Energy Storage Safety and Reliability

Thermal Runaway Database Development

- Hsin Wang¹, Lianshan Lin¹, Srikath Allu¹
- Loraine Torres-Castro², Yuliya Preger², Valerio De Angelis²

Development of Thermally Sensitive Paint

Hsin Wang¹, Beth Armstrong¹, Chanaka Gamalalaralage¹ Michael Starke¹

¹Oak Ridge National Laboratory
²Sandia National Laboratories

ORNL is managed by UT-Battelle, LLC for the US Department of Energy
Team Members - ORNL

Hsin Wang
Material Science and Technology Division
Material Scientist, Testing

Beth Armstrong
MSTD
Ceramist, Paint Development

Lianshan Lin
MSTD
Mechanical, Database

Chanaka Gamaralalage
MSTD
Chemist, Paint Development

Srikanth Allu
Computational Science & Engineering
Modeling & Simulation

Jianlin Li
Electrification & Energy Infrastructure
Battery Research

Michael Starke
Electrification & Energy Infrastructure
Battery Management System

Isabella Fishman
Northwestern University
DOE SULI Student, Battery Testing
Collaboration: Sandia Laboratories and Others

**Sandia Laboratories:** Protocols development, parallel testing database development

Collaborators: Loraine Torres-Castro, Josh Lamb, Yuliya Preger and Valerio De Angelis

**University of Tennessee:** Accelerating Rate Calorimetry (ARC), thermal runaway reactions and propagation

Collaborator: Professor Peng Zhang @ UT Space Institute Tullahoma TN

**LG&E KU:** Technology Research and Analysis Department, Kentucky’s first and largest utility-scale energy storage system. On-site lithium-ion battery temperature monitoring directly supports the E.W. Brown Solar facility
Project History and Progression

2019

- Safety Database
  - ORNL-Sandia test protocol
  - Large format EV battery testing at both labs

2020

- Safety Database
  - Battery testing from 500 mAh to 33 Ah
  - Journal of Power Sources:
    i. Thermal runaway
    ii. Capacity fade

2021

- New Detection Methods
- Safety Database
  - Database development with Sandia
  - Temperature sensitive paint developed (patent)

2022 ->

- New Detection Methods
- Safety Database
  - Thermal runaway severity scores
  - Metal particle-based paint: 60-80°C thiol release
Safety Database

Thermal Runaway Severity

**Project Goal:** Develop a thermal runaway database to rank/predict hazard severity
Mechanical Induced Short Circuit

- Mechanically induced internal short circuit
  - Nail penetration
  - **Single-side indentation**
    - Pinch test (two indenters)
    - Pinch-torsion, indent-torsion

- **Real-time Monitoring:**
  - Load, displacement, $V_{OC}$ and temperature

- **Post-mortem Examination:**
  - X-ray computed tomography (XCT)
  - Open cell examination
ORNL and Sandia Testing Facility: Large Format Cells

Nissan Leaf Cell in Sandia Test Chamber

Nissan Leaf Cell After Indentation
Extracting Li-ion Cells from Electrical Vehicles at ORNL (Chevy VOLT, Nissan Leaf and FORD Focus EV)
Li-ion Cells: Disassembled EVs and Commercial Sources

Large-format Prismatic Cells Tested at ORNL and Sandia

2017 Chevy VOLT (26 Ah)  2013 Nissan Leaf (33 Ah)  Commercial NMC Cells (10 Ah)  Commercial LFP Cells (10 Ah)

10 NMC Cells (5 SOC x 2) after Testing
Left to right: 0% SOC -> 100% SOC

10 LFP Cells (5 SOC x 2) after Testing
Left to right: 0% SOC -> 100% SOC
Updated ORNL-Sandia Test Procedures and Standards

Internal Short-circuit Induced Thermal Runaway
• Mechanical abuse (indentation)

Updated Test Protocols:
• Cycle cell 3-5 times at C/2 between 3.0-4.2V to determine SOC and discharge to test SOC
• Hydraulic or servo-motor driven load frame
• 6 mm punch (most sensitive, small contact)
• 0.05 inch per minute compressive loading
• 25 mV $V_{oc}$ drop
• Hold the punch after short circuit
• Temperature measurement:
  • 5 mm from the indenter
  • At cell corners when possible

Thermocouple Locations on Large-format Cells

Select the most sensitive test to allow safety risk ranking
Thermal Runaway Risks for Li-ion Batteries (ORNL-Sandia)

**Small Cells Testing at ORNL:**
- SOC: 20%, 40%, 60%, 80%, 100%
- Capacity at 500, 1500, 200 mAh
- Number of Cells: 4 cells/condition

