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

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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.

Heating Pattern at Different Resistance-Shorts

- 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

\[ Q_d = \frac{V_{ocv}^2 R_o}{M (R_o + R_s)^2 M} \]

- **Small cell**
  - \( R_o = 100\text{mΩ (0.4Ah)} \)
- **Large cell**
  - \( R_o = 1\text{mΩ (40Ah)} \)
Understanding Heating Response Differences

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

\[ \text{Short Heating} = \text{Heat from Cell Discharge} + \text{Joule Heat at Short} \]

Qualitative Representation for Heating Pattern

10 mΩ Short + 10 Ω Short

\[ Q_d = \frac{V_{ocv}^2 R_o}{(R_o + R_s)^2 M} \]

\[ Q_s = \frac{V_{ocv}^2 R_s}{(R_o + R_s)^2} \]

Small cell

Large cell
Understanding Heating Response Differences

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

Short Heating =

- Global
- Local

Qualitative Representation for Heating Pattern

<table>
<thead>
<tr>
<th>10 mΩ Short</th>
<th>10 Ω Short</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large cell: localized heating</td>
<td>Small cell: global heating</td>
</tr>
</tbody>
</table>

- Large cell: localized heating
- Small cell: global heating

**Joel Heat at Short**

\[ Q_s = \frac{V_{ocv}^2 R_s}{(R_o + R_s)^2} \]

**Heating from Cell Discharge**

\[ Q_d = \frac{V_{ocv}^2 R_o}{(R_o + R_s)^2} \]

Graphs showing the relationship between short resistance and heat generation for different cell sizes.
Understanding Heating Response Differences

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

\[ Q_d = \frac{V_{ocv}^2 R_o}{(R_o + R_s)^2 M} \]

\[ Q_s = \frac{V_{ocv}^2 R_s}{(R_o + R_s)^2} \]

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

Small cell
Large cell

R_o = 100mΩ (0.4Ah)
R_o = 1mΩ (40Ah)
Observations from Literature:

Various Short Resistances

- Small resistance short (bypassing cathode)
- Medium resistance short (bypassing cathode)
- Large resistance short (flow through cathode)

**No Particle**
1. Al → LiC6
2. Al → C6
3. Al → Cu
4. LCO → LiC6
5. Cu → LCO

*Small Cell with Shut-Down Separator*

Easier Explore and Fire

Very Difficult to Explore and Fire

Cell shut-down

Joule Heat at Short

Heat for Discharge

John Zhang, Celgard, AABC08

A POLYPORE Company

Celgard LLC
Observations from Literature:

**Various Short Resistances**

- Small resistance short (metal to metal)
- Medium resistance short (bypassing cathode)
- Large resistance short (flow through cathode)

*Small Cell with Shut-Down Separator*

- 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)

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

\[ R_{\text{short}} \approx 10 \, \text{m\Omega} \]
\[ I_{\text{short}} \approx 300 \, \text{A (15 C-rate)} \]

Current density field near short

Electric potential distribution at shorted metal foil layers

Diverging current at Cu foil

Converging current at Al foil
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

Exothermic Reaction Heat [kW] vs. Time [sec]

- 0 sec: Temperature $T$ and Reaction Heat $Q$ are both low.
- 10 sec: Temperature $T$ starts to increase significantly, indicating the onset of exothermic reaction.
- 20 sec: Reaction Heat $Q$ continues to rise, confirming the reaction propagation.
- 30 sec: Temperature $T$ reaches a peak, suggesting the maximum reaction rate.
- 40 sec: Reaction Heat $Q$ starts to diminish as the reaction slows down.
- 50 sec: Temperature $T$ begins to decline, indicating the end of the exothermic reaction.
- 60 sec: Reaction Heat $Q$ becomes negligible, and temperature $T$ approaches ambient levels.

$T$: Temperature | $Q$: Reaction Heat
Short Between Cathode and Anode Electrodes

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

\[
\begin{align*}
R_{\text{short}} & \sim 20 \, \Omega \\
I_{\text{short}} & \sim 0.16 \, A \ (< 0.01 \, \text{C-rate})
\end{align*}
\]

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
• 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

Issue on Structural Integrity of Separator
Impact of Separator Structural Integrity

Separator Hole Propagation

1 mm x 1 mm → 3 cm x 3 cm

\[ R_{\text{short}} \approx 20 \, \Omega \]
\[ I_{\text{short}} \approx 0.16 \, A \quad (< 0.01 \, \text{C-rate}) \]

\[ R_{\text{short}} \approx 30 \, m\Omega \]
\[ I_{\text{short}} \approx 100 \, A \quad (5 \, \text{C}) \]
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.

Myung Hwan Kim, LG Chem, AABC08

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

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

\[
R_{\text{short}} \sim 2\,\Omega  \\
I_{\text{short}} \sim 1.8\,\text{A (} < 0.1\,\text{C)}
\]

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

\[ R_{\text{short}} \approx 7 \text{ m}\Omega \]
\[ I_{\text{short}} \approx 34 \text{ A (85 C-rate)} \]

- Large cell (20Ah)

\[ R_{\text{short}} \approx 10 \text{ m}\Omega \]
\[ I_{\text{short}} \approx 300 \text{ A (15 C-rate)} \]
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
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