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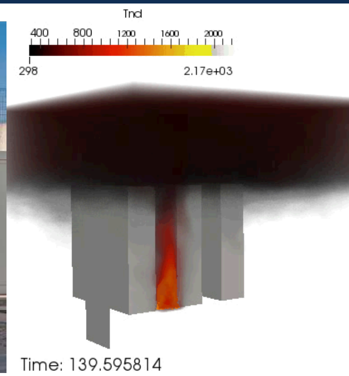

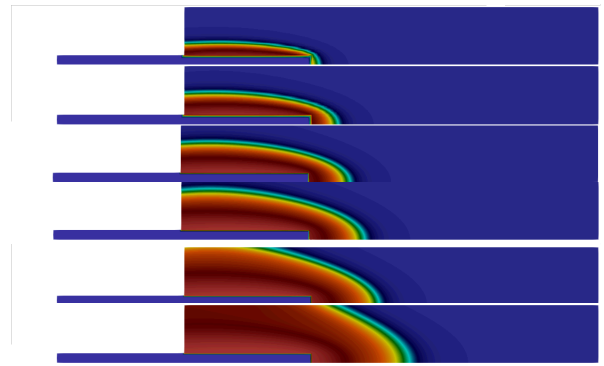

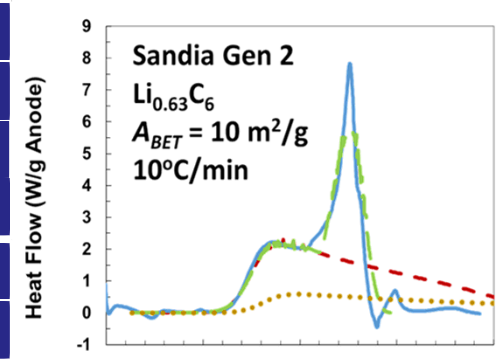

Predictive modeling for energy-storage safety in abnormal thermal scenarios

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Sandia National Laboratories

Office of Electricity Peer Review

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SAND2017-XXXX C

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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

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- 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.

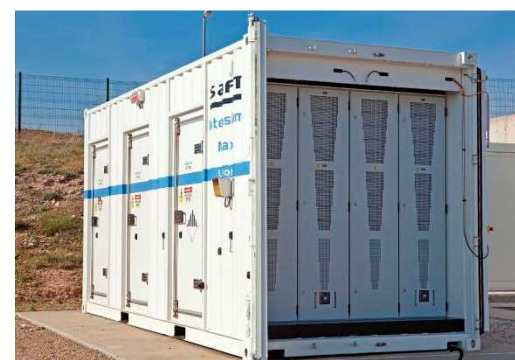
- How do we decrease the risk?

Single Cell
~0.5-5 Ah

Strings and large format cells
~10-200 Ah

EV Battery Pack 100s-1000s cells
10-50 kWh

Stationary storage system 1000s or more individual cells
MWh+



www.nissan.com
www.internationalbattery.com
www.samsung.com
www.saft.com

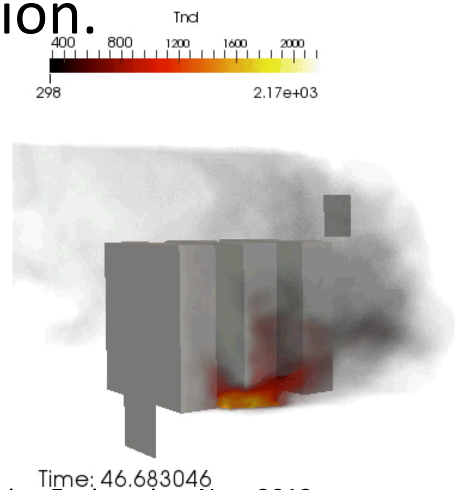
Approaches to designing in safety

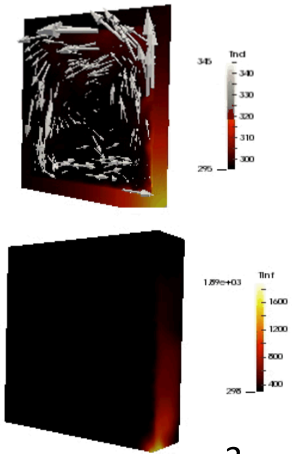
The current approach is to test our way into safety[1]

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

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

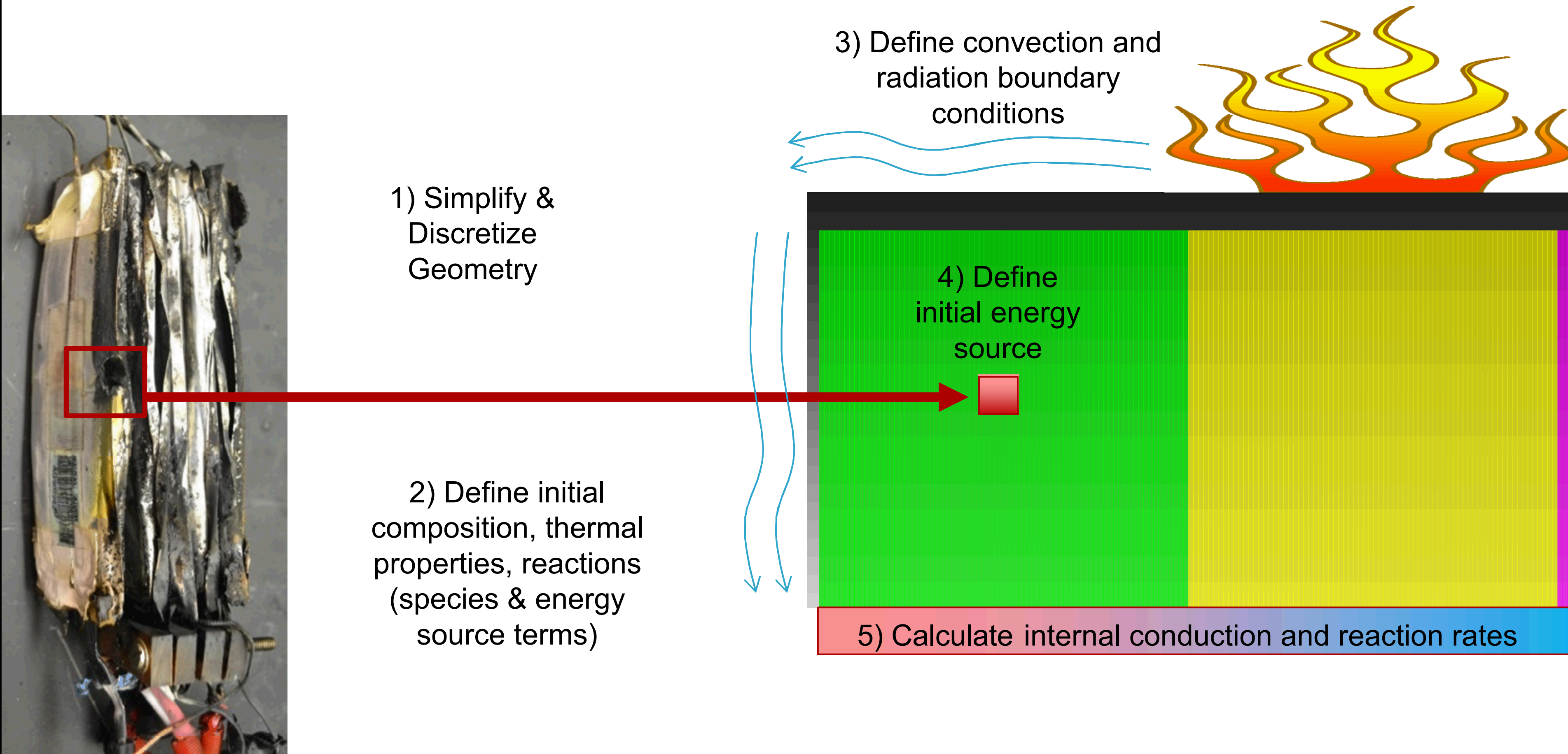
- Develop multi-physics models to predict failure mechanisms and identify mitigation.
- Build capabilities with small/medium scale measurements.
- Still requires some testing and validation.





[1] 'Power Grid Energy Storage Testing Part 1.' Blume, P.; Lindenmuth, K.; Murray, J. EE – Evaluation Engineering. Nov. 2012.

How Do We Model Thermal Runaway in Batteries?



