NREL National Renewable Energy Laboratory
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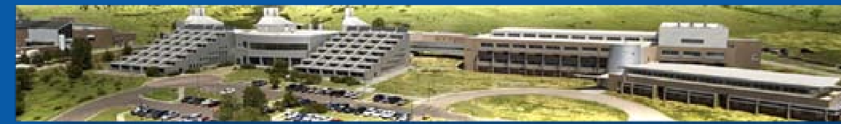

Lithium-Ion Battery Safety Study Using Multi-Physics *Internal Short-Circuit* Model

The 5th Intl. Symposium on
Large Lithium-Ion Battery Technology and Application
in Conjunction with AABC09

June 9-10, 2009, Long Beach, CA

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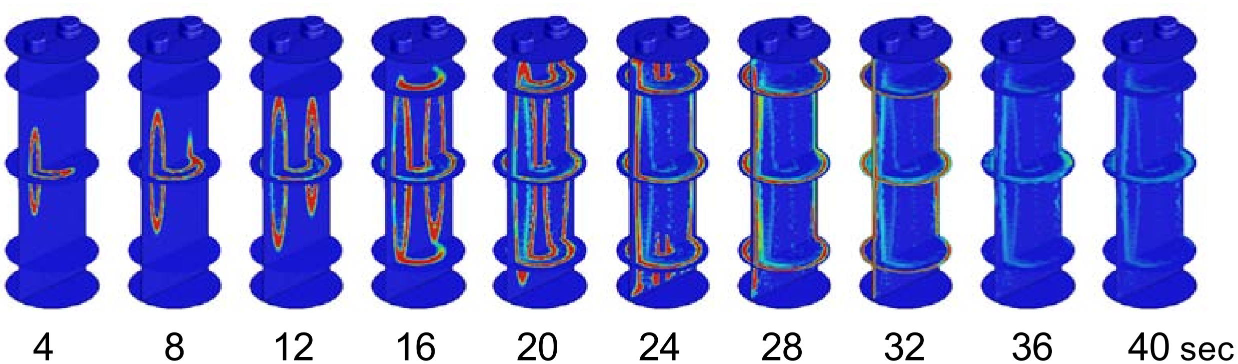
NREL/PR-540-45856

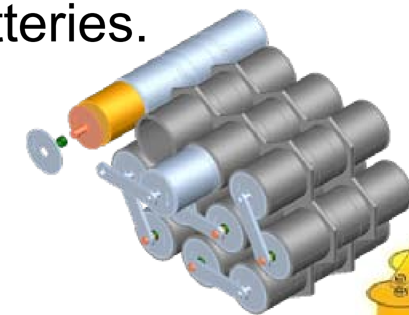
Background

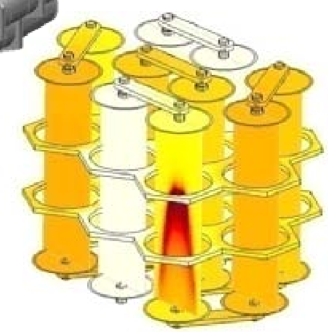
- NREL's Li-ion thermal abuse modeling study was started under the Advanced Technology Development (ATD) program; it is currently funded by Advanced Battery Research for Transportation (ABRT) program.

- NREL's previous model study
  - ✓ focused on understanding 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







Focus Here: Internal Short-Circuit

- Li-Ion thermal runaway due to internal short-circuit is a major safety concern.
  - Other safety concerns may be controlled by electrical and mechanical methods.

- Initial latent defects leading to later internal shorts may not be easily controlled, and evolve into a hard short through various mechanisms:
  - separator wear-out,
  - metal dissolution and deposition on electrode surface, or
  - extraneous metal debris penetration, etc.

- Thermal behavior of a lithium-ion battery system for an internal short-circuit depends on various factors such as nature of the short, cell capacity, electrochemical characteristics of a cell, electrical and thermal designs, system load, etc.

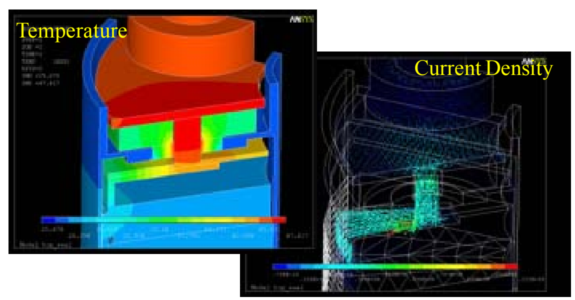
- Internal short-circuit is a multi-physics, 3-dimentional problem related to the electrochemical, electro-thermal, and thermal abuse reaction kinetics response of a cell.

Approach:

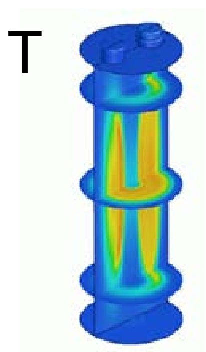
Understanding of Internal Short Circuit Through Modeling

- Perform 3D multi-physics internal short simulation study to characterize an internal short and its evolution over time
- Expand understanding of internal shorts by linking and integrating NREL's electrochemical cell, electro-thermal, and abuse reaction kinetics models

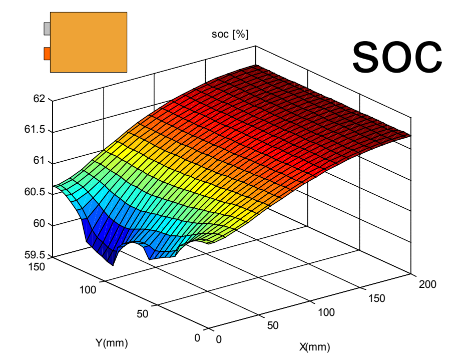
Electro-Thermal Model

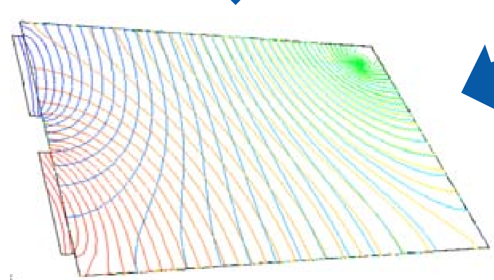


Abuse Kinetics Model



Electrochemical Model





Internal Short Model Study

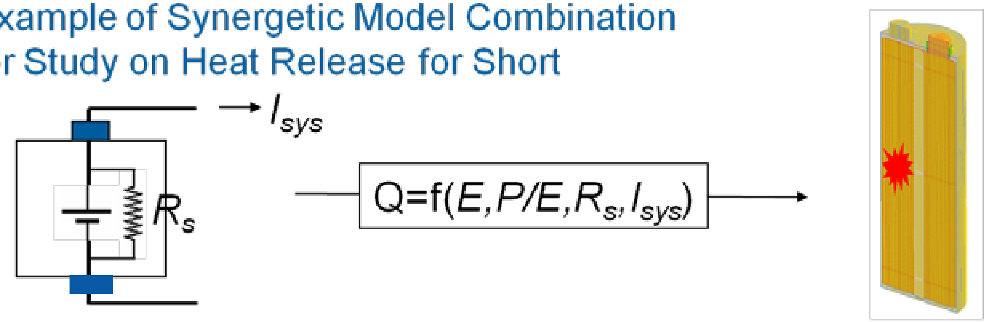
Research Focus Is on …

- Understanding electrochemical response for short
- Understanding heat release for short event
- Understanding exothermic reaction propagations
- Understanding function and response of mitigation technology designs and strategies

Heating Pattern Change

- A multi-physics model simulation demonstrates that heating patterns at short events depend on the nature of the short, cell characteristics such as capacity and rate capability.

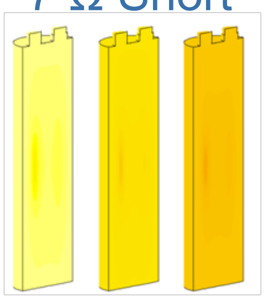
Example of Synergetic Model Combination
for Study on Heat Release for Short



Electrical(Electrochemical) Short Cell Model *3D Abuse Reaction Model*

<u>Heating Pattern at Different Resistance-Shorts</u>

7 Ω Short

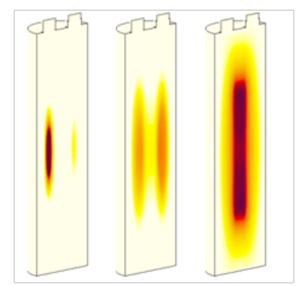


3 min 6min 9 min

Can slow down the evolution?

Can suppress?

30 mΩ Short



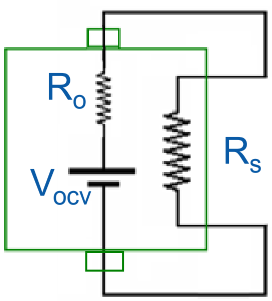
4s 8s 12s

Affected by external thermal conditions

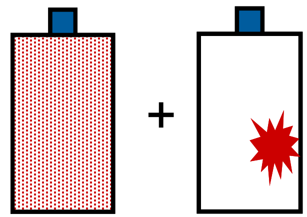
Undetectable from external probes

Understanding Heating Response Differences

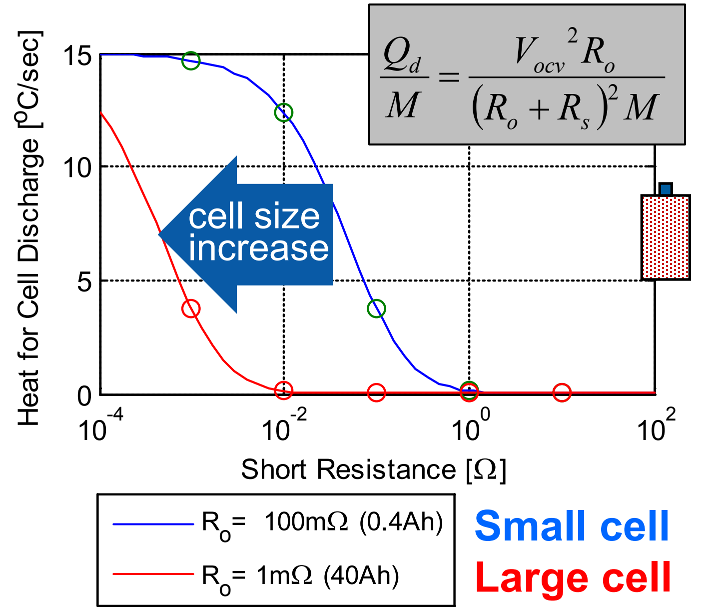
Heating from Short Circuit = Heat from Cell Discharge + Joule Heat at Short



