NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Prediction of Multi-physics Behaviors of Large Lithium-ion Batteries During Internal and External Short Circuit

Battery 2010
Safety
November 3, 2010
Boston, MA

Battery Safety 2010
In conjunction with
6th Lithium Mobile Power
Boston, MA, Nov 3rd, 2010

Gi-Heon Kim[1,*], Kyu-Jin Lee[1], Lawrence Chaney[1], Kandler Smith[1], Eric Darcy[1,2], Ahmad Pesaran[1]

[1]National Renewable Energy Laboratory, Golden, CO, USA
[2]NASA Johnson Space Center, Houston, TX, USA

NREL/PR-5400-49864

*: gi-heon.kim@nrel.gov

Performance, Durability and Safety

Physics of Li-Ion Battery Systems in Different Length Scales

Atomic Scale

Thermodynamic properties
Lattice stability
Material-level kinetic barrier
Transport properties

Particle Scale

Li diffusion in solid phase
Interface physics
Particle deformation & fatigue
Structural stability

Electrode Scale

Charge balance and transport
Electrical network in composite electrodes
Li transport in electrolyte phase

Cell Scale

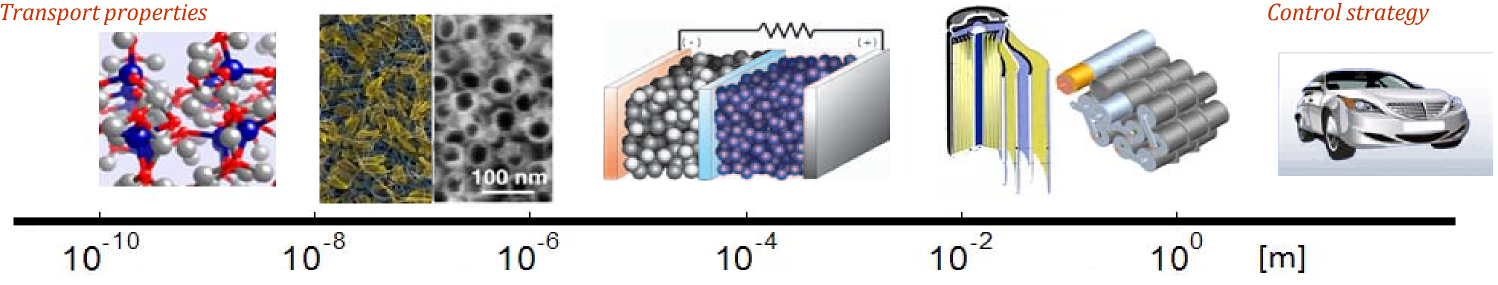
Electronic potential & current distribution
Heat generation and transfer
Electrolyte wetting
Pressure distribution

Module Scale

Thermal/electrical inter-cell configuration
Thermal management
Safety control

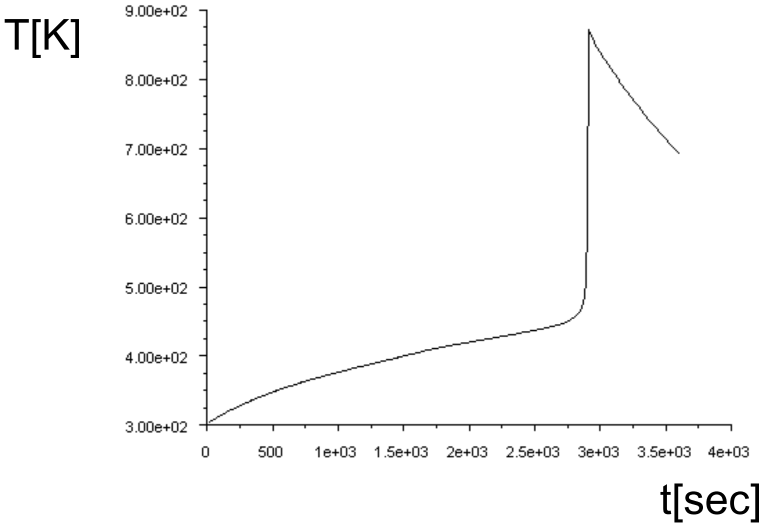
System Scale

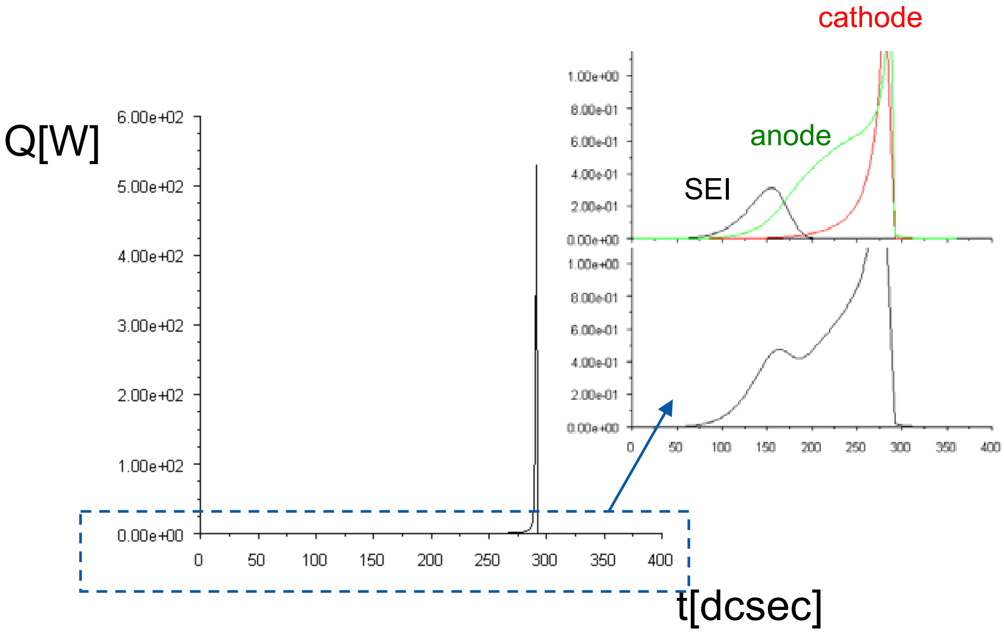
System operating conditions
Environmental conditions
Control strategy



Thermal Runaway

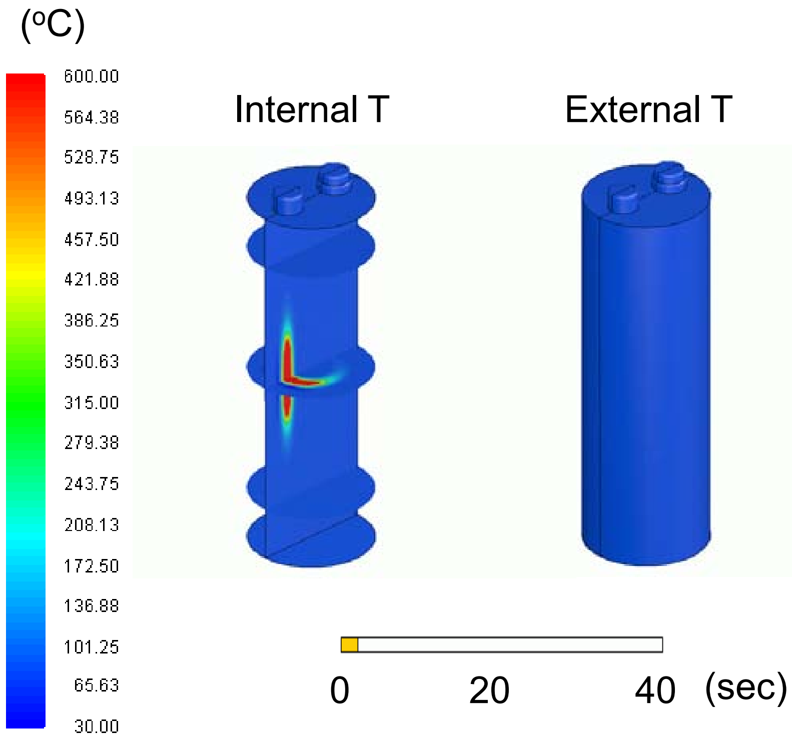
Temperature ⟷ Exothermic Reactions

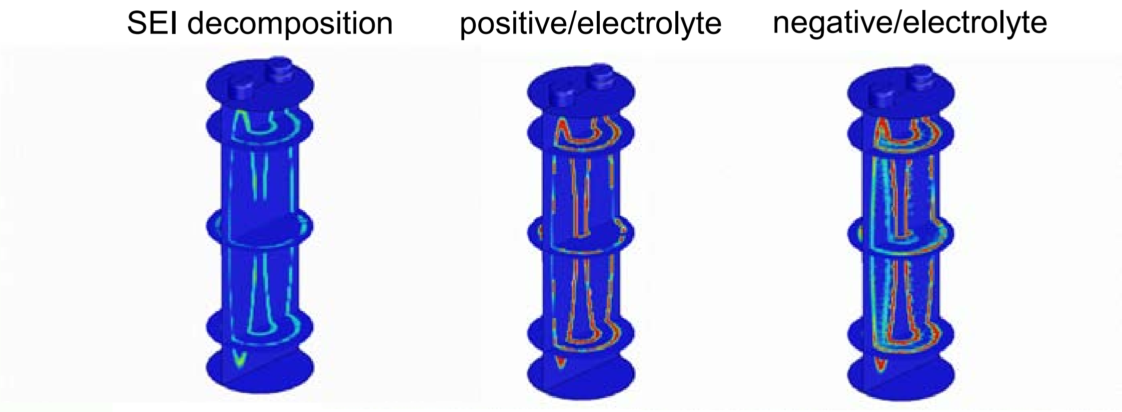




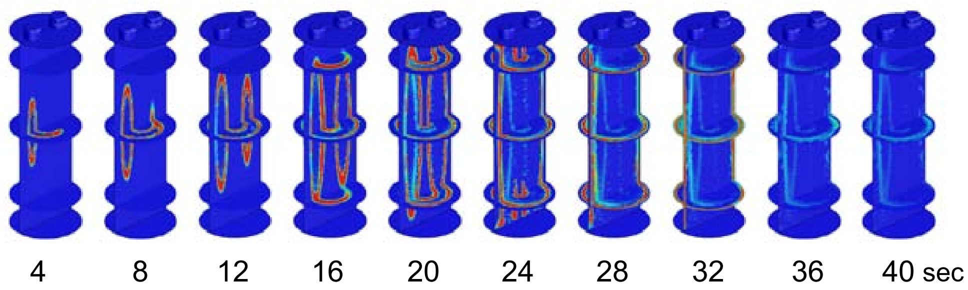
Modeling Thermal Runaway

- ✓ Constructed empirical reaction models using calorimetry data for component decompositions; Approach practiced by J. Dahn’s group
- ✓ Enhanced understanding of the interaction between heat transfer and exothermic abuse reaction propagation for a particular cell/module design, and
- ✓ provided insight on how thermal characteristics and conditions can impact safety events of lithium-ion batteries.





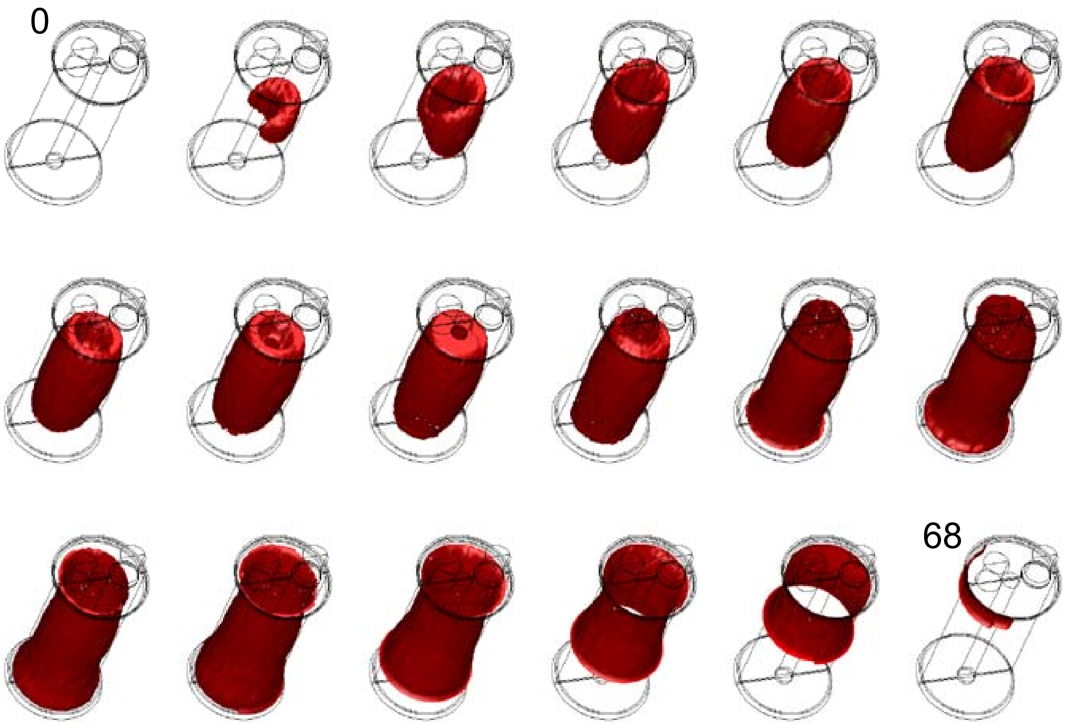
Total volumetric heat release from component reactions

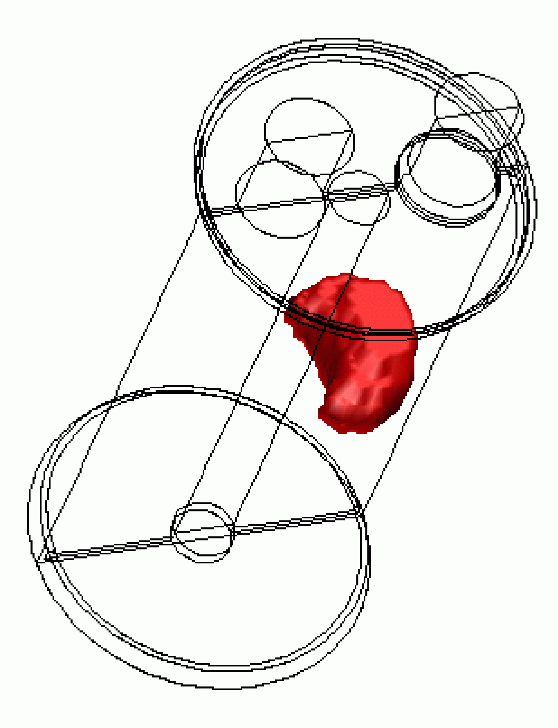


Reaction Propagation

- Propagates Initially in azimuthal direction
- Forms hollow cylinder shape reaction zone
- Center axis zone starts to react
- Finally reaction goes further in outer radius cylinder zone

