NREL
NATIONAL RENEWABLE ENERGY LABORATORY

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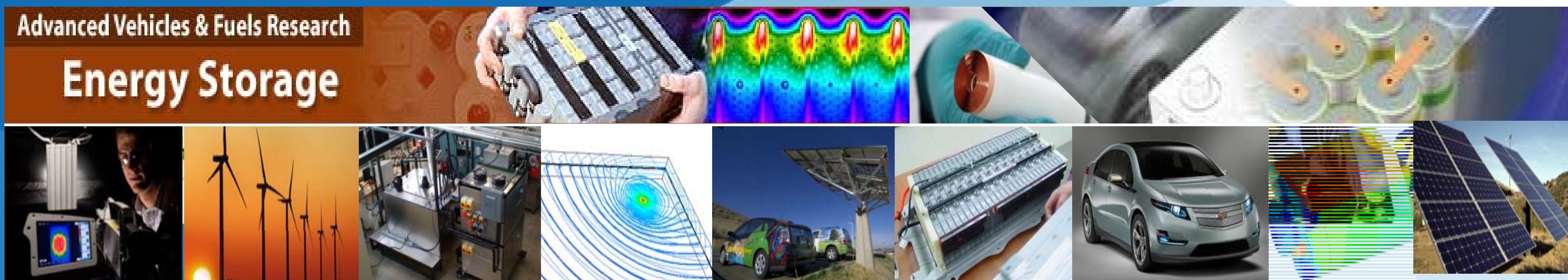

Thermal Runaway Propagation Modeling in Lithium Ion Modules with and without PCM

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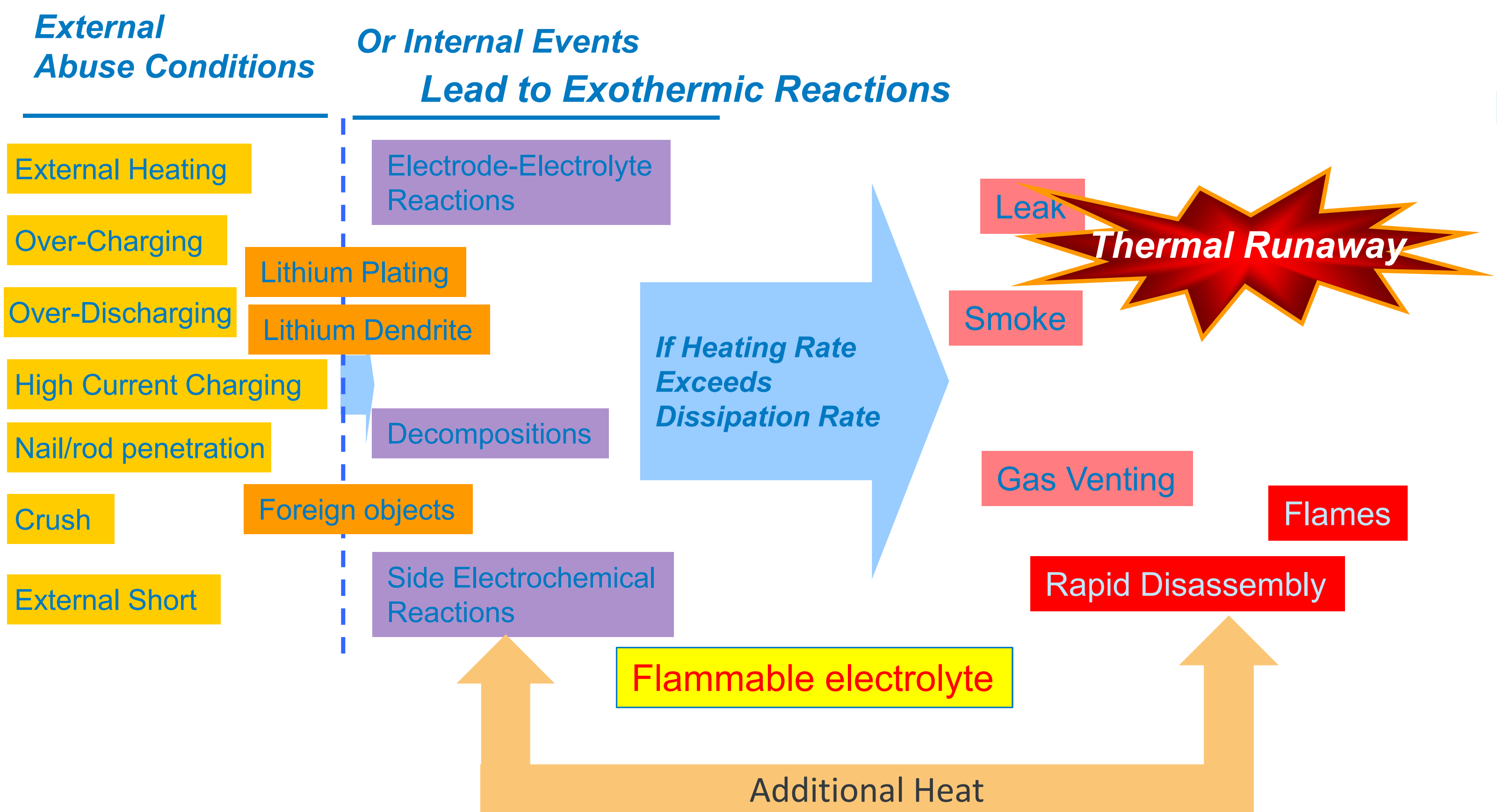
Li-Ion Battery Safety is a Concern for Many Applications

Various Factors Could Lead to Thermal Runaway (TR) of a Cell



Depends on:

- Chemistry
- Electrolyte
- Additives
- Separator
- Cell design
- Safety features
- Environment
- State of charge

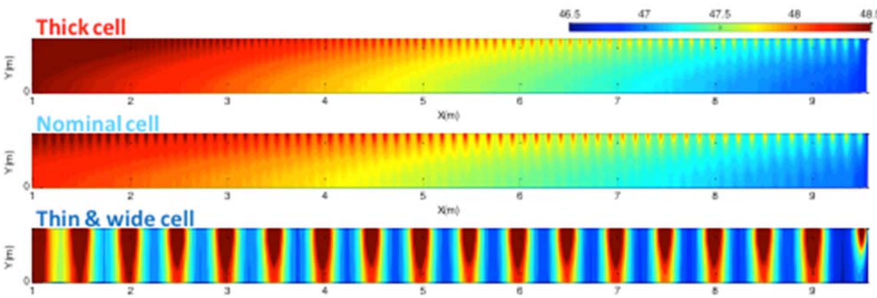
Module/Pack Thermal Runaway – a larger concern than cell TR

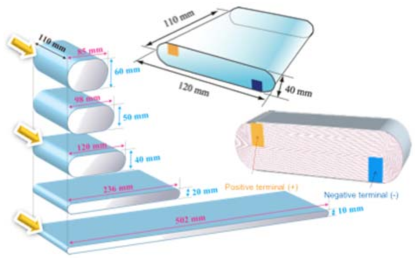
- Millions of lithium ion cells are produced everyday – production growing
- Even with six sigma quality control, some cells may have inherent defects that may lead to field failure later
- During operation one or more cells may experience some kind of abuse
- Can single cell thermal runway be avoided – safer chemistries & designs?
- Single cell abuse has lead to thermal runaway and fire in modules with small number of cells (Boeing 787 and laptops)
- In modules/packs with significant large number of cells (vehicles and grid), probability of cell TR increases
- Cell-to-cell thermal runway in modules and packs leading to a larger safety event is of much more concern (loss of assets& revenue; damage to brand)
- Can diagnostics and monitoring systems warn about impending failures in a module/pack for preventive or corrective actions?
- Can cell-to-cell thermal runaway be avoided - safer designs?

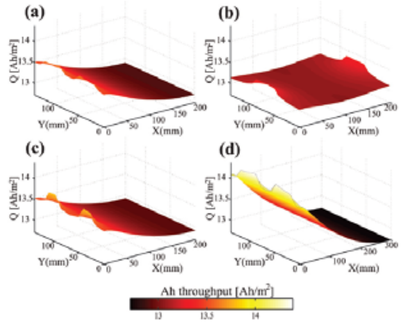
This presentation - Modeling

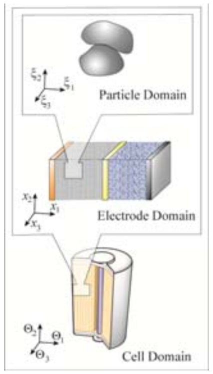
NREL Lithium Ion Battery Safety Portfolio - 1

- Electrochemical-thermal (ETC) models (offered by NREL)

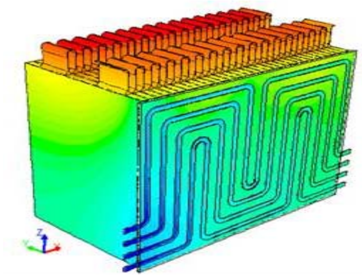


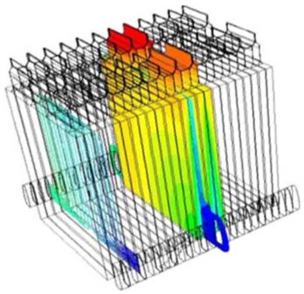


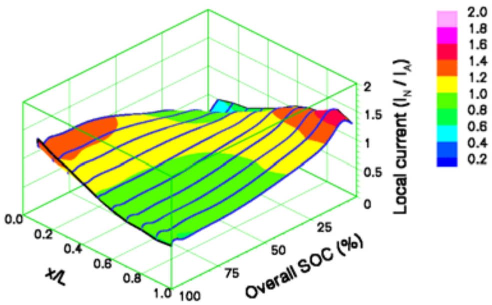


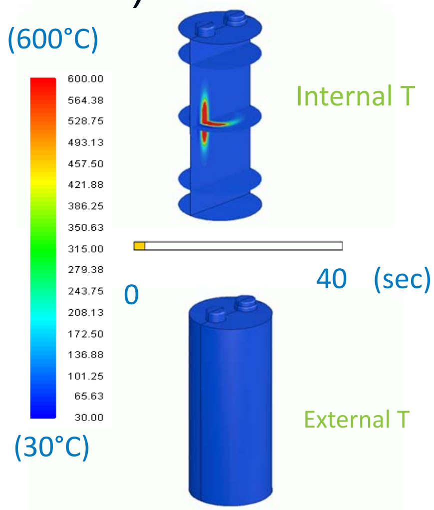


- Computer Aided Engineering for Batteries (CAEBAT) (the first and second generation of these tools are now offered by ANSYS, CD-adapco, EC Power)