Short Heating =

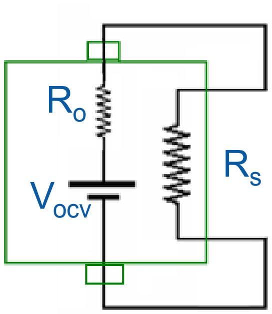


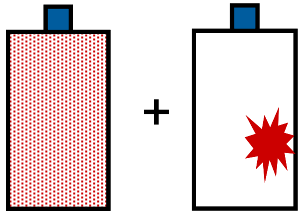
Global **Local**

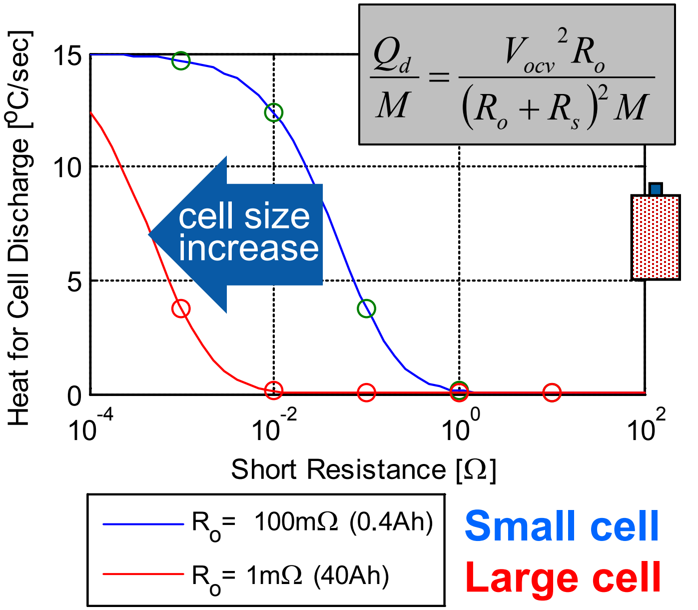


Understanding Heating Response Differences

Heating from Short Circuit = Heat from Cell Discharge + Joule Heat at Short

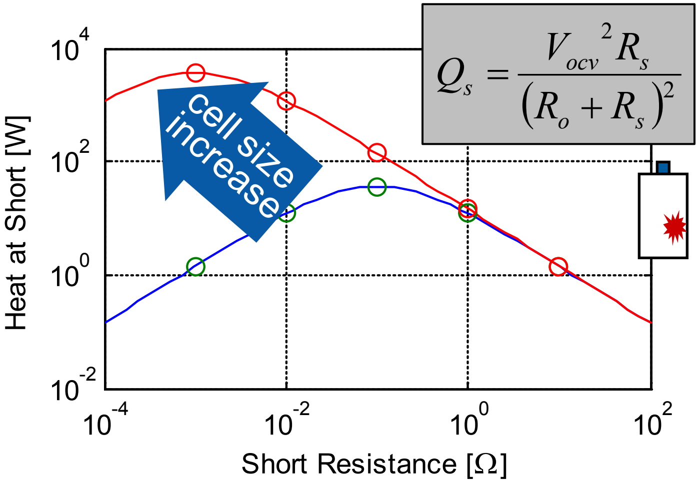






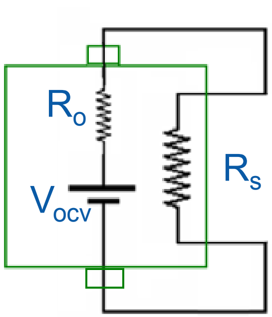
<u>Qualitative Representation for Heating Pattern</u>

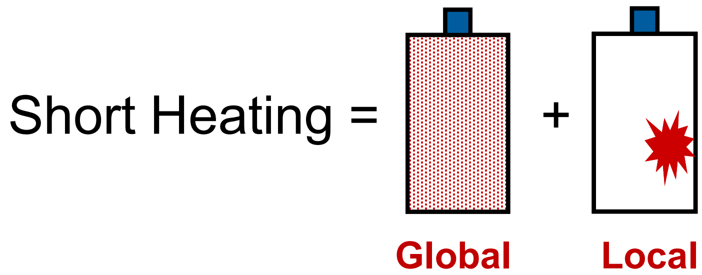
10 **m**Ω Short 10 Ω Short

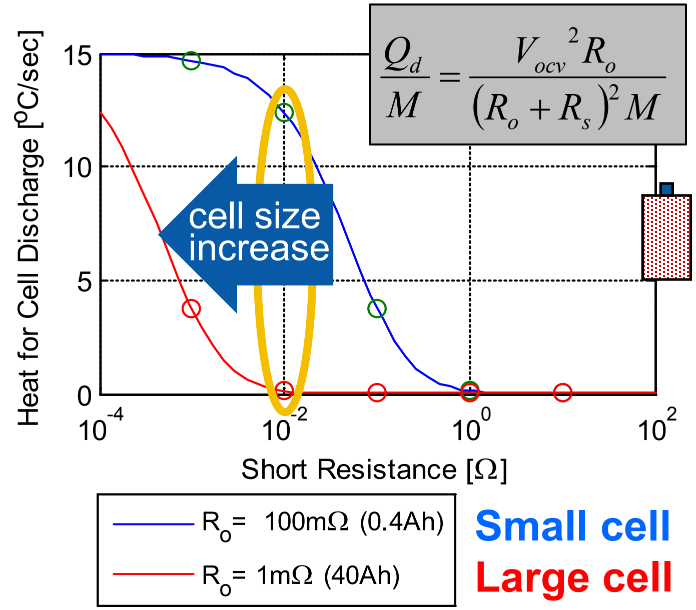


Understanding Heating Response Differences

Heating from Short Circuit = Heat from Cell Discharge + Joule Heat at Short

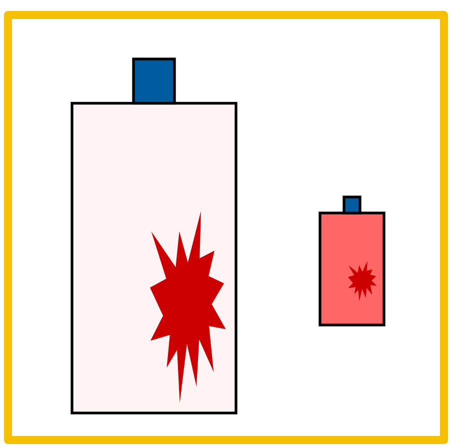




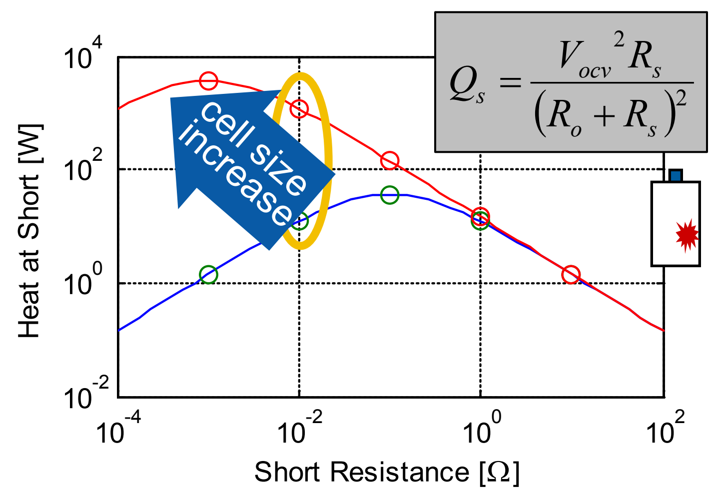


Qualitative Representation for Heating Pattern

10 mΩ Short | 10 Ω Short

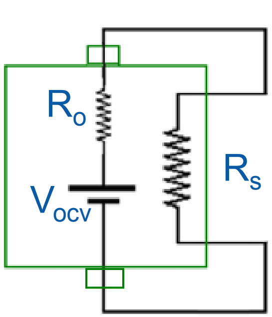


Large cell: localized heating
Small cell: global heating

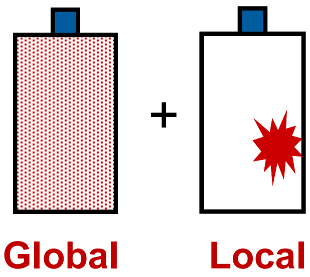


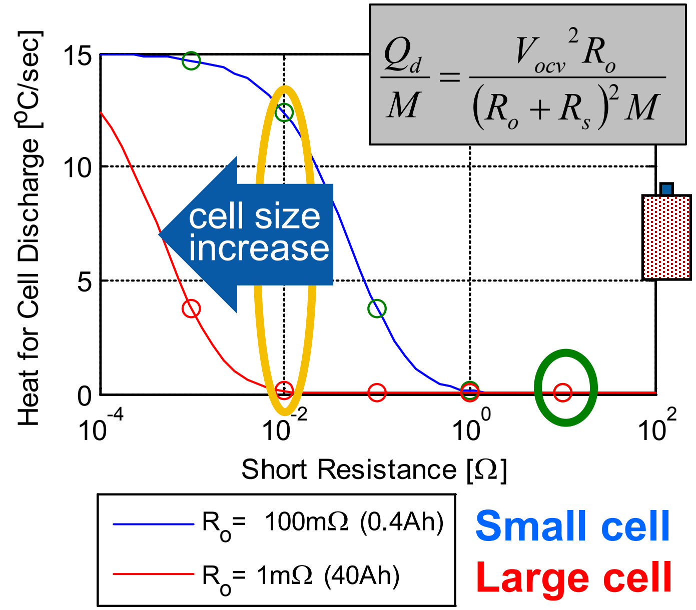
Understanding Heating Response Differences

Heating from Short Circuit = Heat from Cell Discharge + Joule Heat at Short



Short Heating =

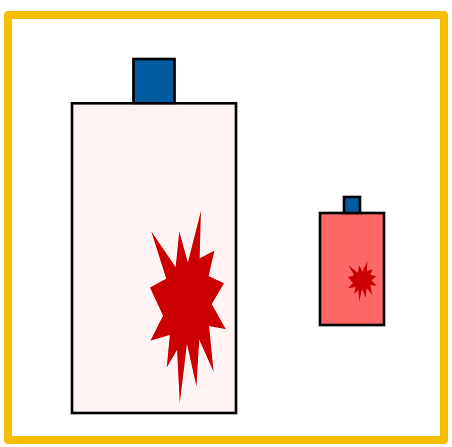




Small cell
Large cell

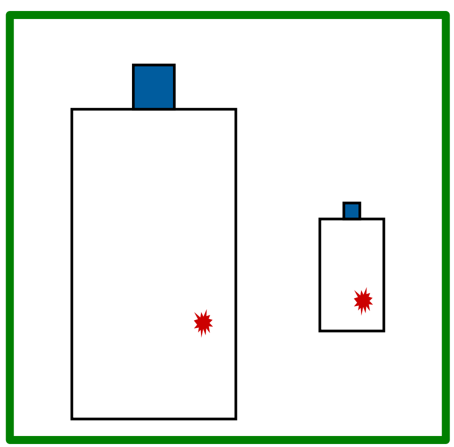
Qualitative Representation for Heating Pattern