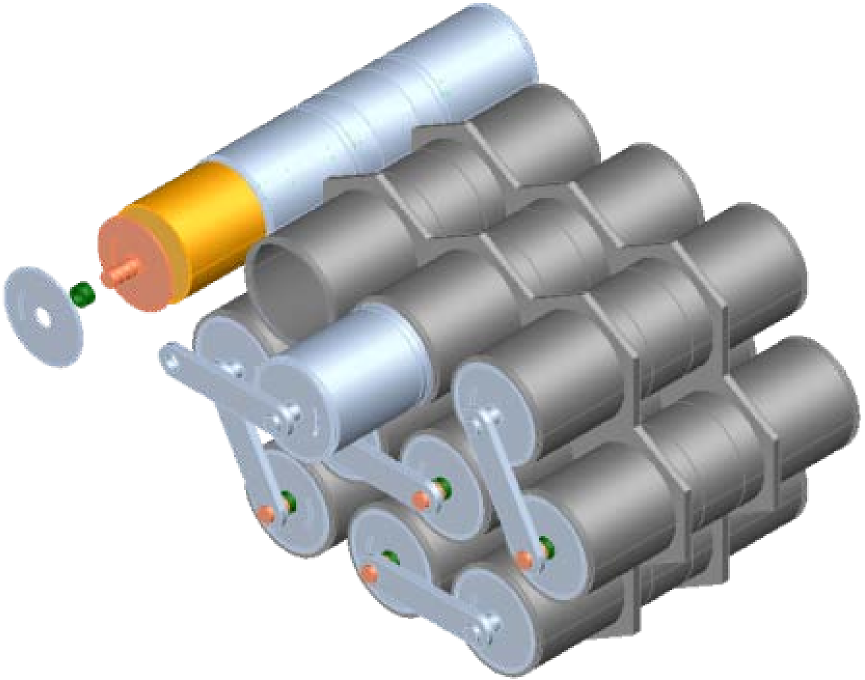
SEI decomposition reaction front

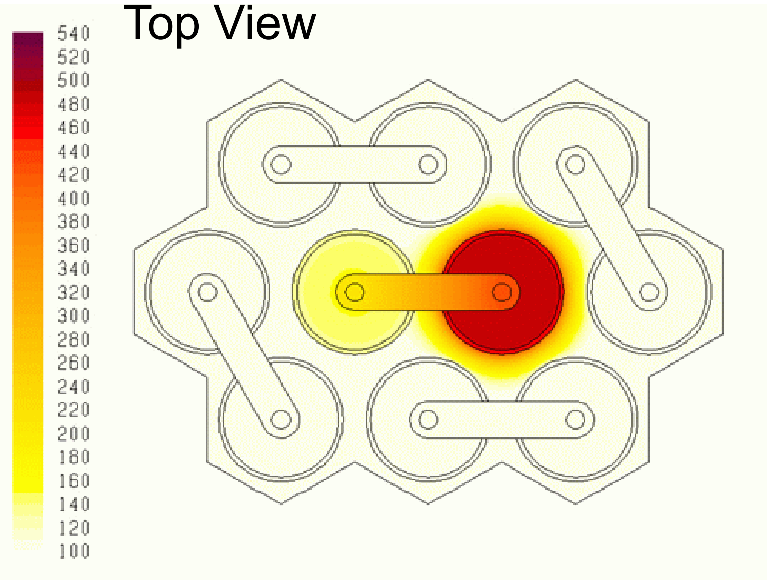


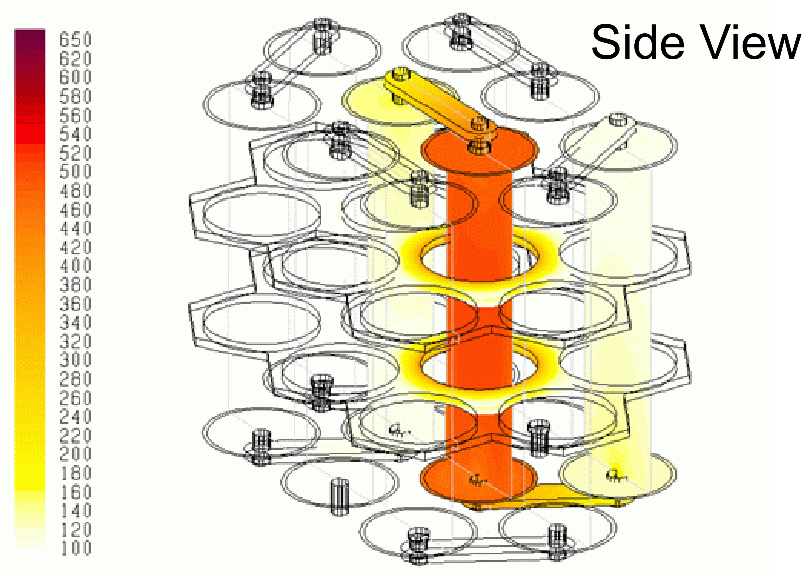


Runaway Propagation

In a multi-cell module

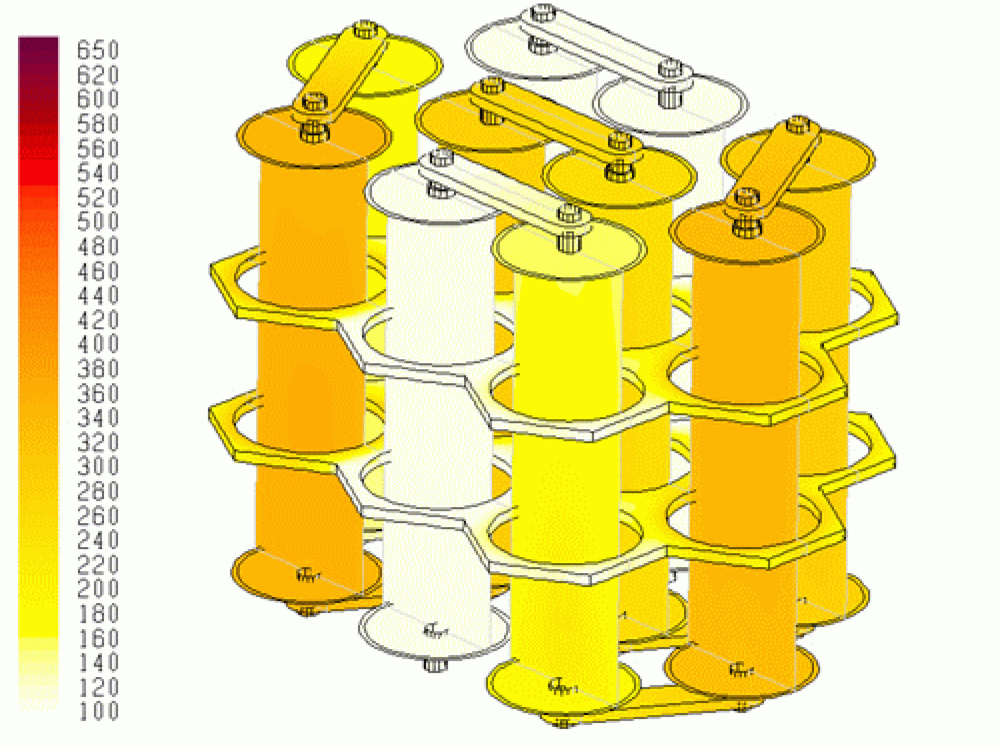






5 minutes apart between each frame

Closer Look at Reaction in an Individual Cell

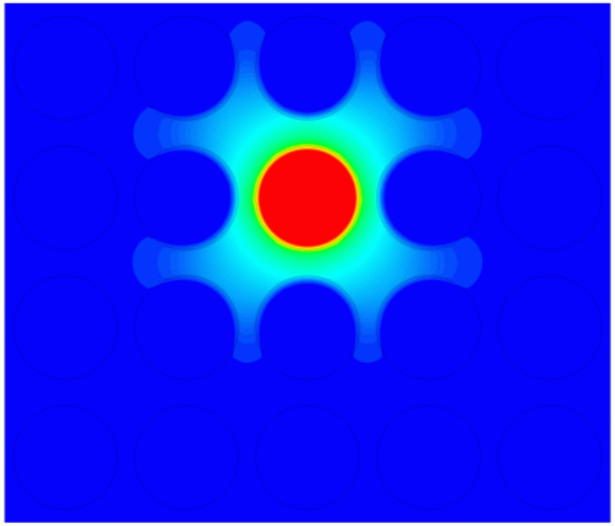


2 seconds apart between each frame

Fast Heat Dissipation

✓ Small cell module: 20 x 18650

✓ Highly conductive carbon matrix wetted with phase change materials

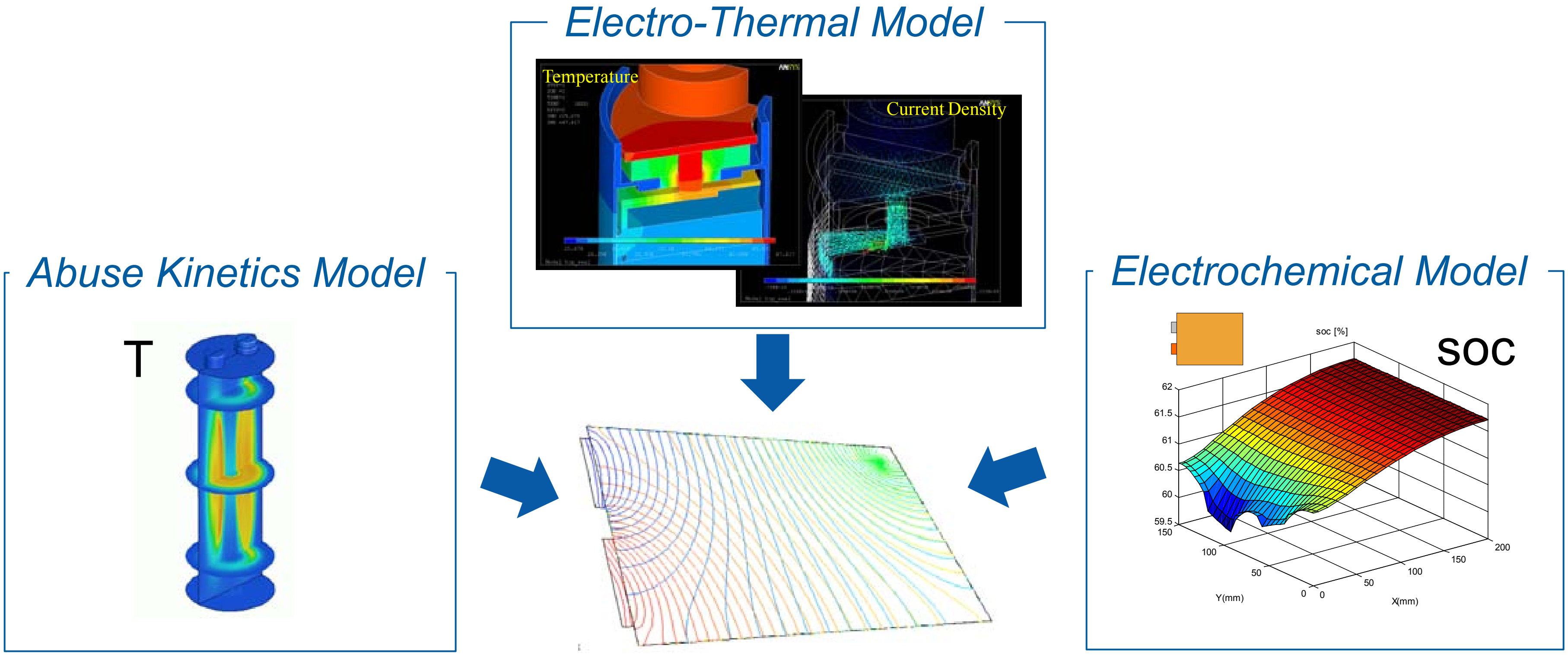


Temperature

Heat of SEI decomposition

Multi-Physics Internal Short Circuit Model

- Developed an integrated model for multi-physics internal short circuit of lithium-ion cells by linking and integrating NREL's unique electrochemical, electro-thermal, and abuse reaction kinetics models
- Performed 3D multi-physics internal short simulation study to characterize an internal short and its evolution over time



Electro-Thermal Model

Abuse Kinetics Model

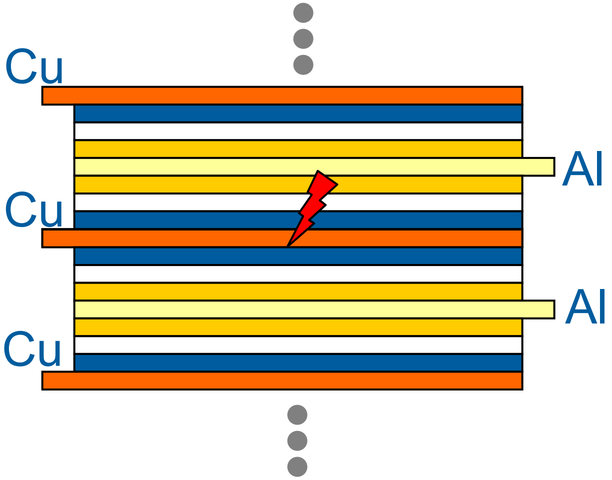
Electrochemical Model

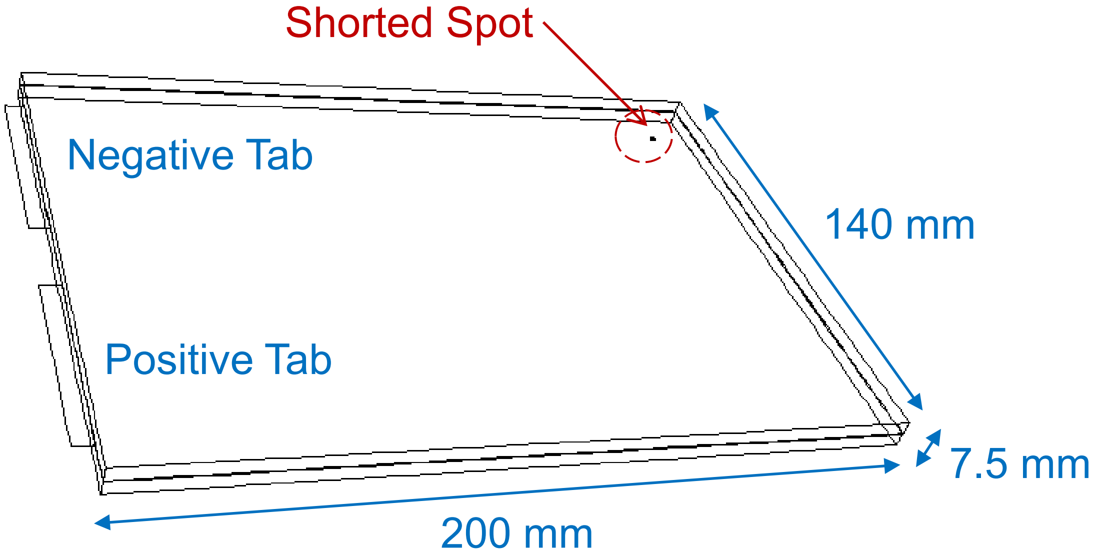
Internal Short Circuit Model Study

Performed Case Study with A 20Ah Prismatic Cell

To investigate impacts of various short natures and cell characteristics

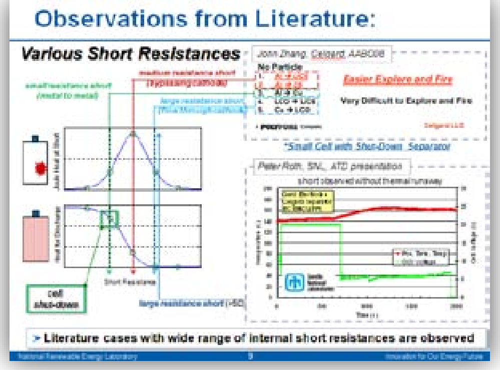
- Case Studies – 20Ah Stacked Prismatic Cell
  - ISC between metal (Al & Cu) current collector foils
  - ISC between electrode (cathode & anode) layers
    - Impact of short area – separator hole propagation
  - ISC between Al to anode – short bypassing cathode
  - Impact of Cell Size
    - Comments on Shutdown Separator
  - Impact of ISC location





Results Agree Well with Laboratory Observations

The simulation results have reasonably reproduced the experimental observations from other research groups/companies including SNL, Exponent, Celgard, LGchem, and Sony



Observations from Literature:

Various Short Resistances

John Zhang, Celgard, AABC08

No Particle

Easier Explore and Fire

Very Difficult to Explore and Fire

"Small Cell with Shut-Down Separator

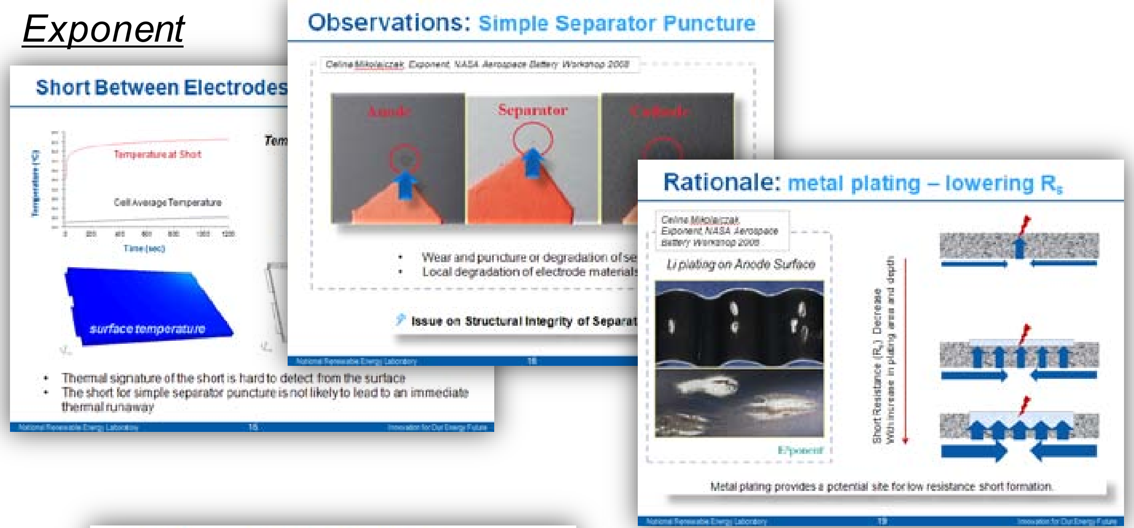
Peter Roth, SNL, ATD presentation

short observed without thermal runaway

- Literature cases with wide range of internal short resistances are observed

Sandia National Lab, Celgard

Exponent



Short Between Electrodes

- Thermal signature of the short is hard to detect from the surface
- The short for simple separator puncture is not likely to lead to an immediate thermal runaway

Observations: Simple Separator Puncture

Celina Mikolajczak, Exponent, NASA Aerospace Battery Workshop 2008

- Wear and puncture or degradation of se
- Local degradation of electrode materials

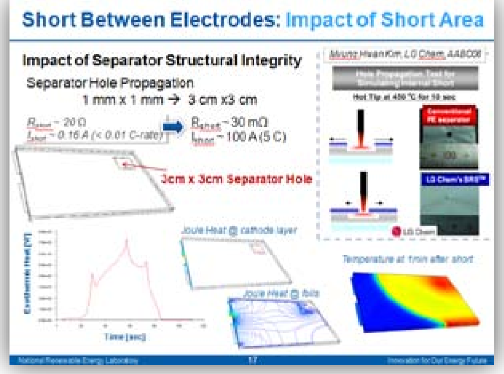
Issue on Structural Integrity of Separat

Rationale: metal plating – lowering R_s

Celina Mikolajczak, Exponent, NASA Aerospace Battery Workshop 2008

Li plating on Anode Surface

Metal plating provides a potential site for low resistance short formation.



