Predicting and mitigating cascading failure of thermal runaway in stacks of Li-ion pouch cells

Presented by
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Thermal runaway and cascading failure

Validated reliability and safety is one of four critical challenges identified in 2013 Grid Energy Storage Strategic Plan

- Failure rates as low as 1 in several million
- Potentially many cells used in energy storage
- Moderate likelihood of ‘something’ going wrong

Increased energy densities and other material advances lead to more reactive systems

A single cell failure that propagates through the pack can have an impact even with low individual failure rates.

How do we decrease the risk?
Approaches to designing in safety

The current approach is to test our way into safety
- Large system (>1MWh) testing is difficult and costly.

Supplement testing with predictions of challenging scenarios and optimization of mitigation.
- Develop multi-physics models to predict failure mechanisms and identify mitigation strategies.
- Build capabilities with small/medium scale measurements.
- Still requires some testing and validation.
Cascading failure testing with passive mitigation

LiCoO$_2$ 3Ah pouch cells

5 closely packed cells with/without aluminum or copper spacer plates

- Spacer thicknesses between 1/32” and 1/8”
- State of charge (SOC) between 50% and 100%

Failure initiated by a mechanical nail penetration in the outer cell (cell 1)

Thermocouples (TC) between cells and spacers (if present)
Cascading failure testing
Finite element model for full cells in thermal runaway

Discretization in one direction ($x$)

Modeled as a quasi 1-D domain of thin hexahedron elements

Multi-layered system
  - Lumped battery material
  - Spacers
  - End block insulators

Convective heat transfer to surroundings (scaled by surface area to volume ratio for thin domain)

Heat conduction with chemical sources inside battery material
Finite element model equations

Energy conservation:

\[ \rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) + \dot{q}''' \]

Mass conservation for species \( i \) with \( N_r \) reactions:

\[ \frac{\partial \rho_i}{\partial t} = \sum_{j=1}^{N_r} (\nu''_{ij} - \nu'_{ij}) r_j \]

Energy source:

\[ \dot{q}''' = - \sum_{j=1}^{N_r} \Delta H_j r_j \]
Chemical source terms for thermal runaway

Preliminary chemistry model from literature

- Based on Dahn group (1999-2001)
- Derived from calorimetry
- Good onset predictions
- Under-predicts peak temperature

Empirical chemical reactions:

- SEI decomposition (Richard 1999)
  \[(CH_2O\text{CO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{gas}\]

- Anode-electrolyte (Shurtz 2018)
  \[2\text{C}_6\text{Li} + \text{C}_3\text{H}_4\text{O}_3 \rightarrow 2\text{C}_6 + \text{Li}_2\text{CO}_3 + \text{gas}\]

- Cathode-electrolyte (Hatchard 2001)
  \[\text{CoO}_2 + \frac{2}{15}\text{C}_3\text{H}_4\text{O}_3 \rightarrow \frac{1}{3}\text{Co}_3\text{O}_4 + \text{gas}\]

- Short-circuit
  \[\text{C}_6\text{Li} + \text{CoO}_2 \rightarrow \text{C}_6 + \text{LiCoO}_2\]
Anode-electrolyte calorimetry and modeling

Anode-electrolyte calorimetry suggest several regimes during thermal runaway

- Initiation – Plateau – Runaway

Anode-electrolyte reactions generate heat

- Could raise cell temperatures \( \sim 650 ^\circ C \)
- Nominal reaction:

\[
2 \text{LiC}_6 + \text{C}_3\text{H}_4\text{O}_3 \rightarrow 2\text{C}_6 + \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4
\]

Electron-Tunneling Limited Plateau

Anode thermal runaway

RD, 1999 model
More predictions with the comprehensive model

Predicting the full range of behavior over a range of particle sizes

Increasing specific area

$z_t$-scaling $= \frac{1}{\sqrt{\text{BET}}}$

$E_2 = 135 \text{ kJ/mol}$

$A_2 = 7.9 \times 10^{15} \text{s}^{-1}$

$C_t = 72.5, z_{crit} = 5.8$

Park & Lee 2009
Sample G1

$\alpha_{BET} = 13.4 \text{ m}^2/\text{g}$

LiC$_6$ at 10°C/min

Park & Lee 2009
Sample G2

$\alpha_{BET} = 12.9 \text{ m}^2/\text{g}$

LiC$_6$ at 10°C/min

Park & Lee 2009
Sample G3

$\alpha_{BET} = 2.95 \text{ m}^2/\text{g}$

LiC$_6$ at 10°C/min

Park & Lee 2009
Sample G4

$\alpha_{BET} = 0.95 \text{ m}^2/\text{g}$

LiC$_6$ at 10°C/min
Many predictions with the comprehensive model
24 x DSC, 5 x ARC