10 mΩ Short

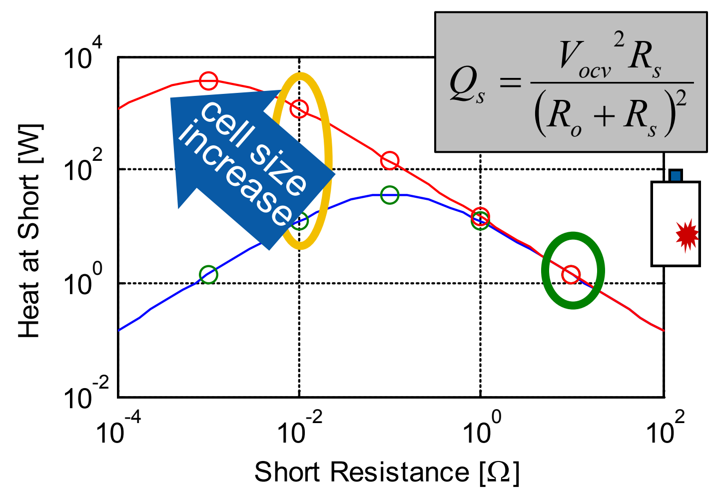


Large cell: localized heating
Small cell: global heating

10 Ω Short

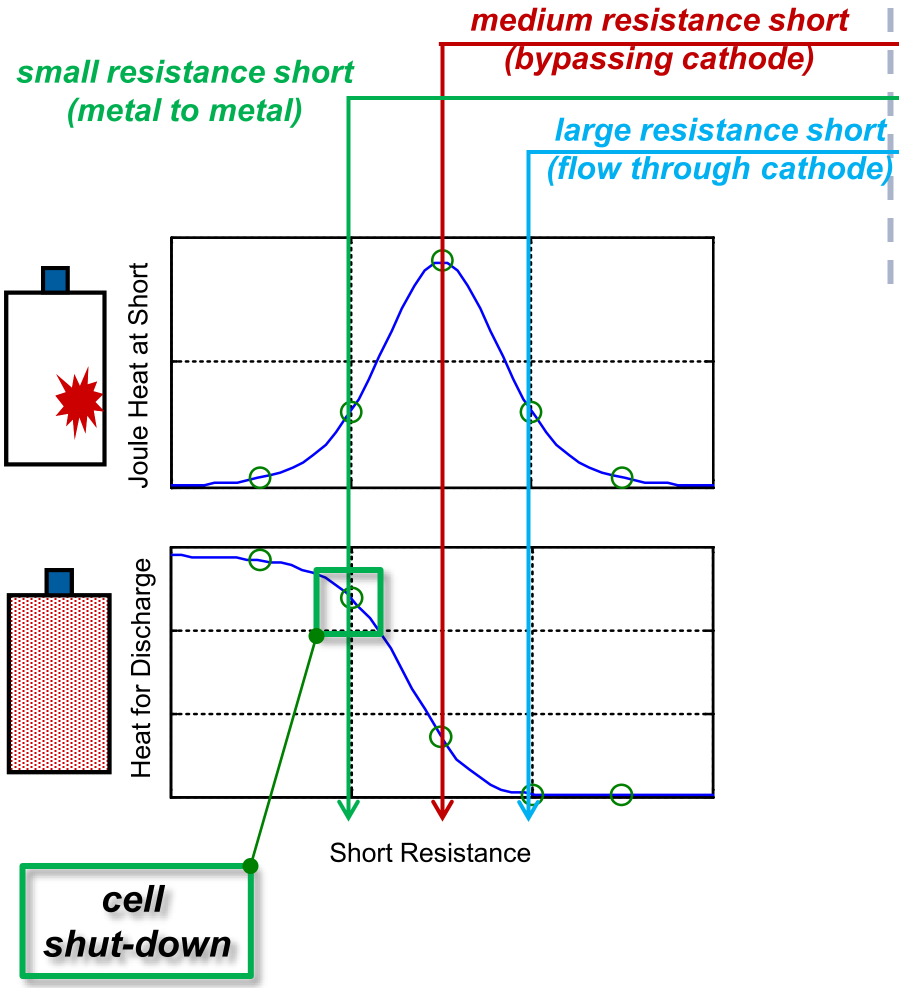


Same local heating, and
Negligible global heating for both



Observations from Literature:

Various Short Resistances



John Zhang, Celgard, AABC08

No Particle

1. Al → LiC6
2. Al → C6
3. Al → Cu
4. LCO → LiC6
5. Cu → LCO

Easier Explore and Fire

Very Difficult to Explore and Fire

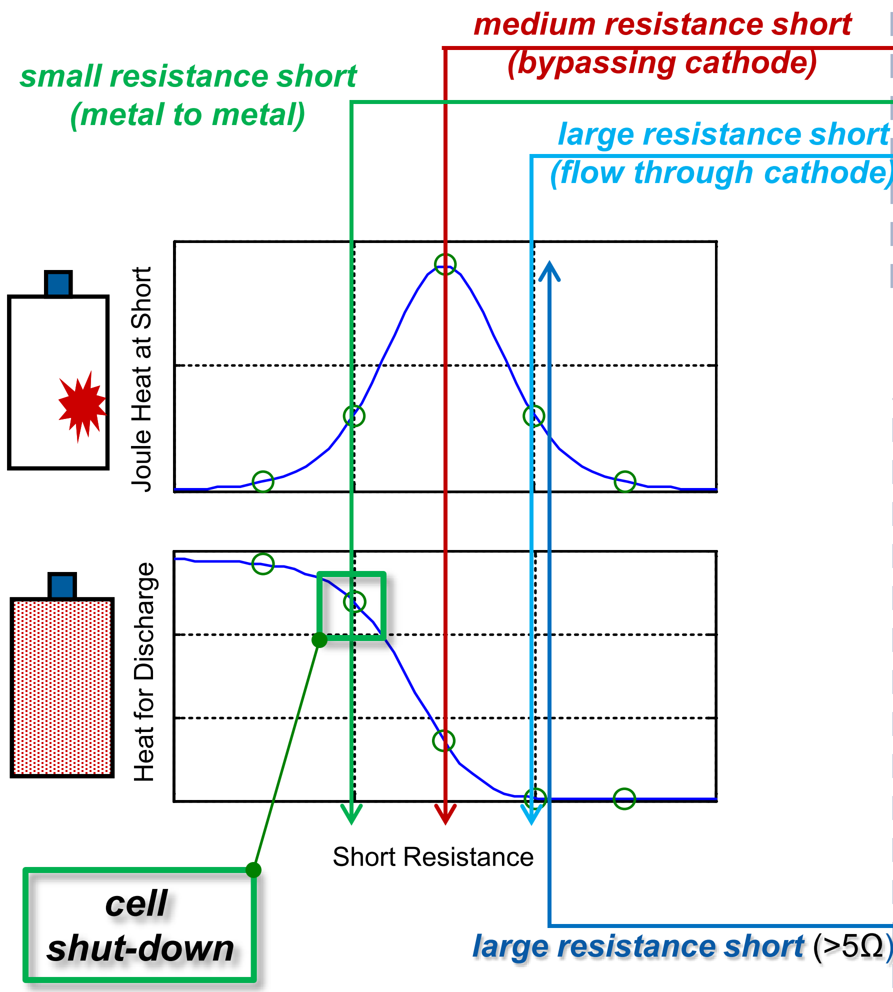
A POLYPORE Company

Celgard LLC

*Small Cell with Shut-Down Separator

Observations from Literature:

Various Short Resistances



John Zhang, Celgard, AABC08

No Particle

1. *Al → LiC6*
2. *Al → C6*
3. Al → Cu
4. LCO → LiC6
5. Cu → LCO

Easier Explore and Fire (1–2)

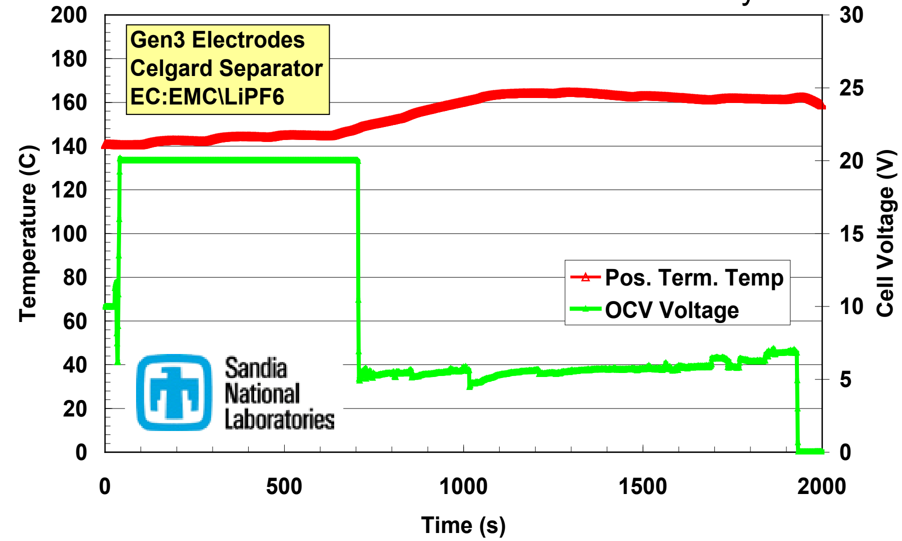
Very Difficult to Explore and Fire (4–5)

A POLYPORE Company — Celgard LLC

***Small Cell with Shut-Down Separator**

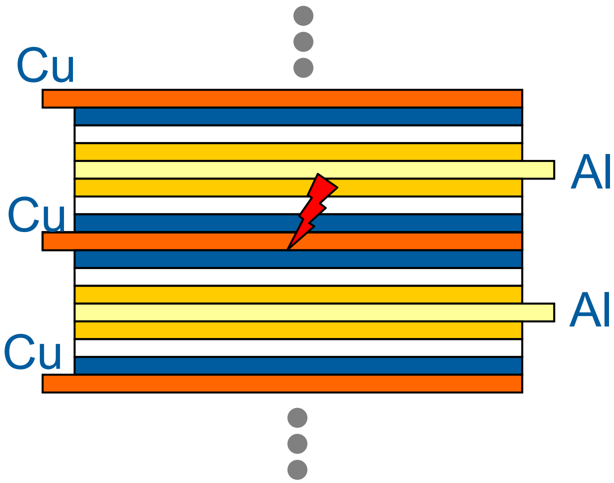
Peter Roth, SNL, ATD presentation

short observed without thermal runaway



➤ **Literature cases with wide range of internal short resistances are observed**