Short Between Electrodes: Impact of Short Area

Impact of Separator Structural Integrity

Separator Hole Propagation

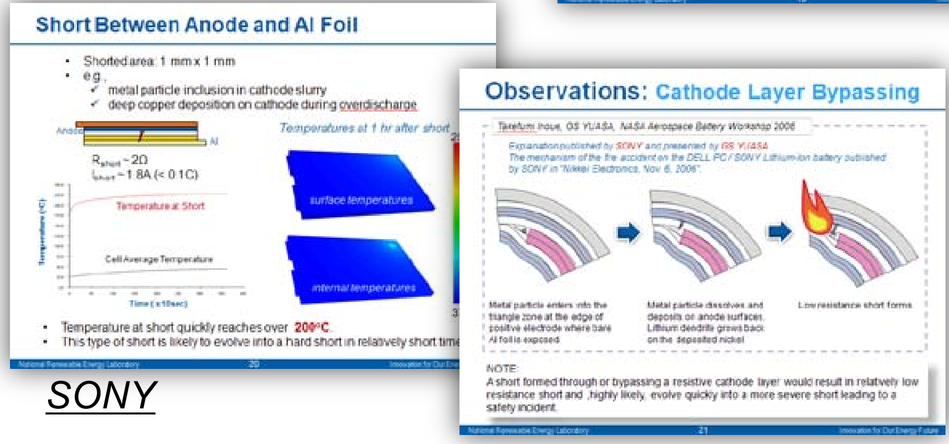
1 mm x 1 mm → 3 cm x3 cm

R_{short} ~ 20 Ω, I_{short} ~ 0.16 A (< 0.01 C-rate) → R_{short} ~ 30 mΩ, I_{short} ~ 100 A (5 C)

Myung Hwan Kim, LG Chem, AABC08

Hot Tip at 450 °C for 10 sec

LG Chem



Short Between Anode and Al Foil

- Shorted area: 1 mm x 1 mm
- e.g.,
  - ✓ metal particle inclusion in cathode slurry
  - ✓ deep copper deposition on cathode during overdischarge

R_{short} ~ 2Ω

I_{short} ~ 1.8A (< 0.1C)

- Temperature at short quickly reaches over 200°C.
- This type of short is likely to evolve into a hard short in relatively short time

Observations: Cathode Layer Bypassing

Takefumi Inoue, GS YUASA, NASA Aerospace Battery Workshop 2008

Explanation published by SONY and presented by GS YUASA

The mechanism of the fire accident on the DELL PC / SONY Lithium-ion battery published by SONY in "Nikkei Electronics, Nov 6, 2006".

Metal particle enters into the triangle zone at the edge of positive electrode where bare Al foil is exposed.

Metal particle dissolves and deposits on anode surfaces. Lithium dendrite grows back on the deposited nickel.

Low resistance short forms

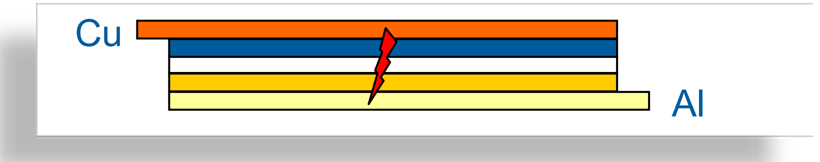
NOTE:

A short formed through or bypassing a resistive cathode layer would result in relatively low resistance short and, highly likely, evolve quickly into a more severe short leading to a safety incident.

SONY

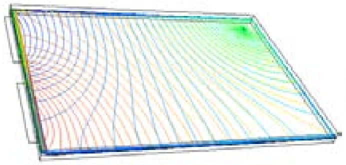
Shutdown Separator for Large Cells?

Short Between Al & Cu Metal Foils



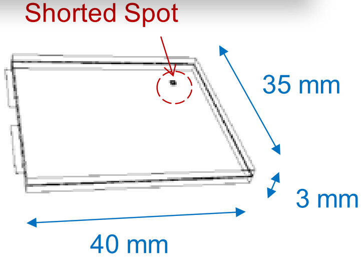
- Cell Capacity: 20 Ah

R_{short} ~ 10 mΩ
I_{short} ~ 300 A (15 C-rate)

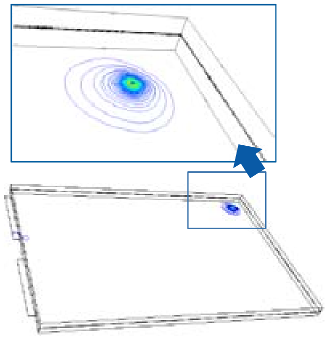


0.4 Ah

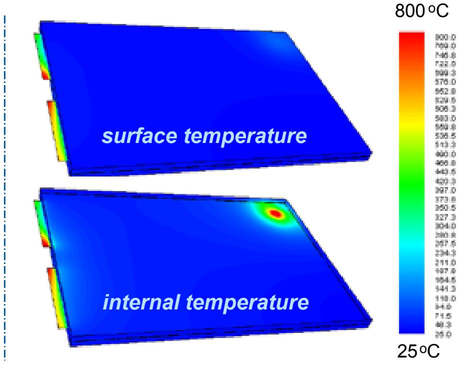
R_{short} ~ 7 mΩ
I_{short} ~ 34 A (85 C-rate)

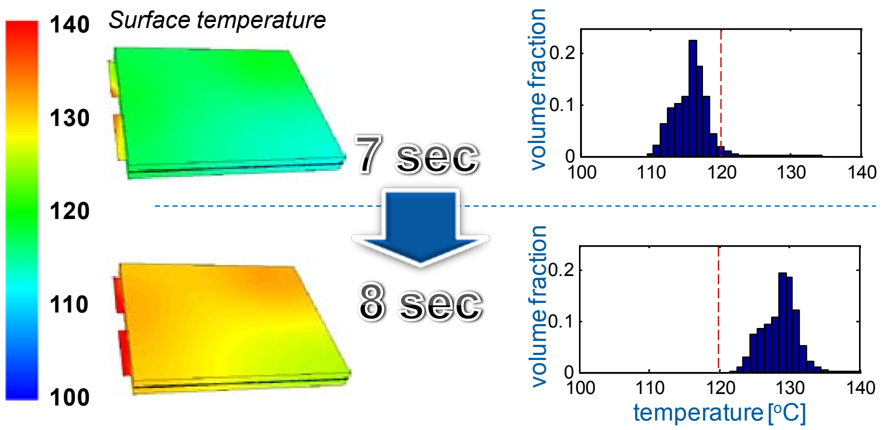


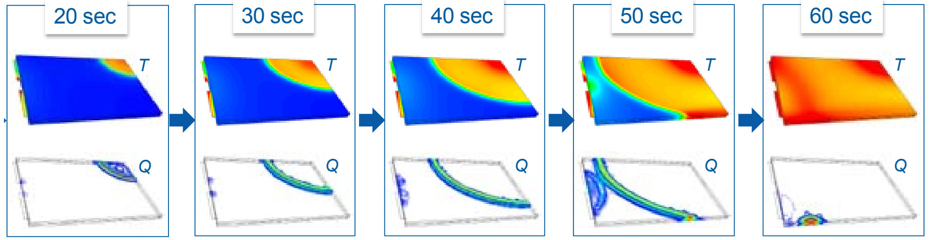
Joule heat for short

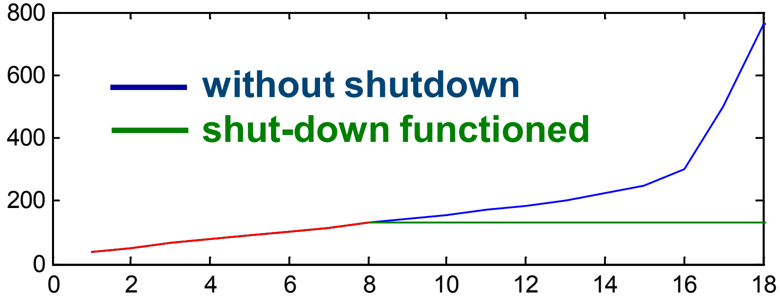


Temperature @10 sec after short

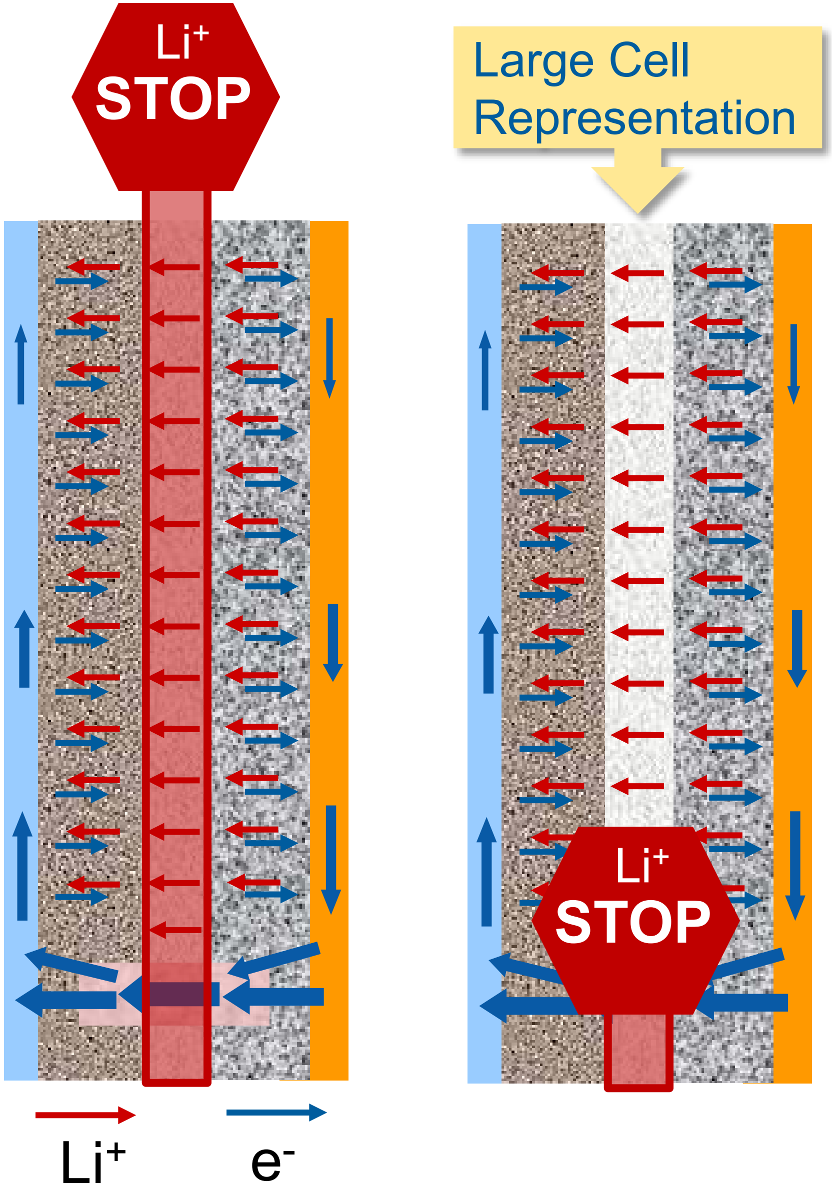








Shutdown Separator Limitation



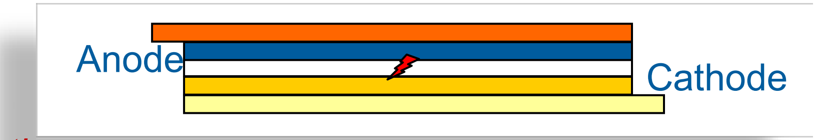
- Thermally triggered
- Block the ion current in circuit

Difficult to apply in

- Large capacity system
- High voltage system

Ceramic Reinforced Separator

Short Between Cathode and Anode Electrodes

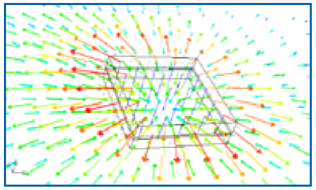


separator hole propagation

- Shorted area: 1 mm x 1 mm

3 cm x3 cm

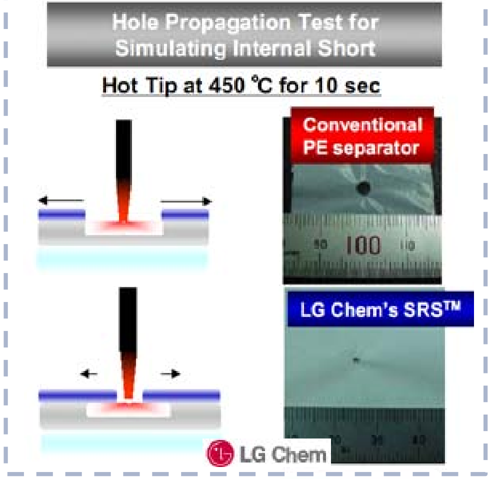
R_{short} ~ 20 Ω
I_{short} ~ 0.16 A (< 0.01 C-rate)