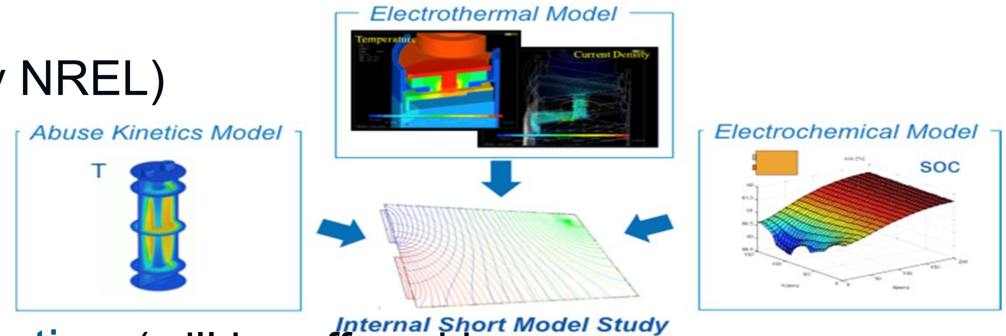




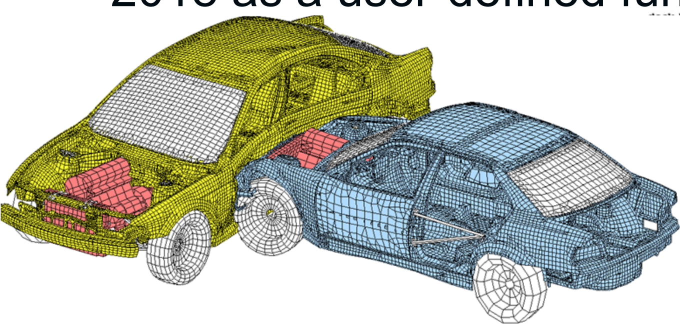
- Abuse reaction kinetics modeling (now offered by ANSYS)
- Overheating (thermo-chemical) simulations (offered by NREL)

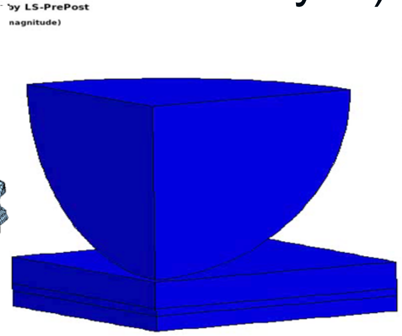
NREL Lithium Ion Battery Safety Portfolio - 2

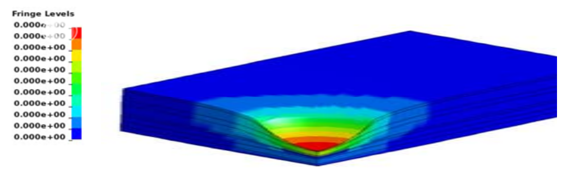
- Internal short circuit modeling (offered by NREL)

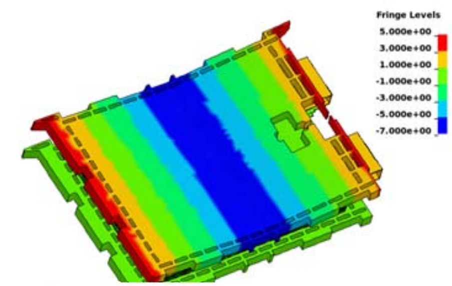


- Mechanical-ETC models for crush simulation (will be offered in 2018 as a user-defined function in LS-Dyna)

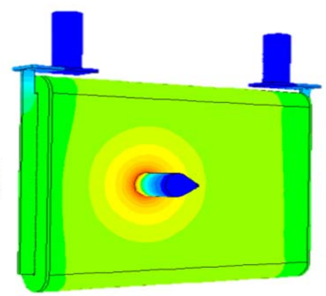




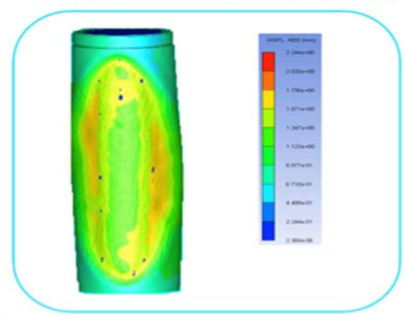




- Nail penetration modeling (offered by NREL)



Deformation due to Pressure-Distribution within an 18650 cell

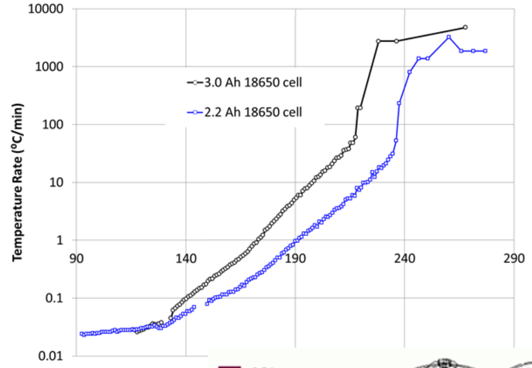


- Overcharge modeling and testing (offered by NREL)

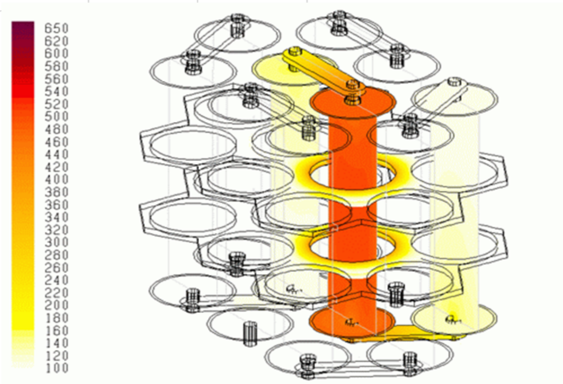
NREL Lithium Ion Battery Safety Portfolio - 3

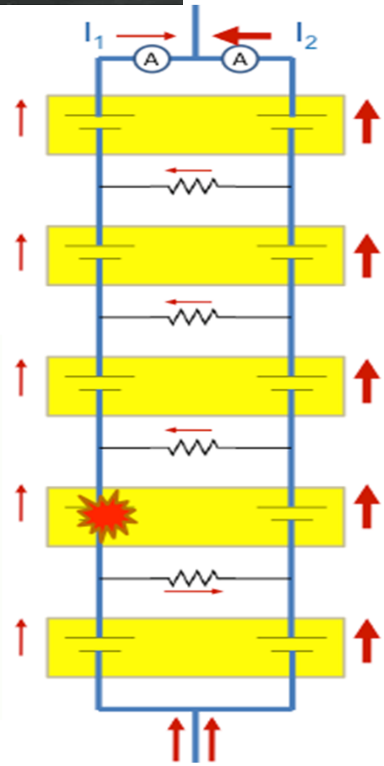
- Battery internal short circuit instigator device (offered by NREL)

- Accelerating rate calorimeter testing



- Fail safe design architecture for multi-cell strings (under development)

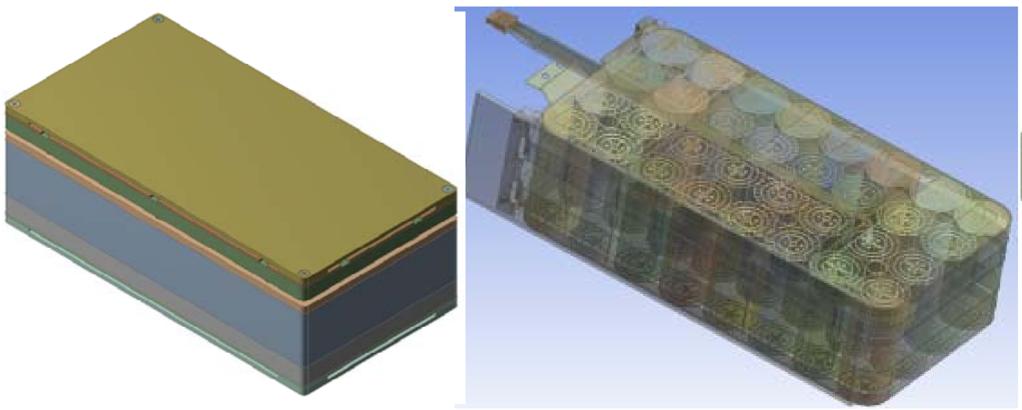




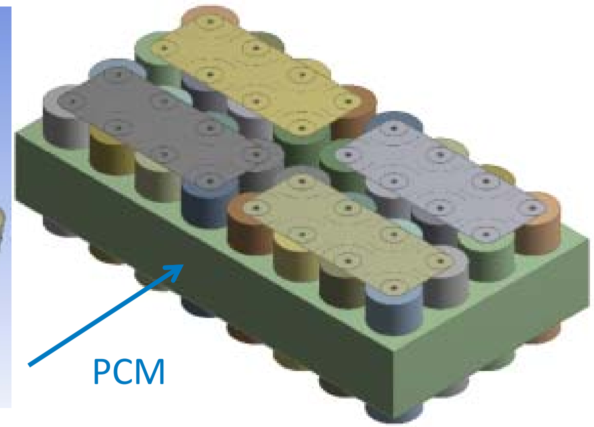
- **Cell-to-cell thermal propagation modeling (non-mechanical)**

Battery Module Modeled (4P8S)

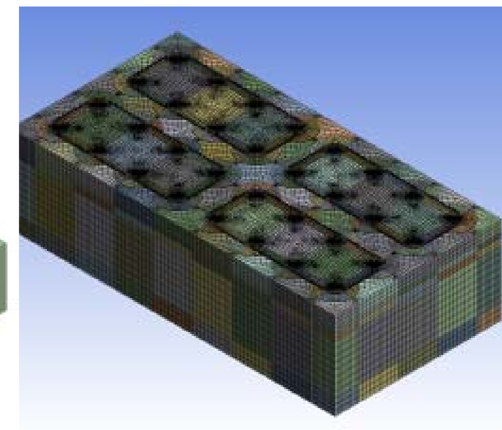
4P8S Battery Module



4P8S 3D Geometry



4P8S 3D Mesh



- Module designed by ECI Labs per NAVAIR spec.
- Geometry and fine mesh of battery module were created in ANSYS Workbench. Plastic enclosure applied at top and bottom of battery module
- **Objective of this study is to understand the effectiveness of PCM on mitigation of cell-cell thermal propagation after short circuit occurs in a cell**

