.org/

Discussion

- A cell may exhibit dramatically different failure response when in a string, module or pack than during single cell abuse testing
- Propagation can be mitigated through system engineering, however the results can be unpredictable. Further, electrical design will play a role in susceptibility to failure testing.
- Failure testing of large, complex systems is fairly resource intensive. Model based design presents a potential remedy to this, allowing us to infer a large amount of information from a relatively small number of tests.

Acknowledgements

- Phil Gorney (DOT – NHTSA)
- Steve Summers (DOT – NHTSA)
- Dave Howell (DOE)
- Brian Cunningham (VTO)
- Samm Gillard (VTO)
- Jack Deppe (DOE)
- Ahmad Pesaran (NREL)
- Shriram Santhanagopalan (NREL)
- Christopher Orendorff
- John Hewson
- Kyle Fenton
- Eric Allcorn
- Lorie Davis
- Mani Nagasubramanian
- Jill Langendorf

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

- Heather Barkholtz
- Josh Lamb
- John Hewson
- Chris LaFleur
- Alice Muna
- David Rosewater
- Loraine Torres-Castro
- Randy Shurtz
- Jill Langendorf
- Armando Fresquez

- Michael Hargather (NMT)
- Frank Austin (NMT)
- Scott Roberts
- Julian Medina
- Sergei Ivanov
- Dave Conover (PNNL)
- Pam Cole (PNNL)

Battery Safety R&D Program at Sandia: http://energy.sandia.gov/?page_id=634
DOE Office of Electricity
Office of Vehicle Technologies

Acknowledgements

- Dr. Imre Gyuk for supporting energy storage safety work
- Summer Ferreira, Babu Chalamala, Josh Lamb, Leigh Anna Steele, Loraine Torres-Castro, June Stanley, Chris Grosso, Jerry Quintana, Jill Langendorf, John Hewson, Randy Shurtz
- 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).

- **Identify** the location and type of system
- **Shutdown** the battery ESS if necessary
- **Watch out** for high voltage and other hazard

IDENTIFY

LABELS:

Battery Disconnect

Emergency Stop (ESTOP)

Battery Room

COMPONENTS:

Battery racks or cabinets

Gas detection equipment

SDS's

SHUTDOWN

If system is on fire or other life safety/property hazard exists

Locate emergency stop, disconnect or circuit breaker

Shutdown the BESS

WATCH OUT

Stay away from open bus bars (shock hazards)

Monitor for re-ignition with thermal imaging camera (TIC)

Look for electrolyte spills

Monitor air for toxic/flammable gases

Ventilate as required

Images from NFPA and www.esstechsafety.org

Safety through Codes and Standards

- Many ESS safety related issues are identical or similar to those associated with other technologies
- Some safety issues are unique to energy storage in general and others only to a particular energy storage technology
- Current codes and standards provide a basis for documenting and validating system safety
  - prescriptively
  - through alternative methods and materials criteria
- Codes and standards are being updated and new ones developed to address gaps between ESS technology/applications and criteria needed to foster initial and ongoing safety

Safety-Related Issues

- ESS 'product' configuration and how safety validation is addressed
- New versus existing systems and new versus existing building/facility applications
- Siting (location, loads, protection, egress/access, maximum quantities of chemicals, separation, etc.)
- Ventilation, thermal management, exhausts (when necessary, flow rates, etc.)
- Interconnection with other systems (electrical, any non-electrical sources)
- Fire protection (detection, suppression, containment, smoke removal, etc.)
- Containment of fluids (from the ESS and from incident response)
- Signage

Materials R&D for Energy Storage System Safety

- Major research areas
  - Materials origin of safety and reliability
  - Device level failures
  - Cascading failures
- Advanced simulation and modeling of energy storage systems
- Further
  - Software's role as a critical safety system
  - Better control of cell behavior through power electronics

Improving Storage Safety

Development of Inherently Safe Cells

- Safer cell chemistries
- Non-flammable electrolytes
- Shutdown separators
- Non-toxic battery materials
- Inherent overcharge protection