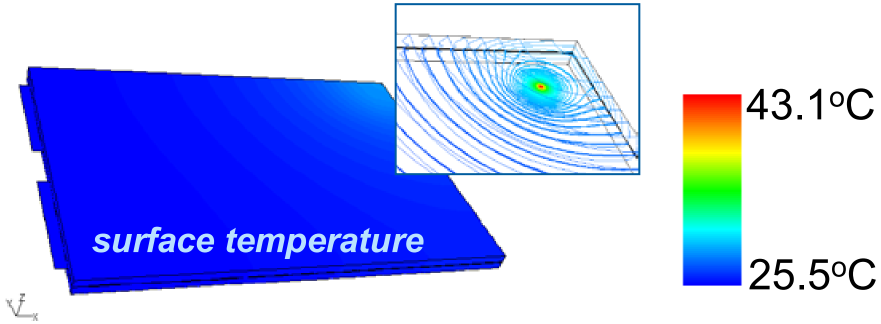


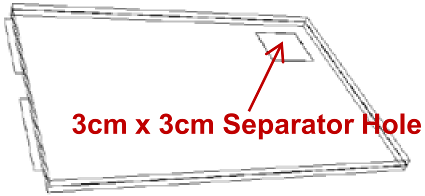
current density field near short

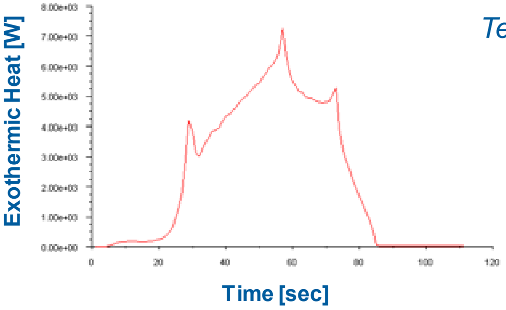
R_{short} ~ 30 mΩ
I_{short} ~ 100 A (5 C)

Myung Hwan Kim, LG Chem, AABC08

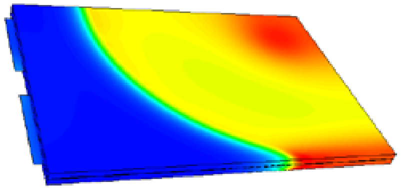








Temperature at 1min after short



- Thermal signature of the short is hard to detect from the surface
- The short for simple separator puncture is not likely to lead to an immediate thermal runaway

- Maintaining structural integrity of separator seems critical to delay short evolution

External Short of Multi-Cell Battery

Background

- Cell **PTC** device proven effective control for over-current hazards at Li-Ion cell and small battery level
- Known as ineffective in high-voltage or large capacity battery designs
- Need to verify if NASA's spacesuit battery design (16P-5S) array could depend on cell PTC devices to tolerate an external short

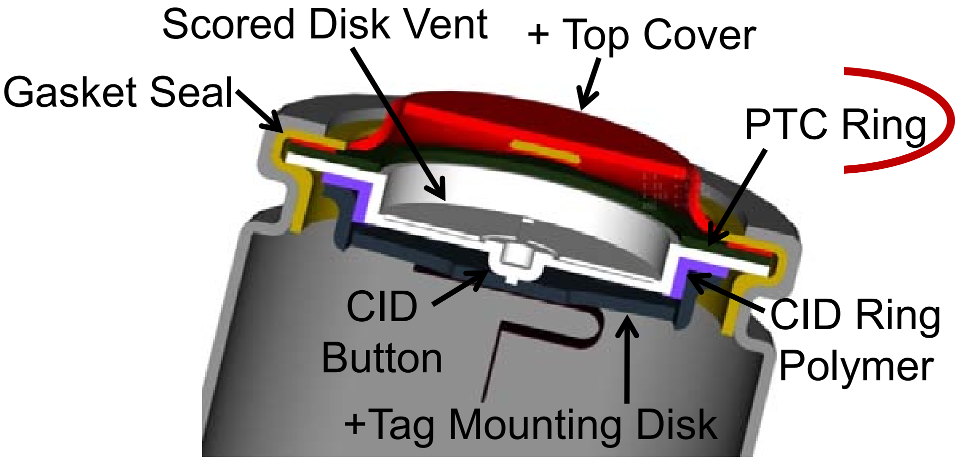
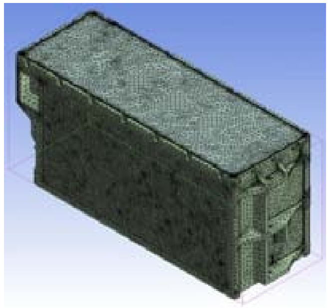


Photo: NASA



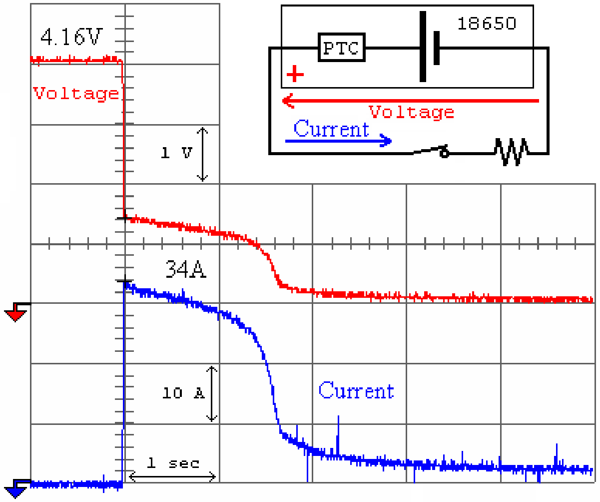
PTC Device

- Commercial lithium ion 18650 cells typically have a current-limiting PTC (positive temperature coefficient) device installed in the cell cap to limit external currents in the event of an external short to the cell.

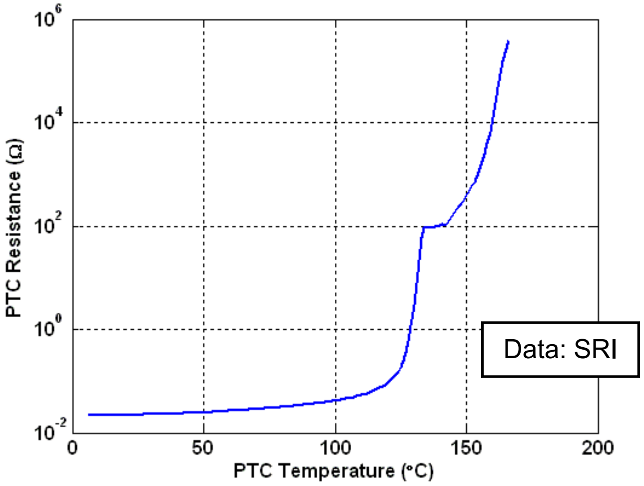
- The PTC device consists of a matrix of crystalline polyethylene containing dispersed conductive particles, usually carbon black. The resistance of the PTC device increases sharply with temperature.

- Once triggered, PTC behaves as a thermal regulator

- PTC device often fails to function in high voltage / high capacity systems

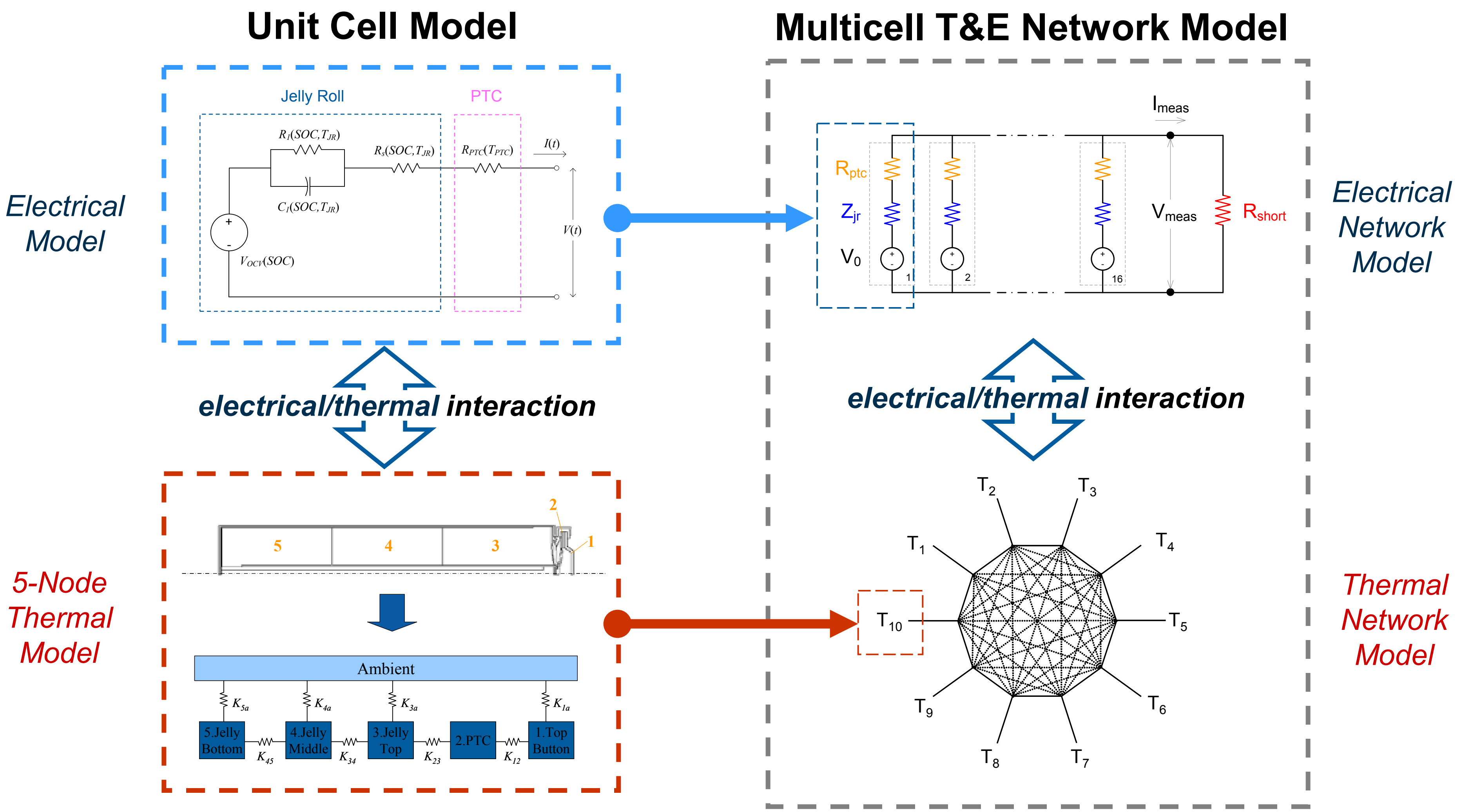


PTC Resistance vs. Temp



Model Development Approach

Integrated Thermal and Electrical Network Model *of a Multicell Battery for Safety Evaluation of Module Design with PTC Devices during External Short*



Unit Cell Model

Multicell T&E Network Model

Electrical Model

Electrical Network Model

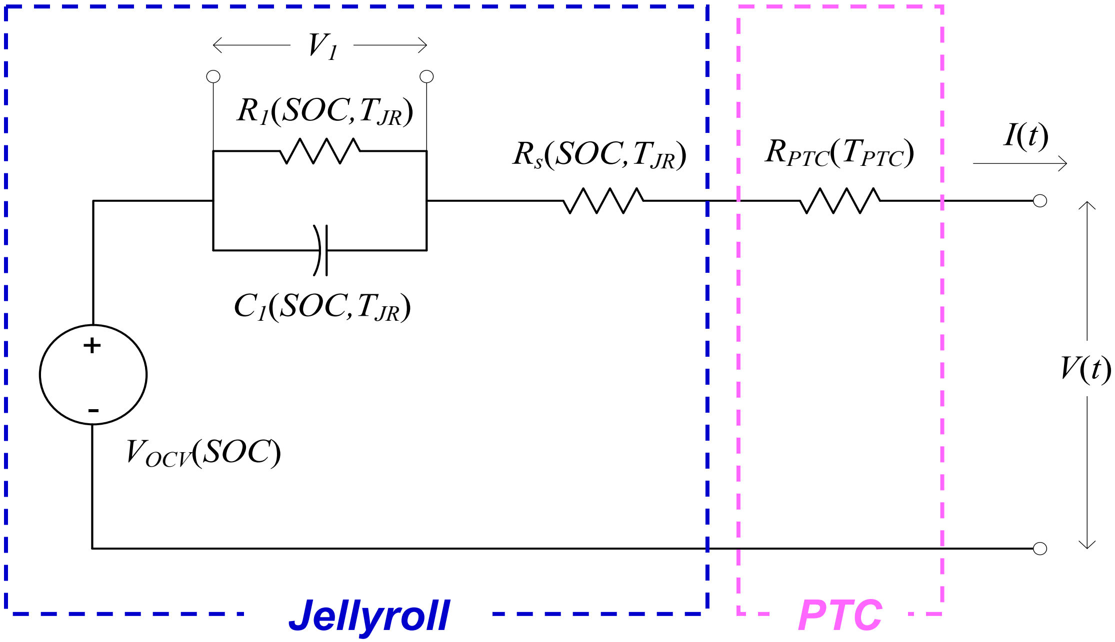
electrical/thermal interaction

electrical/thermal interaction

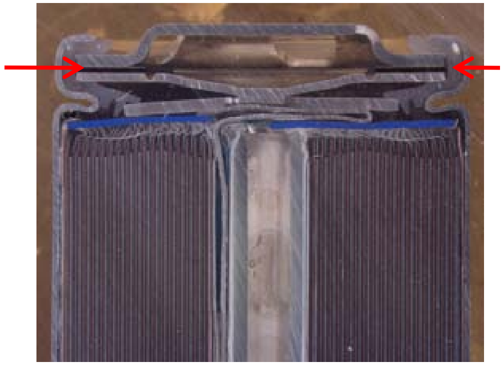
5-Node Thermal Model

Thermal Network Model

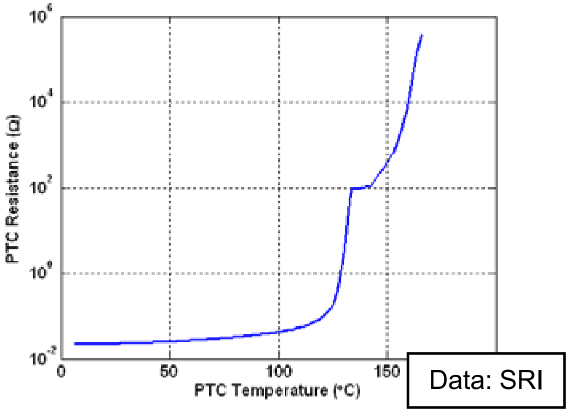
Unit Cell Model – Electrical



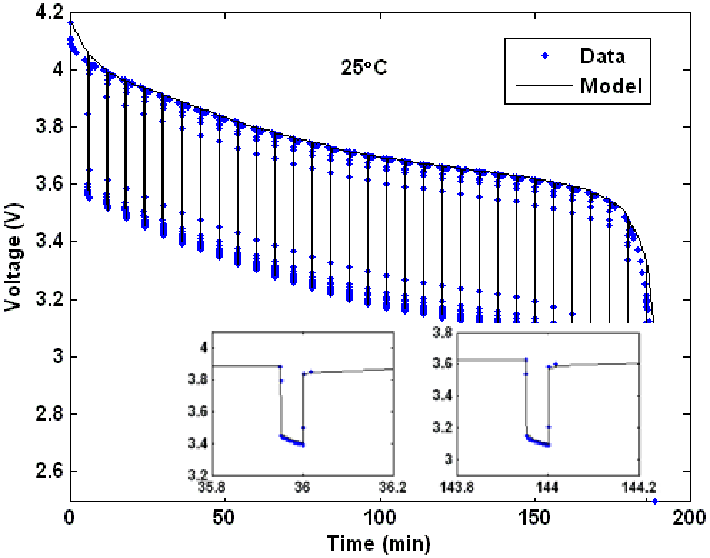
ECM including PTC device



PTC Resistance vs. Temp.