Specifications of Battery Module

Chemistry	LFP/Gr	NMC/Gr
Number of Cell	32	32
Structure	4 Parallel 8 Series	4 Parallel 8 Series
Volume (L)	2	2
Weight (kg)	3.3	3.5
Nominal Voltage (V)	13.2	14.8
Capacity (Wh)	264	521

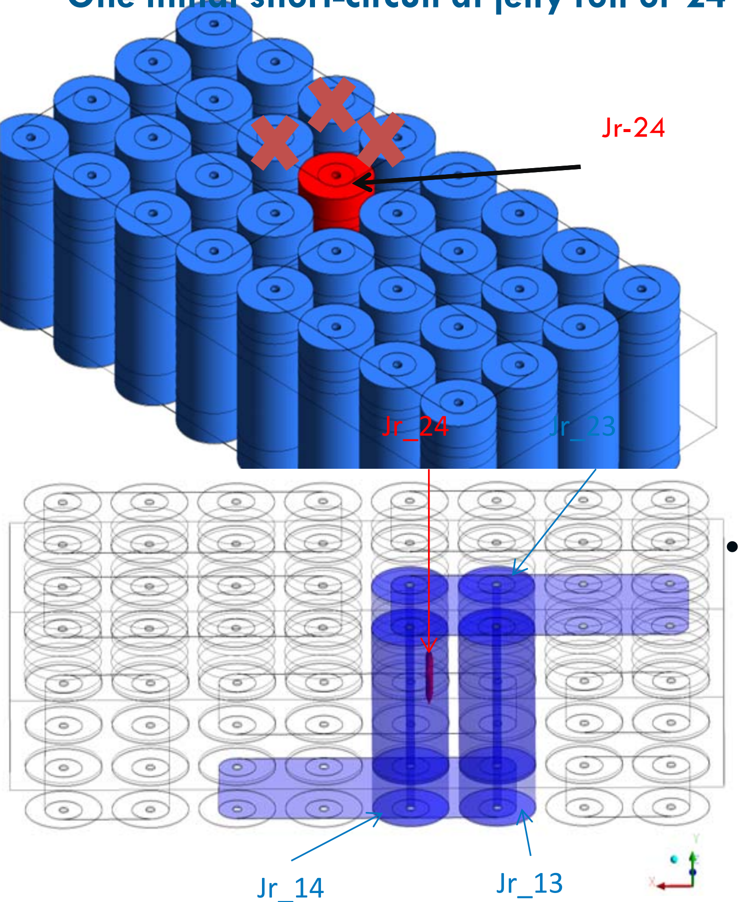
Cell Specifications and Material Thermal Properties

26650 Cylindrical Cell		
Cathode Active Material	LFP	NMC
Anode Active Material	Graphite	Graphite
Weight (g)	76	82
Nominal Capacity (Ah)	2.5	4.4
Nominal Voltage (V)	3.3	3.7
Energy Density (Wh/kg)	108.1	198.5
k (W/m-K) (Radial, Tangential and Axial)	0.8, 27, 27	0.8, 27, 27

Material Thermal Properties	PCM	Plastic
Density (kg/m^3)	870	900
Cp (J/kg-K)	1877 (Solid) / 2399 (Liquid)	1800
k (W/m-K) (Radial, Tangential and Axial)	0.4	0.22
Phase Transition Temperature (°C)	72 – 73	N/A
Heat of Fusion/Melting (J/g)	180	N/A

3D Cell-to-Cell Thermal-Propagation Simulation

One initial short-circuit at jelly roll of 24



Active Cells:
Jr_13, Jr_14, Jr_23, Jr_24

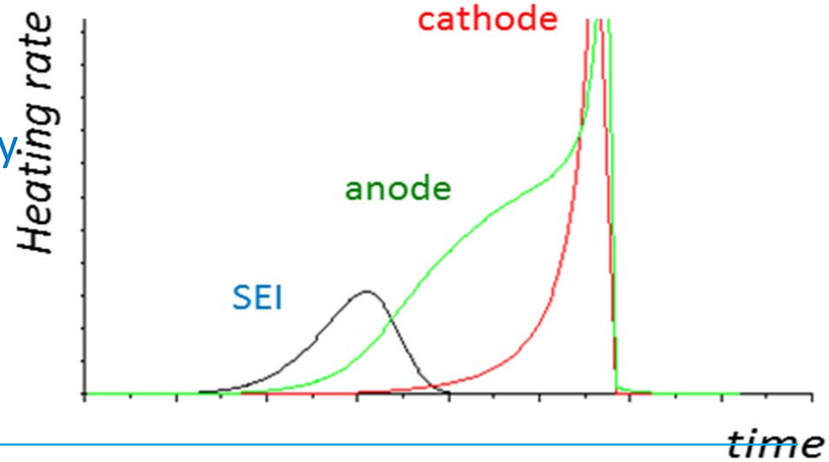
- **Assumptions**
  - One cell in a 4P group develops a internal short circuit.
  - Cascading short is induced by localized internal temperature. Separator shutdown occurs at 120°C. Separator breaks down at 160°C
  - Battery module is not under load, but the cells in one 4P group get discharged
  - Heat released due to thermal runaway in estimated using NREL Abuse reaction kinetics (ARK)
  - All TR heat goes into cells (no venting or outside combustions)
- **Initial conditions**
  - Short circuit occurs in Jr_24 with initial short resistance of 4 mΩ
  - All cells in battery module have a SOC of 100% and initial temperature of 25°C
  - Natural convection cooling on all surfaces (T_{amb}=25°C; h=5 W/°C/m^2)

Thermal only analysis; Simulation of electrical behaviors of 4P8S module is not included

TR Heat Release for **NMC** Cells - Abuse Reaction Kinetics Model

Bottom-up approach

- Abuse reactions among cell components superimposed
- Incorporates exothermic component reactions commonly addressed; readily accommodates other abuse reactions
- Empirical reaction model
  - Built from accelerating rate calorimetric test data
- Evaluates the rate of heat generated from exothermic decomposition reactions



	Ea (J/mol)	A (s^{-1})	m	n	p
For NMC/Gr	**2.80E5**	**5.14E25**	**0**	**0.0991**	**2.1145**

ARK Model Equations

$$\begin{cases} S = HW\dfrac{d\alpha}{dt} \\ \dfrac{d\alpha}{dt} = k(T)f(\alpha) \\ k(T) = Ae^{-\frac{Ea}{RT}} \\ f(\alpha) = \alpha^m(1-\alpha^n)(-\ln(1-\alpha))^p \end{cases}$$

S : volumetric reaction heat generated

H : heat of reaction

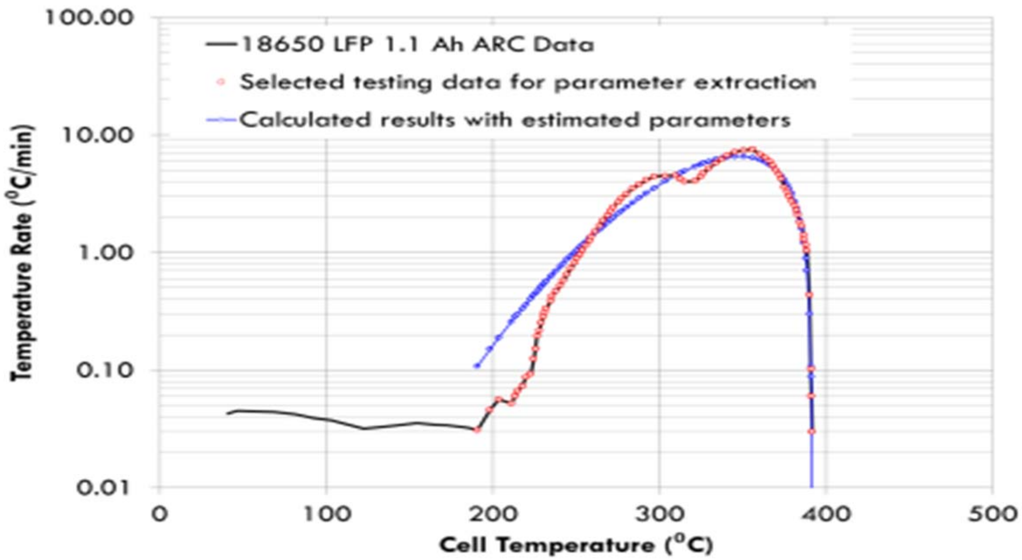
$d\alpha/dt$: reaction rate

$k(T)$: temperature-dependent rate constant

For Estimating exothermic heat of NMC, there are four decomposition reactions, including SEI, NE, PE, and ELE. The heat is 257, 1714, 314, and 155 (J/g), respectively. The onset temperatures for SEI is 90°C-120°C, PE is larger than 120°C, and ELE is greater than 200°C.

Published data: Kim, G. , Pesaran, A. , and Spotnitz, R. , 2007, " A Three-Dimensional Thermal Abuse Model for Lithium-Ion Cells," J. Power Sources, 170(2), pp. 476–489.

TR Heat Release for **LFP** Cells - Abuse Reaction Kinetics Model



Cell	26650 LFP 2.5 Ah
Onset Temperature	190^{0}C
Exothermic Heat	220.73 J/g
Ea	9.18E4 J/mol
A	1.95E5 s^{-1}
m, n, p	0, 1.25, 0

Andrey W. Golubkov, et al, Thermal Runaway Experiments on Consumer Li-Ion Batteries with Metal-oxide and Olivine-Type Cathodes, RSC Adv., 2014, 4,3633

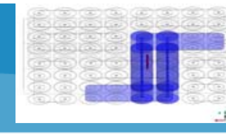
- Abuse reaction kinetics model was developed based on ARC test data to extract kinetics parameters of cell-level abuse reactions occurring at elevated temperatures
- Literature review indicates onset temperatures of LFP cells varies from 90°C to 190°C. 190°C is defined as the onset temperature in this study because heat released below 190°C has low rates.

