Thermal Abuse Modeling of Li-Ion Cells and Propagation in Modules

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Outline

Methodology for Understanding Impacts of Battery Design Parameters on Thermal Runaway in Lithium-Ion Cells/Modules

- Background
- Objectives
- Simulating Internal Short in a Cell
  - Parametric runs
  - Results
- Propagation in a Module
- Summary
Background

• Last year, in LLIBTA-3, we introduced our approach for modeling Li-ion thermal abuse\(^1\)
  – Chemical reactions at elevated temperatures
    • SEI decomposition
    • Negative-solvent reaction
    • Positive-solvent reaction
    • Electrolyte decomposition
  – Captured real 3-D geometries and boundary conditions
  – Performed oven heat test simulations
  – Simulated localized heating – cell internal short
  – Cell-to-cell propagation in a module
    • Balance between discrete heat sources and thermal network
    • Heat transfer through radiation, conduction, and convection

\(^1\)G.-H. Kim, A. Pesaran “Analysis of Heat Dissipation in Li-ion Cells & Modules for Modeling of Thermal Runaway,” 3\(^{rd}\) Large Lithium Ion Battery Technology and Application, May 2007, Long Beach, CA
Thermal Runaway - Background

*External Abuse Conditions*

- External Heating
- Over-Charging
- Over-Discharging
- High Current Charging
- Nail penetration
- Crush
- External Short
Thermal Runaway - Background

External Abuse Conditions
- External Heating
- Over-Charging
- Over-Discharging
- High Current Charging
- Nail penetration
- Crush
- External Short

Causing or Energizing Internal Events or Exothermic Reactions
- Electrode-Electrolyte Reactions
- Decompositions
- Electrochemical Reactions

If Heating rate exceeds Dissipation rate
External Abuse Conditions

Causing or Energizing Internal Events or Exothermic Reactions

If Heating rate exceeds Dissipation rate

Focus of the modeling

Thermal Runaway - Background

External Heating
Over-Charging
Over-Discharging
High Current Charging
Nail penetration
Crush
External Short

Lithium Plating
Internal Short Circuit
Electrode-Electrolyte Reactions
Decompositions
Electrochemical Reactions

Leak
Smoke
Gas Venting
Flames
Rapid Disassembly

Focus of the modeling
Background - Approach

- Formulated **Exothermic Reactions** at elevated temperatures

  Reproduce thermal abuse modeling of Li-ion cells provided by Hatchard et al. (J. Electrochem. Soc. 148, 2001);
  Bob Spotnitz provided insight for reaction formulation

  ➔ Component reactions were fitted to Arrhenius type reactions.
  ➔ Kinetic parameters were determined from ARC/DSC literature data.

- Extended to **multi-dimensional models** capturing **actual thermal paths** and geometries of cells and modules.

  ➔ A commercial finite-volume method (FVM) solver, FLUENT, was used.
Background - 3D Oven Heat Test

Small Cell (D18H65)*

*D18H65: Diameter of 18 mm, Height of 65 mm

Although oven test is not a highly multidimensional phenomenon, it still demonstrates noticeable spatial distribution, especially in large cells.

P/S: positive/cathode-solvent
N/S: negative/anode-solvent

Averge Temp after cell exposed to 155 °C.
Objectives of this Study

Continue to explore thermal abuse behaviors of Li-ion cells and modules that are affected by local conditions of heat and materials

- Use the 3D Li-ion battery thermal abuse “reaction” model developed for cells to explore the impact of the location of internal short, its heating rate, and thermal properties of the cell.

- Continue to understand the mechanisms and interactions between heat transfer and chemical reactions during thermal runaway for Li-ion cells and modules.

- Explore the use of the developed methodology to support the design of abuse-tolerant Li-ion battery systems.
Cell Level Thermal Runaway Analysis

• Internal Short Simulation
  ✓ Impact of short location in a cell
  ✓ Impact of thermal property of cell materials
  ✓ Impact of heating rate at short event
Model Description

Hot-Spot

- Localized energy is released in a short period of time in a very small volume of the core.
  - Initially we assumed 5% of stored electric energy released
- Simulation of details of initial process of short is challenging, but we are trying to predict what happens after short happens.