Data: SRI



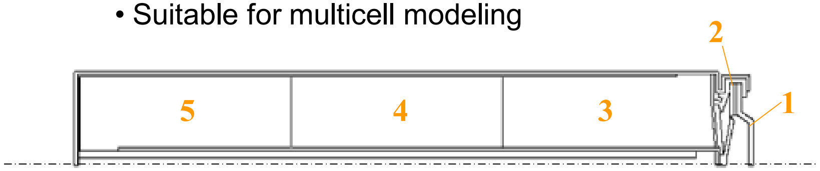
Unit Cell Model – 5-node Thermal

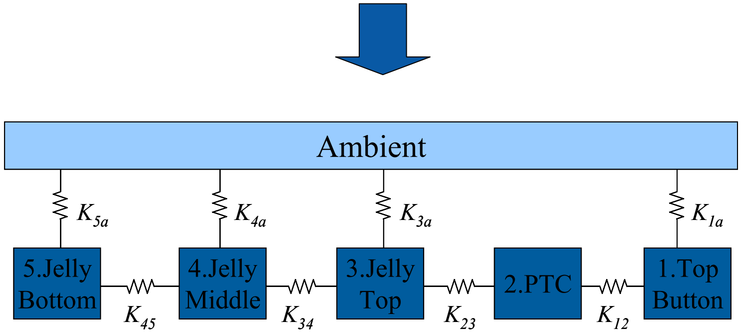
Detailed Cell Thermal Model

- Large computational requirement
- Not suitable for multicell modeling

5-Node Cell Thermal Model

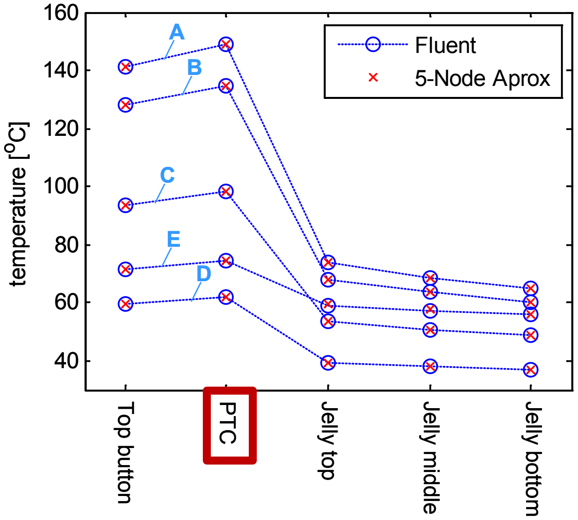
- Low order dynamic model
- Suitable for multicell modeling





Comparison of Detailed and 5-Node Models

for different heat generation conditions



A PTC:3.38W, Jelly:0.0093W
B PTC:3.0W, Jelly:0.0093W
C PTC:2.0W, Jelly:0.0093W
D PTC:1.0W, Jelly:0.0093W
E PTC:1.0W, Jelly:1.0W

Steady Form

$$Q_i = \sum_j K_{ij}\left(T_i - T_j\right)$$

Unsteady Form

$$Q_i = \sum_j K_{ij}\left(T_i - T_j\right) + MCp_i \frac{dT_i}{dt}$$

Multicell Network Model – Thermal

Thermal Network Model

Thermal Mass: Identifying thermal mass at each node
Heat Generation: PTC heat, discharge/charge heat (, abuse reaction heat)
Heat Transfer: Quantifying heat exchange among the nodes

$$Q_{transport,i} = \sum_{j=1, j\neq i} -Q_{ij}, \quad Q_{ij} = Q_{ij,radiation} + Q_{ij,connector\_conduction} + Q_{ij,convection} \cdots$$

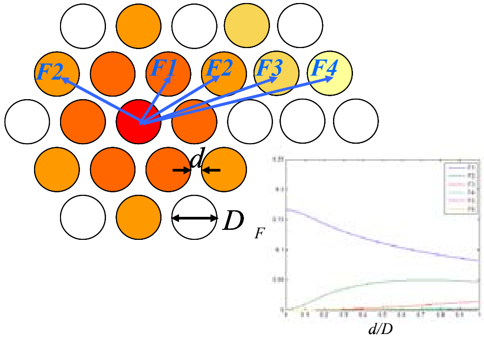
Cell-to-Cell Irradiative Heat Transfer

Transverse Heat Transfer Through Plates

Heat Conduction Through Air Gap

Heat Rejection Through Wires

Heat Transfer to Ambient



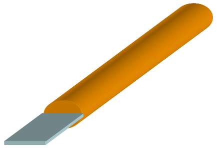



Photo: NASA ISS01E5361

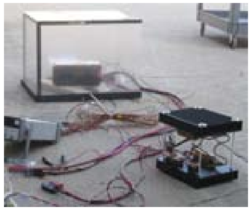


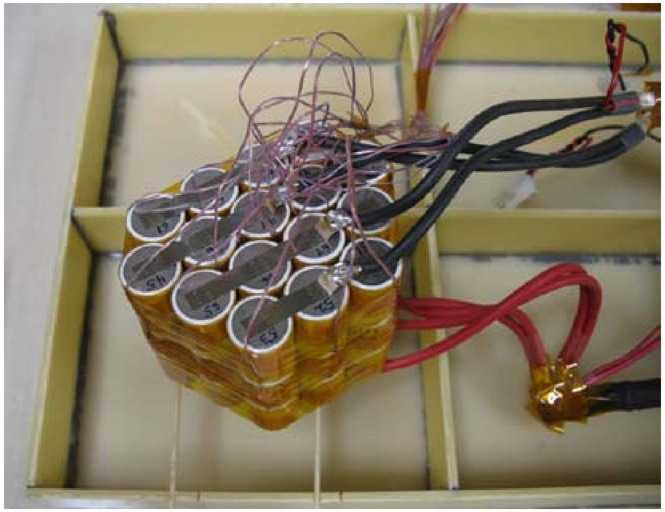
Photo: ABSL

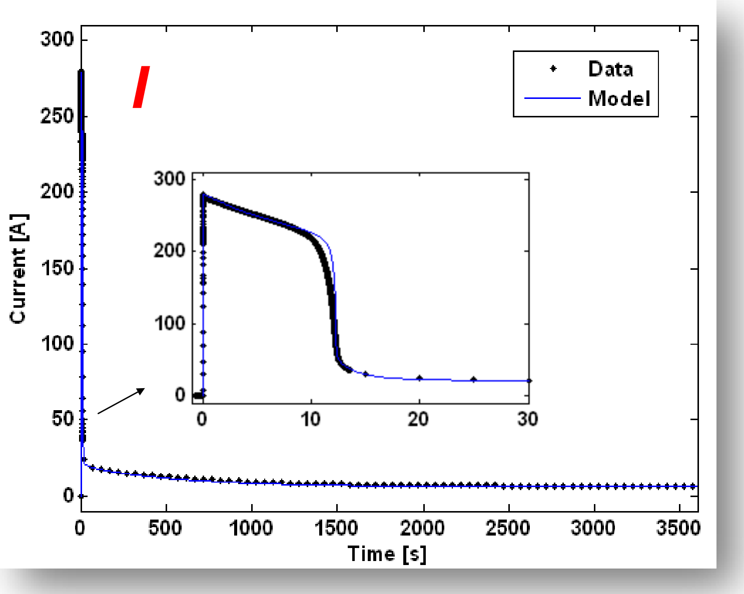
Experimental Model Validation: 16P Bank

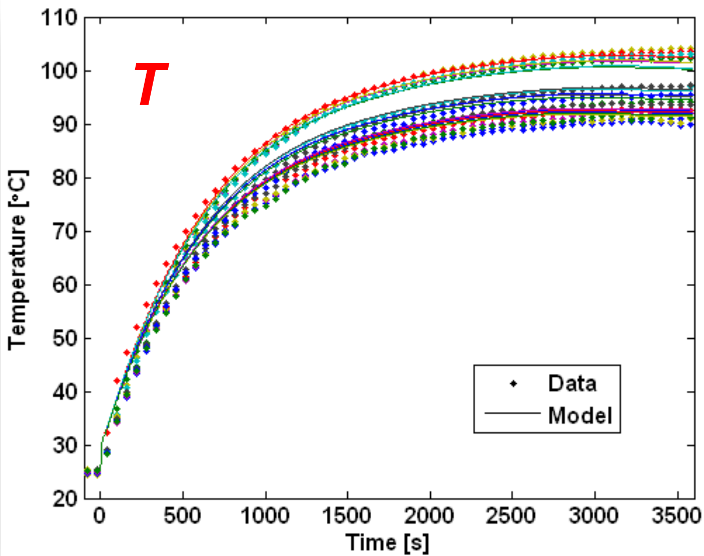
16P model validated against a bank short test

- 10 mΩ external short
- Peak inrush current
- PTC device trip time
- Steady-state behavior
- Temperature rise profiles for all 16 cells

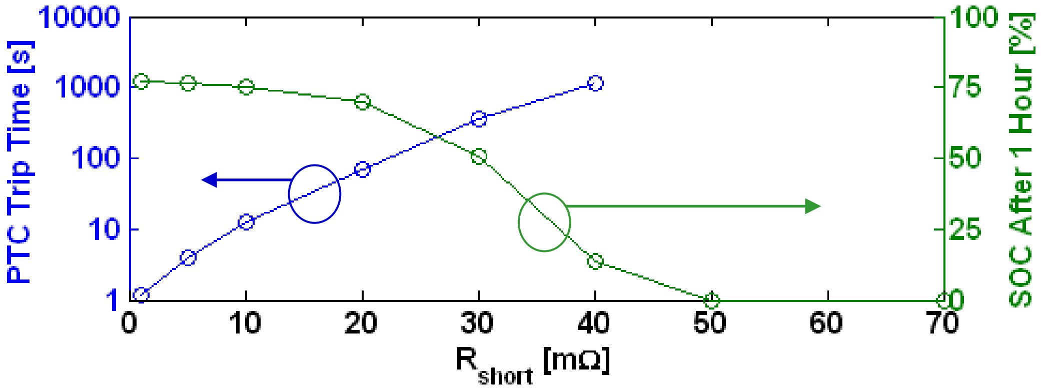
Test Data & Photo: SRI



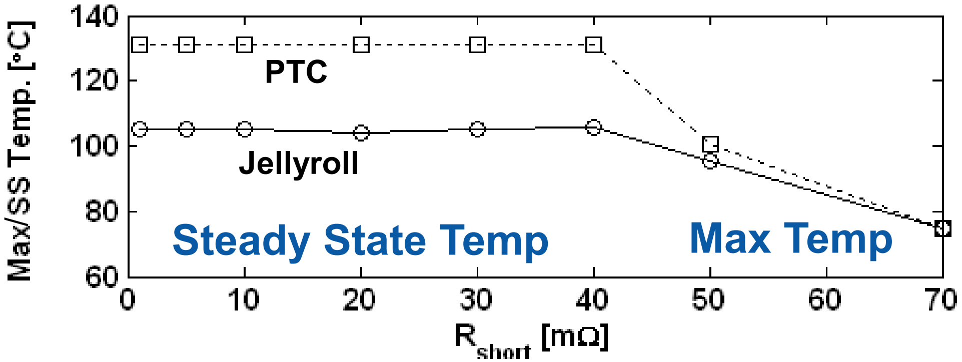




Simulation Results at Various Values of R_{short}



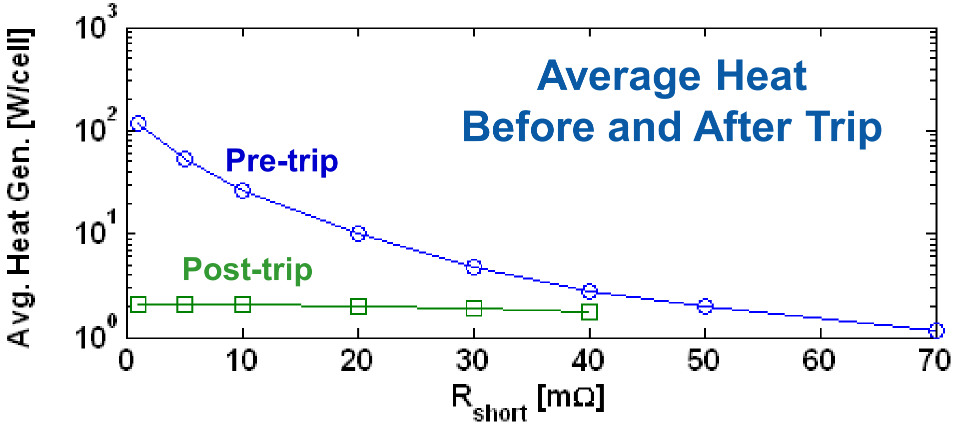
- Rshort ≤ 40 mΩ: PTC-limited
- Rshort ≥ 50 mΩ: SOC-limited



- Tripped PTC device serves as thermal regulator

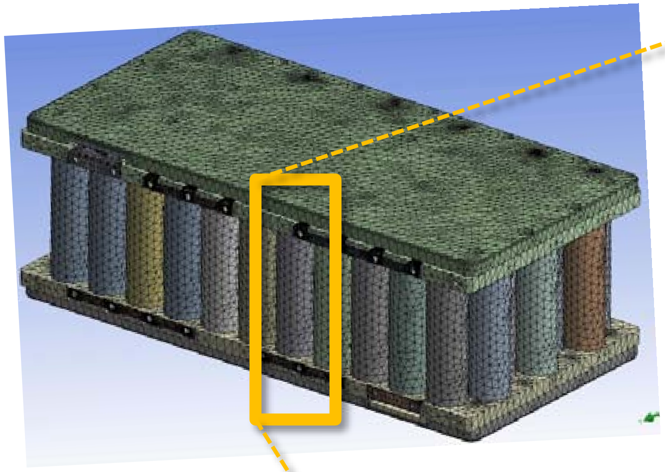
  [dRPTC/dT]130˚C = 3 Ω /˚C

  (5 orders of magnitude > than at 25˚C)

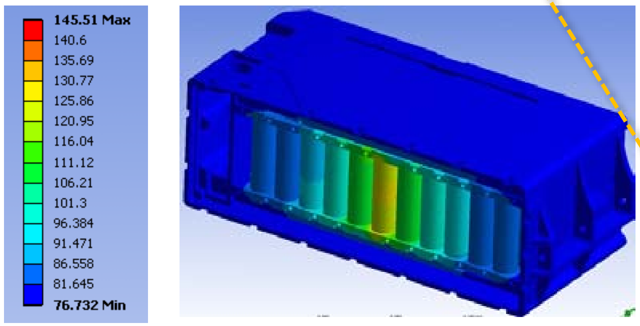


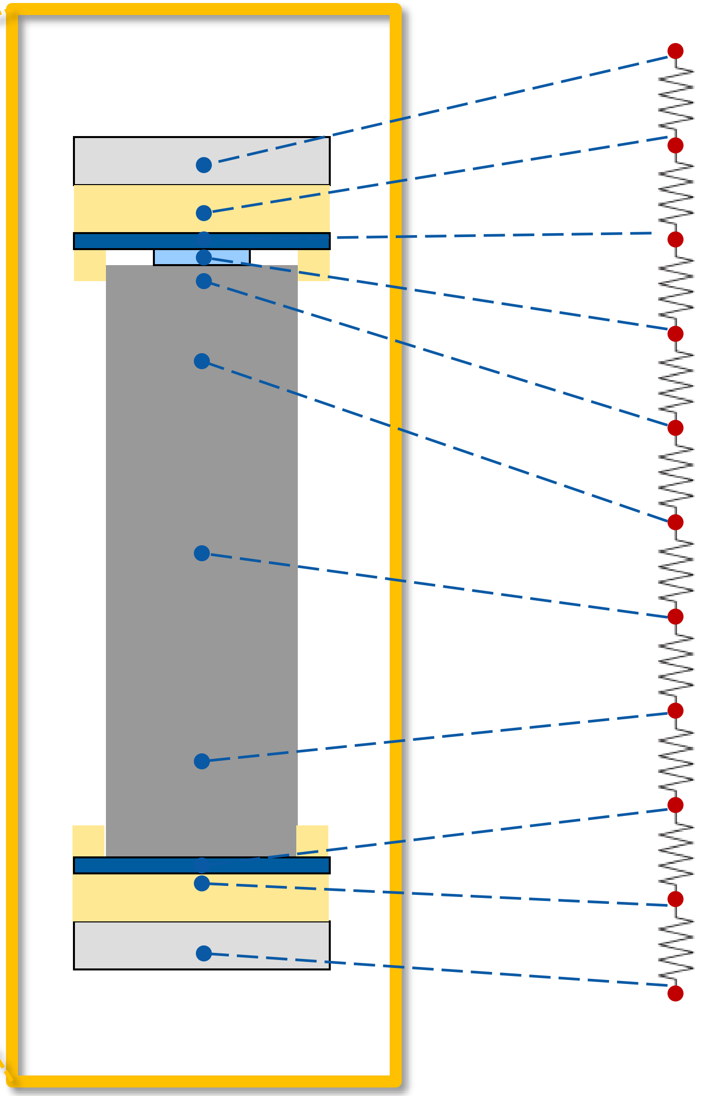
- Large pre-trip heat rates are safe provided that they have
  - Short duration
  - Sufficient thermal mass
  - Sufficient heat dissipation