Safety Devices and Systems

- Cell-based safety devices
  - current interrupt devices
  - positive T coefficient
  - Protection circuit module
- Battery management system
- Charging systems designed

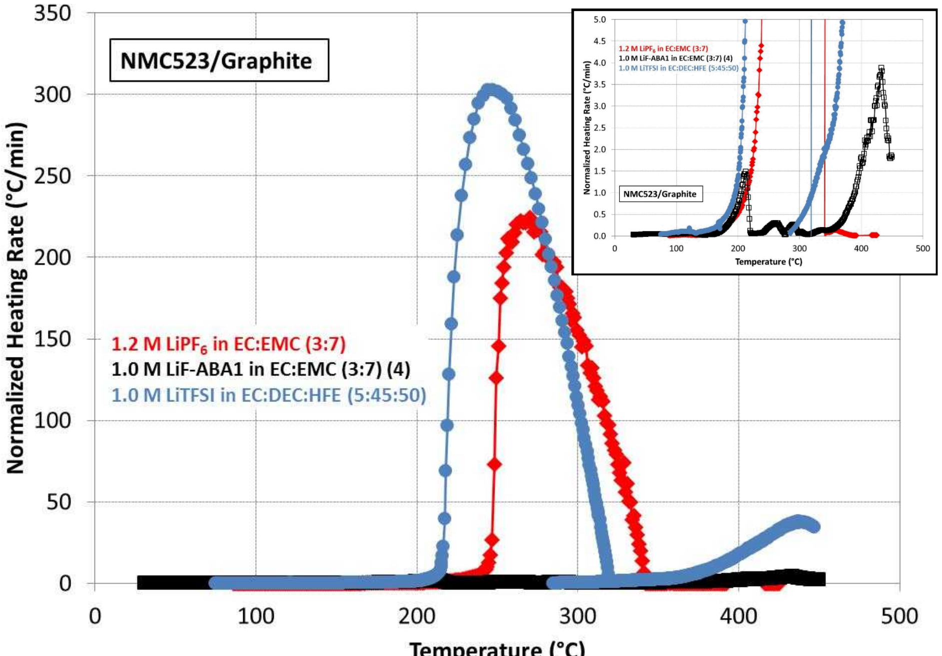
Effective Response to Off-Normal Events

- Suppressants
- Containment
- Advanced monitoring and controls

Abuse Tolerance of Li-ion Cells

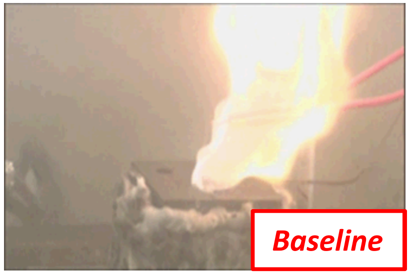
Sandia National Laboratories

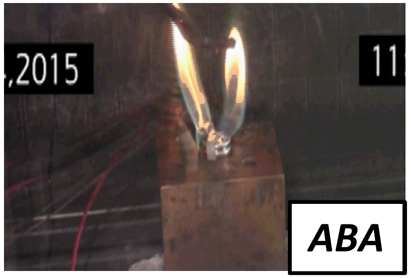
Accelerating Rate Calorimetry (ARC)



- *Significant reduction in the thermal runaway free energy of NMC cells with LiF/ABA electrolytes*
- *HFE electrolytes are measured to be nonflammable in a cell vent failure scenario*

Cell Vent Flammability Measurements





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Role of SOC on Thermal Runaway