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 $2\ ROCO_2Li \rightarrow Li_2CO_3 + \text{prod}$
  - Cathode-electrolyte $CoO_2 + C_3H_4O_3 \rightarrow \frac{1}{3}Co_3O_4 + \text{prod}$
  - Electrolyte-salt $C_3H_4O_3 + LiPF_6 \rightarrow \text{prod}$
  - Anode-electrolyte $C_6Li + C_3H_4O_3 \rightarrow Li_2CO_3 + \text{prod}$

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

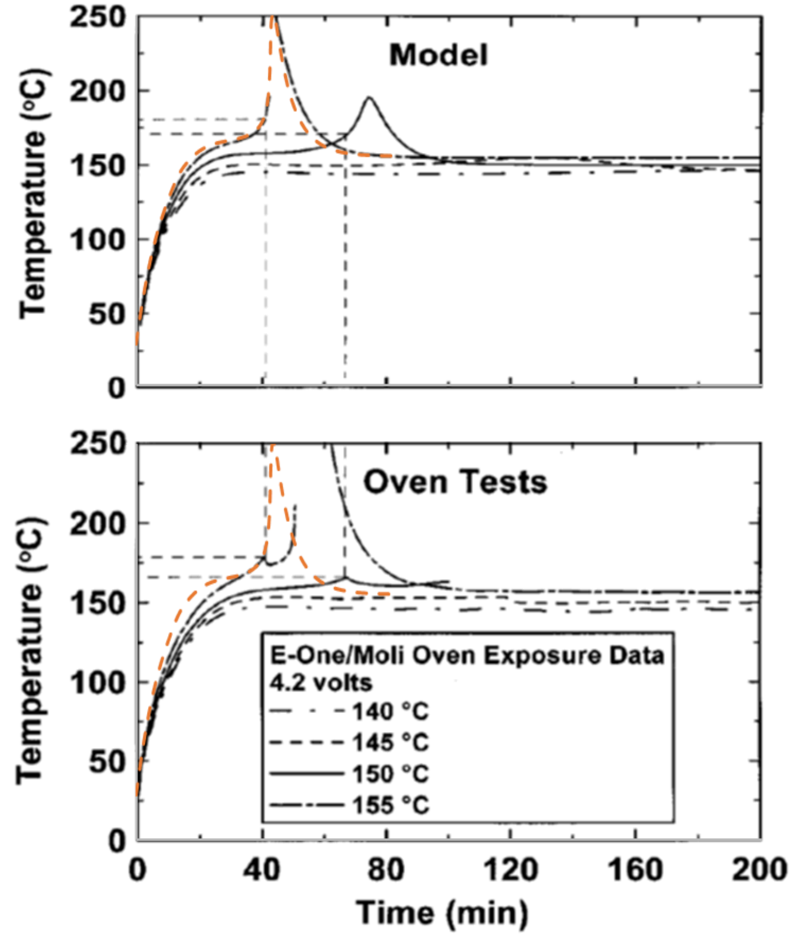
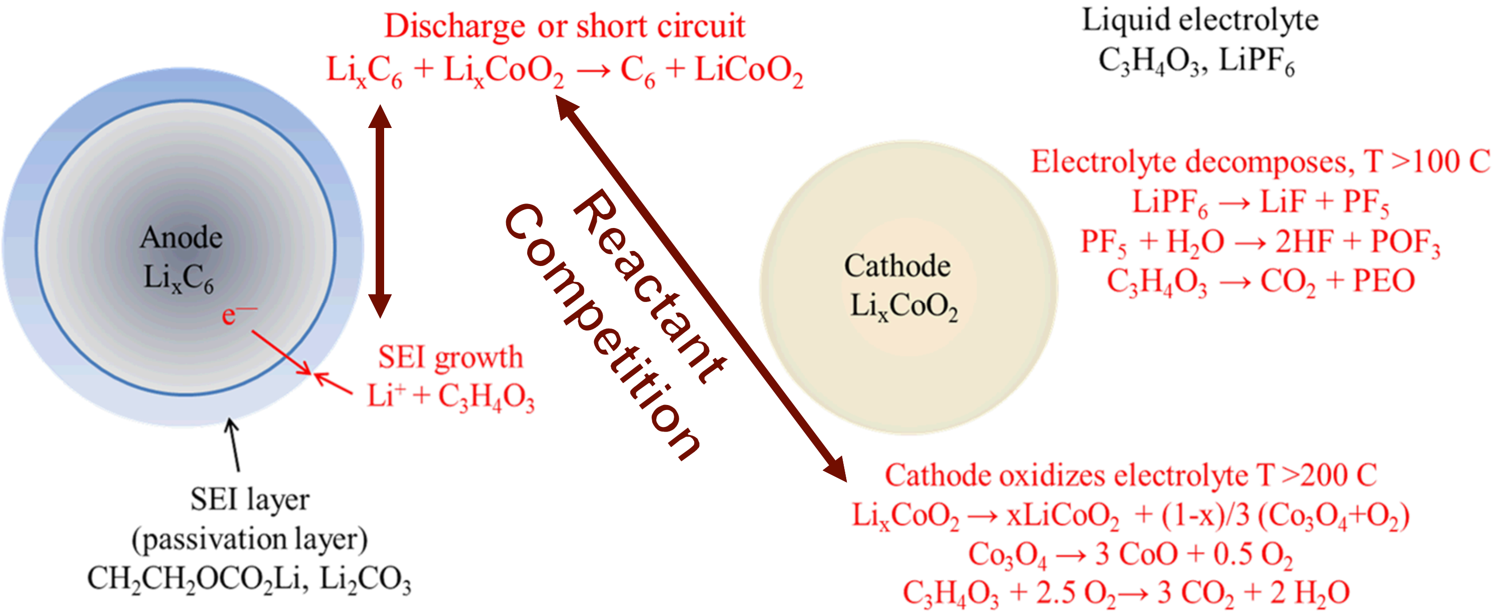
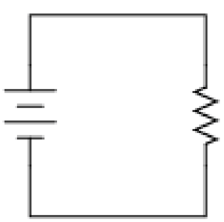


Figure 2. A comparison of oven exposure test results to model predictions: (top) model predictions and (bottom) oven test results for 18650 E-One/Moli Energy cells charged to 4.2 V.

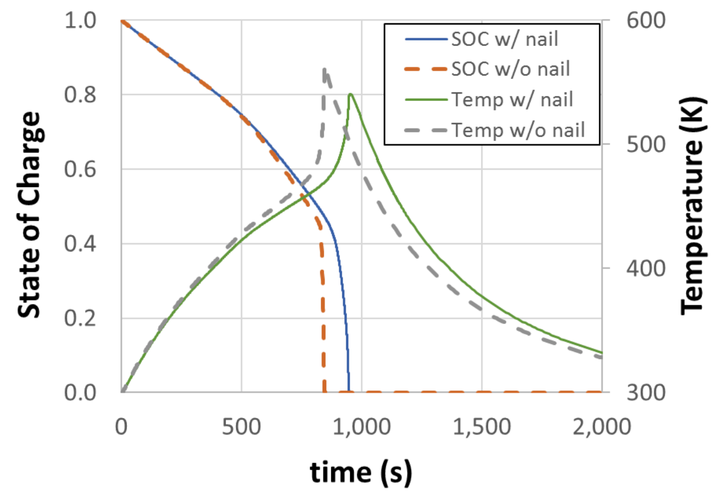
Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society **148**(7): A755-A761.

Thermal and electrochemical reactants are same





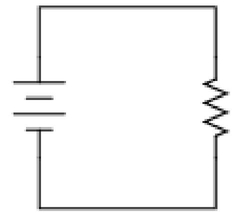
Simulated short circuit plus thermal runaway