Extend Validated 16P Model for 16P-5S Pack



- 11 nodes are vertically placed at 80 cell locations
- Node thermal connections are defined considering various heat transfer modes
- Aluminum enclosure box is considered thermally lumped
- 11 x 80 + 1 = 881 node system





Aluminum Plate

Glass Reinforced Plastic Plate

Nickel Bus Plate

Top Button

PTC

Jelly Roll Node 1

Jelly Roll Node 2

Jelly Roll Node 3

Nickel Bus Plate

Glass Reinforced Plastic Plate

Aluminum Plate

Model Validation for Pack External Short

ABSL experiment: Bank 3 short through external resistor

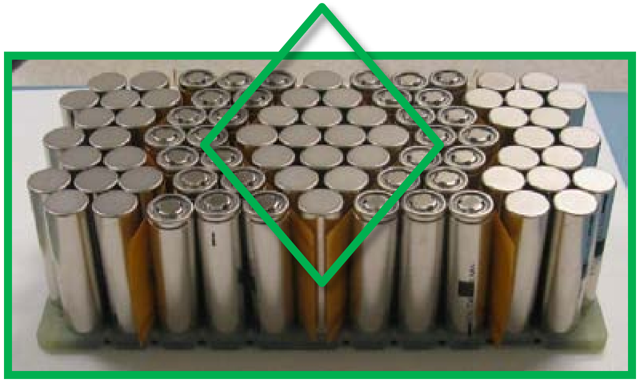
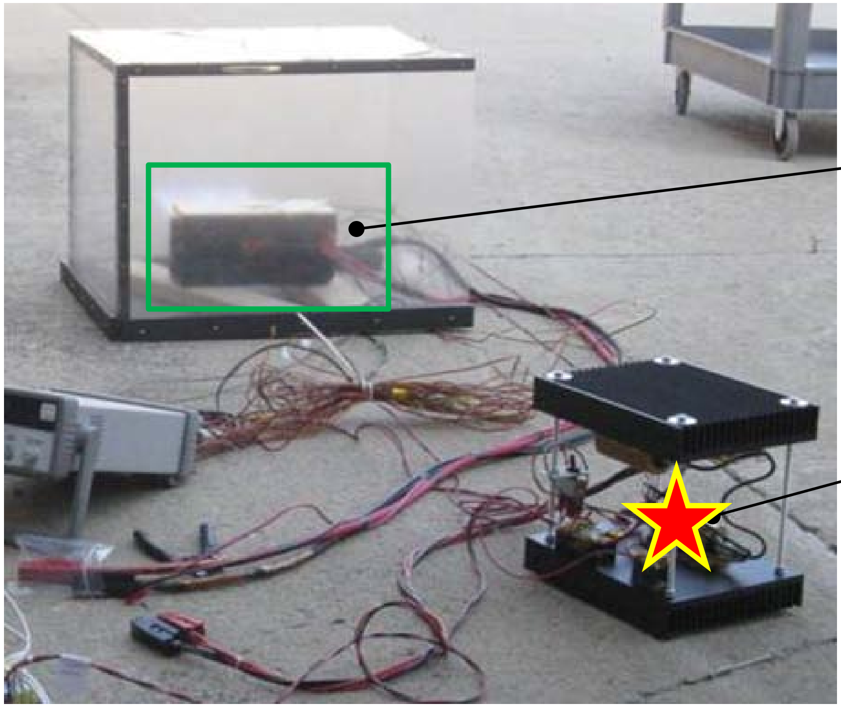


