Predictive modeling for energy-storage safety in abnormal thermal scenarios

John Hewson, Randy Shurtz
Babu Chalamala, Summer Ferreira, Josh Lamb, Heather Barkholtz, Lorraine Torres-Castro
Sandia National Laboratories

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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,

- 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?

www.nissan.com
www.internationalbattery.com
www.samsung.com
www.saft.com
Approaches to designing in safety

The current approach is to test our way into safety\(^1\)

- Large system (>1MWh) testing is difficult and costly.

Consider supplementing testing with predictions of challenging scenarios and optimization of mitigation.

- Develop multi-physics models to predict failure mechanisms and identify mitigation.
- Build capabilities with small/medium scale measurements.
- Still requires some testing and validation.

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How Do We Model Thermal Runaway in Batteries?

1) Simplify & Discretize Geometry

2) Define initial composition, thermal properties, reactions (species & energy source terms)

3) Define convection and radiation boundary conditions

4) Define initial energy source

5) Calculate internal conduction and reaction rates
Models Need Parameters

- Preliminary chemistry model from literature
  - Based on Dahn group from 2000, 2001
  - Derived from calorimetry data (ARC and DSC)
  - Needs to be recalibrated

- Empirical chemical reactions
  - SEI decomposition: \(2 \text{ROCO}_2\text{Li} \rightarrow \text{Li}_2\text{CO}_3 + \text{prod}\)
  - Cathode-electrolyte: \(\text{CoO}_2 + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \frac{1}{3}\text{Co}_3\text{O}_4 + \text{prod}\)
  - Electrolyte-salt: \(\text{C}_3\text{H}_4\text{O}_3 + \text{LiPF}_6 \rightarrow \text{prod}\)
  - Anode-electrolyte: \(\text{C}_6\text{Li} + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{prod}\)

- This model form has been utilized repeatedly, but requires calibration for each system because it is not expressed in terms of fundamental cell characteristics.
Thermal and electrochemical reactants are same

Simulated short circuit plus thermal runaway
Limits of thermal runaway in high-temperature environments and under internal short-circuits

Simulated oven test

Simulated short circuit analogy with oven temperature

\[ P = \frac{V^2}{R} \]

\[ T_{eff} = T_{\infty} + P / h_{net} A \]

Energy required for initial heating unavailable for runaway
Short-circuit induced runaway in meshed 18650 with nail

- Effects of inhomogeneity increase as scale increases beyond the lumped-capacitance regime.
Relative importance of short-circuit versus thermal reactions

R = 1.4 ohm, h = 7 W/m²/K, Meshed 18650 with 50% heat release in nail

Time: 1004.759876

Thermal Reaction Cathode Product

Short Circuit Cathode Product
How Much Cooling to Suppress Runaway with Internal Short Circuit?

- Models can be used to estimate cooling requirements
  - Simulation shows homogeneous heating of 18650 cells (varying short resistance and cooling)
  - Internal temperature variation will be worse for large format systems and localized shorts
Cascading Propagation Observed in Li-Ion Packs

- Experimental propagation in 5 stacked pouch cells at Sandia
- Investigating effects of
  - State of charge
  - Intermediate layers
  - Cell geometry
- Good pack-scale model validation cases

High-Fidelity Models Required for Cascading Failure

- Propagation predictions will improve with fidelity of high-temperature chemistry

Prior models provided incomplete accounting of heat release – example for anode.

Key anode model improvements

Area-Scaled Model

- SEI Passivation layer inhibits lithium reduction of electrolyte, \( \exp(-z) \).
- \( H_{rxn} \) thermodynamically consistent with \( 2\text{LiC}_6 + \text{EC} \rightarrow 2\text{C}_6 + \text{C}_2\text{H}_4 + \text{Li}_2\text{CO}_3 \).
- Reaction scales with effective surface area.

\[
\frac{dz}{dt} \propto \frac{A_{rxn,ref}}{A_{rxn}} \approx \left( \frac{A_{BET,ref}}{A_{BET}} \right)^{n_1}, \quad n_1 < 1
\]