Heat Sources

- Exothermic reaction heat
- No resistive/Joules heating

½ Model with Symmetry Plane

- MESH
  - Computational grid: 200K
  - Grid size: ~1 mm by 1 mm by 1 mm
  - Max: 2.01 mm³; min: 0.31 mm³

Thermal Boundary Conditions

- Natural/forced convection
- Gray-body radiation

Core Material

- Cylindrically orthotropic properties
Temperature Evolution after a Short

Delay between measuring external temperature and internal event, external sensing may be too late.

5% of stored electric energy released in a short time at a small portion of active volume.

Local internal temperatures of core could exceed 600°C

Short in the middle of cell
Volumetric Heat Generation after a Short (Total and due to various reactions, showing how reactions propagate)

5% of stored electric energy released in a short time at a small portion of active volume.
Impact of the **Location of the Short**

Layered structure of electrodes

→ *Preferred directions of reaction propagation*

Initial location of short and thermal paths and material distributions

→ *Propagation pattern*

→ *Heat release duration*

5% of stored electric energy released in a short time at a grid point.
Short Near Exterior Surface vs. Short Near Center of Cell

Heat dissipation is dependent on the location of heat release and thermal paths.

Snapshots of temperature distribution at interior (top) and surface (bottom) 38 seconds after short
Short Near Surface vs. Near Center

- Location of short has impact on how heat flows and abuse reactions propagate (e.g., delay in abuse reaction heat release for near-surface case).

**Temperatures**

- Near surface
- Near center

**Heat Generation (kW)**

- Near surface
- Near center

**Time (sec)**: 0 10 20 30 40 50 60 70 80

**Heat Generation (kW)**: 0 2 4 6 8 10 12

**Near surface**

- 2 sec: 30.00°C
- 20 sec: 664.38°C
- 38 sec: 628.75°C
- 54 sec: 493.13°C

**Near center**

- 2 sec: 350.63°C
- 20 sec: 315.00°C
- 38 sec: 279.38°C
- 54 sec: 243.75°C
Short Near Bottom of Cell vs. Short Near Top of Cell

Heat dissipation is dependent on the location of heat release and thermal paths.

Snapshots of temperature distribution at interior (top) and surface (bottom) 25 seconds after shorting.

Total heat released (area under each curve) is about the same for three cases.
Short near top .vs. Short near bottom

Temperatures: near-top short

Heat dissipation is dependent on the location of heat release and thermal paths.

Temperatures: middle short
Impact of Thermal Properties

Heat Capacity

5% less $C_p$ 5% more

Thermal Conductivity

50% less $k$ 50% more

Electrode/current collector thicknesses and relative amount of component materials

→ Volumetric heat generation
→ Thermal properties of electrode sandwich
Heat Capacity Impact on Cell Thermal Runaway

Reaction propagation is faster in a cell with smaller heat capacity.

5% of stored electric energy released in a short time at a small portion of active volume.
Core Thermal Conductivity Impact on Cell Thermal Runaway

Reaction propagation is slower in a cell with smaller thermal conductivity

Temperatures

Small $k$

2 14 26 38 sec

Large $k$

Thermal Conductivity

50% less $k$ 50% more

Heat Generation (kW)

Time (sec)
Impact of Amount of Released Heat

Heat: % of cell energy release at a very small volume

No thermal runaway with smaller heat release

Heat dissipates quickly without triggering thermal runaway.

Pattern of initial heat release at short events need to be investigated.

We did an in-depth analysis.
Impact of Heating Rate in Short Events

Heat Release at a Short Event is affected by†:

- Electrical Resistance of the Short
- Cell Power Rate (Power/Energy ratio)
- Cell Size (Capacity)

†This is based on our ongoing analysis and the details are beyond scope of this presentation. The next few slides look at a case with high-resistance short. Details of low-resistance case will be presented at other upcoming conferences.
Quantifying Heat Release at Short Event
Using Electrochemical Cell Model

**Total Heat** [W] = Volumetric Heat for Current Production + Heat Release at Short (Short Heat)

High-resistance Short Cases (3Ω, 7Ω, 10Ω) Observed from SNL Data

- Short current is determined by the short resistance rather than by the power rate or by the size of a cell.
- Relatively low c-rate for high resistance shorts
- Volumetric heat from current production is small
- Most released heat is local to the short site
Thermal Behavior of a Cell at High-Resistance Short Events