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

Simulated oven test

high
temp
environ



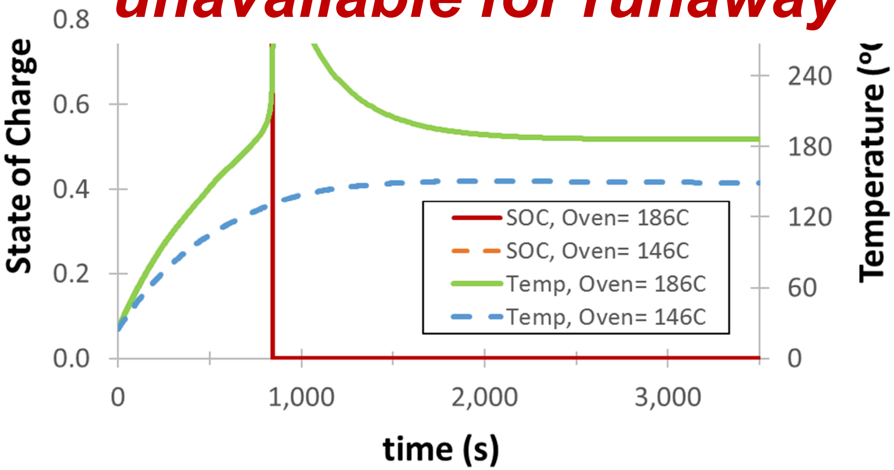
Simulated short circuit

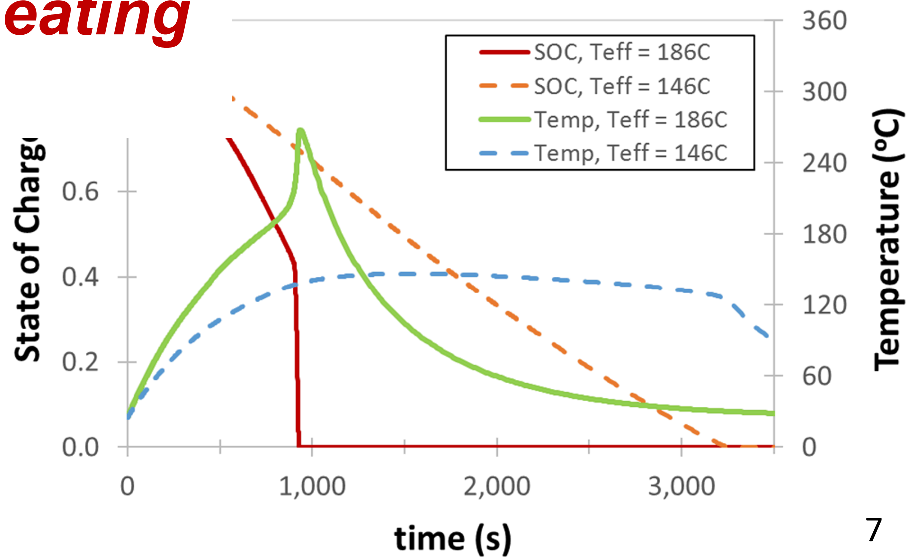
analogy with oven temperature

$$P = \frac{V^2}{R}$$

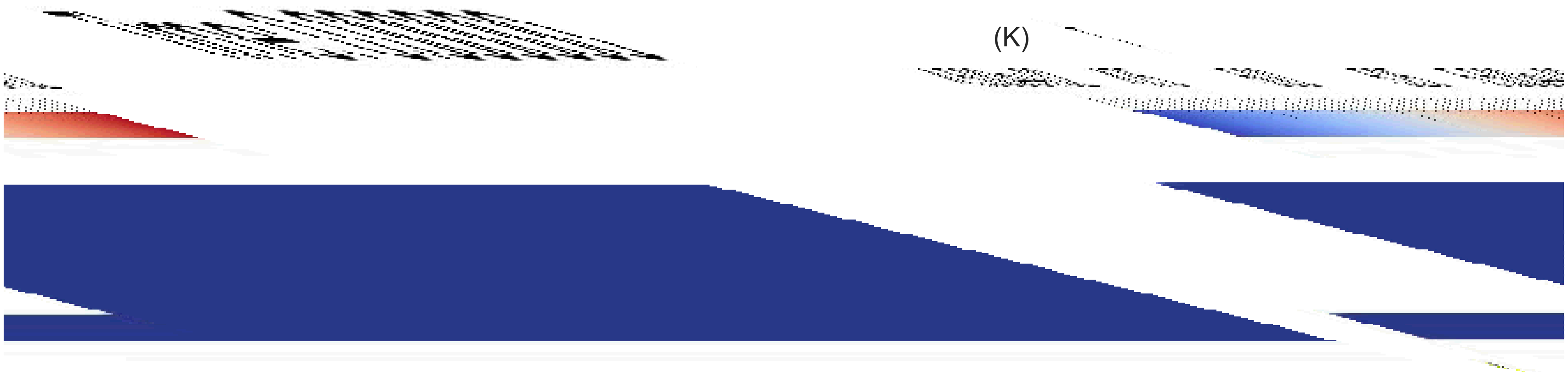
$$T_{eff} = T_\infty + P / h_{net} A$$

Energy required for initial heating unavailable for runaway

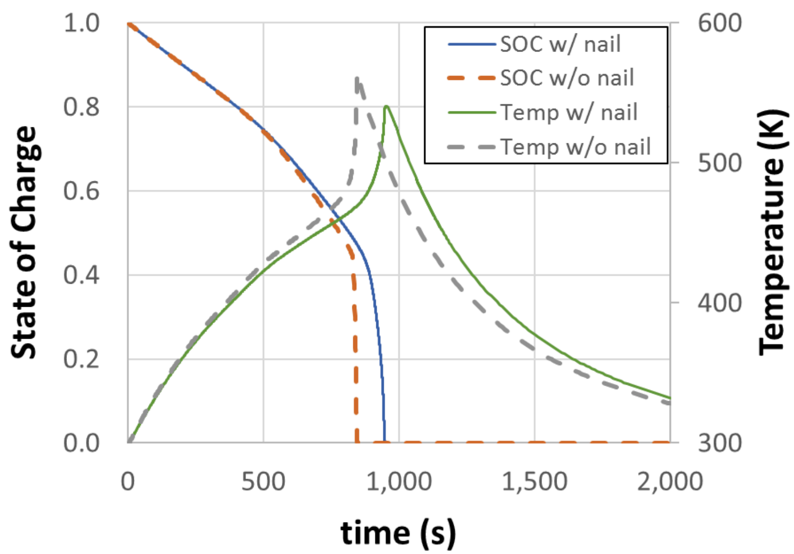


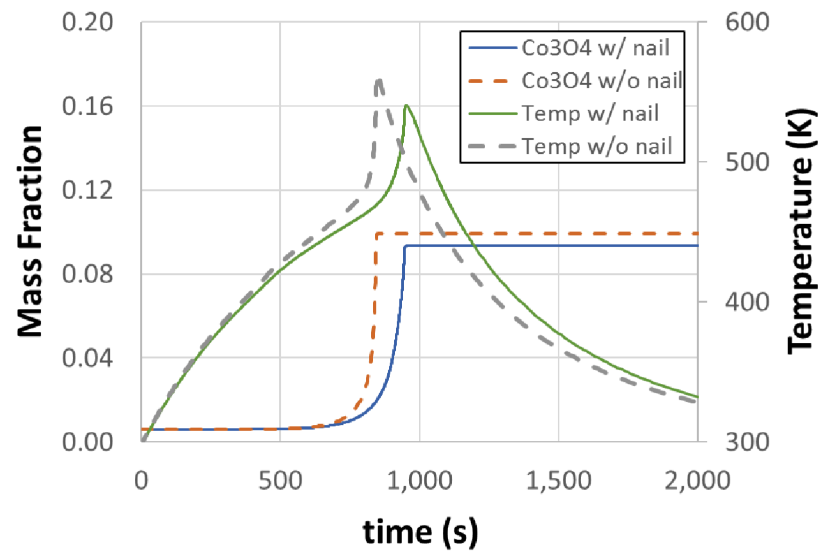


Short-circuit induced runaway in meshed 18650 with nail



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

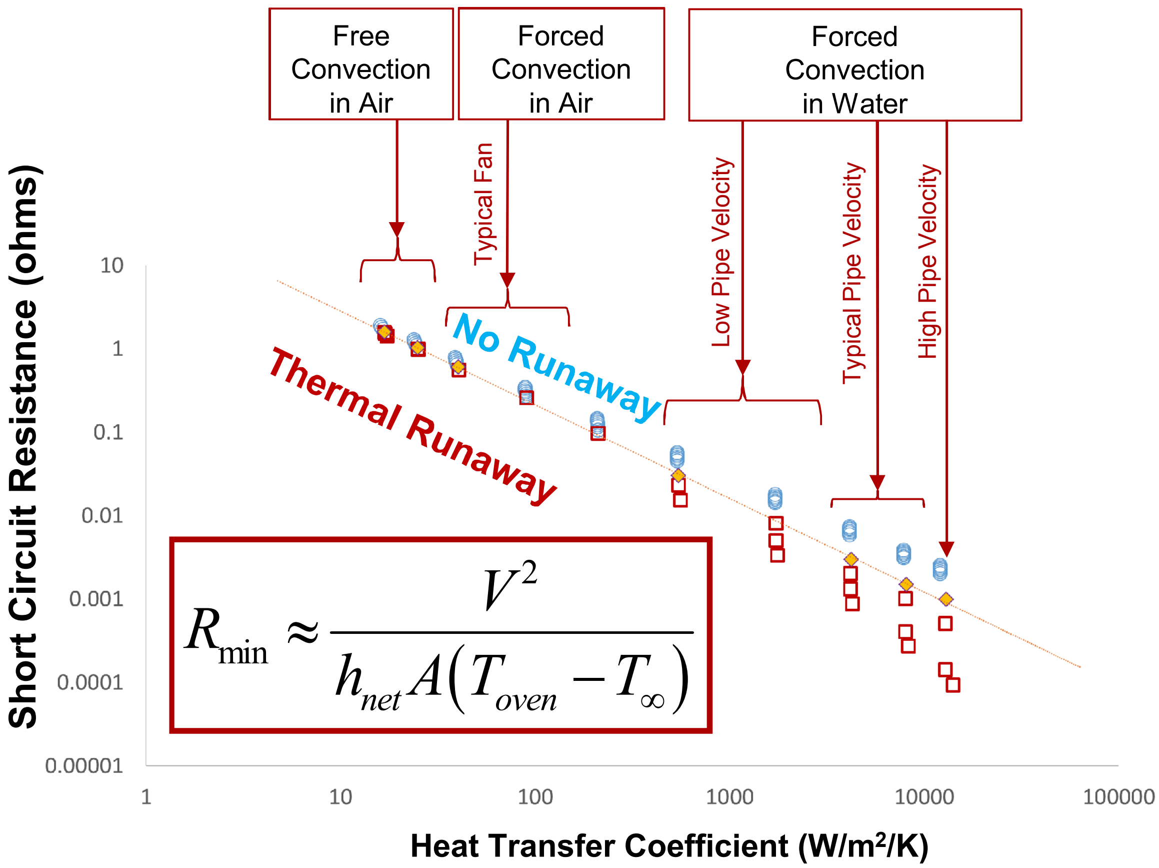