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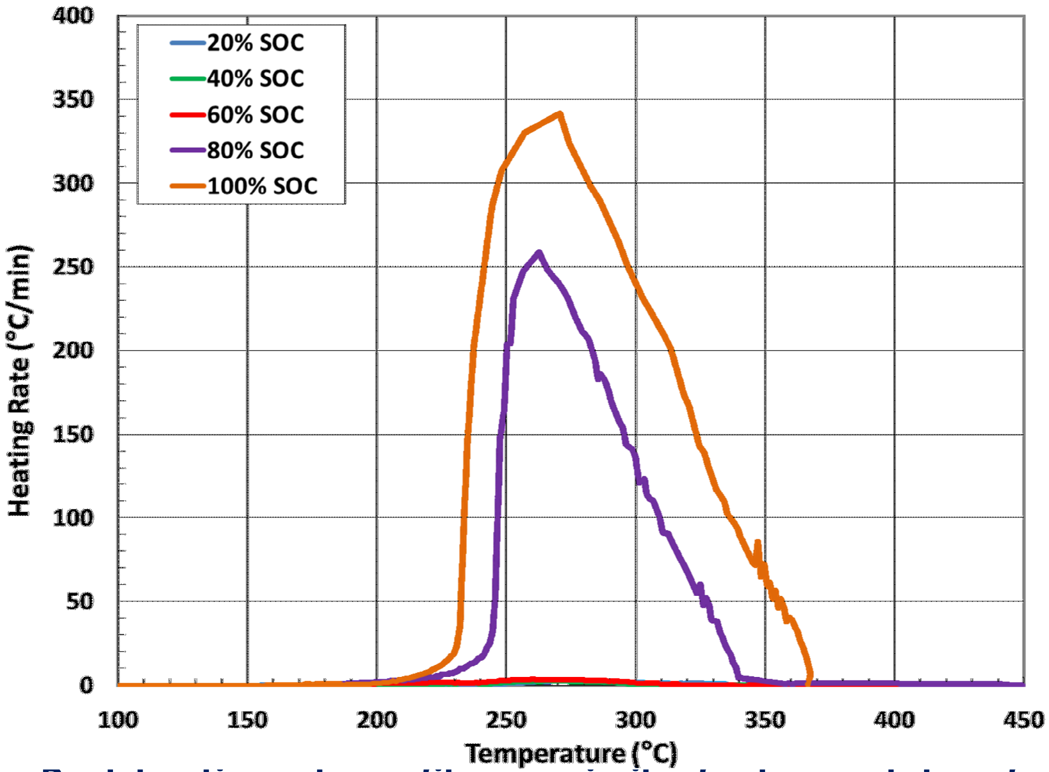
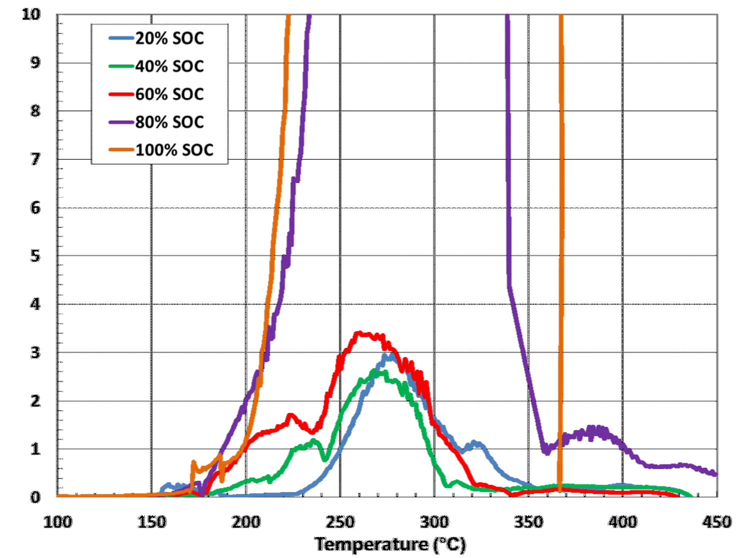
18650 cells 20-80% SOC (80-20%DOD)