Prismatic Stack Cell Short Simulation



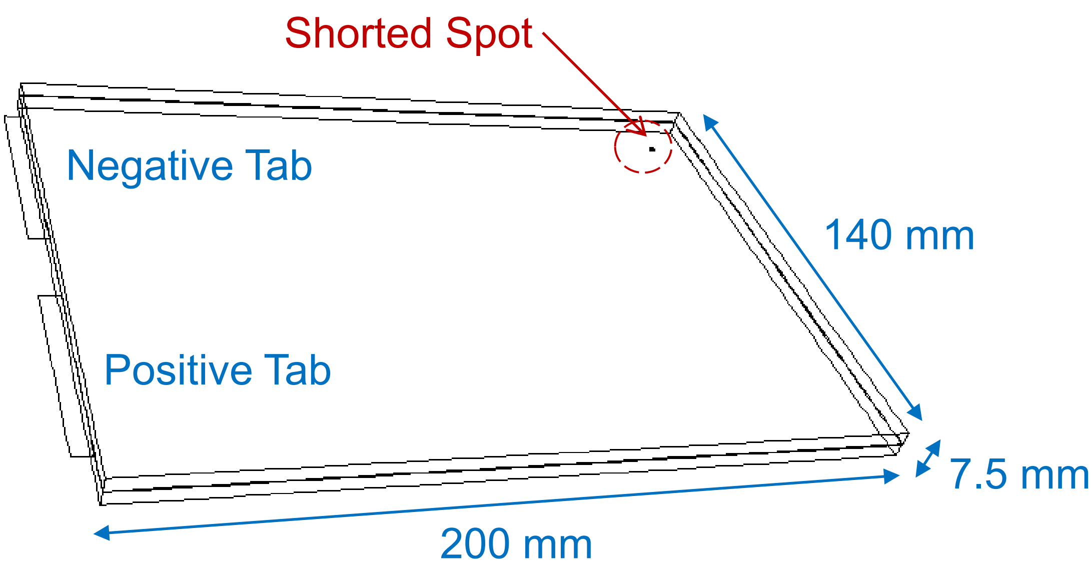
- 20 Ah
- P/E ~ 10 h^{-1}
- Stacked prismatic
- Form factor: 140 mm x 200 mm x 7.5 mm
- Layer thickness: (Al-Cathode-Separator-Anode-Cu)
  15 µm-120 µm-20 µm-135 µm-10 µm
- Multi-physics model parameters
  - ✓ Electrochemistry model: a set evaluated at NREL
  - ✓ Exothermic kinetics: Hatchard and Dahn (1999)
  - ✓ Electronic conductivity: Srinivasan and Wang (2003)

Modeling Objectives

- **Characterize short natures**
- Predict cell responses
- Predict onset of thermal runaway

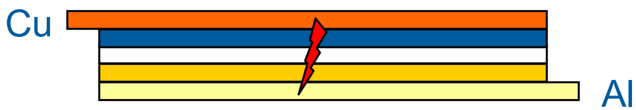
Assumptions

- Short remains same
- Structurally intact
- No venting and no combustion

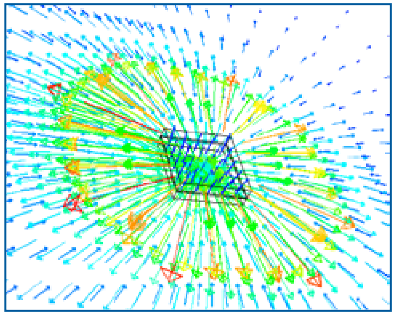


Short Between Al & Cu Current Collector Foils

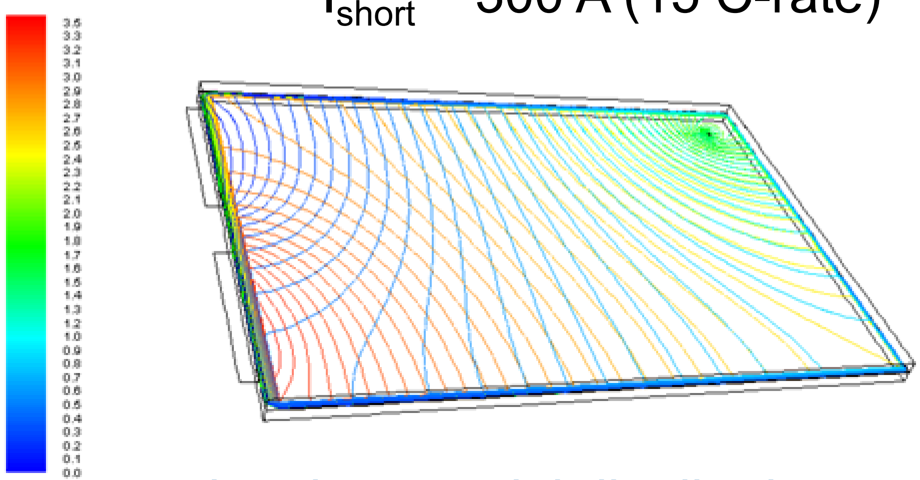
- Shorted area: 1 mm x 1 mm
- e.g.,
  - ✓ metal debris penetration through electrode & separator layers
  - ✓ contact between outermost bare Al foil and negative-bias can



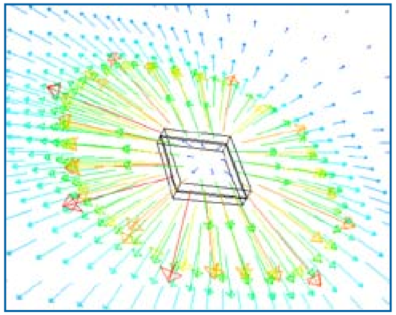
R_{short} ~ 10 mΩ
I_{short} ~ 300 A (15 C-rate)