18650 CoO$_2$/graphite

30°C ambient, heat transfer coefficient on cell surface (h) = 7 W/m$^2$K

Heat Dissipation vs Heat Release

**Temperature**

- **3Ω**, **7Ω**, **10Ω**

**Reaction Heat**

- **3Ω**, **7Ω**, **10Ω**

Strong natural convection in air
Comparison of Thermal Behavior Between two High-Resistance Short Events

Temperature

<table>
<thead>
<tr>
<th>Temperature Component Reaction Heat</th>
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<tbody>
<tr>
<td>SEI Decomposition</td>
</tr>
<tr>
<td>Negative/Electrolyte</td>
</tr>
<tr>
<td>Positive/Electrolyte</td>
</tr>
<tr>
<td>NET</td>
</tr>
</tbody>
</table>

- **7Ω Short**
  - Led to thermal runaway.

- **10Ω Short**
  - Did not lead to thermal runaway.

18650 CoO₂/graphite Cell

30°C ambient, (h) = 7 W/m²K

Can a short have such a high resistance?
Observed Events

**Internal Short** (may or may not lead to thermal runaway)

### 18650 Cells

Short & Thermal Runaway observed by SNL

- **Heat release was much faster than dissipation.**
- **Low resistance short** ($<<1\Omega$) is likely

#### SNL Data: From presentations at DOE’s Advanced Technology Development Meetings

(E. Peter Roth and Tom Wunsch)
Module-Level Analysis of Cell-to-Cell Thermal Runaway Propagation

How can a module be more resistive to cell-to-cell thermal runaway propagation?
Background

We proposed that *Cell-to-Cell Propagation* in a module is a result of the **INTERACTION** between the distributed chemical sources and the thermal transport network through a module.

**Approach** for the analysis of this system

- Formulated *exothermic chemical reactions* of a cell at elevated temperatures.
- Quantified *heat transfer among the cells* in a module
  - Radiation heat transfer
  - Conduction heat transfer
  - Convection heat transfer
- We used multi-node lumped approach last year; this year we have looked at 3D approach
Impact of a Highly Conductive Heat Transfer Medium

Rather than the air used in the base case (left), a highly conductive PCM/graphite matrix was used to fill the space between the cells in the module (right).

Base case (air)

Graphite matrix impregnated with PCM

It appears that a very conductive medium may reduce the chance for propagation.

NOTE: * PCM/graphite matrix is a highly porous graphite structure that is impregnated with phase-change material (PCM) (based on information from S. Al-Halaj et al.).
3D Module Propagation Model

Objective: Developing a 3D cell and module geometry capturing cell-to-cell interconnects

CAD drawing of a 10-cell module (Each cell is in its own individual sleeve)

Top view

Bottom view

Grid for the 10-cell module
Close Look at Reaction in an Individual Cell in the 10-cell Module

2 seconds apart between each frame
Reaction Propagation in a Module with 10 Cells in Series

The order at which cells go into thermal runaway depends on the cell interconnect configurations.

Top view

Side view
On-going Work
Module-Level Research in Progress
Adding the electrical network modeling

- Impact of thermal transport network + electrical network

6 Parallel, 4 Series
Summary

• Li-ion thermal abuse reaction chemistry was implemented in a finite-volume 3D cell model to address various design elements.
  ✓ Examined impact of cell design parameters
  ✓ Investigated impact of short location and thermal properties
    ✓ Some shorts may not lead to thermal runaway
    ✓ Heat dissipation is important, but depending on the amount of heat release from abuse

• Propagation of abuse reaction through a module was simulated.
  ✓ A complicated balance between the heat transfer network and dispersed chemical sources
  ✓ Balance is affected by module design parameters such as cell size, configuration and size of cell-to-cell connectors, and cell-to-cell heat transfer medium
Future Work

• Improve model through comparisons with experimental data from other laboratories
• Continue examining the impact of design variables
• Address the limitation of the model
• Expand the model capability to address various chemistries and materials, such as iron phosphate
• Investigate internal/external short by incorporating an thermally coupled electrochemistry model into the three-dimensional cell model
• Use the models to investigate the impact of (shut-down) separators
• Work with developers on specific cell and module designs
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