Similar response observed in 18650

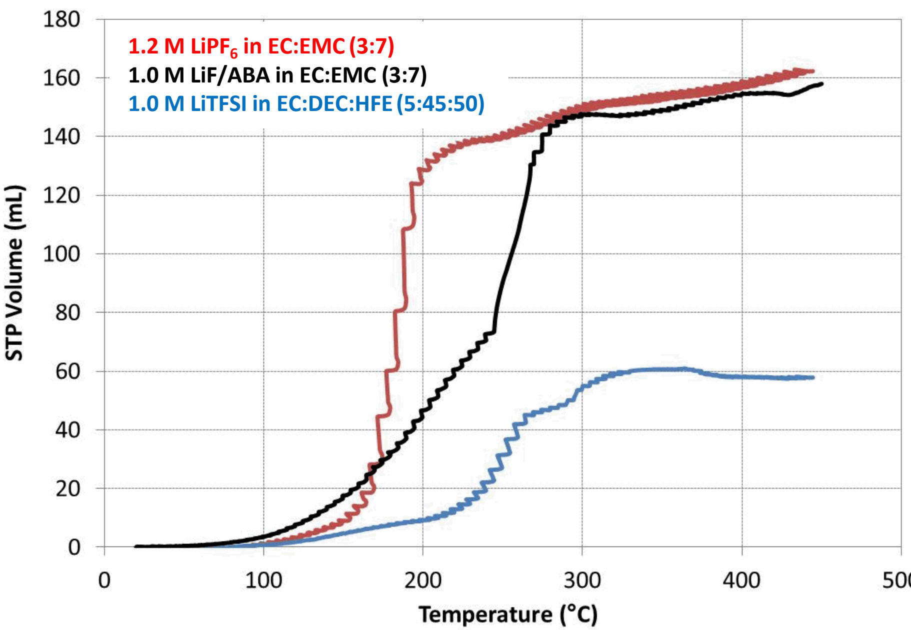


- **Peak heating rate profiles are similar for lower states of charge (20-60%) then drastically increase at 80% and 100% SOC. The onset of thermal runaway increases as the %SOC decreases**

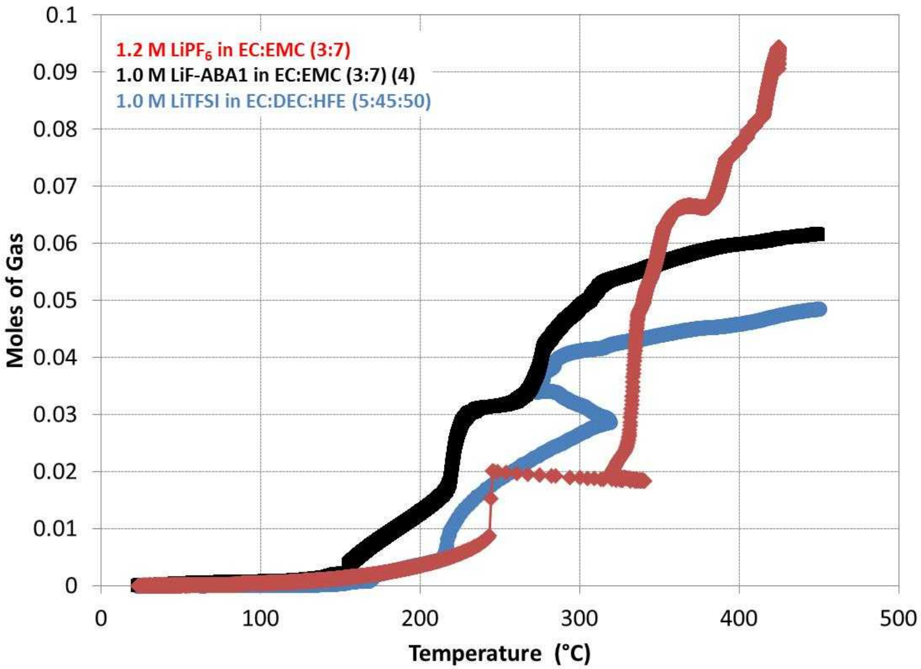
Chris Orendorff, John Lamb and Leigh Ann Steel

Electrolyte Gas Generation

Electrolyte ARC bomb gas volume



Cell ARC gas volume



~60% reduction in gas volume between baseline and HFE electrolyte
~40% reduction in gas volume at the cell-level between baseline and HFE electrolyte
~30% reduction in gas volume at the cell-level between baseline and LiF/ABA electrolyte