Simulation Matrix

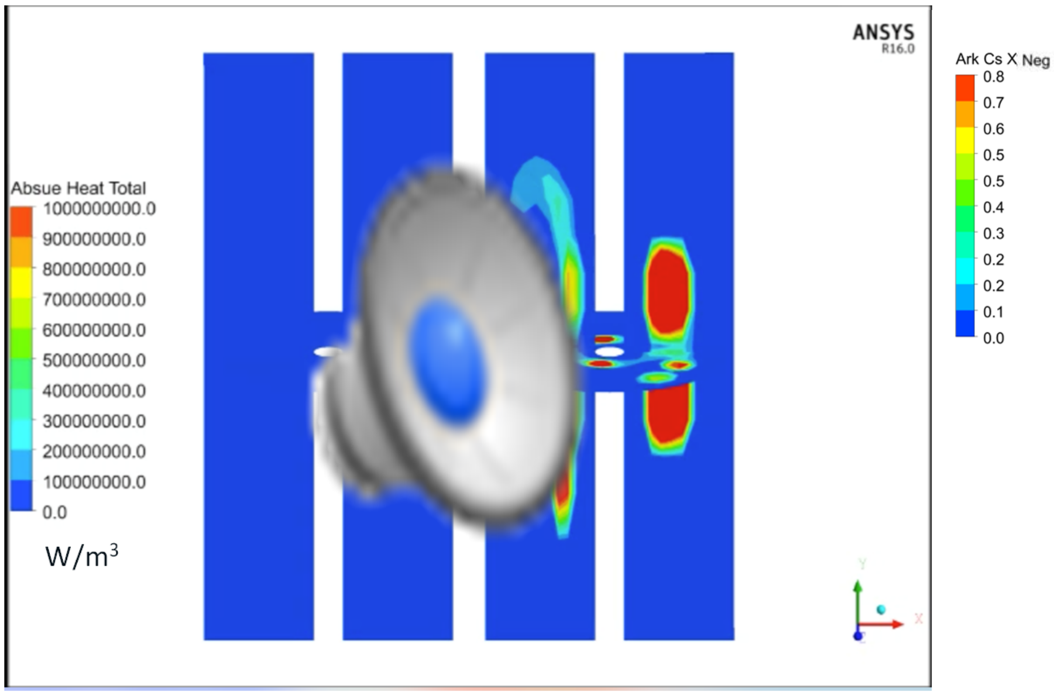
Case No.	Chemistry	PCM Volume*	PCM Melting Point	Initial Short	Location of Cell
1	NMC	50 %	72 °C	4 mΩ	Jr_24 (center)
2	LFP	50 %	72 °C	4 mΩ	Jr_24
3	NMC	100 %	72 °C	4 mΩ	Jr_24
4	NMC	0 %	72 °C	4 mΩ	Jr_24
5	NMC	50 %	120 °C	4 mΩ	Jr_24
6	NMC	50 %	72 °C	2 mΩ	Jr_24
7	NMC	50 %	72 °C	4 mΩ	Jr_11 (corner)

Effect of Parameters on Thermal Propagation	Case No.
Chemistry	1 Vs. 2
PCM Volume (0% Vs. 50% Vs. 100%)	1 Vs. 3 Vs. 4
Melting Point of PCM	1 Vs. 5
Initial Short Resistance	1 Vs. 6
Location of Shorted Cell	1 Vs. 7

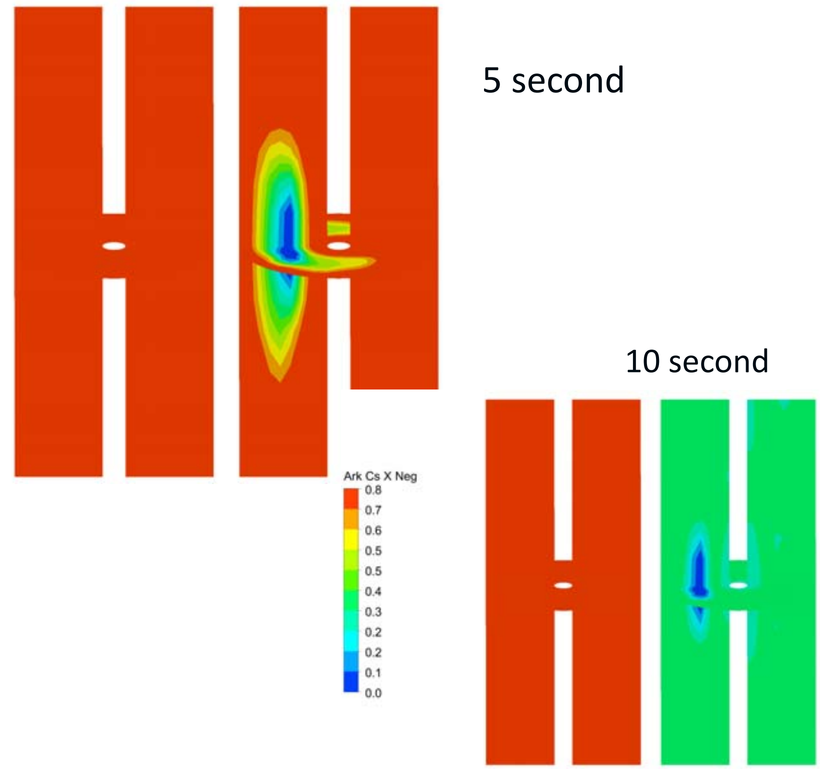
Case 1. Propagation of Thermal Runaway in Source Cell (Jr_24)



Propagation of Thermal Runaway

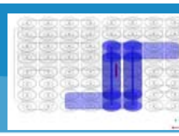


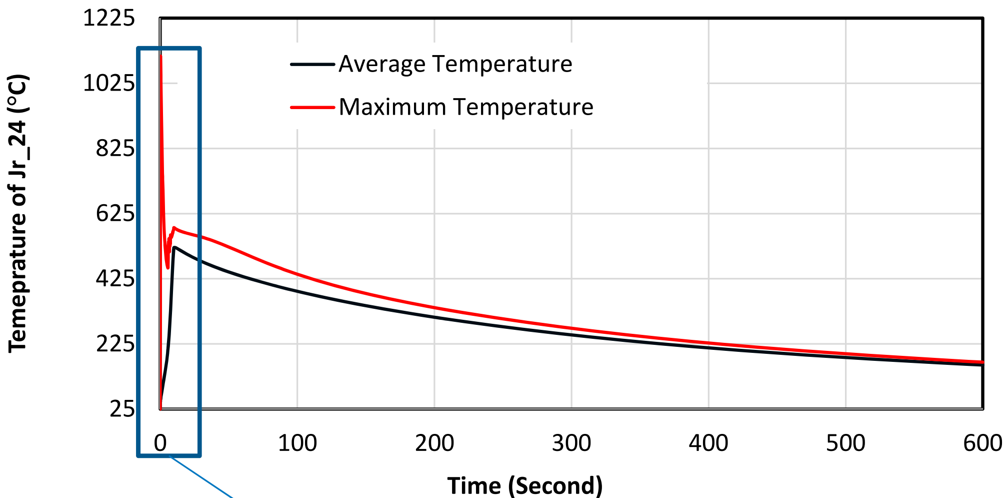
Contours of Electrolyte Concentration for Abuse Heat

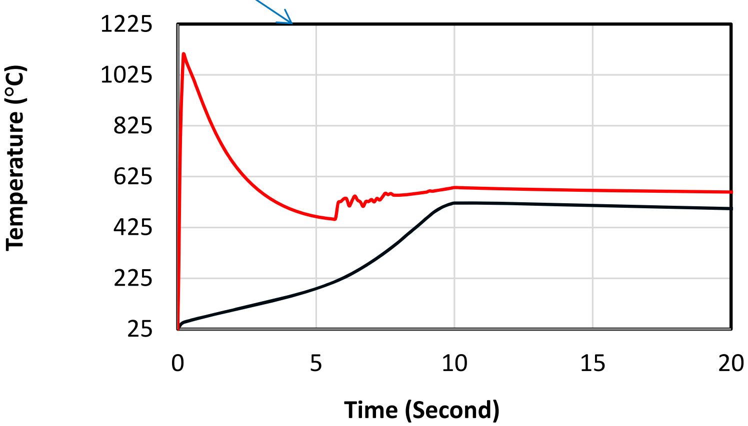


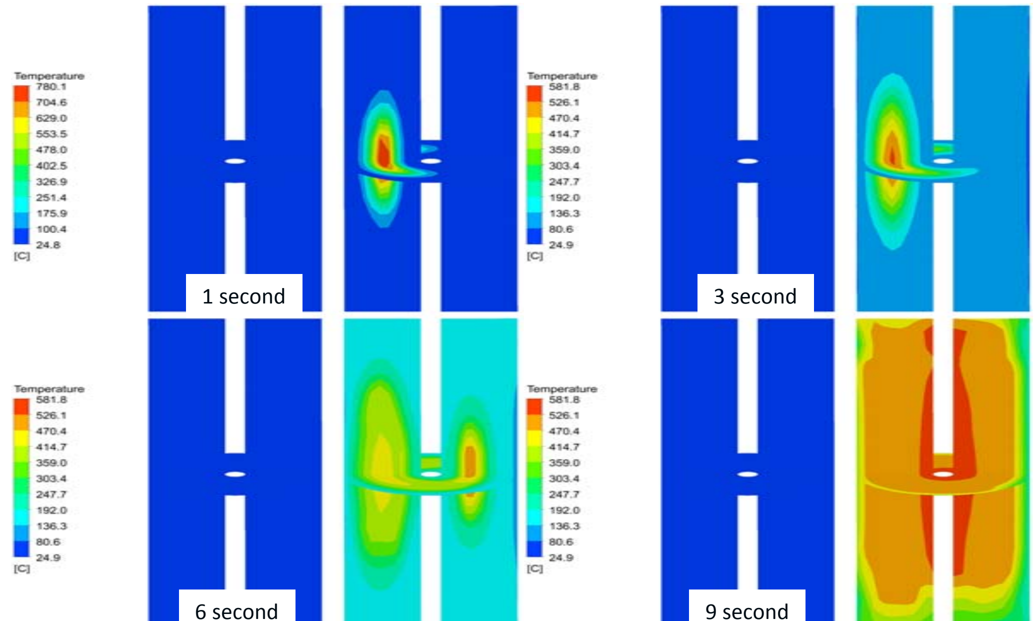
- Abuse heat can be found around the internal short circuit region in the beginning, then it propagates along azimuthal direction, abuse heat distributes along axial and radial direction in the end .
- At the 10 second, concentration of electrolyte is close to 0.3, which indicates thermal runaway has been done in source cell

Case 1. Distribution of Temperature in Source Cell (Jr_24)