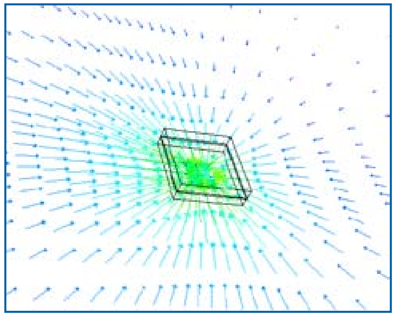
current density field near short



electric potential distribution at shorted metal foil layers



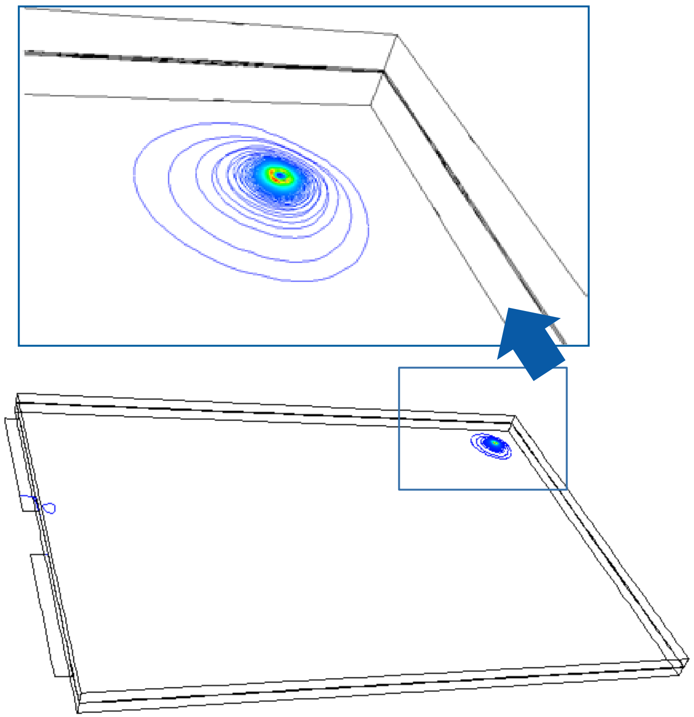
diverging current at Cu foil



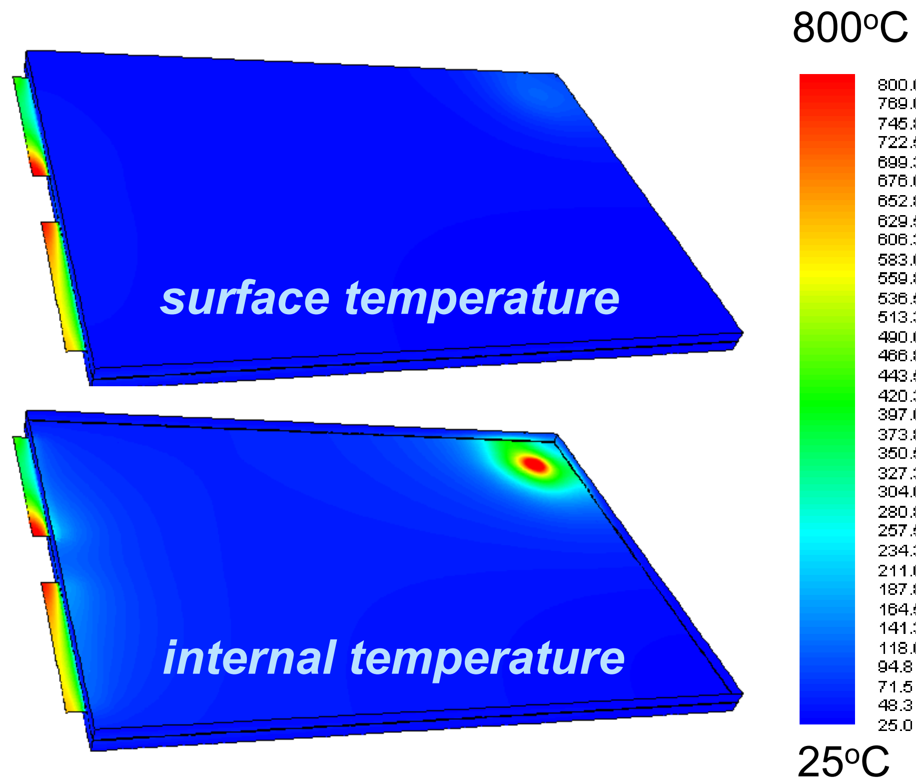
converging current at Al foil

Short Between Al & Cu Current Collector Foils

Joule Heat for Short

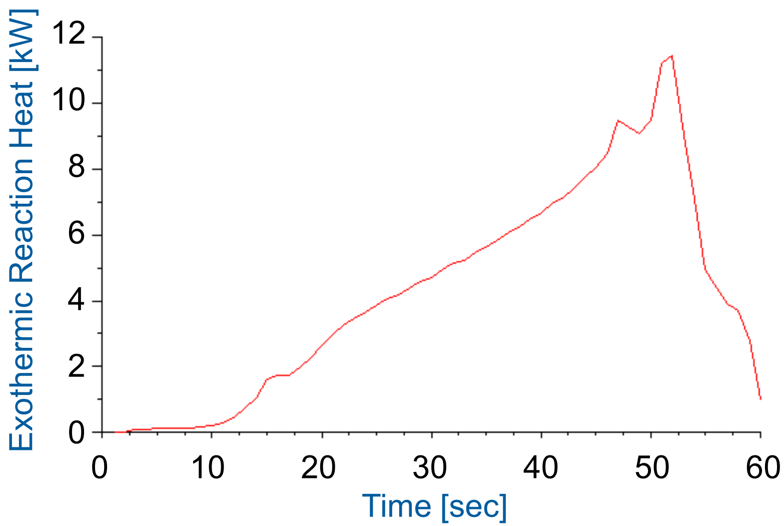


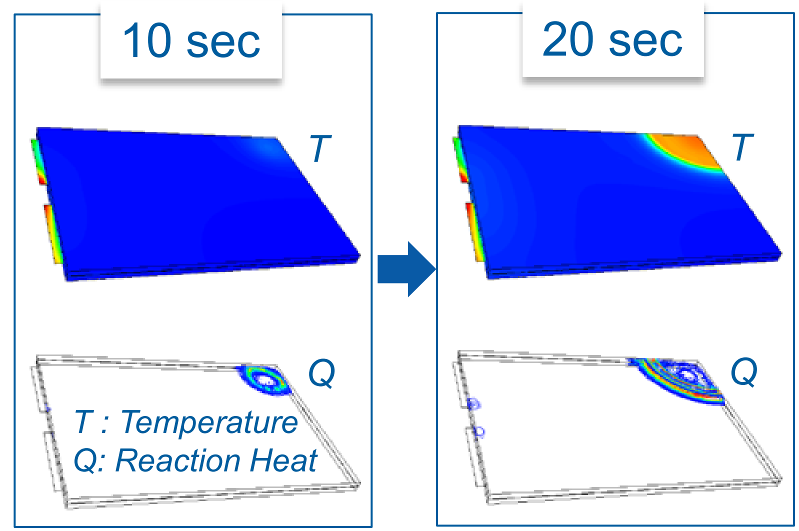
Temperature @10 sec after short

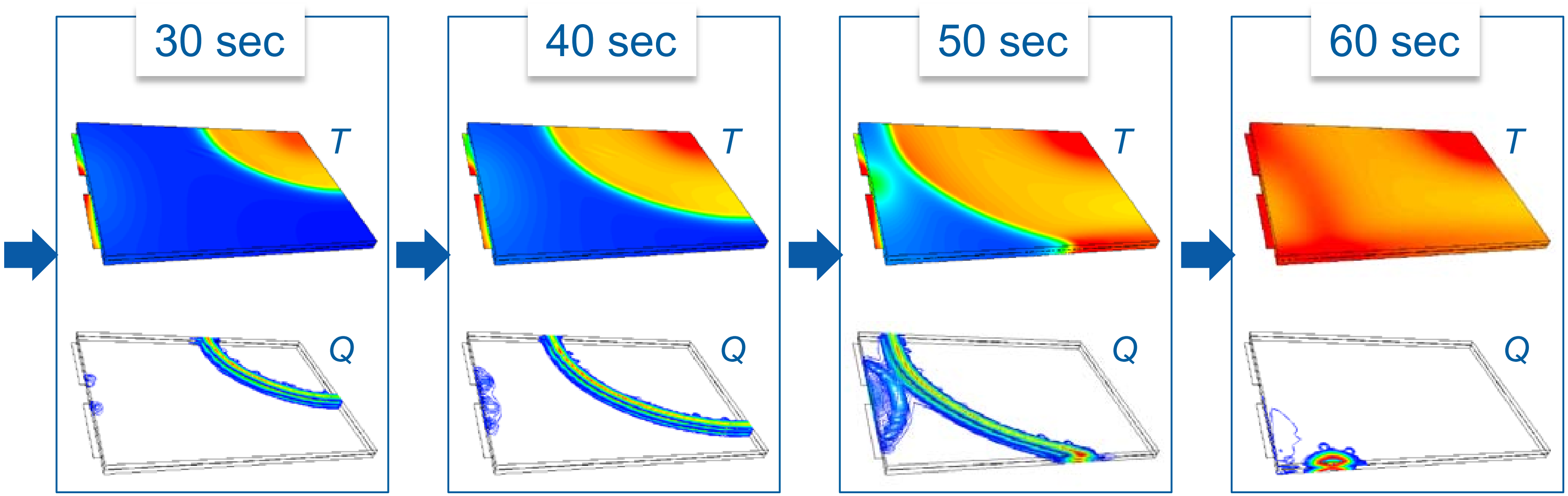


- Joule heat release is localized for converging current near short
- Localized temperature rise is observed.
- Temperature of Al tab appears to reach its melting temperatures (~600°C)

Short Between Al & Cu Foils: Reaction Propagation





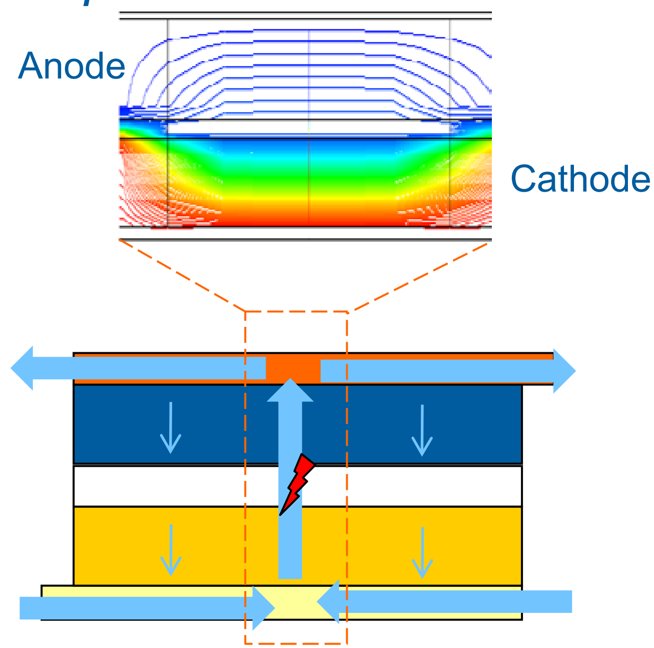


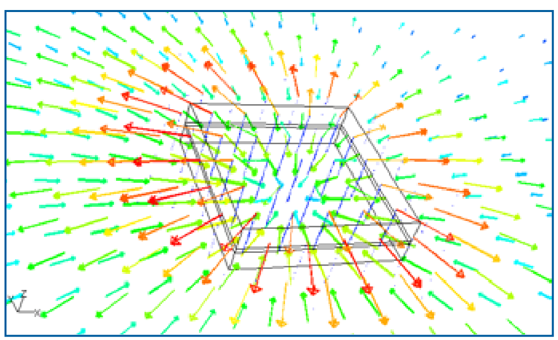
Short Between Cathode and Anode Electrodes

- Shorted area: 1 mm x 1 mm
- e.g.,
  - ✓ separator puncture
  - ✓ separator wearout under electrochemical environment

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

potential near short

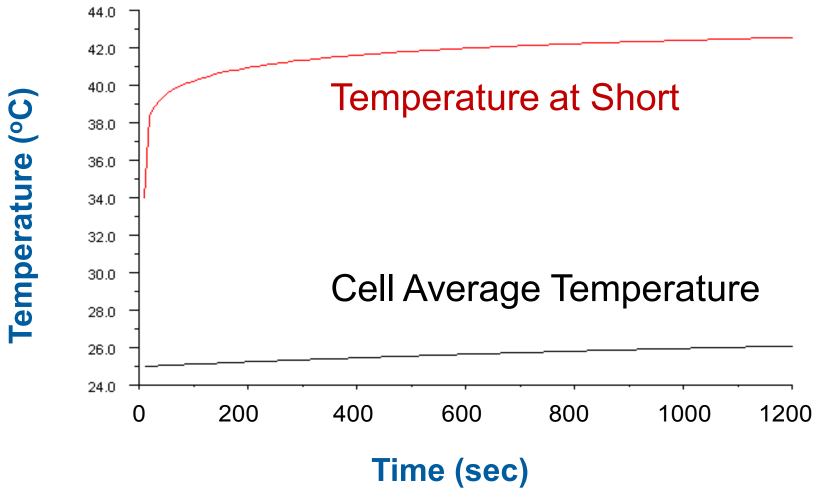


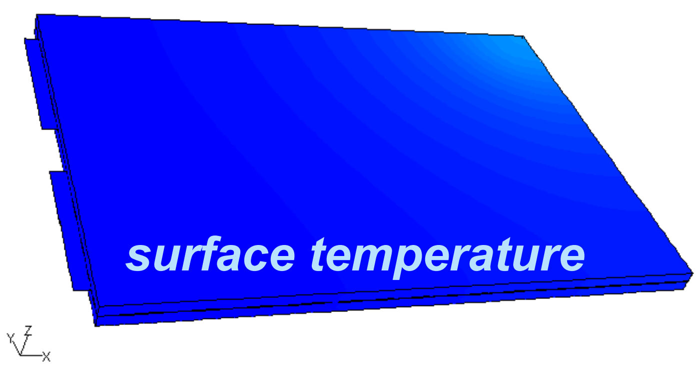


current density field near short

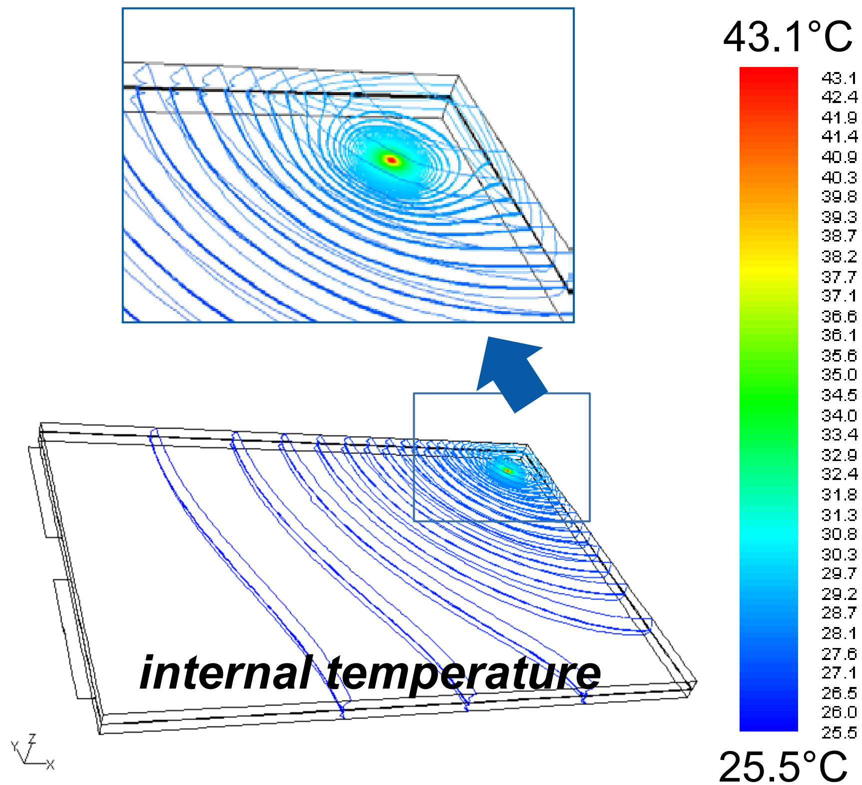
- Electron current is still carried mostly by metal current collectors
- Short current should get through the resistive electrode layers
- Potential drop occurs mostly across positive electrode