Battery safety – stationary storage

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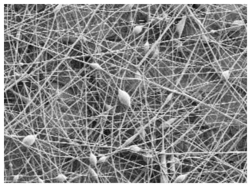
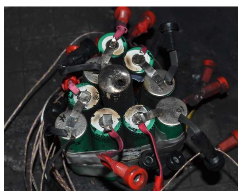
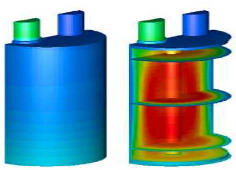
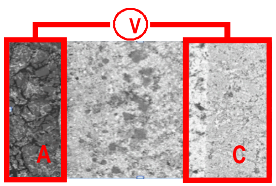



Materials R&D to date:
- Non-flammable electrolytes
- Electrolyte salts
- Coated active materials
- Thermally stable materials

Materials R&D needs:
- Viable flow batteries
- Aqueous electrolyte batteries
- High specific heat suppressants
- Vent gas composition




Testing
- Electrical, thermal, mechanical abuse testing
- Failure propagation
- Suppressants and delivery
- Large scale thermal and fire testing (TTC)

Simulations and Modeling
- Multi-scale thermal models
- Validating failure propagation models
- Fire Dynamic Simulations (FDS)

UL ICC IEEE IEC ASME SETTING THE STANDARD CERTIFIED FIRE PROTECTION SPECIALIST NFPA CFPS

Procedures, Policy, and Regulation
- Overarching
- Installations
- Complete systems
- Components
- International

Standards: SNL & PNNL Protocol for Evaluation ES Systems

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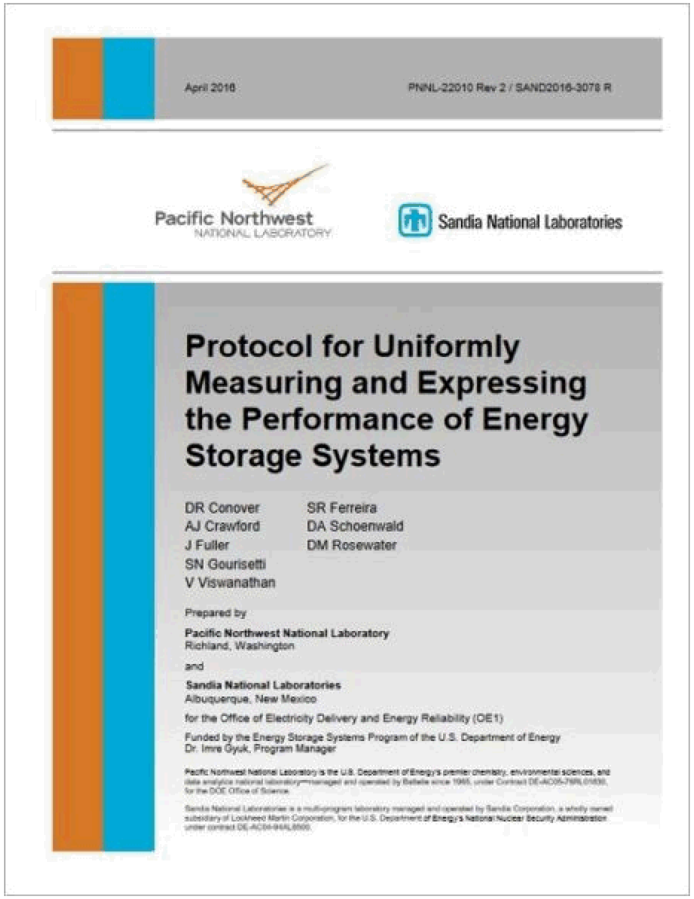
Companies looking for an accurate method to gauge how well large batteries and other grid-scale energy storage systems work now have a new set of evaluation guidelines, called the Energy Storage Performance Protocol, at their disposal. The guidelines currently evaluate three energy storage performance uses:
Peak shaving, Frequency Regulation, and Islanded Microgrids

Additional Lab Protocols:

- **Duty Cycle for ESS Firming**
- **Duty Cycle for PV Smoothing**


April 2016
PNNL-22010 Rev 2 / SAND2016-3078 R

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Protocol for Uniformly Measuring and Expressing the Performance of Energy Storage Systems

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for the Office of Electricity Delivery and Energy Reliability (OE1)
Funded by the Energy Storage Systems Program of the U.S. Department of Energy
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