**ESS Batteries at Various SOCs:**
- Sandia: 30%, 50%, 75%, 100%
- ORNL: 20%, 40%, 60%, 80%, 100%

**Test Data and Cell Information:**
- Cell Capacity
- Loading curve: before & after short
- Cell Voltage: drop and response
- Cell Temperature vs. Time
- Open cell voltage
- Anode thickness
- Cathode thickness
- Separator thickness
- C/2 Charge curve
- 1C discharge curve

<table>
<thead>
<tr>
<th>Cell Name</th>
<th>Chemistry</th>
<th>Capacity (mAh)</th>
<th>Sample Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial LCO</td>
<td>LiCoO₂</td>
<td>500</td>
<td>15</td>
</tr>
<tr>
<td>Commercial LCO</td>
<td>LiCoO₂</td>
<td>1500</td>
<td>10</td>
</tr>
<tr>
<td>Commercial LCO</td>
<td>LiCoO₂</td>
<td>2000</td>
<td>15</td>
</tr>
<tr>
<td>Commercial LCO</td>
<td>LiCoO₂</td>
<td>6400</td>
<td>13</td>
</tr>
<tr>
<td>Control NMC</td>
<td>LiNiMnCoO₂ (811)</td>
<td>5200</td>
<td>12</td>
</tr>
<tr>
<td>Metallized Film Current Collector (MFCC) NMC</td>
<td>LiNiMnCoO₂ (811)</td>
<td>5200</td>
<td>10</td>
</tr>
<tr>
<td>Commercial LFP</td>
<td>LiFePO₄</td>
<td>10000</td>
<td>16</td>
</tr>
<tr>
<td>Commercial NMC</td>
<td>LiNiMnCoO₂</td>
<td>10000</td>
<td>14</td>
</tr>
</tbody>
</table>

Acronyms for cathode chemistry: lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC), lithium iron phosphate (LFP)
## EUCAR Severity Levels

<table>
<thead>
<tr>
<th>Hazard Level</th>
<th>Description</th>
<th>Classification Criteria &amp; Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No effect</td>
<td>No effect. No loss of functionality.</td>
</tr>
<tr>
<td>1</td>
<td>Passive protection activated</td>
<td>No defect; no leakage; no venting, fire, or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.</td>
</tr>
<tr>
<td>2</td>
<td>Defect/Damage</td>
<td>No leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell irreversibly damaged. Repair needed.</td>
</tr>
<tr>
<td>3</td>
<td>Leakage ∆mass &lt; 50%</td>
<td>No venting, fire, or flame; no rupture; no explosion. Weight loss &lt; 50% of electrolyte weight (electrolyte = solvent + salt).</td>
</tr>
<tr>
<td>4</td>
<td>Venting ∆mass ≥ 50%</td>
<td>No fire or flame; no rupture; no explosion. Weight loss ≥ 50% of electrolyte weight (electrolyte = solvent + salt).</td>
</tr>
<tr>
<td>5</td>
<td>Fire or Flame</td>
<td>No rupture; no explosion (i.e., no flying parts).</td>
</tr>
<tr>
<td>6</td>
<td>Rupture</td>
<td>No explosion, but flying parts of the active mass.</td>
</tr>
<tr>
<td>7</td>
<td>Explosion</td>
<td>Explosion (i.e., disintegration of the cell).</td>
</tr>
</tbody>
</table>

## ORNL-Sandia Test Data Based Severity Levels

<table>
<thead>
<tr>
<th>Hazard Severity Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (VL, 0-10)</td>
<td>Very low, instant local Joule heating, detectable voltage drops</td>
</tr>
<tr>
<td>2 (L, 10-25)</td>
<td>Low, localized heating, small voltage drops and recovery</td>
</tr>
<tr>
<td>3 (M, 25-75)</td>
<td>Moderate, localized heating spread, significant voltage drops, continued discharge after recovery</td>
</tr>
<tr>
<td>4 (H, 75-90)</td>
<td>High, heating due to chemical reactions, cell puff and gas release, voltage drop to close zero</td>
</tr>
<tr>
<td>5 (VH, 90-100)</td>
<td>Very high, heating spread to the cell, heavy smoke and possible fire, voltage drops to zero</td>
</tr>
</tbody>
</table>
Calculation of Thermal Runaway Severity Score

Severity Score Calculation Based on Temperature and Voltage

\[
5, \text{ if Max Temperature} < 40 \, ^\circ C \\
\min \left\{ \begin{array}{l}
wA \left( \frac{\text{Max Temperature}}{160} \right)^{0.25} \\
wB \left( \frac{\text{Temperature Increase Rate}}{200} \right) \\
wC \times \text{wCap} \times \text{wSOC} \times \text{Voltage Drop Score} \\
+c_{\text{offset}}, \ 100 \end{array} \right\} \\
100, \text{ if Max Temperature} > 160 \, ^\circ C
\]