Short Between Electrodes: Temperature





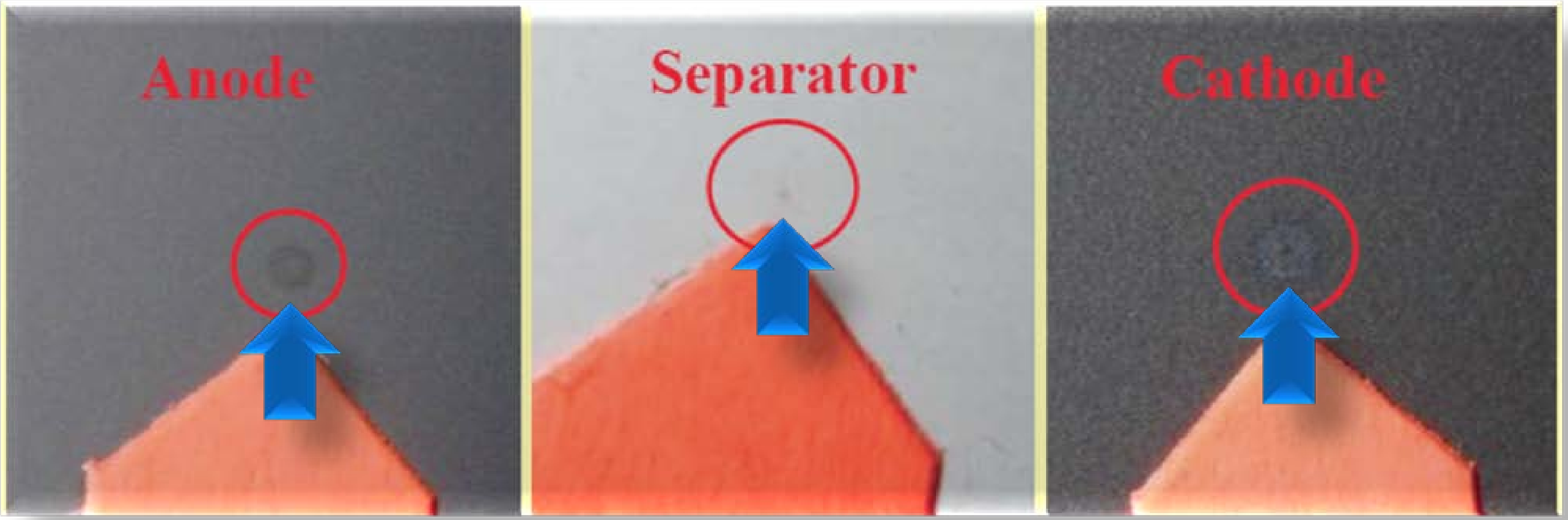
Temperatures at 20 min after Short



- 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

Observations: Simple Separator Puncture

Celina Mikolajczak, Exponent, NASA Aerospace Battery Workshop 2008



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

Exponent

Issue on Structural Integrity of Separator

Short Between Electrodes: Impact of Short Area

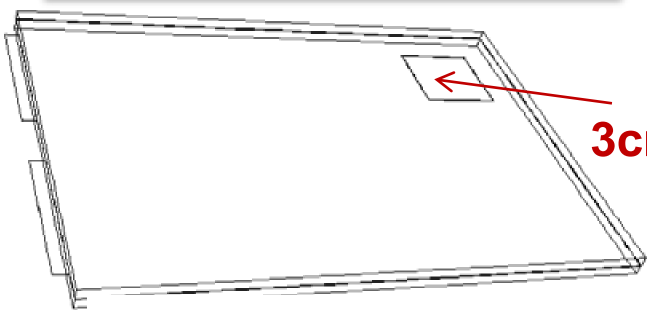
Impact of Separator Structural Integrity

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)

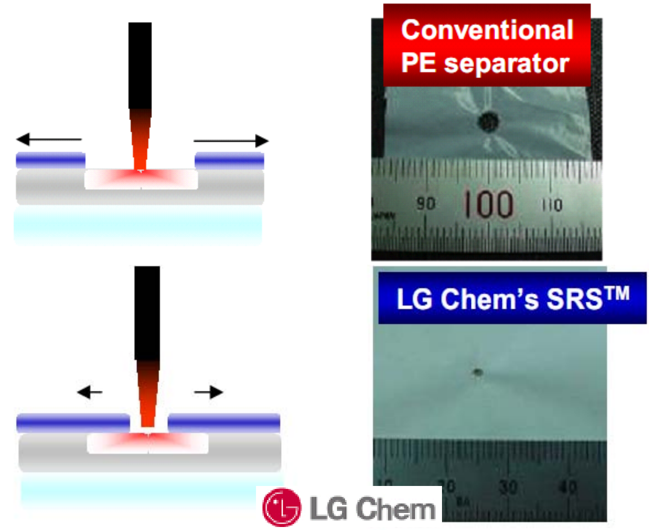


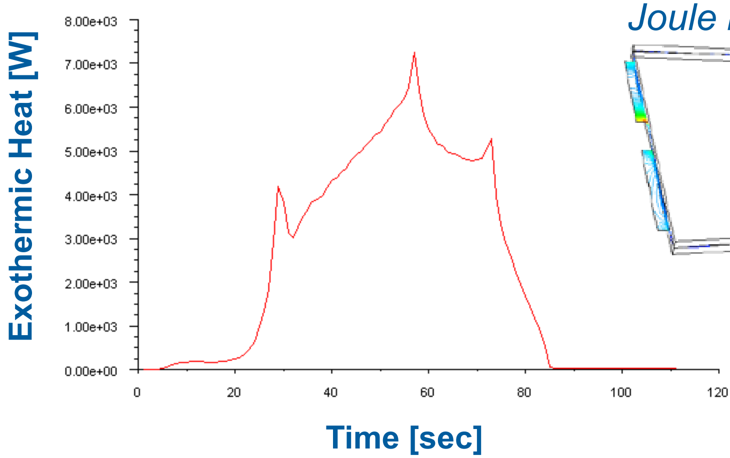
3cm x 3cm Separator Hole

Myung Hwan Kim, LG Chem, AABC08

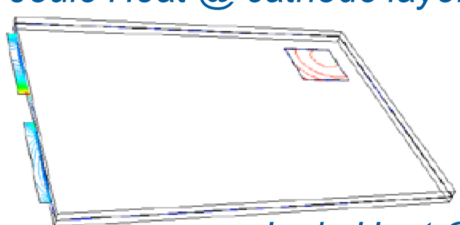
Hole Propagation Test for Simulating Internal Short

Hot Tip at 450 ℃ for 10 sec

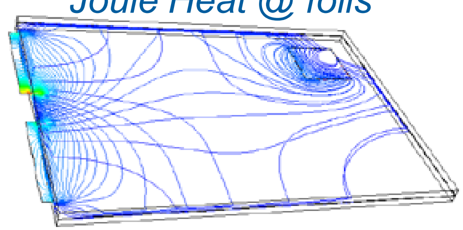




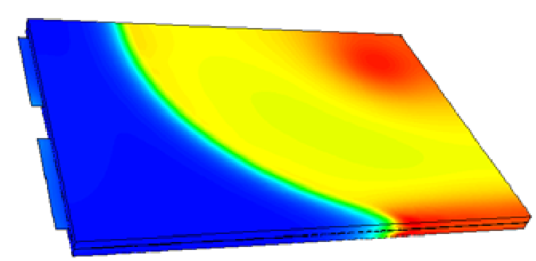
Joule Heat @ cathode layer



Joule Heat @ foils



Temperature at 1min after short



Observations: Structurally Reinforced Separator

Y. Baba, Sanyo Electric, PRIME 2008 (214th ECS)

- Ceramic coated (one-side) functional separator was tested.
- Improvements in safety were **NOT** observed clearly against typical abuse tests.
- Slight performance improvements were reported.

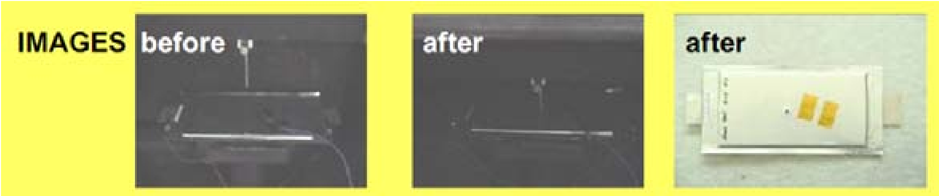
SANYO

VS

Myung Hwan Kim, LG Chem, AABC08

- Mn-spinel based cathode, ceramic coated separator, and laminated packaging provide good abuse-tolerance against typical abuse tests.