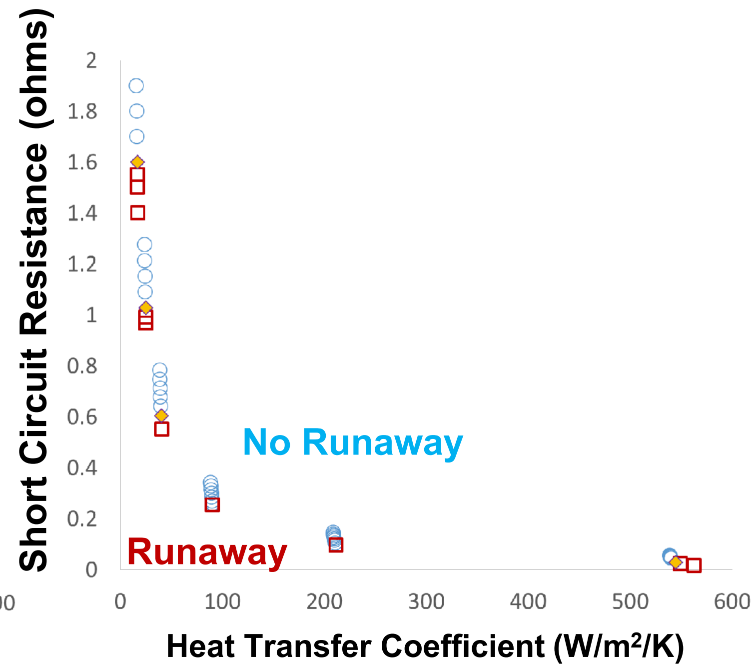
- Effects of inhomogeneity increase as scale increases beyond the lumped-capacitance regime.

How Much Cooling to Suppress Runaway with Internal Short Circuit?

$$T_{eff} = T_{\infty} + P / h_{net} A \qquad P = \frac{V^2}{R}$$



$$R_{min} \approx \frac{V^2}{h_{net} A \left(T_{oven} - T_{\infty} \right)}$$



- 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

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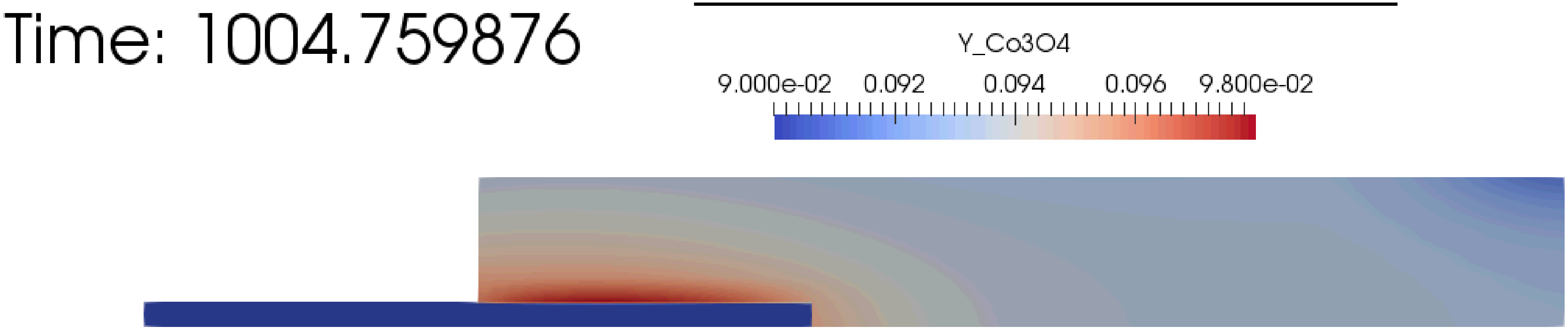
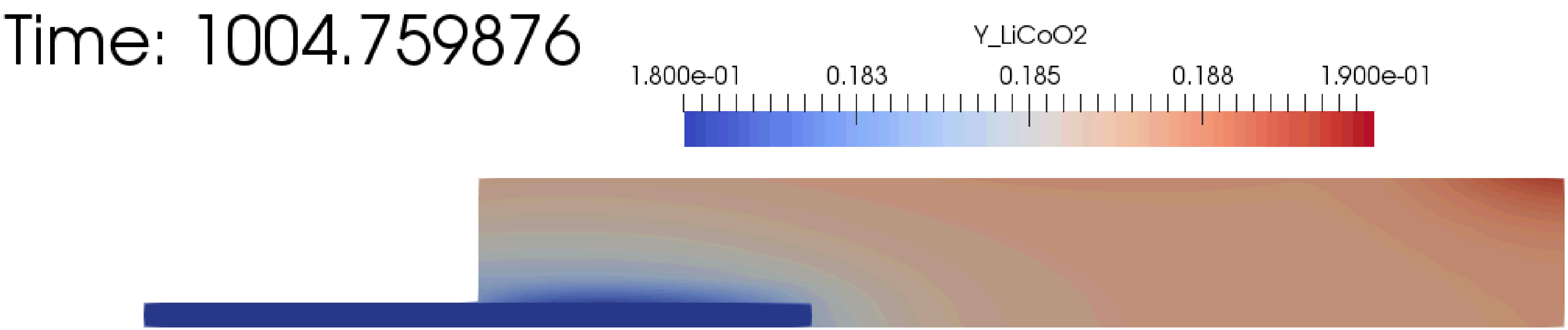
Relative importance of short-circuit versus thermal reactions