Voltage Drop Score:

\[
\begin{align*}
1, & \text{ if } \left( \frac{\text{Voltage Range}}{\text{Initial Voltage}} \right) < 0.2 \\
2, & \text{ if } \left( \frac{\text{Voltage Drop in 2 Seconds}}{\text{Initial Voltage}} \right) > 0.5 \text{ and } \left( \frac{\text{Final Voltage Change}}{\text{Initial Voltage}} \right) < 0.2 \\
3, & \text{ if } \left( \frac{\text{Voltage Drop in 2 Seconds}}{\text{Initial Voltage}} \right) < 0.4 \text{ and } \left( \frac{\text{Final Voltage Change}}{\text{Initial Voltage}} \right) > 0.7 \\
4, & \text{ if } \left( \frac{\text{Voltage Range}}{\text{Initial Voltage}} \right) > 0.7 \text{ and } \left( \frac{\text{Final Voltage Change}}{\text{Initial Voltage}} \right) > 0.7 \text{ and } \left( \frac{\text{Voltage Drop in 5 Seconds}}{\text{Initial Voltage}} \right) > 0.7
\end{align*}
\]

\[
wA = 2.0 \times \text{cScale}, \ wB = 3.0 \times \text{cScale}, \ wC = 2.0 \times \text{cScale}
\]

\[
wC = \frac{\text{Battery Capacity}}{10000}
\]

\[
wSOC = \frac{\text{Battery SOC}}{100}
\]

\[
cScale = 95/6, \ c_{\text{offset}} = 5-c\text{Scale}
\]
Results: Linear Change vs "Step Change"

LCO Batteries: 500 mAh to 6400 mAh

NMC Batteries

LFP Batteries
Thermal Runaway Severity Calculation Workflow

Formatted data file in ‘excel’ folder

Necessary columns

Time Load Voltage Time Temperature

Calculation file

Capacity SOC

Run code

Result worksheet

Severity score

Code behind the worksheet
Search Database by Battery and Abuse Test Metadata (Host: Sandia Labs)
New Detection Methods

Thermally Sensitive Paint Development

(Seedling)

Project Goal:
Thermal runaway avoidance. Early detection of thermal runaway on every cell and large surface area
Indirect Large Area Temperature Monitoring

Temperature-Sensitive Paint for $T_{\text{Threshold}}$ Monitoring

Carriers for paint need to have the following features:

- Stay normal within battery operation temperature
- Release chemical/gas $T > T_{\text{Threshold}}$
- Non-line-of-sight (change of color is not an option)
- Detection via “smell” and gas detector

Li-ion Battery  
Brush or Spray Paint  
Overheating  
Smoke Alarm  
Mercapton Detector  
Special Gas Release for Overheating  
Thermal Runaway  
Heating  

(Web image)
Experimental Setup and Demonstration of Thiol Release

Over-temperature Detection

Sample temperature recording system
Temperature control system
Thiol sensor
Stage temperature display system
Heating stage with sample

Battery pouch foil on the heating stage

Over-temperature Detection

Paint Development

(a) CuCl₂ in ethanol
(b) EtSH addition
(c) Stirred 30 min at RT
(d) Purified using EtOH

Eappable thiolate compound
Copper thiolate coating on battery pouch material

(a) Battery pouch
gal thermal sensitive compound

Temperature sensor
After heating

Coated Pouch on Hot Plate
Future Plan: ESS Reliability Safety Testing and Analysis Facility

Single Cells Database (ORNL-Sandia):
- UL Standard, end-user upload
- Machining learning, prediction of hazard severity

NHTSA Electrical Vehicles -> battery Packs, module and cell:
- Thermal runaway testing
- Thermal runaway propagation studies
- Modeling and Simulations of battery failure

Battery Safety Technology Development and Demonstration:
- Thermal runaway warning system (paint development)
- Gas detection, BMS/TMS control, prevention mechanisms (isolation, lowering SOC, discharge)
Acknowledgements and Outputs

Project Supported by DOE EERE Office of Electricity (OE) (Dr. Imre Gyuk)

Publications, Patent, Presentation:


2. Wei Li, Bobing Xin, Thomas R. Watkins, Yong Xia, Hsin Wang, Juner Zhu, “Mechanical damage of prismatic Lithium-ion cells subject to bending: tests, model, and detection”, *EcoMat*, revised, doi.org/10.1002/eom2.12257, pp1-16, 2022 Impact factor =12.213


One Provisional Patent Filed: ID 4373 “Temperature sensitive paint with gas and chemical release functions” by, BL Armstrong, CI Gamalarage, K. Buddett-Trofimov, GM Veith, H Wang

Invited talk: Battery & EV Congress 2022 (June 8-9, 2022 at the MSU Management Education Center, Troy, Michigan), Title: Thermal Runaway Risk of Li-ion Batteries Used in Electric Vehicles: Testing and Analysis by Hsin Wang et al