Nail Penetration Test



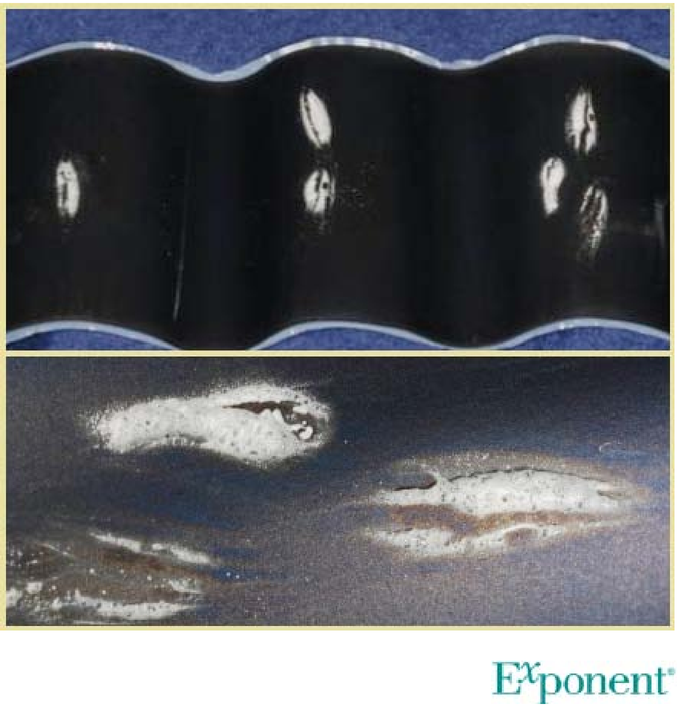
LG Chem

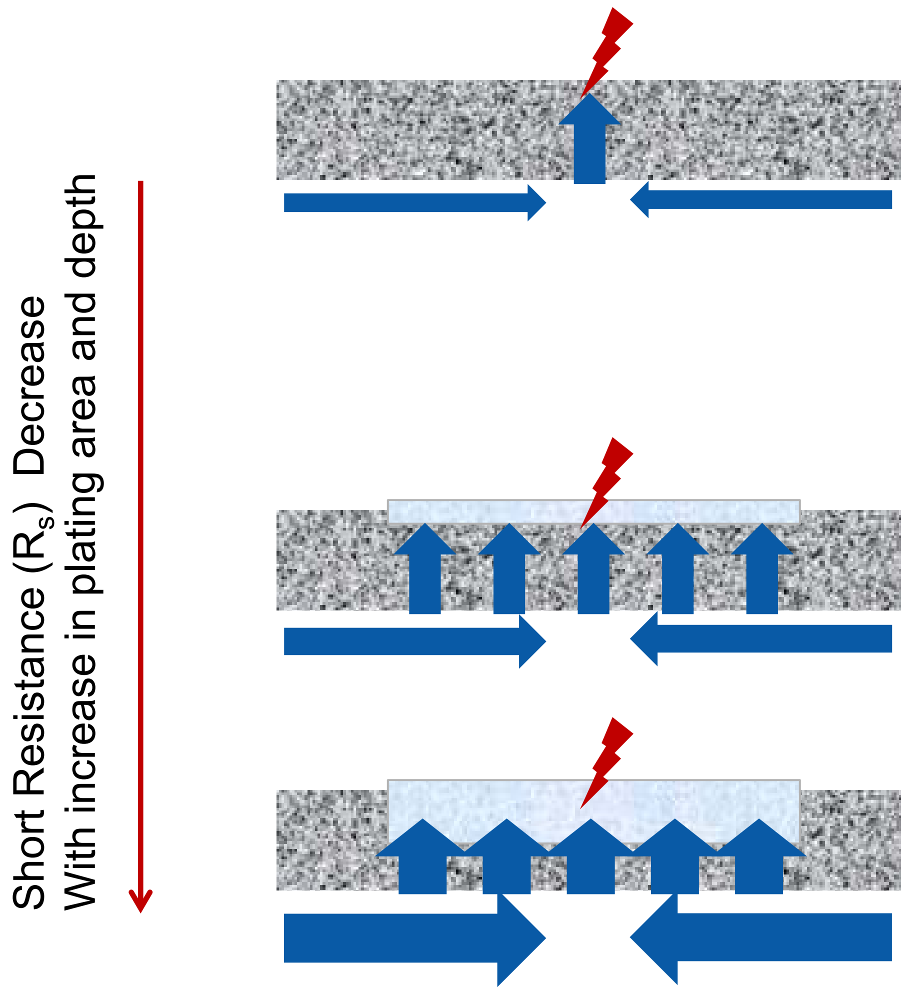
NOTE:
An abuse test such as nail-penetration is not likely to represent the process of formation and evolution of internal short-circuits.

Rationale: metal plating – lowering R_s

Celina Mikolajczak, Exponent, NASA Aerospace Battery Workshop 2008

Li plating on Anode Surface



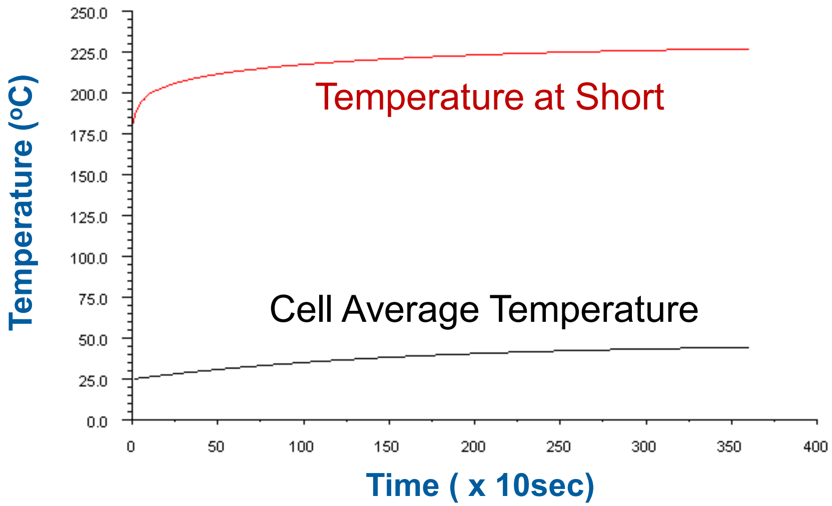


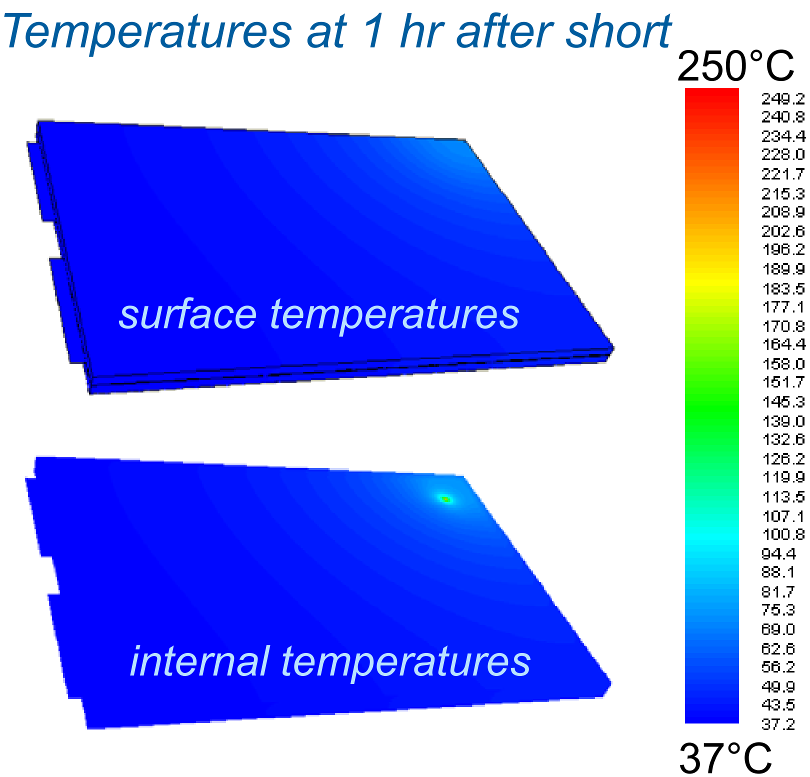
Metal plating provides a potential site for low resistance short formation.

Short Between 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

$R_{short} \sim 2\Omega$
$I_{short} \sim 1.8A\ (< 0.1C)$



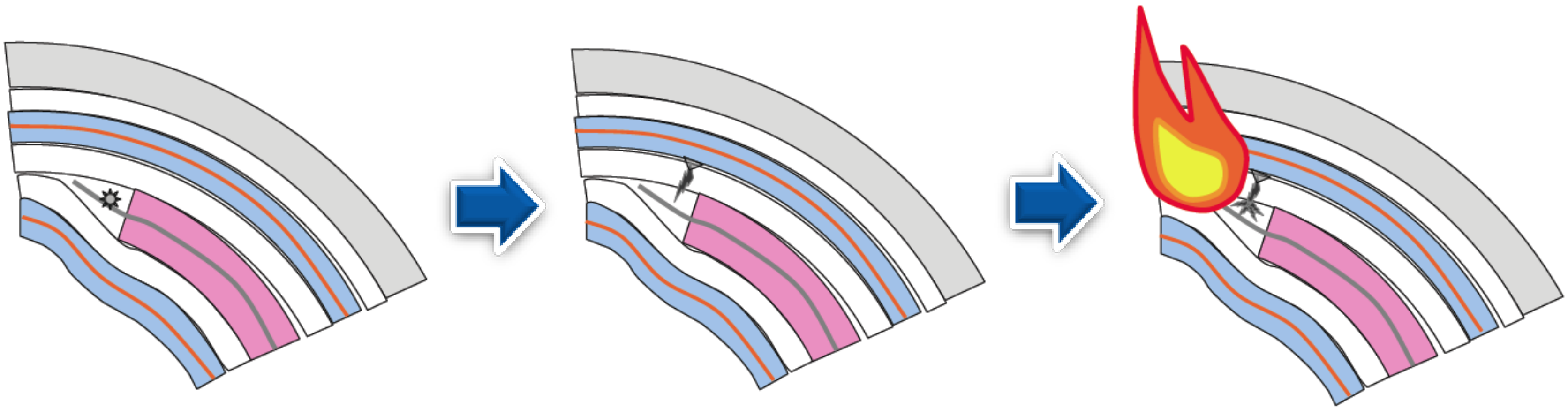


- Temperature at short quickly reaches over **200°C**.
- This type of short is likely to evolve into a hard short in relatively short time.

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.

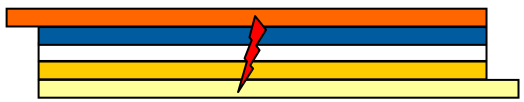
Metal particle dissolves and deposits on anode surfaces. Lithium dendrite grows back on the deposited nickel.

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.