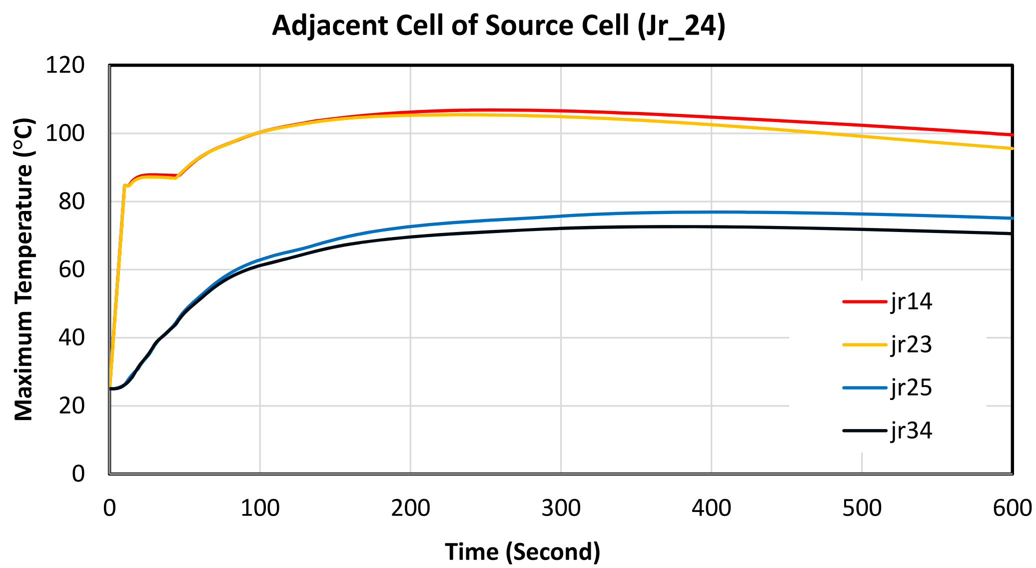


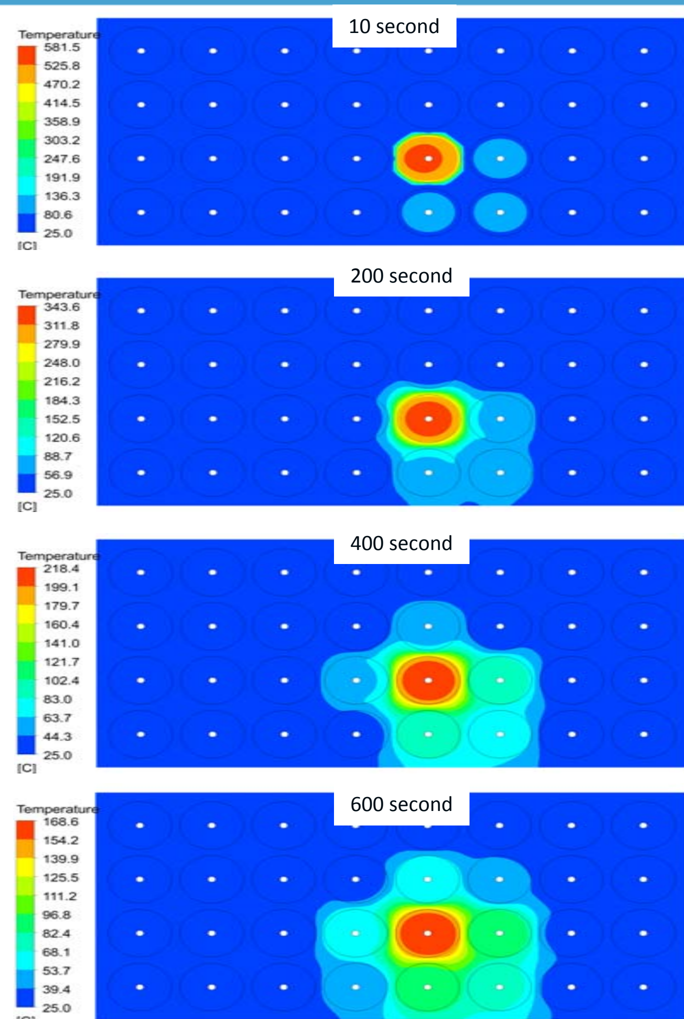




- Internal short circuit in source cell produces a hot spot first, then the high temperature distributes along radial, tangential, and axial directions, and heats the entire fault cell
- With the increasing of average temperature of cell, thermal runaway occurs and makes the maximum temperature of cell rise again
- After 10 second, the potential of fault cell is close to zero due to short circuit and thermal runaway; the temperature of fault cell starts to decrease and distributes the heat to surrounding area

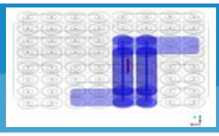
Case 1. Distribution of Temperature in Adjacent Cells

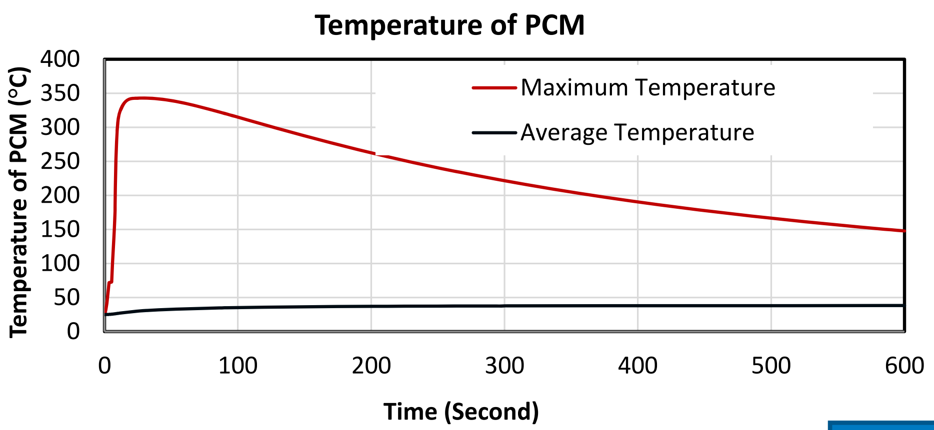


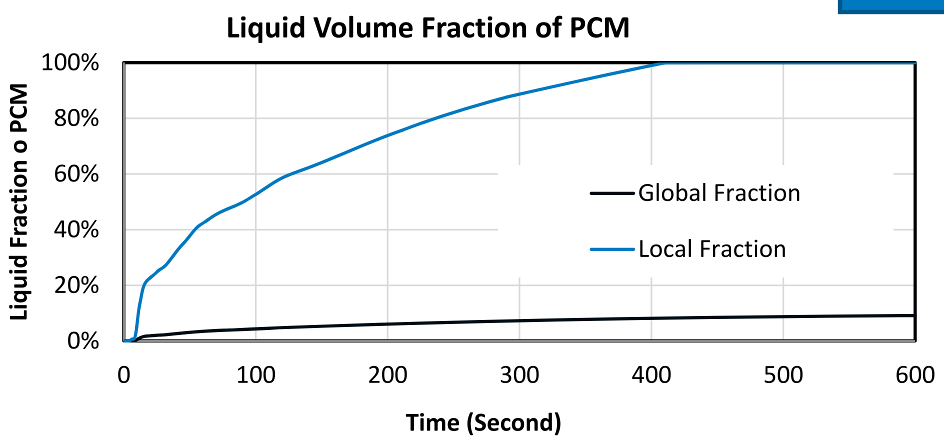


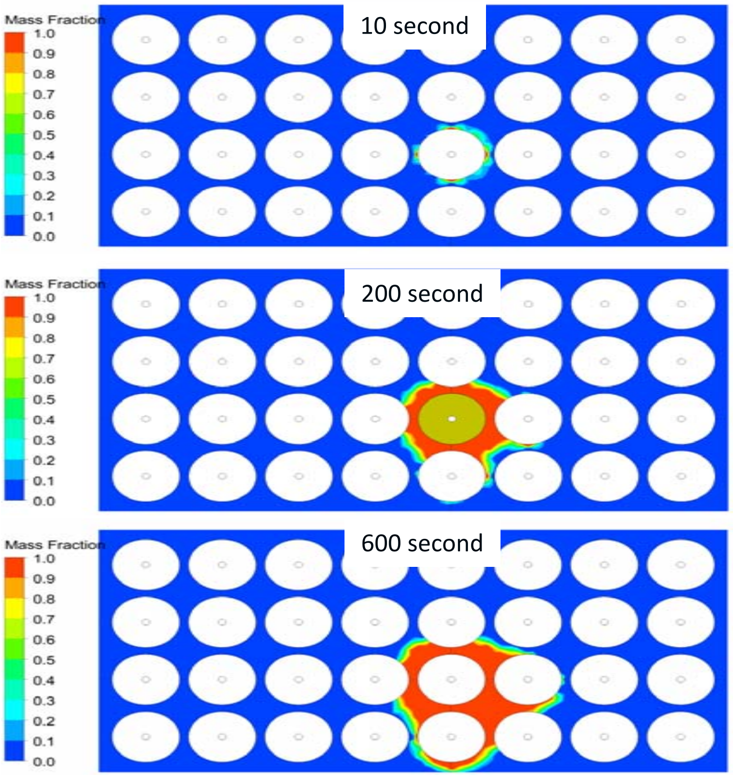
- Jr_14 and Jr_23 are in the same 4P group as source cell (Jr_24); therefore, the temperature are higher than that of Jr_25 and Jr_34
- Maximum temperature of Adjacent cells is less than 110°C, which indicates thermal runaway doesn't propagates to adjacent cell

Case 1. Distribution of Liquid PCM (NMC Module, 50% PCM)