Critical Effective Layer Thickness

\( z = \min(z, z_{crit}) \) where

\[
z_{crit} \propto x_{sei,crit} \left[ \frac{A_{BET}}{A_{BET,ref}} \right]^{n_2}
\]

- Limit to passivation layer growth with heating.
  - Endothermic defoliation (or other process) observed. Fracture, cracking?
  - Defects in SEI more likely on on edges.
New model based on measureable quantities and thermodynamic material properties

Applying the new anode model to cascading failure

Dahn Model (Hatchard et al. 2001)

Applying the new anode model to cascading failure

Publications and presentations

- **Publications**

- **Presentations:**
Future work

- Fit calorimetry data from a variety of battery chemistries (Sandia team and literature) to kinetic models.
- Identify configurations that inhibit initial ignition.
- Continue modeling thermal interaction of battery pack configurations.
  - Cascading versus isolated failure.
  - Inhomogeneous packs with losses.
  - Focus on heat losses required to mitigate propagation.
- Intermediate term
  - Demonstrate simulation as tool for risk-cost trade space studies through distributed sensing versus mitigation response.
  - Predict contributions of battery thermal runaway to overall fire load and as source of hazardous products.
  - Integrate reacting thermal model of battery packs with fire models in Sierra to evaluate safety of representative geometries and scenarios.
- **Ultimate goal:** *Employ modeling as design tool for optimal mitigation strategies.*
In closing

- Thermal runaway is a risk and potential barrier to development and acceptance.
- Heat release rates are moderate relative to potential dissipation.
- Multi-physics thermal models can potentially identify critical ignition and propagation trends.
- Quality measurements are key to parameter identification.
- Progress this term
  - Relate chemical source to fundamental material properties, allowing simultaneous short-circuit and thermal runaway.
  - Identify thermal mitigation to prevent thermal runaway with short circuits.
  - Advance chemical models of thermal runaway processes to predict high-temperature processes.
  - Identification of thermal ignition criterion for cell-to-cell (EESAT).
  - Cell-to-cell propagation and cooling for mitigation along homogenized pack structures (EESAT).
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THANK YOU

QUESTIONS:
JOHN HEWSON
jchewso@sandia.gov
• Results show a nearly linear relationship between total heat release (kJ) and cell SOC – similar to data for cell size this suggests that failure enthalpy is based largely on the stored energy available
• Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC – again this is traditionally thought to cause a greater risk of thermal runaway
• Could a runaway still occur with large numbers of low SOC cells or cells in well insulated conditions?
Increasing stored energy (SOC) leads to exponentially faster heat release rates

- Fully charged cells observed to undergo more violent exothermic reactions.
- Charged fraction of cathode and anode are reactive component.
  - \( \text{CoO}_2 \) vs \( \text{LiCoO}_2 \); \( \text{LiC}_6 \) vs \( \text{C}_6 \)
- Greater heat release associated with greater fractions of active material (greater SOC).

- Higher temperatures give exponentially greater heat release due to Arrhenius rate constants.
How are Different Heat Sources Analogous?

Energy balance on a cell yields:

\[ T_{\text{eff}} = T_\infty + \frac{P}{h_{\text{net}}} A \]

\[ P = \frac{V^2}{R} \]

\[ h_{\text{net}} = h + h_{\text{rad}} = h + \varepsilon \sigma (T_w^2 + T_\infty^2) (T_w + T_\infty) \]

Simulated Oven and Short-Circuit Tests

- **Simple Oven Tests**
  - 100% SOC
  - \( T_{\text{oven}} = T_{\text{eff}} \)

- **Modified Oven Tests**
  - Correspond well to short-circuit tests if both \( T_{\text{eff}} \) and SOC match at onset of runaway for each case

- **Internal Short-Circuit Tests**
  - Ambient \( T_\infty \), varying resistance
  - 100% initial SOC

**Energy required for initial heating unavailable for runaway**
Lumped capacitance previously reported as good approximation for this battery

Transition region becomes more gradual due to inhomogeneous competition for reactants