Small Cell (0.4 Ah) Short: metal to metal

- 0.4 Ah cell
- Shorted area: 1 mm x 1 mm



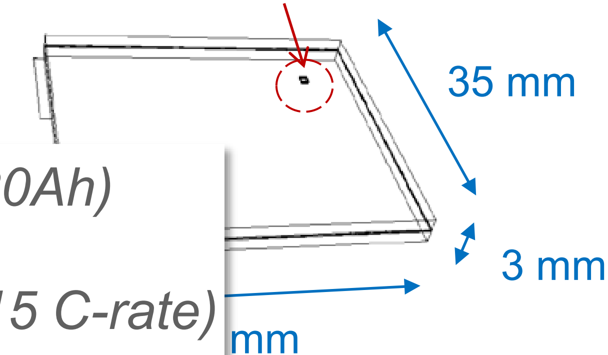
R_{short} ~ 7 mΩ

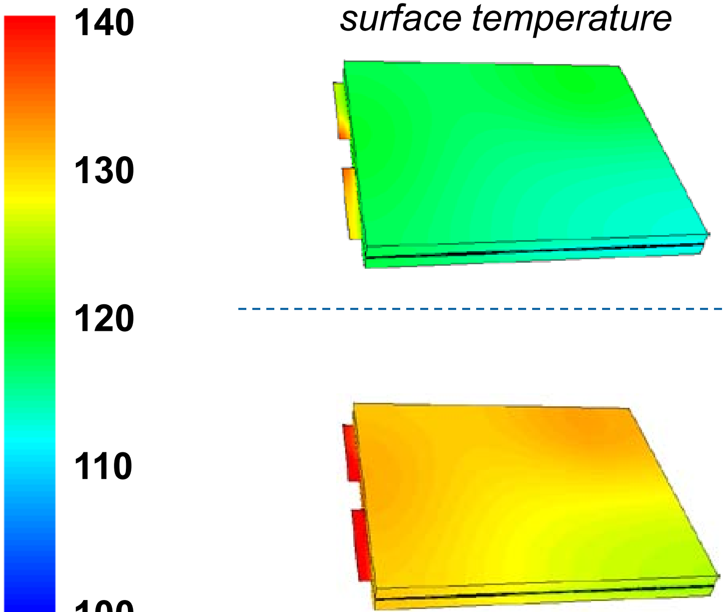
I_{short} ~ 34 A (85 C-rate)

Large cell (20Ah)

R_{short} ~ 10 mΩ

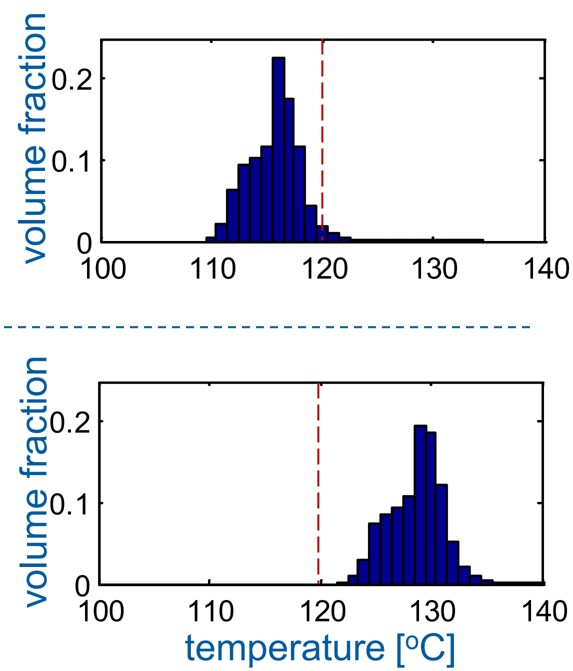
I_{short} ~ 300 A (15 C-rate)



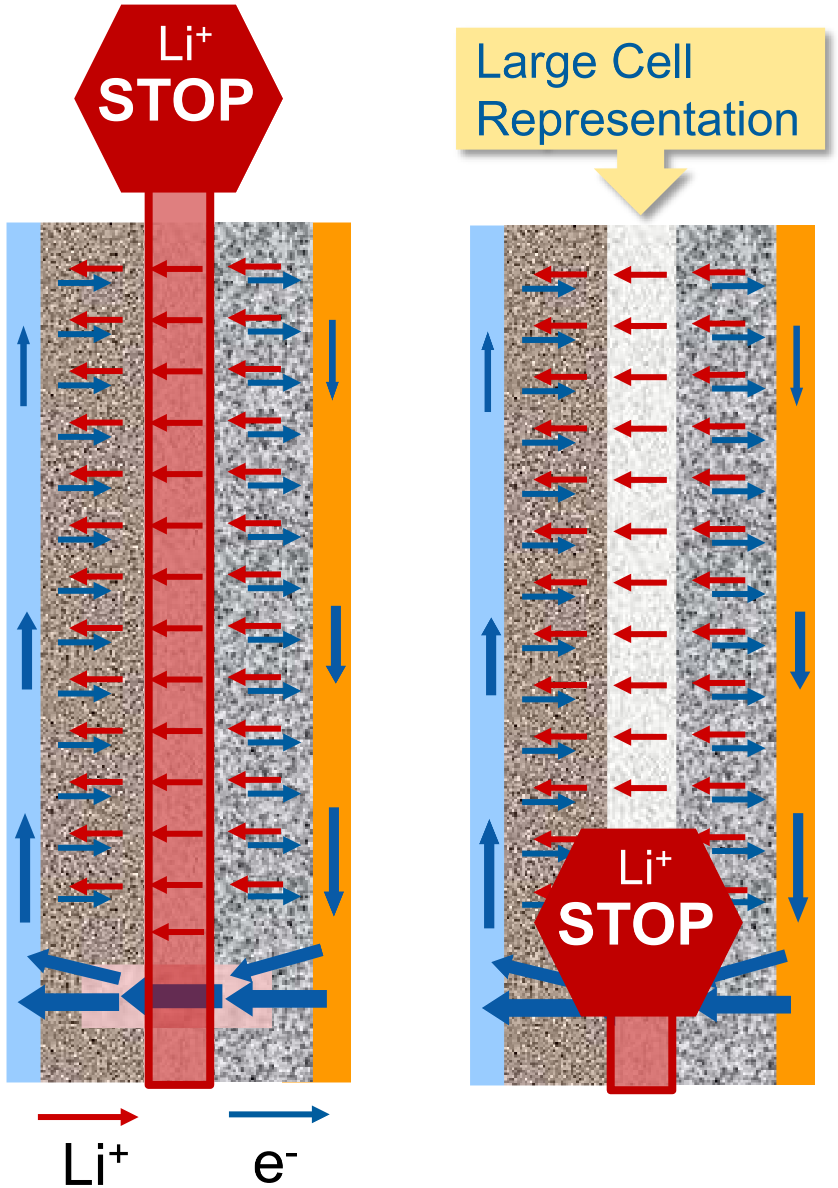


7 sec

8 sec



Shut-Down Separator



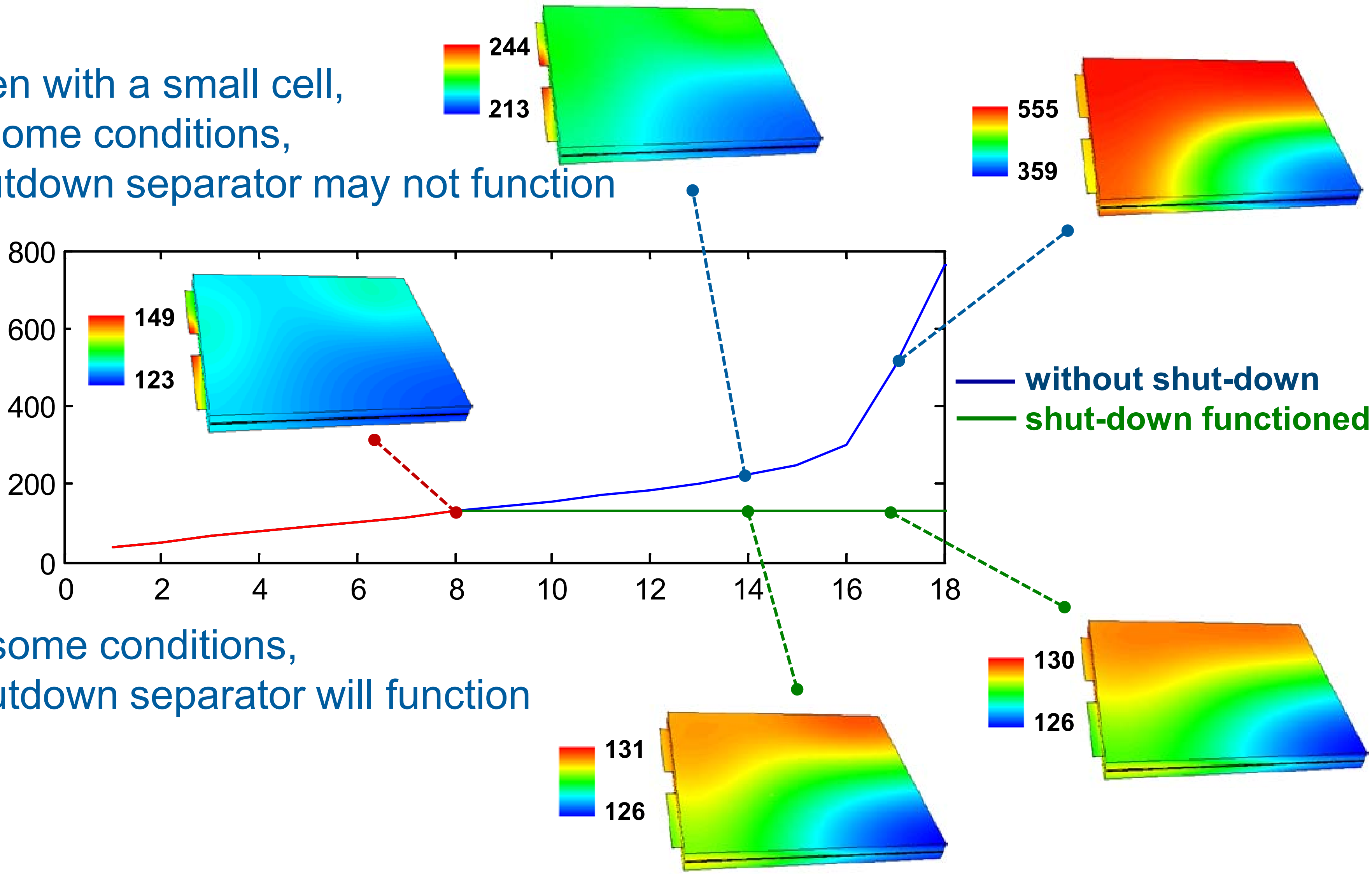
- Thermally triggered
- Block the ion current in circuit

Difficult to apply in

- Large capacity system
- High voltage system

Thermal Behavior of a Small Cell

Even with a small cell,
in some conditions,
shutdown separator may not function



In some conditions,
shutdown separator will function

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 various physical parameters such as nature of short, cell size, rate capability.
- Temperature rise for short is localized in large-format cells.
- Electron 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.
- Electrical, thermal, and electrochemical responses of a shorted cell change significantly for different types of internal shorts.

Future Work

- Perform in depth analysis for evaluating recommended safety designs such as structurally intact separators and shutdown featured device/strategy in relation to cell design parameters (materials, electrode thickness, cell capacity, etc.)

- Design experimental apparatus for model validation through the collaboration with other national labs (Sandia National Laboratory)

- Partner with cell manufacturers and auto industries to help them design safer lithium-ion battery system that appears critical to realize technologies for green mobility

Acknowledgments

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