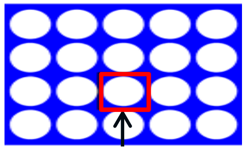






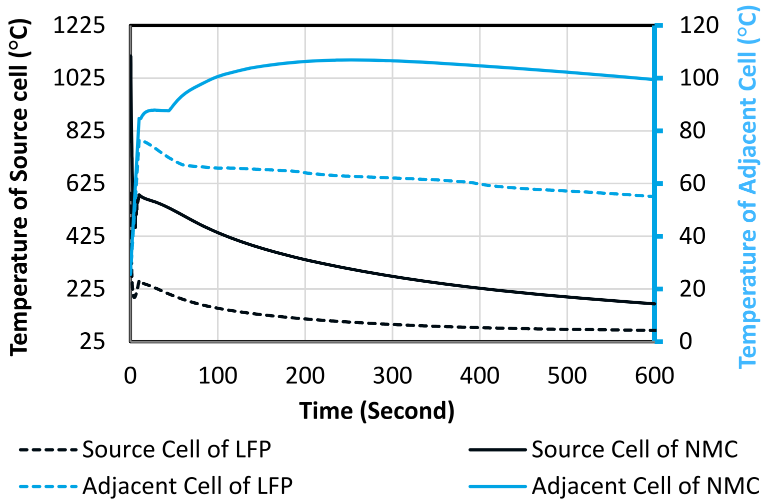


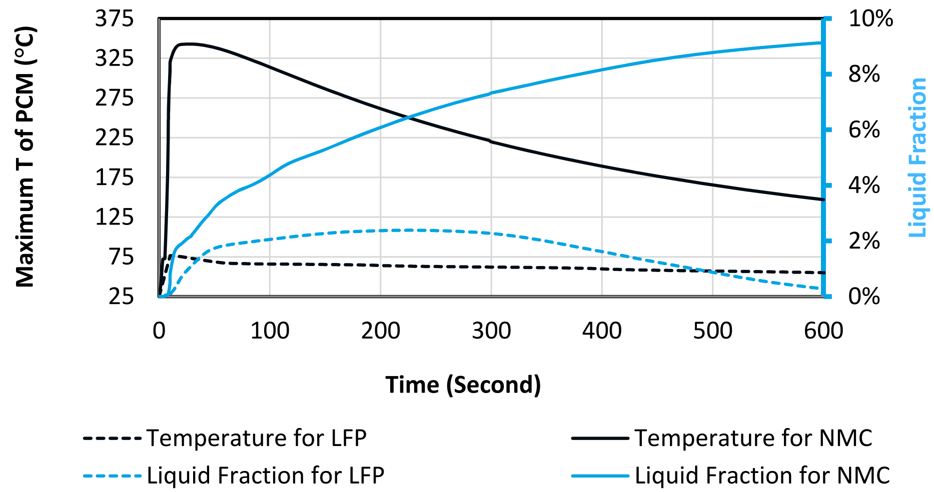
- Most of PCM, which surrounds the source cell (Jr_24), has been melted

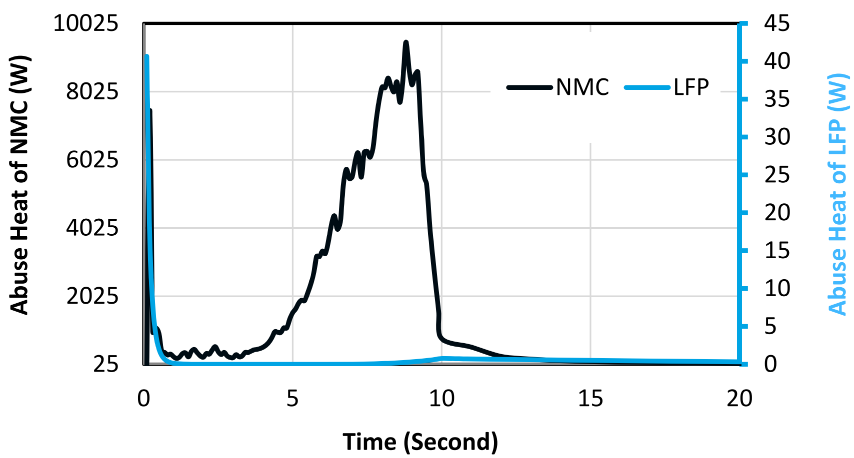


Total volume of local fraction

Case 1. Vs 2. Effects of Cell Chemistry at ISR of 4mΩ (NMC Vs. LFP)

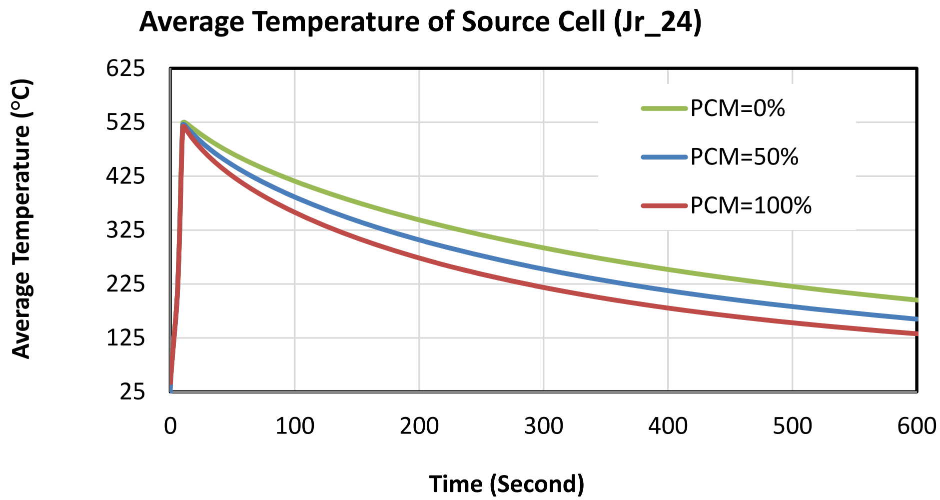


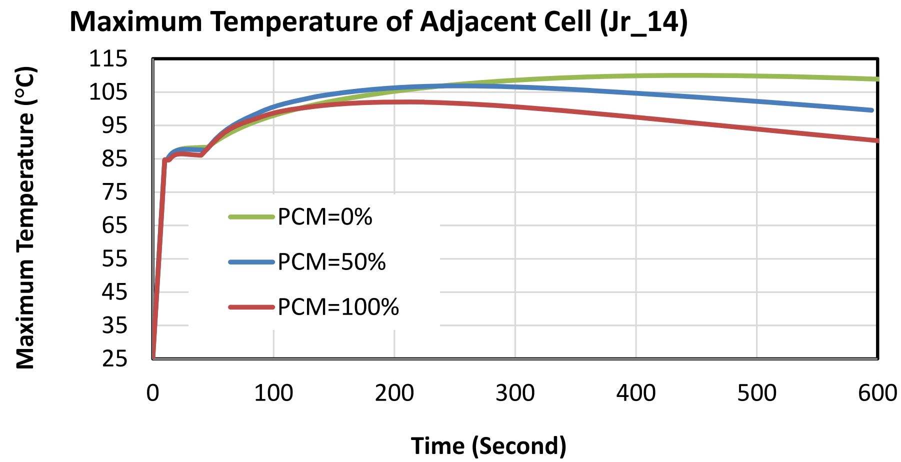


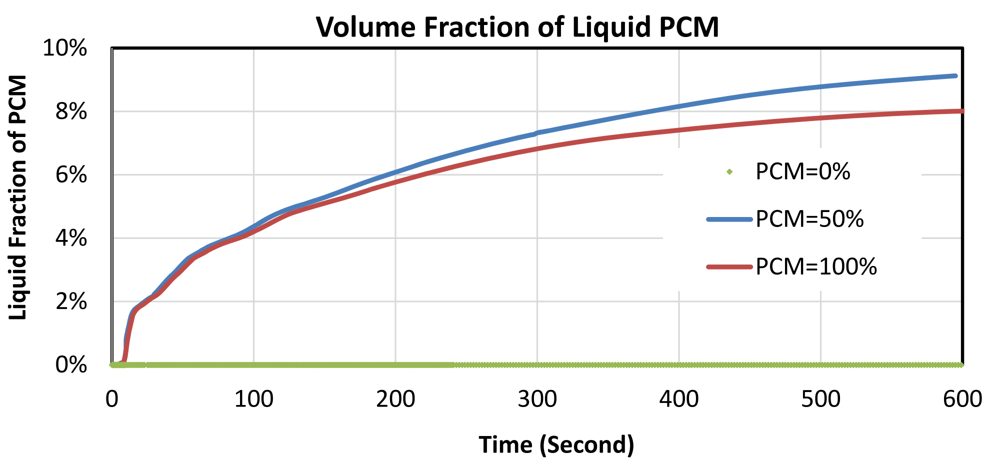


- Due to chemistry difference, maximum temperature of source cell and adjacent cell for LFP battery is much lower than that for NMC battery
- Abuse heat can be found in LFP in the beginning, but the magnitude of abuse heat is very small, and it decays within a short time
- LFP battery is safer than NMC battery in term of magnitude of abuse heat

Effects of PCM Volume for NMC at ISR of 4mΩ (Cases 1, 3, 4)