Shown earlier

Limiting Electrolyte

State of Charge

Detailed area measurements
A comprehensive model for anode-electrolyte runaway

\[ - \frac{dx_i}{dt} = x_i \frac{a_e}{a_0} \frac{m_E}{(m_{50} + m_E)} A_2 \exp \left( - \frac{E_2}{RT} \right) \exp(-z_t) \]

\[ \frac{dz_t}{dt} = - \frac{dx_i}{dt} \frac{C_t}{(a_{BET}/a_0)^n_t} \]

for \( z_t < z_{crit} \), and \( \frac{dz_t}{dt} = 0 \) otherwise

\[ Q \ [W/g] = - \frac{dx_i}{dt} \frac{\Delta H_{rxn}}{W_a} \]

Heat Release with new \( \Delta H_{rxn} \)
Simulation results: 100% SOC, no spacers

- Prediction of peak temperatures and cooling
- Cell crossing speed over-predicted
Deriving propagation times

[Diagram showing space and cell crossing with labeled points and graph representing heating rates over time]
Predicted crossing times: 100% SOC, no spacers

- Experimental cell and space crossing times are on the same order.
- Cell crossing times are under-predicted and space crossing times are over-predicted.
Simulation results: 80% SOC, no spacers

- Insufficient heat generation to initiate thermal runaway outside of the nail penetration region
- Experimental peak temperatures lower than 100% SOC
Simulation results: 100% SOC, 1/32” aluminum spacers

- Temperature difference in TCs on either side of the plates under-predicted
- Cell crossing speed still over-predicted
Simulation results: 100% SOC, 1/16” copper spacers

- No propagation in simulations and experiments
Cascading failure: propagation speeds

Adding spacers *increases* space crossing time, but *decreases* cell crossing time.

Increasing state of charge (SOC) *decreases* both space and cell crossing time.

Interplay between heat capacity of system and energy release.
Heat capacity and SOC: limits of propagation

Interplay between **heat capacity** of system and **energy release:**

\[ \text{Energy/Capacity} = \frac{Q_{\text{cells}}}{(m_{\text{cells}}c_{p,\text{cells}} + m_{\text{spacers}}c_{p,\text{spacers}})} \]

<table>
<thead>
<tr>
<th>Case Description</th>
<th>Energy/Capacity (K)</th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% SOC</td>
<td>940</td>
<td>Propagation</td>
<td>Propagation</td>
</tr>
<tr>
<td>1/32” Aluminum</td>
<td>819</td>
<td>Propagation</td>
<td>Propagation</td>
</tr>
<tr>
<td>1/32” Copper</td>
<td>778</td>
<td>Propagation</td>
<td>No Propagation</td>
</tr>
<tr>
<td>80% SOC</td>
<td>752</td>
<td>Propagation</td>
<td>No Propagation</td>
</tr>
<tr>
<td>1/16” Aluminum</td>
<td>725</td>
<td>Cell 2 Failure</td>
<td>No Propagation</td>
</tr>
<tr>
<td>75% SOC</td>
<td>705</td>
<td>Cell 2 Failure</td>
<td>No Propagation</td>
</tr>
<tr>
<td>1/16” Copper</td>
<td>663</td>
<td>Cell 2 Failure</td>
<td>No Propagation</td>
</tr>
<tr>
<td>1/8” Aluminum</td>
<td>590</td>
<td>No Propagation</td>
<td>No Propagation</td>
</tr>
<tr>
<td>1/8” Copper</td>
<td>512</td>
<td>No Propagation</td>
<td>No Propagation</td>
</tr>
<tr>
<td>50% SOC</td>
<td>470</td>
<td>No Propagation</td>
<td>No Propagation</td>
</tr>
</tbody>
</table>
Summary

Finite element model with chemical source terms was tested against experimental data.
- Captures trends at 100% SOC, over-predicts propagation velocity through cells.
- Model is under-conservative with predictions when heat capacity is increased and SOC is decreased.

There is a need for validated chemical source models tested at higher heat release rates.

Ongoing work to improve mechanistic understanding of thermal and chemical time scales.
- Comprehensive cathode models
- Transport limited reaction kinetics
Acknowledgements

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