R = 1.4 ohm, h = 7 W/m^2/K, Meshed 18650 with 50% heat release in nail

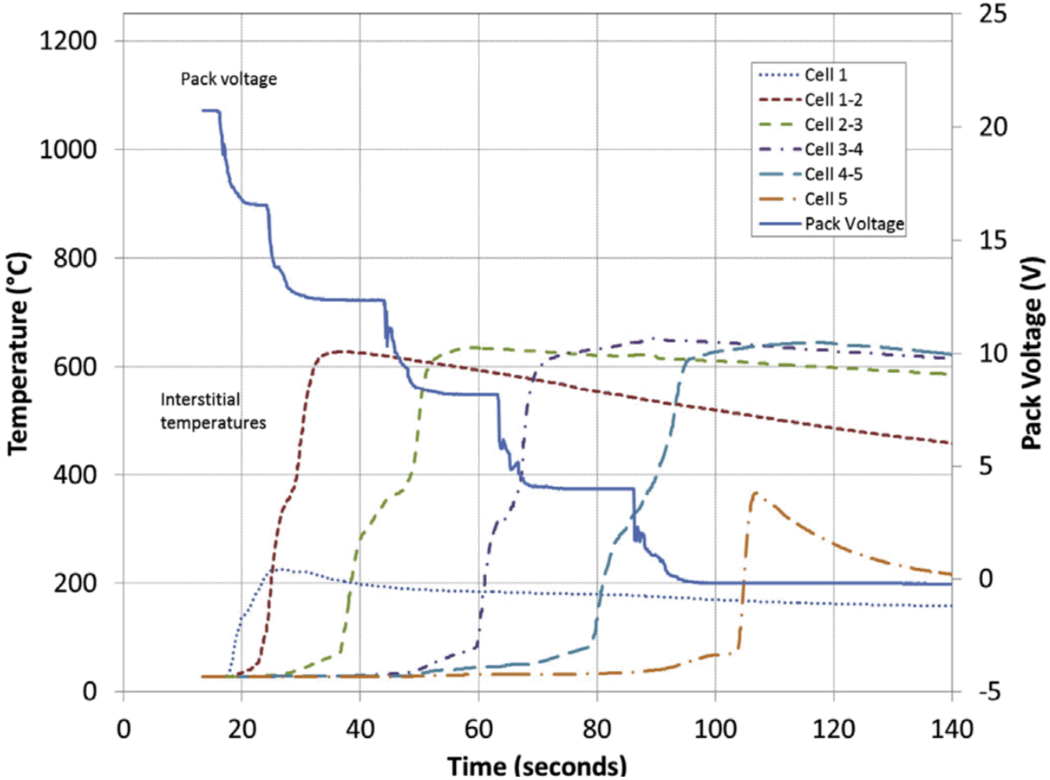
Thermal Reaction Cathode Product

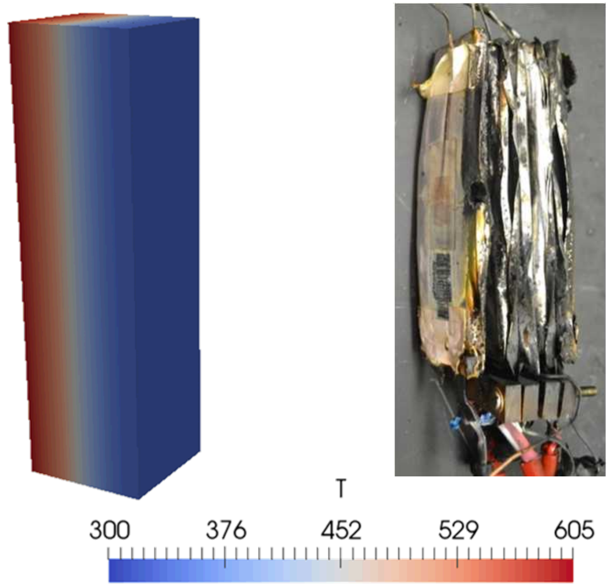


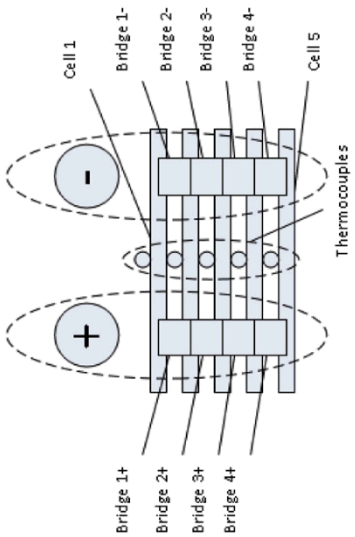
Short Circuit Cathode Product



Cascading Propagation Observed in Li-Ion Packs

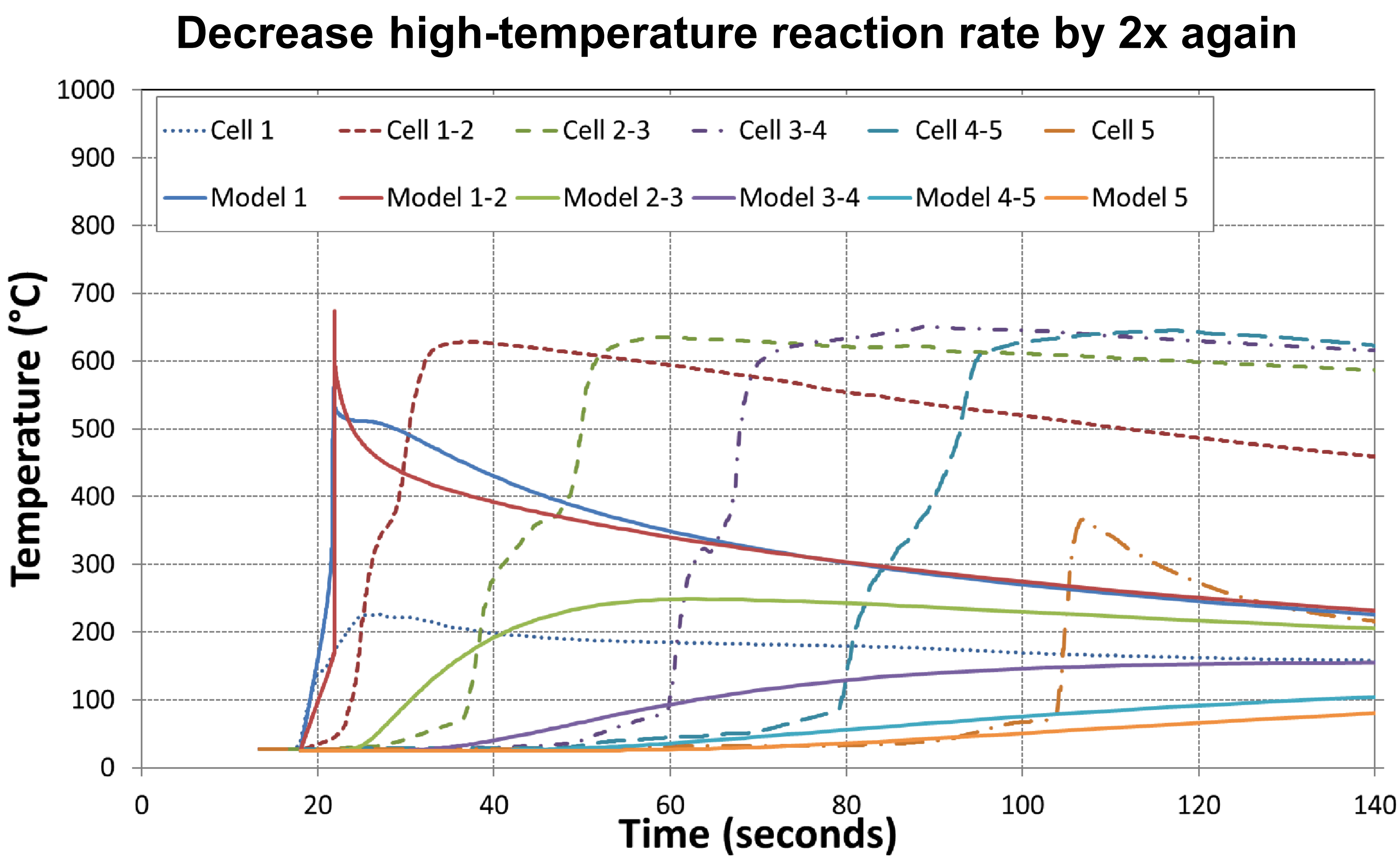






- Experimental propagation in 5 stacked pouch cells at Sandia
- Investigating effects of
  - State of charge
  - Intermediate layers
  - Cell geometry
- Good pack-scale model validation cases

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.