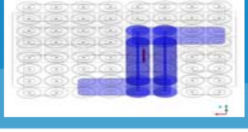


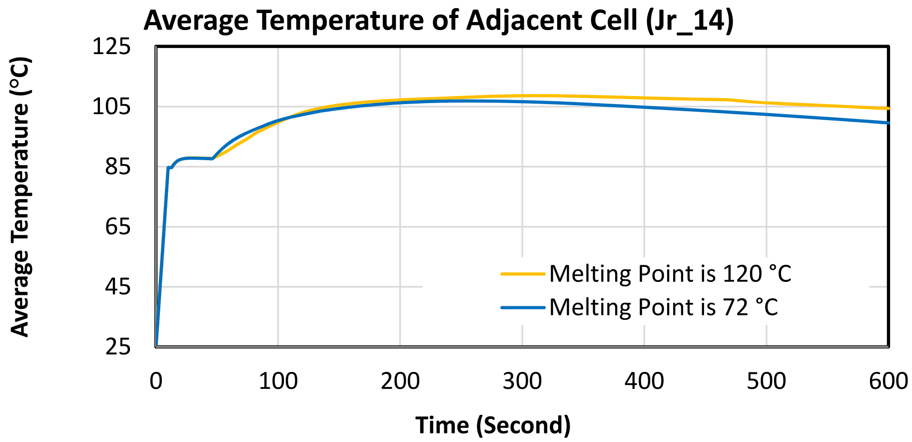


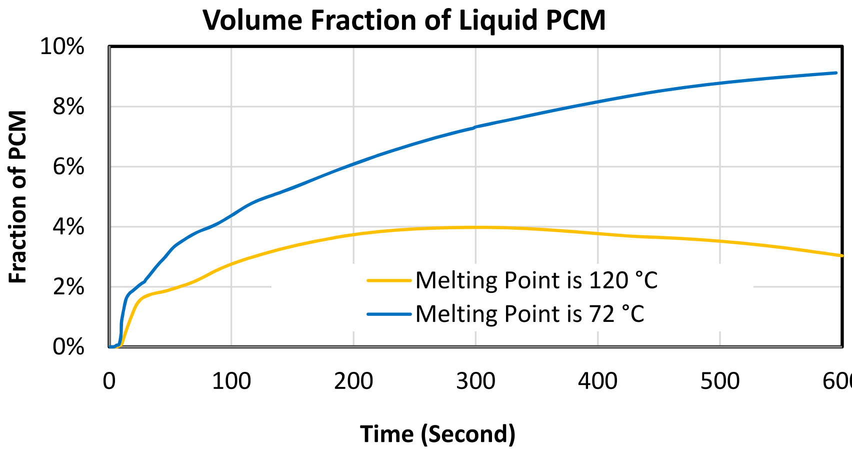


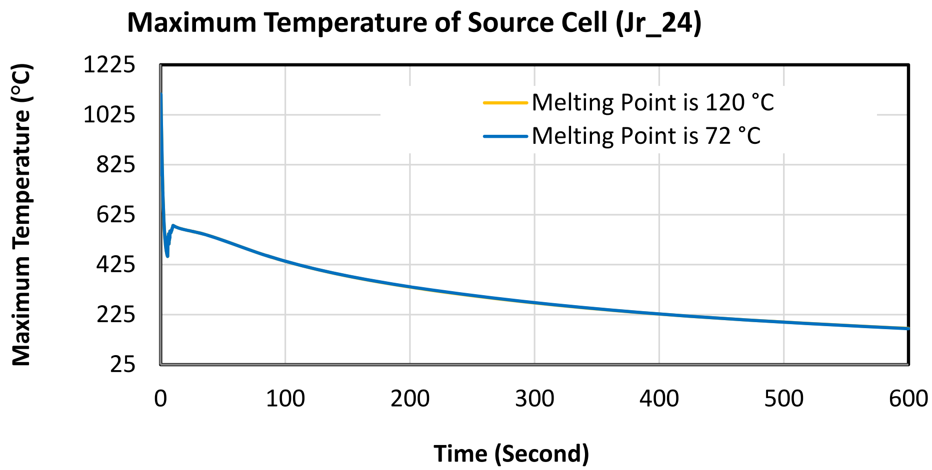
- PCM starts to work after 10 second
- PCM is 0% means the phase-change material is substituted by plastic
- Average temperature of source cell and Adjacent cell is decreasing with volume of PCM increasing
  - Abuse heat doesn't propagates to adjacent cell in plastic case too because of insulating effect of the surrounding the cell (0.22W/m °C)

Effects of Melting Point of PCM (Cases 1 &5)



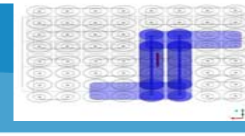


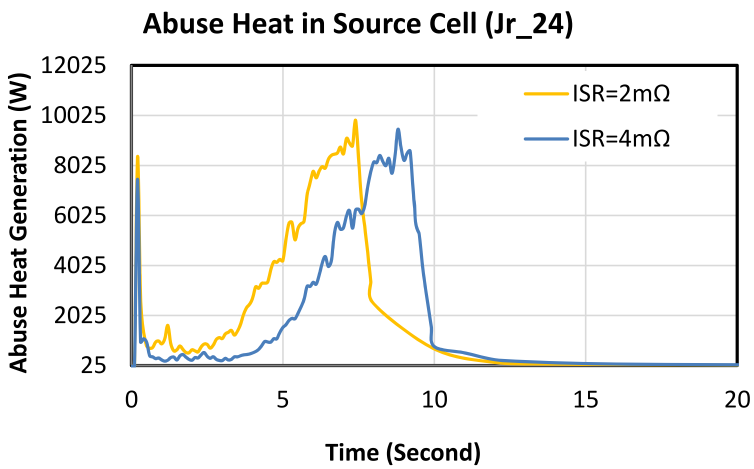


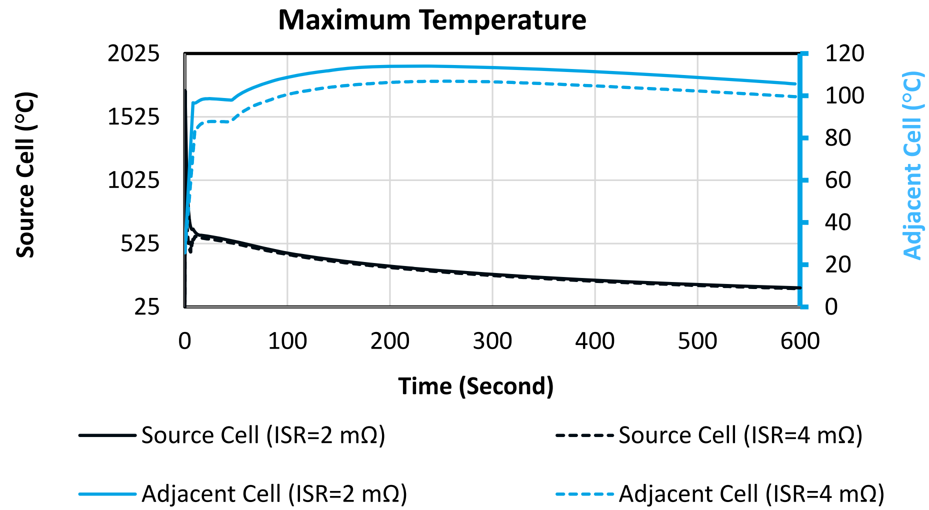


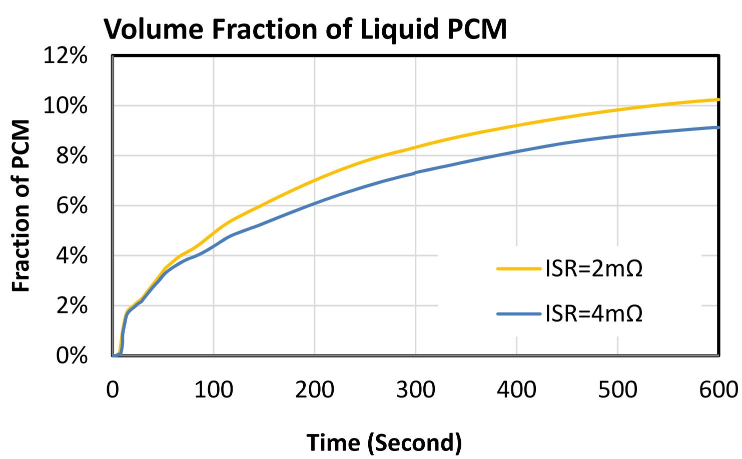
- Average temperature of adjacent cell is lower when melting point of PCM is 72 °C
- Low melting point of PCM provides a better performance
- Maximum temperature of source cell is not affected by melting point

Effects of Initial Short Resistance (2mΩ Vs. 4mΩ) (Cases 1 & 6)



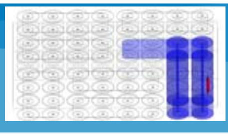




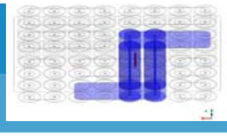


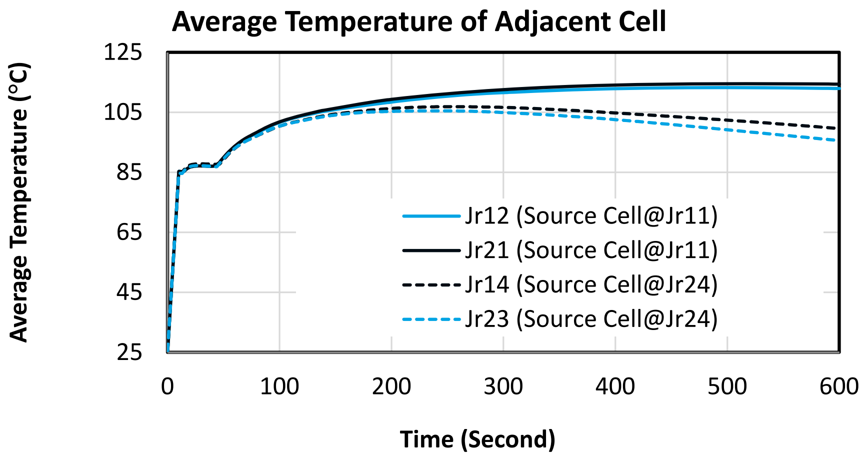
- Abuse heat propagates faster when ISR is 2 mΩ
- Maximum temperature of adjacent cell for ISR of 2mΩ is greater than that for ISR of 4 mΩ , but adjacent cell is still safe (T < 120 °C)

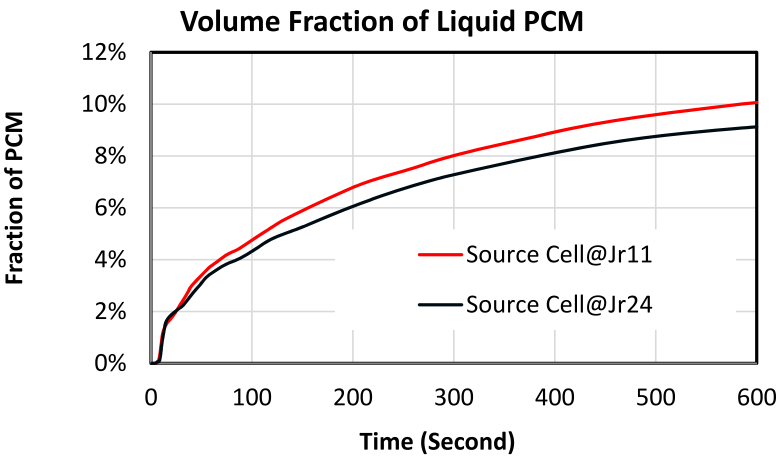
Effects of Location of Shorted Cell (Cases 1 & 7)

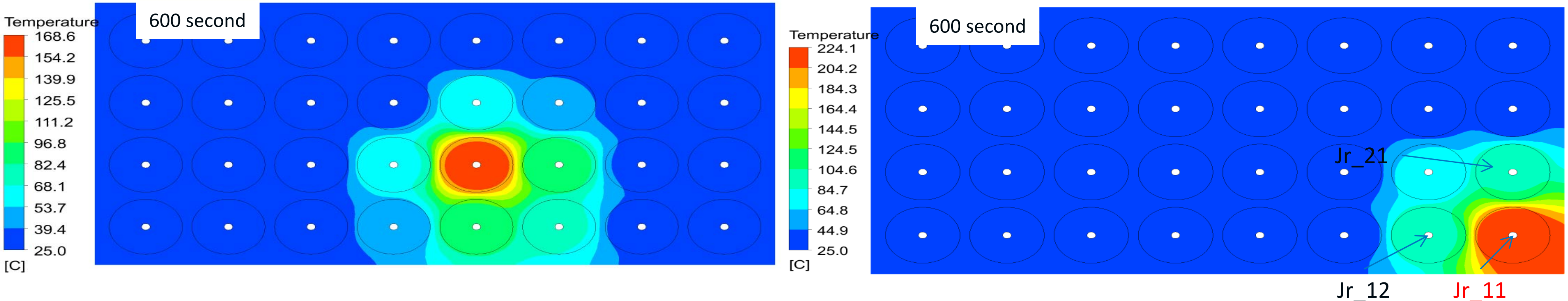


Vs.