Photo: ABSL

Photo: NASA



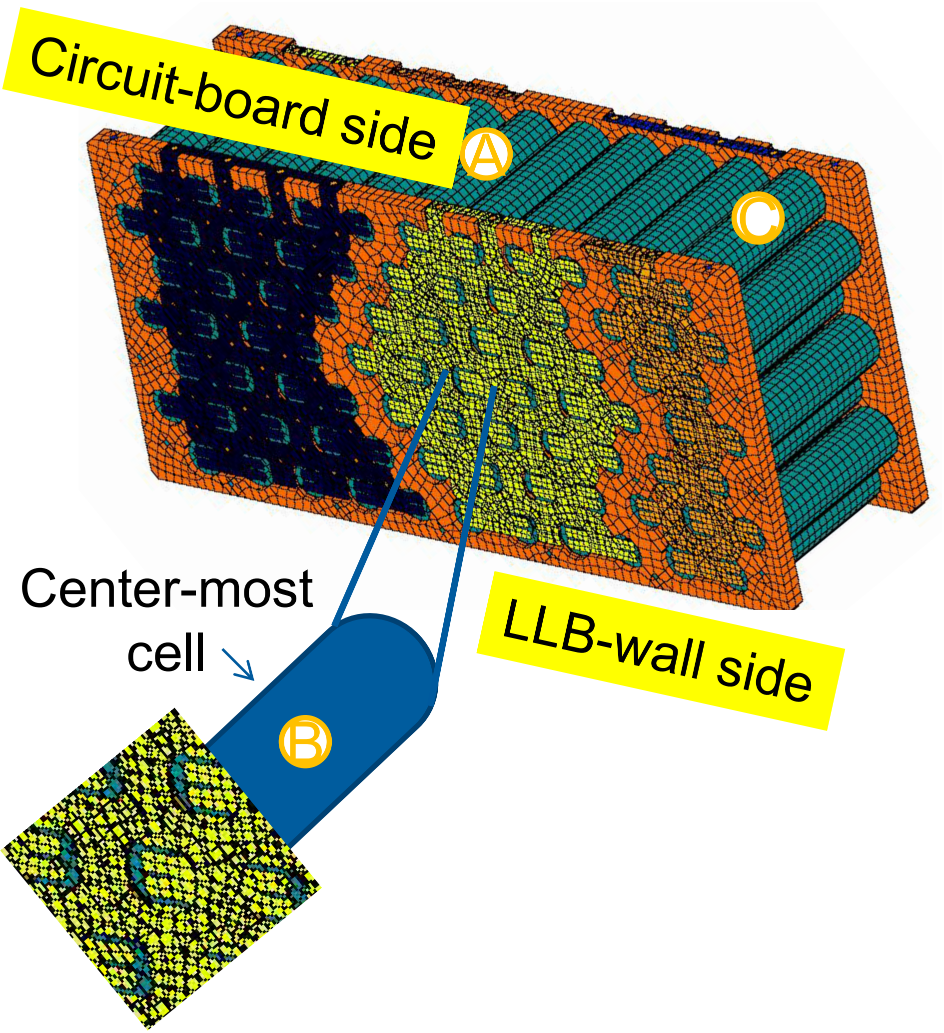
80 cell battery in test enclosure

10 mΩ resistor

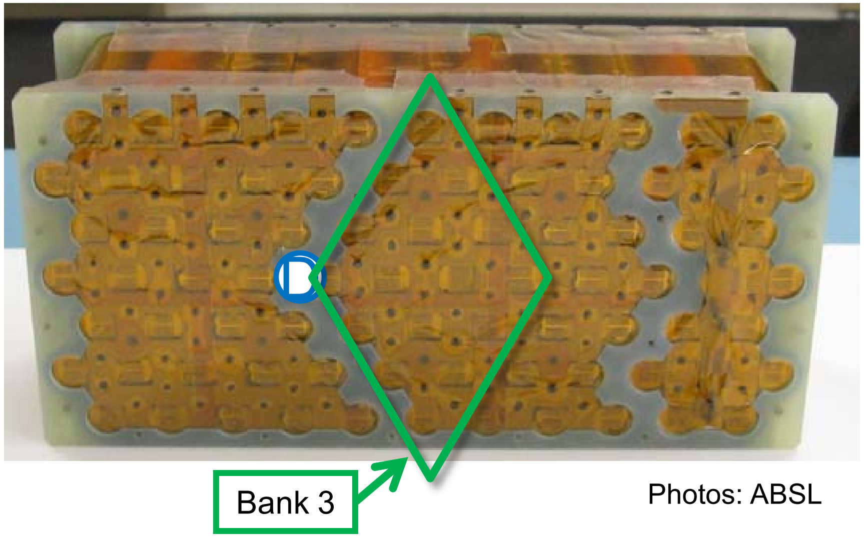
Photo: ABSL

ABSL Instrumentation

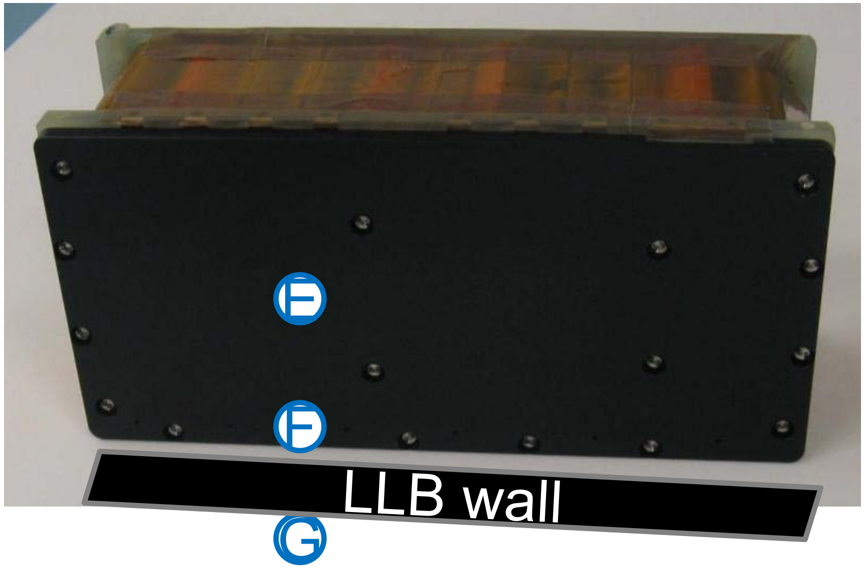
Cell Temperature Sensor Locations



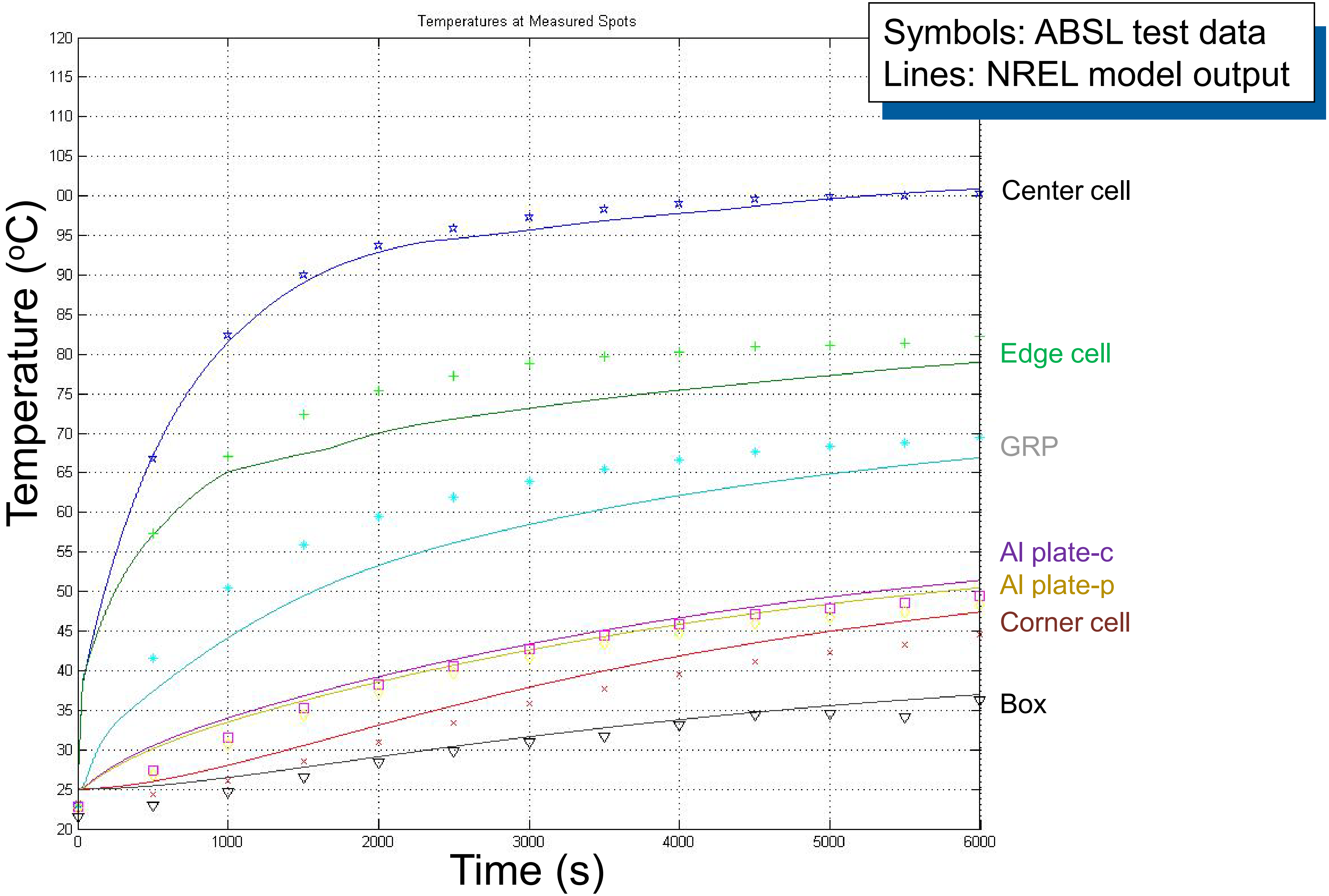
Brick Temperature Sensor Locations



Photos: ABSL



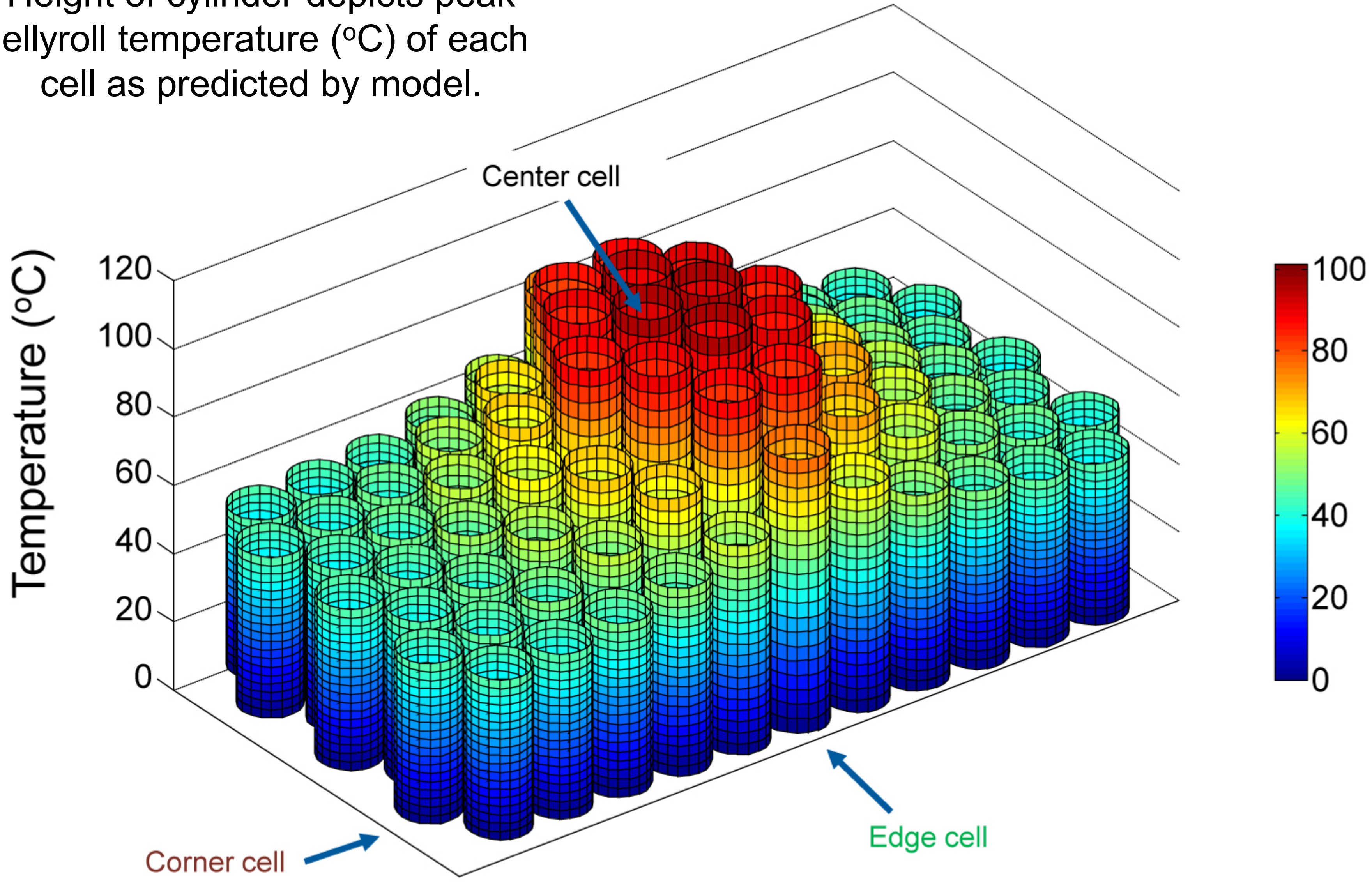
Model Validation – First 6000 seconds



Symbols: ABSL test data
Lines: NREL model output

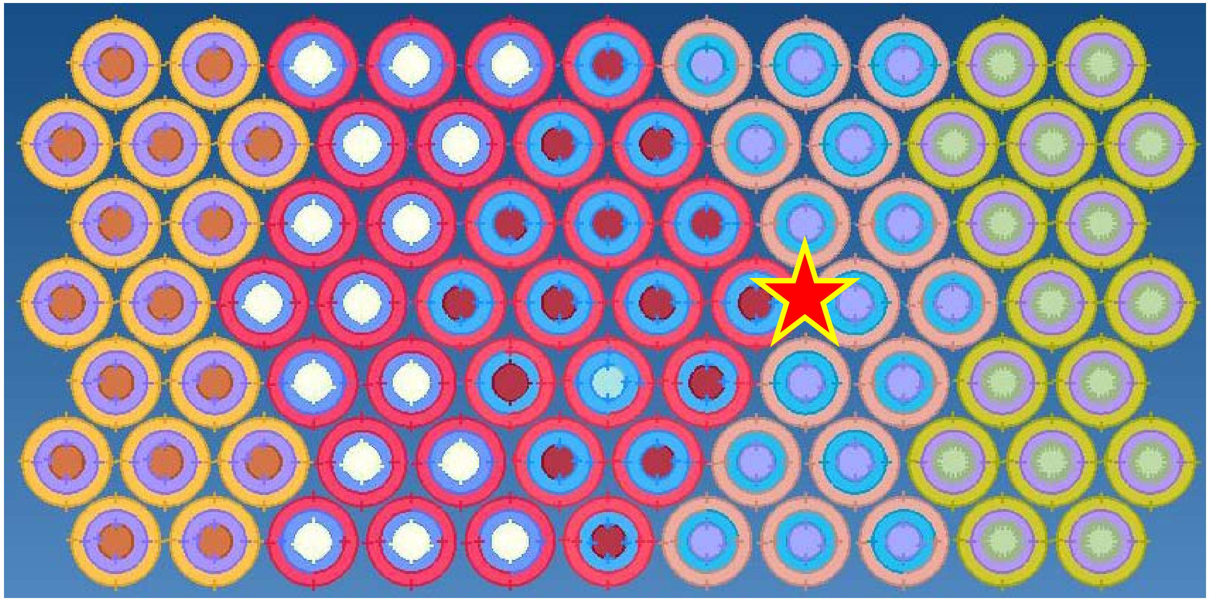
Cell Temperature Distribution at 6000 seconds

Height of cylinder depicts peak jellyroll temperature (°C) of each cell as predicted by model.



Model Analysis for Pack-Internal Shorts

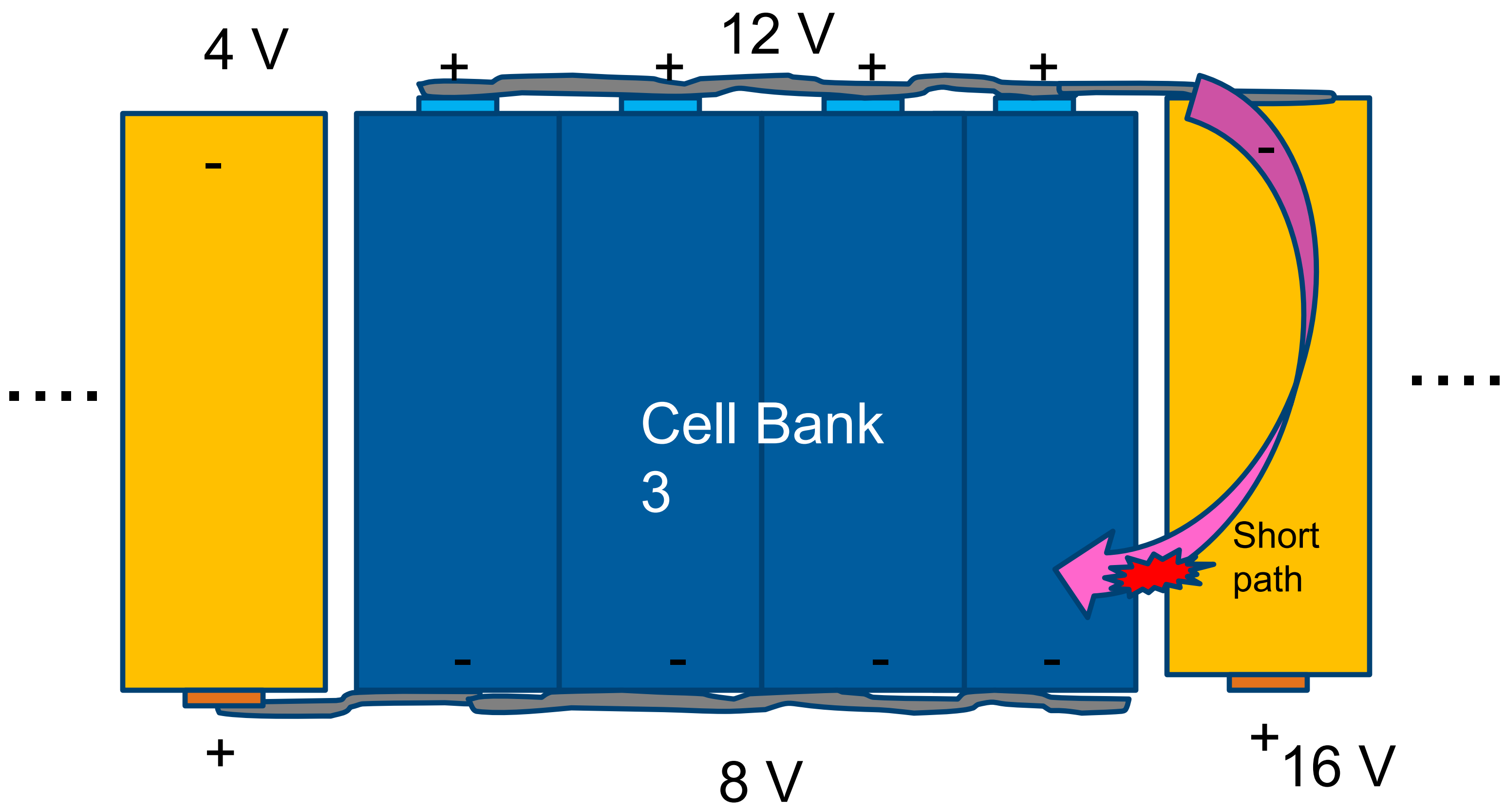
E.g., bank 3 short is caused by foreign object between banks 3 and 4*



Bank 1	Bank 2	Bank 3	Bank 4	Bank 5
+	-	+	-	+

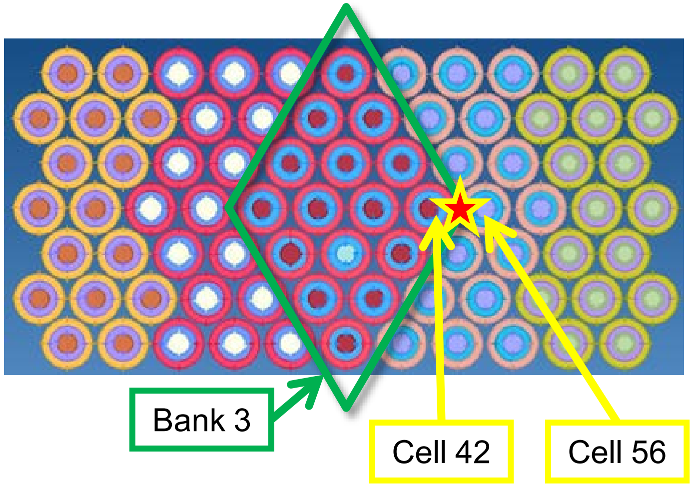
* Requires more than two faults: Introduction of foreign object debris & penetration of Kapton/Nomex/Kapton divider between banks

Schematic of Shorted Middle Cell Bank



- Short runs through can of cell from adjacent bank 4
- Bare walls of cells are negatively biased
- Note that 3-layer (Kapton-Nomex-Kapton) bank-to-bank insulator is omitted for clarity

Bank 3 Short from 100% SOC



- Cell 42 (bank 3) participates in electrical discharge
- Cell 56 (bank 4) does not electrically discharge; its external can wall serves as a path for short current
- Model assumes ohmic heat of short shared equally by cells 42 and 56

- Internal-to-pack short more thermally severe than external-to-pack
- Thermal mass dominates – negligible dependence on Earth vs. space boundary conditions
- Runaway possibly prevented at 10 mΩ
- Runaway predicted at 20,30 mΩ with collateral damage

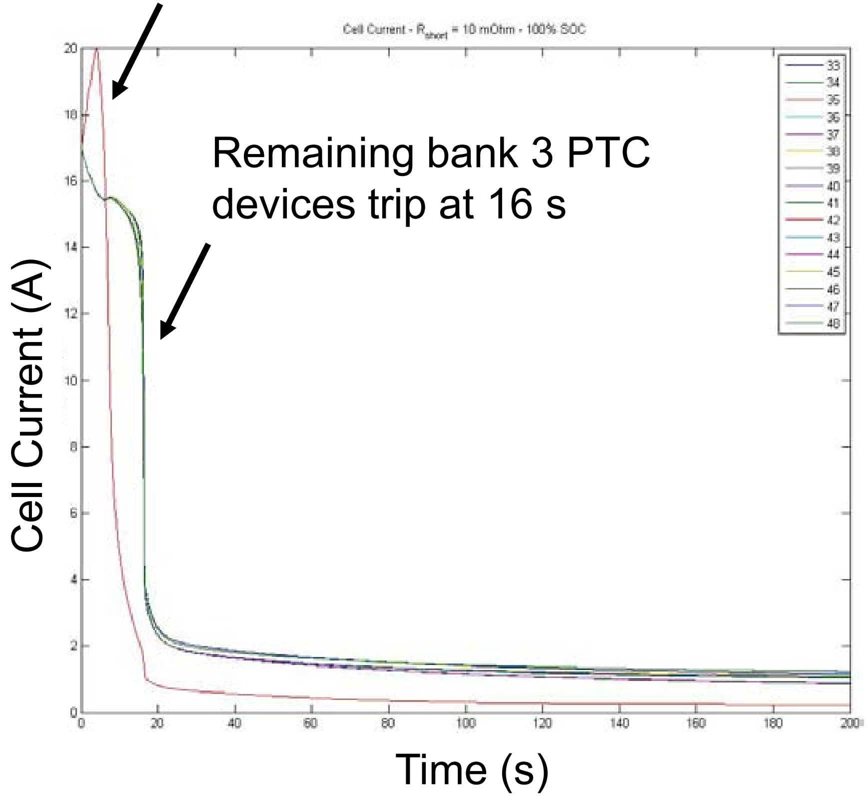
R_{short}	**Short Condition** (SOC_0 = 100%)	**Cell 42 T_{max}** (Bank 3)	**Cell 56 T_{max}** (Bank 4)
10 mΩ	External-to-pack, earth	97°C @ 6000-s	75°C @ 6000-s
	Internal-to-pack, earth	150°C @ 16-s	146°C @ 16-s
	Internal-to-pack, space	153°C @ 16-s	147°C @ 16-s
20 mΩ	Internal-to-pack, space	525°C @ 110-s	522°C @ 110-s
30 mΩ	Internal-to-pack, space	595°C @ 240-s	591°C @ 240-s

Bank 3 Short from 100% SOC: 10 mΩ vs. 20 mΩ

10 mΩ:

Bank 3 PTC devices trip quickly and uniformly because high inrush current causes PTC self-heating

Cell 42 PTC trips at 8 s

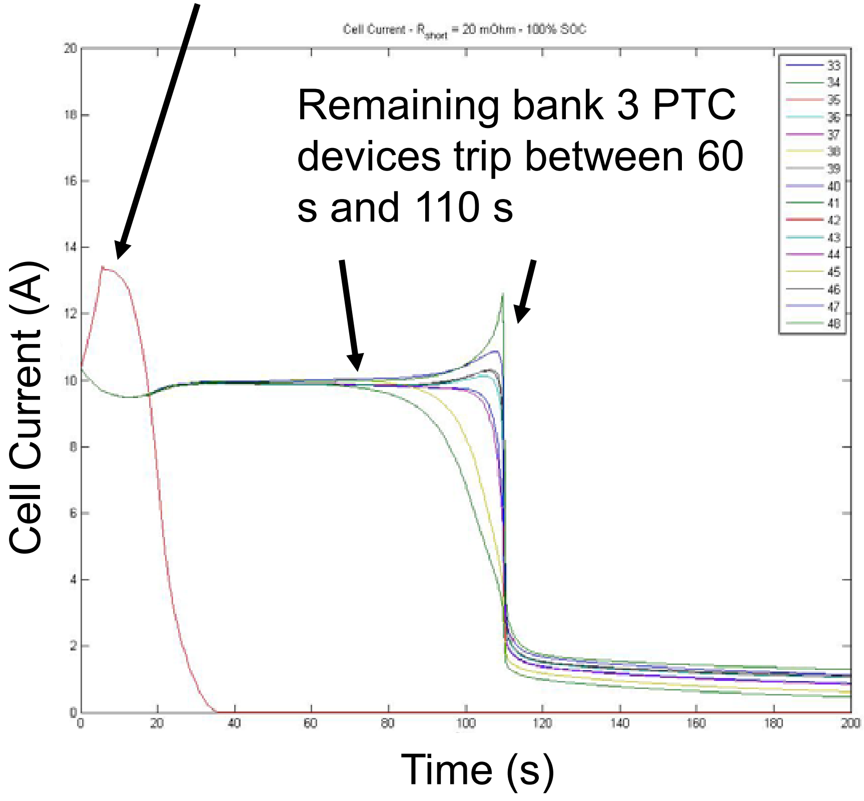


Remaining bank 3 PTC devices trip at 16 s

20 mΩ:

Bank 3 PTC devices trip slowly at different times, depending upon bank 3 temperature distribution