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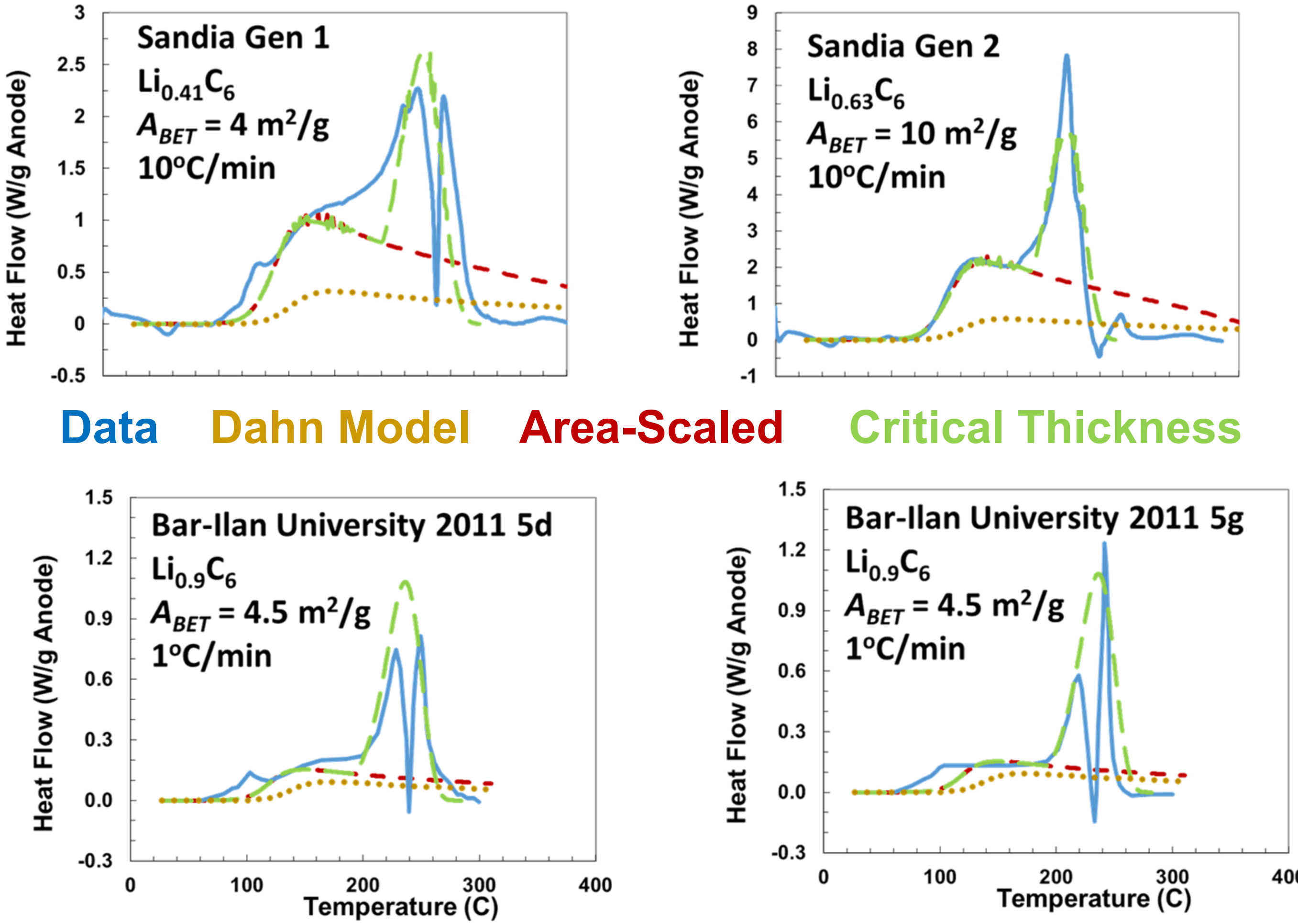


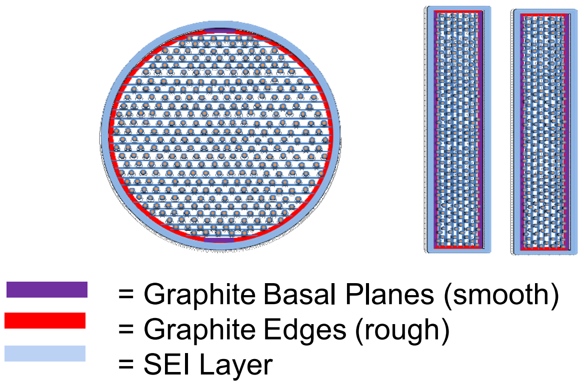
Data from Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

Key anode model improvements

Area-Scaled Model

- SEI Passivation layer inhibits lithium reduction of electrolyte, exp(-z).
- H_{rxn} thermodynamically consistent with $2LiC_6 + EC \rightarrow 2C_6 + C_2H_4 + Li_2CO_3$
- Reaction scales with effective surface area.

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

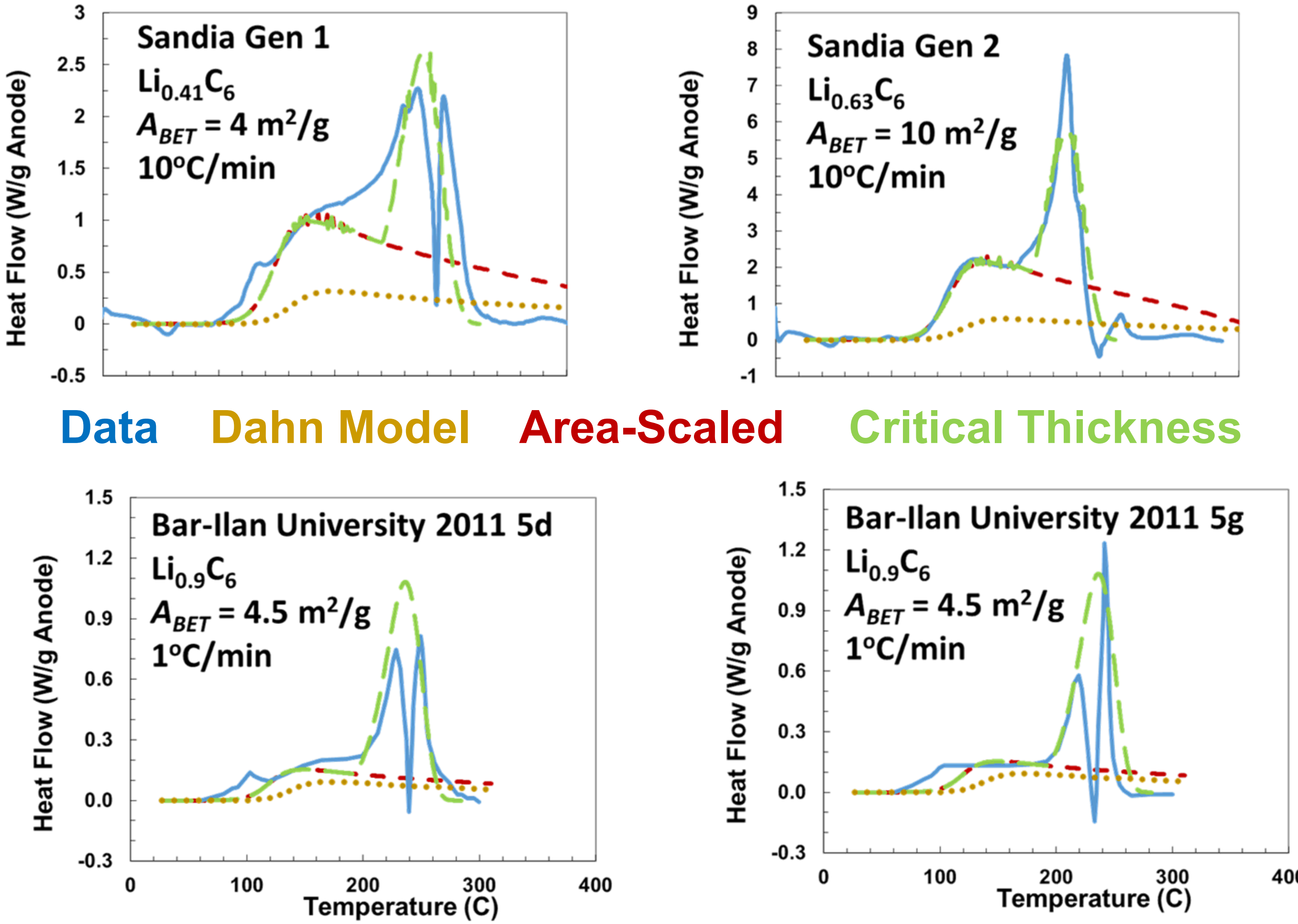


Critical Effective Layer Thickness

$$z = min(z, z_{crit}) \quad \text{where} \quad z_{crit} \propto x_{sei,crit} \left[\frac{A_{BET}}{A_{BET,ref}}\right]^{n_2}$$

- Limit to passivation layer growth with heating.
  - Endothermic defoliation (or other process) observed. Fracture, cracking?
  - Defects in SEI more likely on on edges.