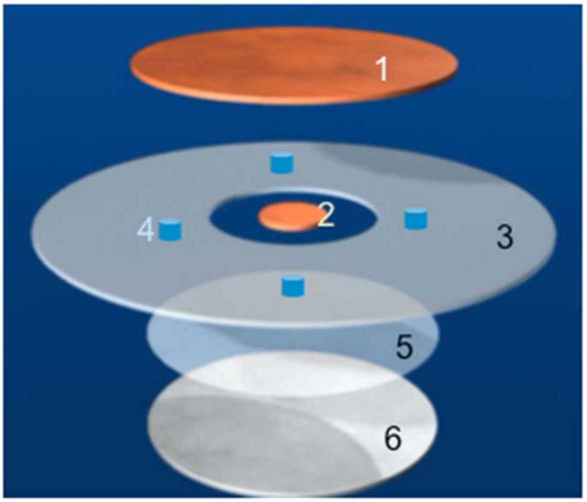


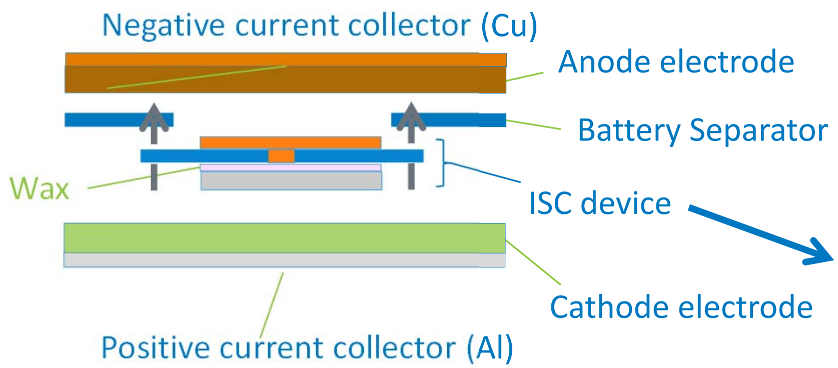
- When shorted cell locates in the center of module, average temperature of adjacent cell is lower than the case which shorted cell locates at the corner of battery module

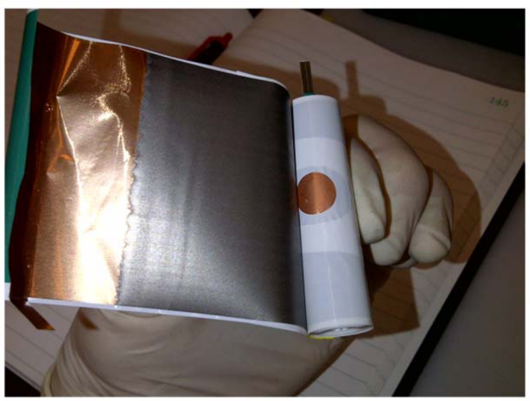
Validating Cell-to-Cell Thermal Propagation in Module

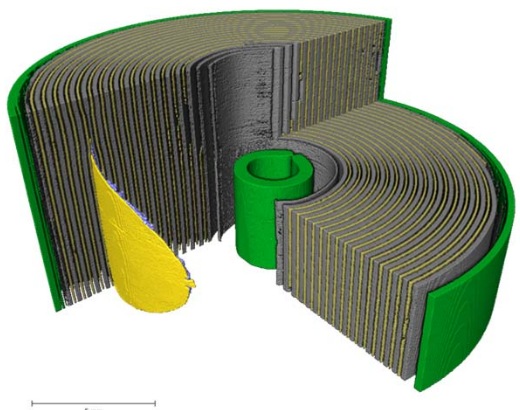
- To validate the thermal propagation model with hardware testing, one or two cells need to be sent to thermal runaway?
- What are approaches in sending cells into thermal away?
  - Overheating of a cell with heaters (uniformly or localized)
  - Overcharging of a cell
  - Nail/rod penetration into one cell (side or top)
  - Localizing heating of a cell with laser (SNL investigating)
  - Trigger a cell embedded into TR with NREL Battery Internal Short Circuit Instigator Device

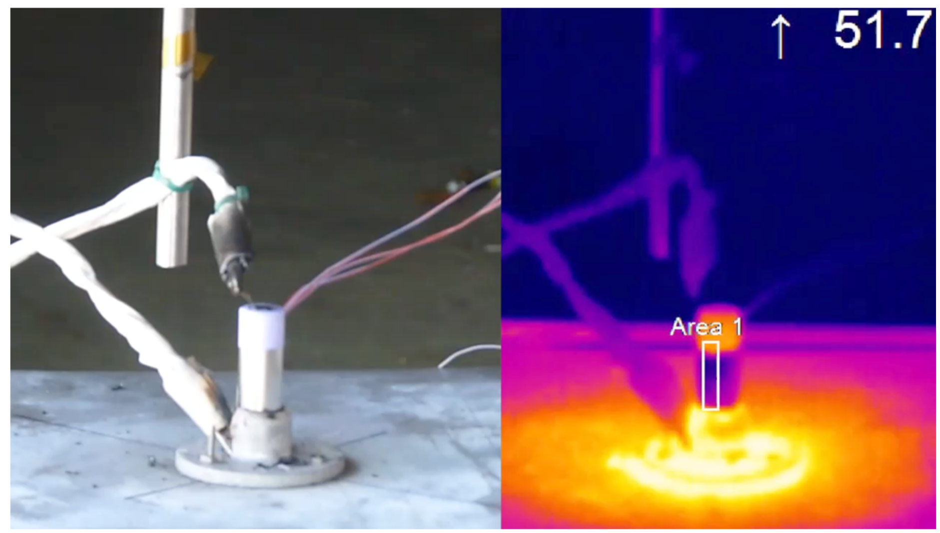
NREL ISC Device for Instigating Internal Short Circuit in Li-Ion Cells









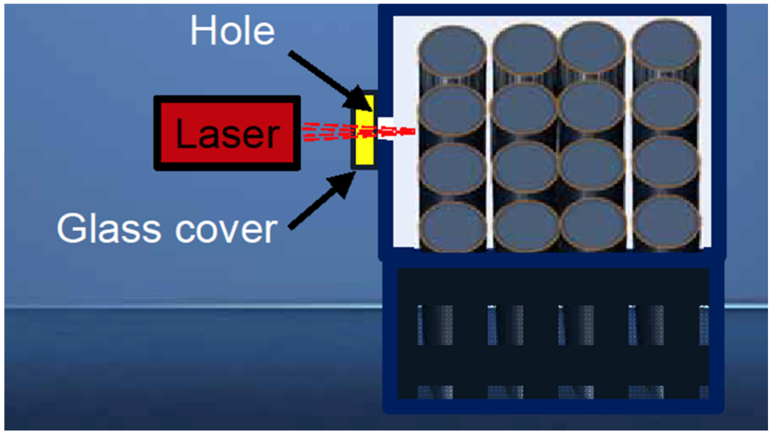


Validating Cell-to-Cell Thermal Propagation in Module

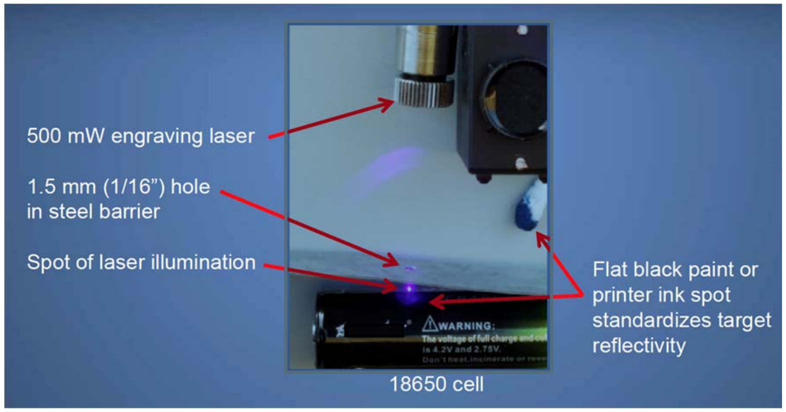
- To validate the thermal propagation model with hardware testing, one or two cells need to be sent to thermal runaway?
- What are approaches in sending cells into thermal away?
  - Overheating of a cell with heaters (uniformly or localized)
  - Overcharging of a cell
  - Nail/rod penetration into one cell (side or top)
  - Localizing heating of a cell with laser (SNL investigating)
  - Trigger a cell embedded into TR with NREL Battery Internal Short Circuit Instigator Device
- Overheating, overcharge, and nail/rod penetration may generate much more heat to the adjacent cells and will make them pre-disposed to thermal runaway
- NREL ISC device trigger simulates a realistic short – but need access to cell/module
- Localized heating of a cell in a module with a laser may present an interesting opportunity (no modification)

NTSB’s Proposed Method to Induce Cell-to-Cell Propagation with Laser

- Sandia National Lab has shown that an appropriately sized laser can send a pouch cell to thermal runaway *(Lamb, et. al. BSC, 1/12/2017)*
- *Robert Swaim* of NTSB has proposed the following:
  - Drill a 1 mm hole through the module/pack casing
  - Minimize reflectivity of the visible cell by applying black paint or ink
  - Cover hole with a laser-transparent glass piece
  - Fire a laser with appropriate power at cell seen through the hole to send it to thermal runaway
  - Initial proof of concept shown that a cell in a string of 18650 Li-Ion cells expose to a laser beam through a cover hole can go into thermal runaway



Cells in battery case



Summary

- NREL has a portfolio of tools to understand safety issues and how solutions might work
- We modeled cell-to cell-thermal propagation in a 32-cell module
- Localize heating (similar to internal short circuit was simulated)
- The model include chemical kinetics reactions happening in a cell depending on chemistry
- LFP and NMC chemistries were modeled (NMC resulted in higher temperatures)
- Results show that phase change material could be effective in preventing propagation when a cell abused
- Corner cells if go into TR could results in higher temperature in adjacent cells than middle cells
- Need to evaluate thermal performance under normal operation
- The model needs to be validated with hardware under abuse testing
- Two single cell TR methods could be used for validation: NREL ISC Device or laser ignition of a cell

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