Cell 42 PTC trips at10 s

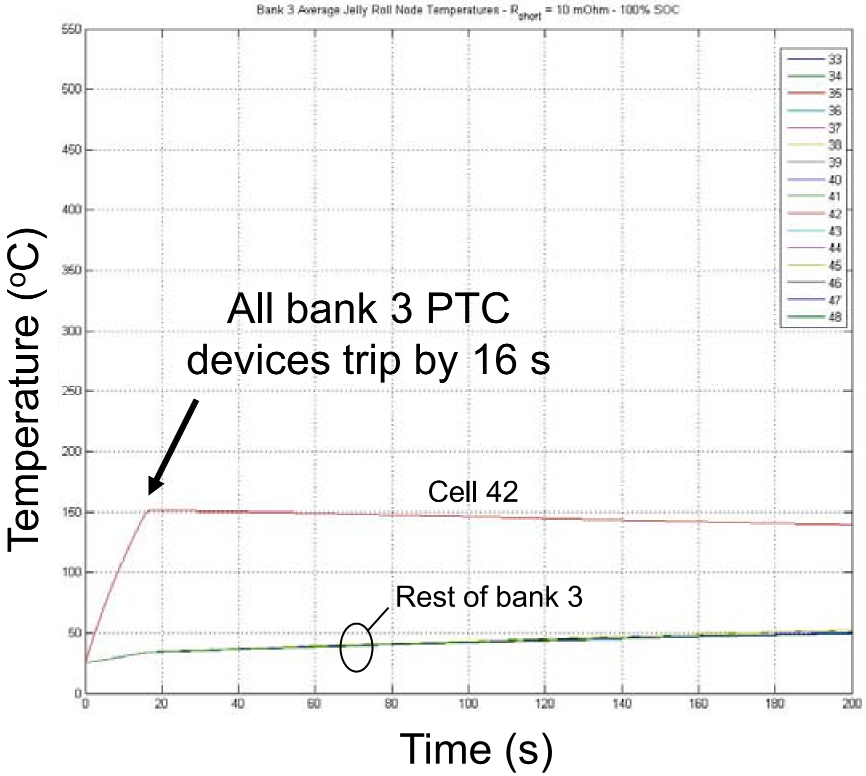


Remaining bank 3 PTC devices trip between 60 s and 110 s

Bank 3 short from 100% SOC: 10 mΩ vs. 20 mΩ

10 mΩ:

Bank 3 PTC devices trip quickly and uniformly due to high in-rush current causing PTC self-heating



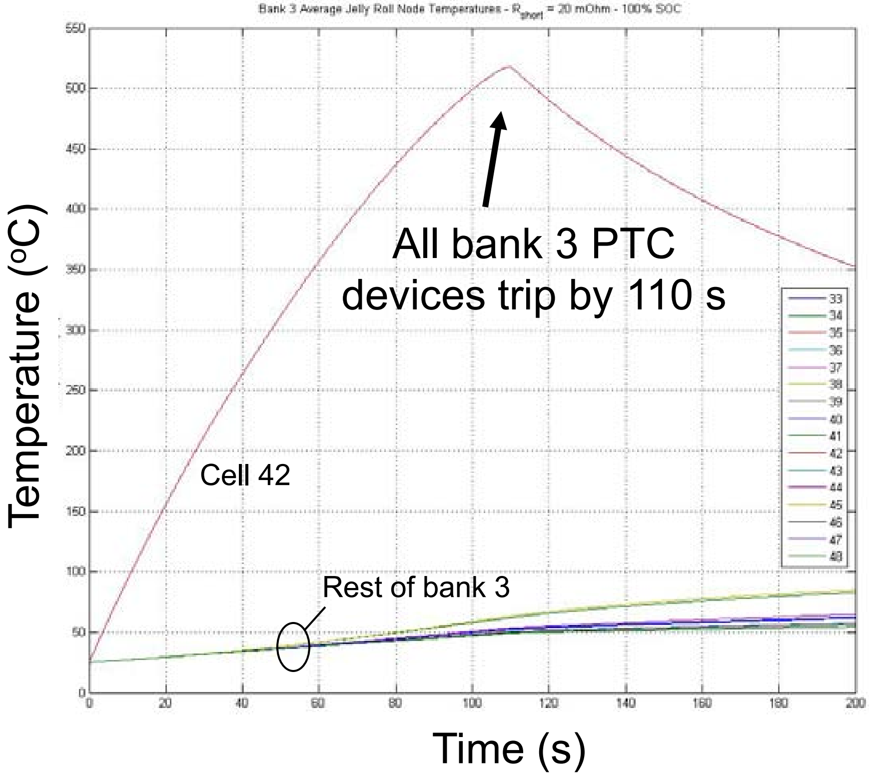
All bank 3 PTC devices trip by 16 s

Cell 42

Rest of bank 3

20 mΩ:

Bank 3 PTC devices trip slowly, at different times dependent upon bank 3 temperature distribution

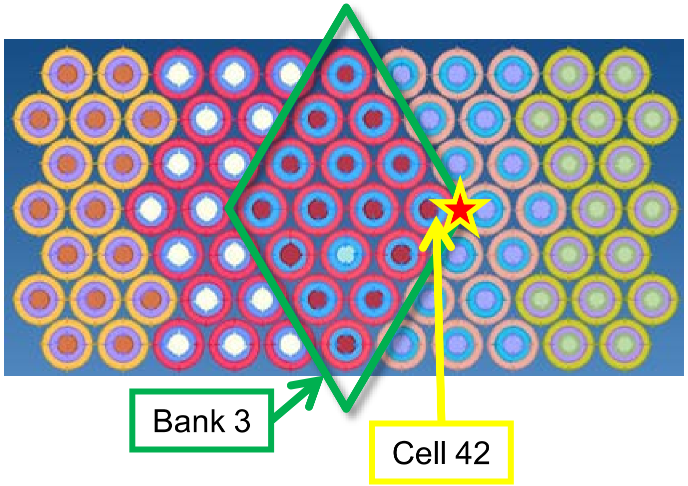


All bank 3 PTC devices trip by 110 s

Cell 42

Rest of bank 3

Bank 3 Short from 100% SOC: Cell-to-Cell Radiation



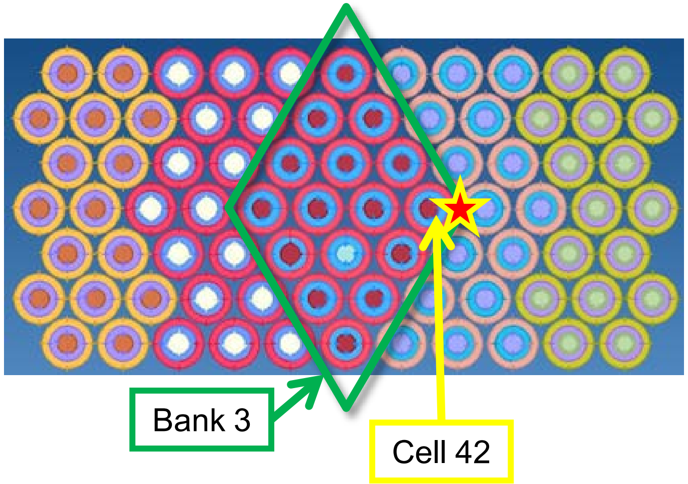
Design question:
Would a high-emissivity coating applied to bare cell walls help limit thermal excursion?

R_{short}	**Short Condition** (SOC$_0$ = 100%)	**Cell wall emissivity**	**Cell 42 T_{max}** (Bank 3)
20 mΩ	Internal-to-pack, earth	ε = 0.3 (Nominal)	525°C @ 110 s
		ε = 0.9 (Coating)	410°C @ 102 s

(Insufficient impact)

Bank 3 Short: SOC Dependence

Is battery design tolerant to pack-internal shorts when stored at low SOCs?



R_{short}	Short Condition	Initial SOC	Initial OCV	Cell 42 T_{max} (Bank 3)
20 mΩ	Internal-to-pack, earth	1.5%	3.428 V	117°C @ 85 s
		0.5%	3.346 V	83°C @ 80 s

No thermal runaway when stored at 0% SOC (3.25 OCV).

Summary

- NREL performed an internal short model simulation study to characterize an internal short and its evolution over time by linking and integrating NREL's electrochemical cell, electro-thermal, and abuse reaction kinetics models.
- Initial heating pattern at short events depends on nature of short, cell characteristics, and system configuration.
- Temperature rise for short is localized in large capacity cells.
- Short current is carried mostly by metal collectors.
- A simple puncture in the separator is not likely to lead to an immediate thermal runaway of a cell.
- Maintaining the integrity of the separator seems critical to delay short evolution.
- PTC device is an effective thermal regulator. Maximum cell temperature (final state) is very similar for a variety of initial and boundary conditions.

Summary

- 80-cell spacesuit battery electrical/thermal model
    - Captures relevant physics for cell-external shorting events, including PTC behavior
    - Agrees well with pack-external bank 3 short experiment run by ABSL
    - Predicts that design will tolerate all pack-external short resistance conditions

- Relocating short from pack-external (experimental validation) to pack-internal (modeling study) causes substantial additional heating of cells that can lead to cell thermal runaway
    - Negligible sensitivity to earth/space boundary conditions (thermal mass dominates)
    - Large sensitivity to R_{short}
        - $R_{short} < 10\ m\Omega$: 16P bank PTC devices trip quickly, most likely preventing runaway
        - $10\ m\Omega < R_{short} < 60\ m\Omega$: Thermal runaway appears likely
    - Nevertheless, this finding re-emphasizes the general imperative of battery pack assembly cleanliness

- Design is tolerant to pack-internal short when stored at 0% SOC

Acknowledgments

Vehicle Technology Program at DOE

- Dave Howell

NASA Johnson Space Center

- NASA JSC under Interagency Agreement NNJ08HC04I
- Technical discussion: Sam Russell, Frank Davies

Symmetry Resources Inc.

- Brad Strangways

ABSL

- Craig Flora

Thank you for your attention!

Digital Battery Innovation

Multi-physics design and analysis paving the road for future automotive batteries

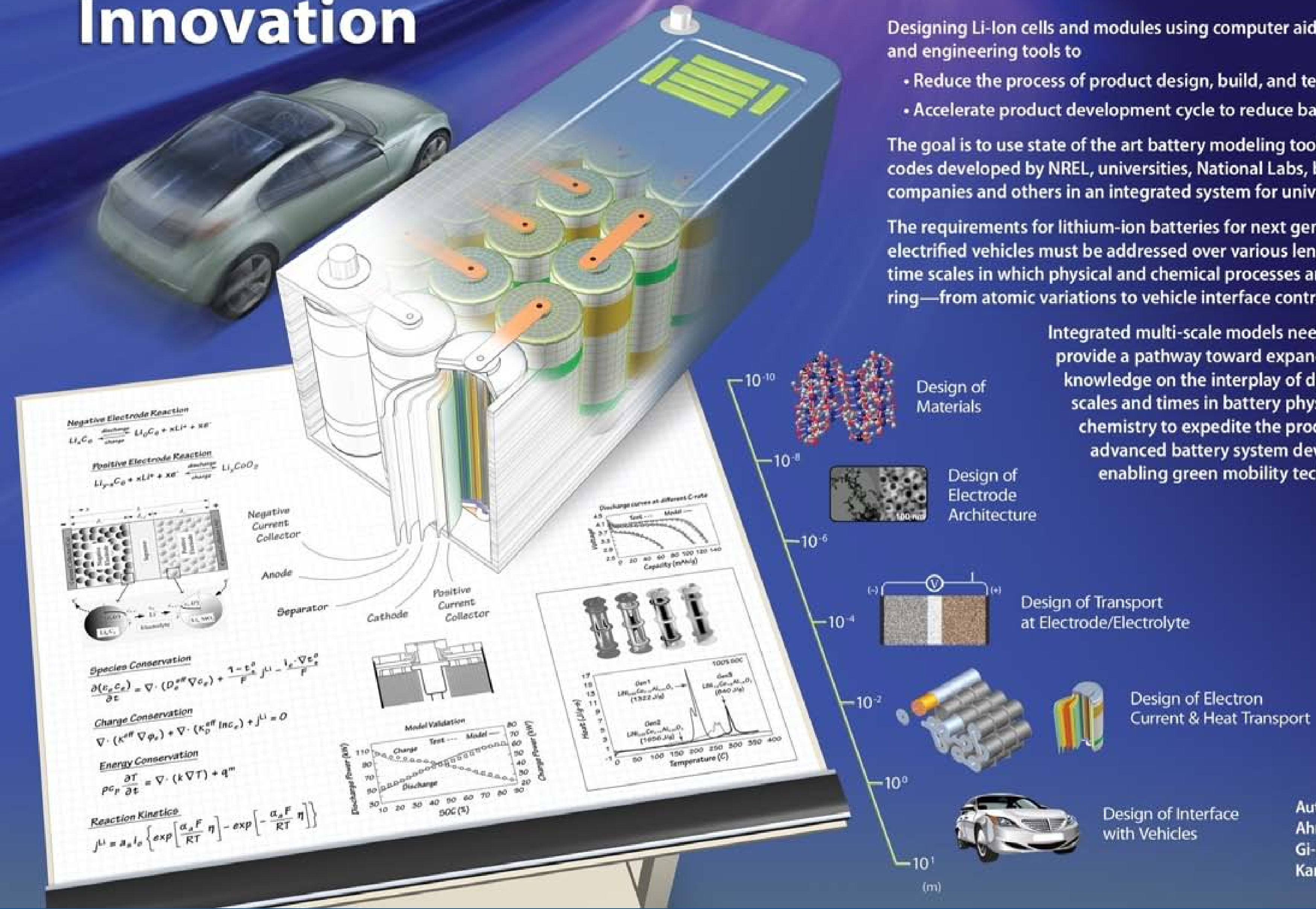
Designing Li-Ion cells and modules using computer aided design and engineering tools to

- Reduce the process of product design, build, and test cycle.
- Accelerate product development cycle to reduce battery cost.

The goal is to use state of the art battery modeling tools and codes developed by NREL, universities, National Labs, battery companies and others in an integrated system for universal use.

The requirements for lithium-ion batteries for next generation electrified vehicles must be addressed over various length and time scales in which physical and chemical processes are occurring—from atomic variations to vehicle interface controls.

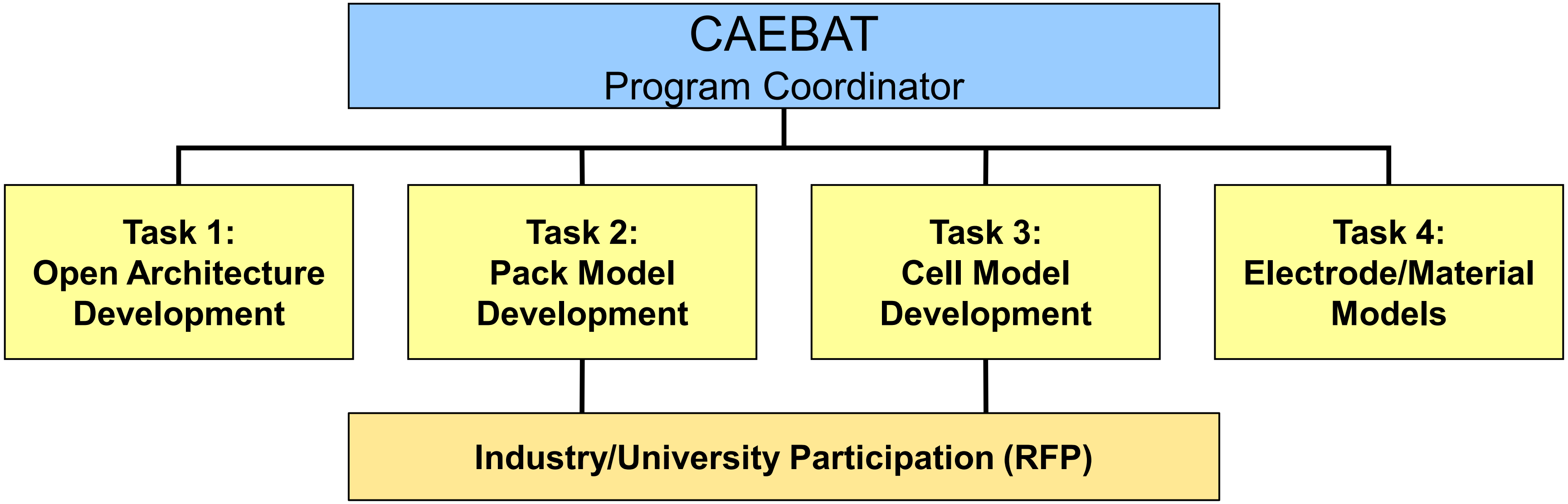
Integrated multi-scale models need to provide a pathway toward expanding knowledge on the interplay of different scales and times in battery physics and chemistry to expedite the process of advanced battery system development enabling green mobility technologies.



Authors:
Ahmad Pesaran,
Gi-Heon Kim,
Kandler Smith

DOE's New CAEBAT Program

- Will integrate the accomplishments of battery modeling activities in national lab programs and make them accessible as design tools for industry
- Will shorten time and cost for design and development of EDV battery systems



CAEBAT
Program Coordinator

Task 1:
Open Architecture Development

Task 2:
Pack Model Development

Task 3:
Cell Model Development

Task 4:
Electrode/Material Models

Industry/University Participation (RFP)