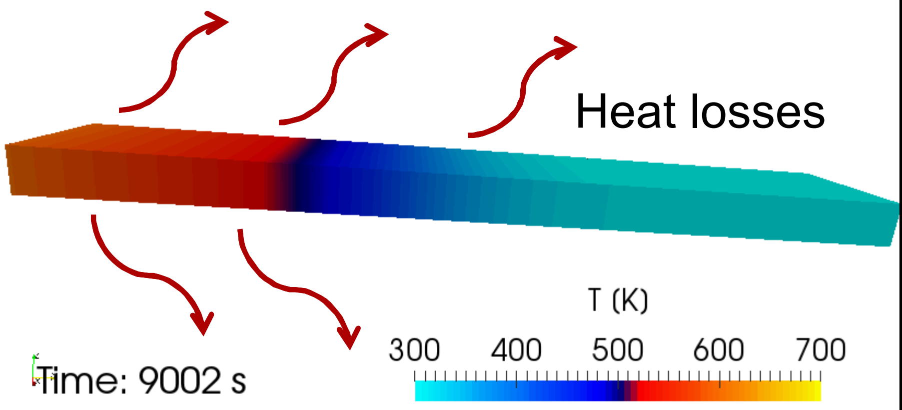
New model based on measureable quantities and thermodynamic material properties



Data from Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

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.***

Publications and presentations

- Publications
  - J. C. Hewson, R. Shurtz, "Modeling Thermal Runaway in Lithium-ion Packs as a Function of Scale and Heat Source," *Proceedings of the 10th US National Combustion Meeting*, 2017.
  - Hewson, J.C., *Understanding the limits of thermal runaway in lithium-ion battery systems*, in *Interflam*. 2016: London, UK.
  - Ferreira, S.R., et al., *Fundamental aspects of the safety of large-scale energy storage systems, Paper 5.3*, in *Power Sources Conference*. 2016: Orlando, FL.
- Presentations:
  - Shurtz, R. and J. Hewson, "Modeling Thermochemical Sources for a Broader Range of Materials and Conditions," 231st Electrochemical Society Meeting, New Orleans, (May 28-June 2, 2017)
  - Shurtz, R. and J. Hewson, "Modeling Thermal Runaway in Li-ion Packs as a Function of Scale and Heat Source," 231st Electrochemical Society Meeting, New Orleans, (May 28-June 2, 2017)
  - J. C. Hewson, R. Shurtz, "Modeling for understanding and preventing cascading thermal runaway in battery packs," FAA Triennial Fire and Cabin Safety Research Conference, Atlantic City, NJ, October 2016.
  - J. C. Hewson, R. Shurtz, "Understanding and preventing cascading thermal runaway in battery packs," 2017 Energy Storage Systems Safety & Reliability Workshop in Santa Fe, NM, February 2017.
  - J. C. Hewson, R. Shurtz, "Modeling Thermal Runaway in Lithium-ion Packs as a Function of Scale and Heat Source," *Proceedings of the 10th US National Combustion Meeting*, April 2017.

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).

Acknowledgements

- Supported by Imre Gyuk and the OE Electrical Energy Storage Program.

- Collaborative discussions with Heather Barkholtz, Lorraine Castro, Summer Ferreira, Josh Lamb, Chris Orendorff and Dave Ingersoll have been instrumental in understanding the range of possible topics that might be addressed.

THANK YOU

QUESTIONS:

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How do we evaluate thermal runaway in realistic scenarios?

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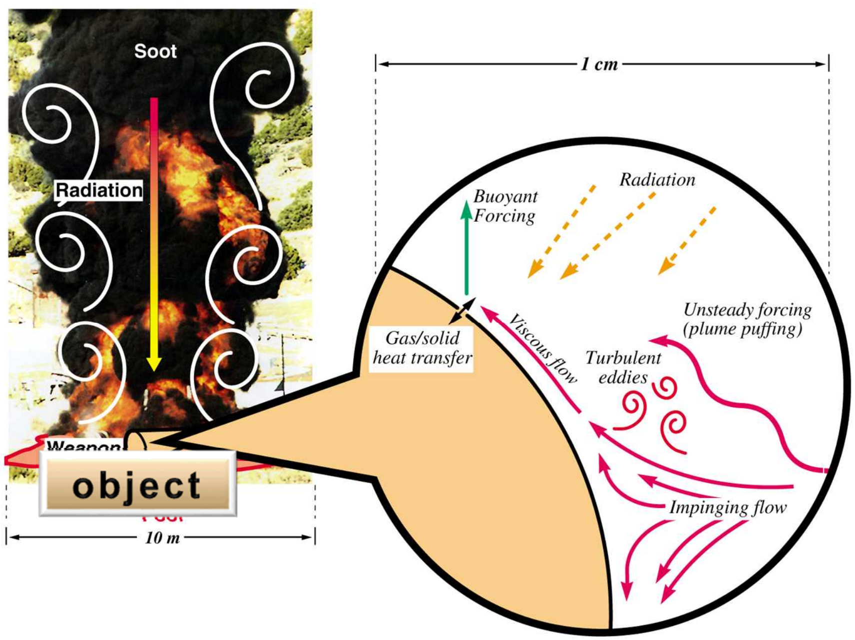
- Leverage the large DOE-NNSA Investments in Sierra-Mechanics Integrated Code simulation tools developed at Sandia National Laboratories under the Advanced Scientific Computing (ASC) program for Science-based Stockpile Stewardship by applying these tools to battery safety analysis

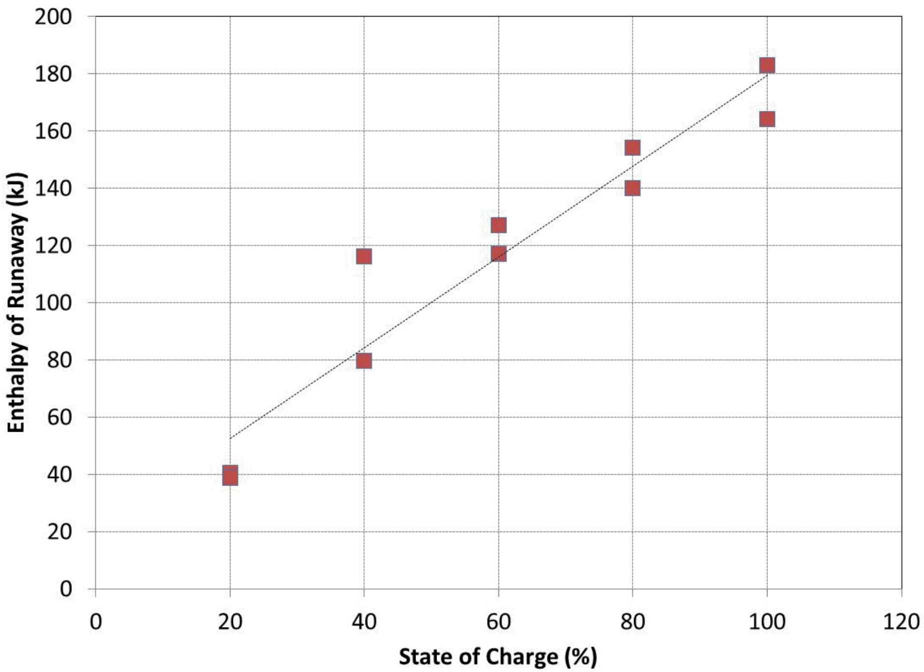


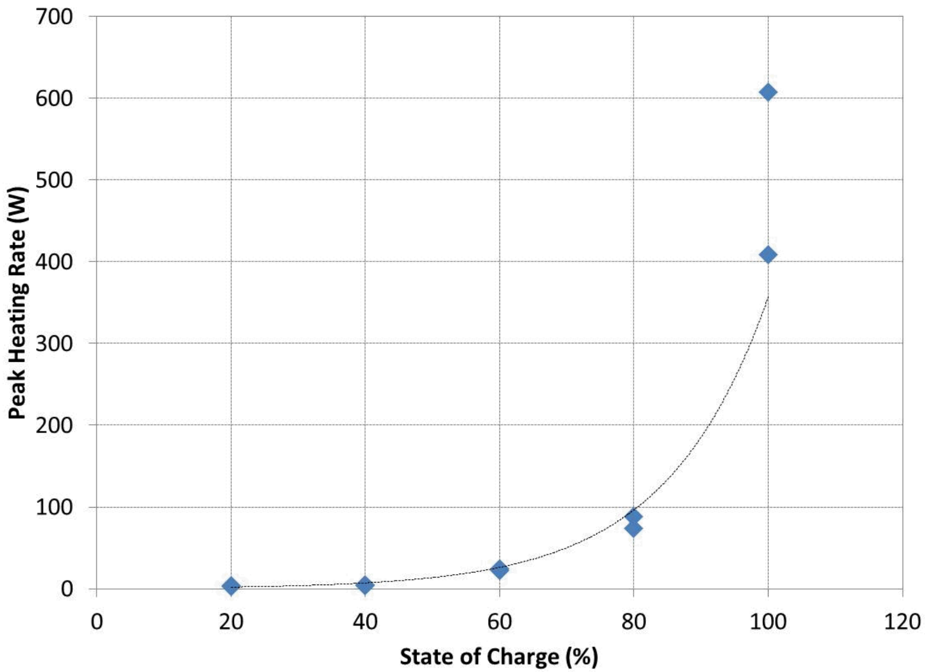
Heat transfer mechanisms in a fire

Physics:

- Turbulent fluid mechanics (buoyant plumes)
- Participating Media Radiation (PMR)
- Reacting flow (hydrocarbon, particles, solids)
- Conjugate Heat Transfer (CHT)
- The simulation tool *predicts* the thermal environment and object response

Impact of SOC on Runaway – Josh Lamb Expts.

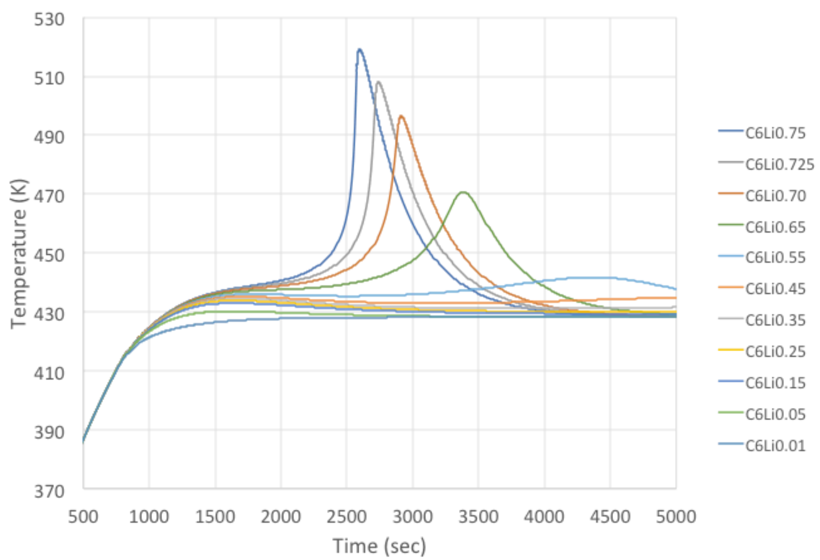


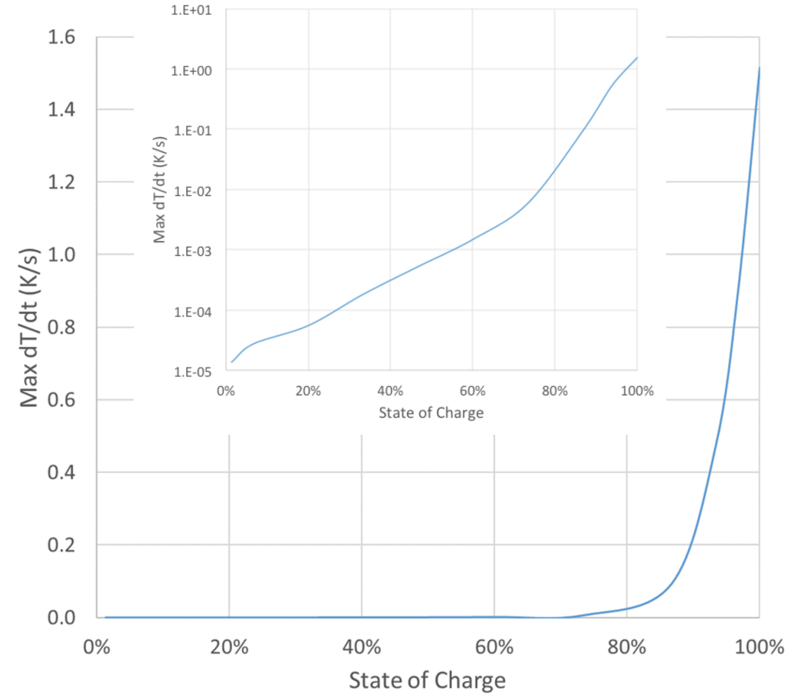


- **Results show a nearly linear relationship between total heat release (kJ) and cell SOC – similar to data for cell size this suggests that failure enthalpy is based largely on the stored energy available**
- **Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship 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.
  - CoO_2 vs $LiCoO_2$; LiC_6 vs C_6
- Greater heat release associated with greater fractions of active material (greater SOC).

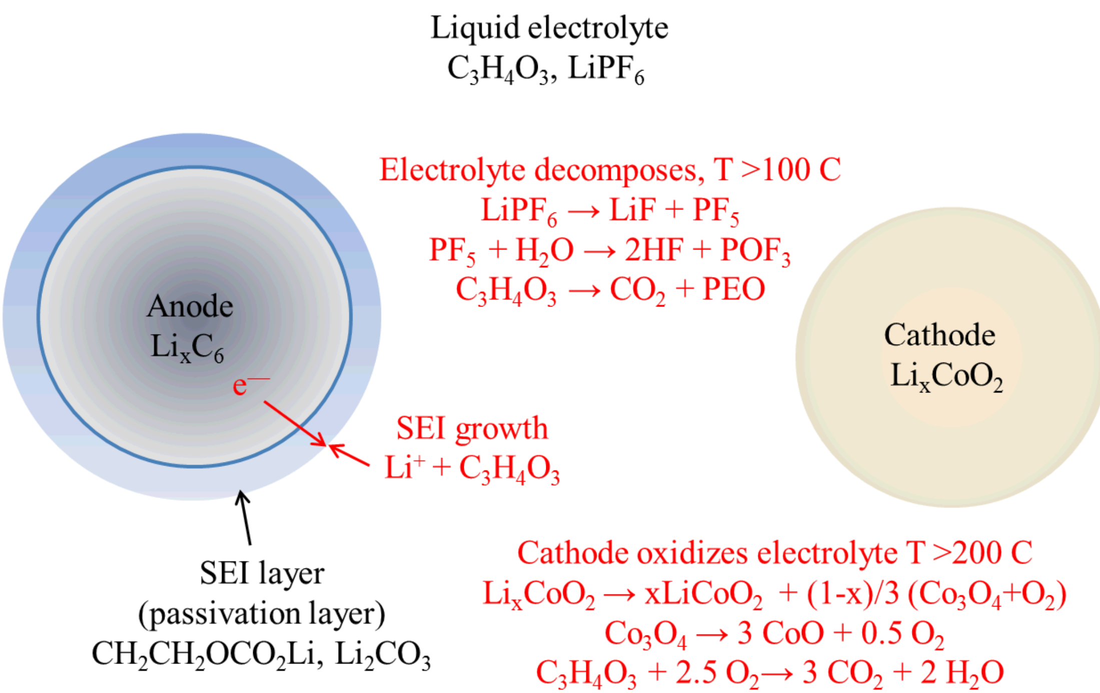




- Higher temperatures give exponentially greater heat release due to Arrhenius rate constants.

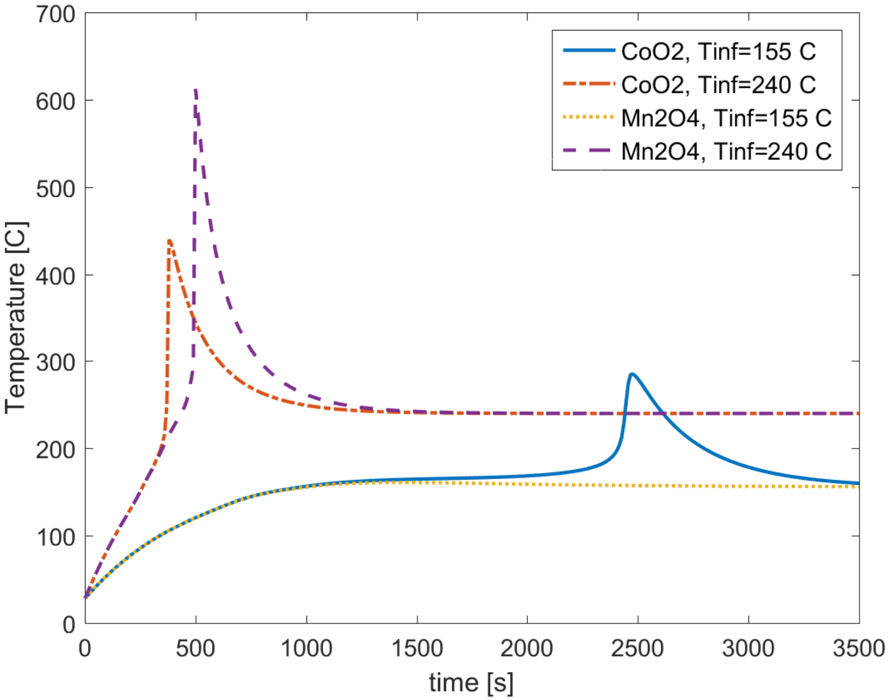
The drive to greater energy density and efficiency

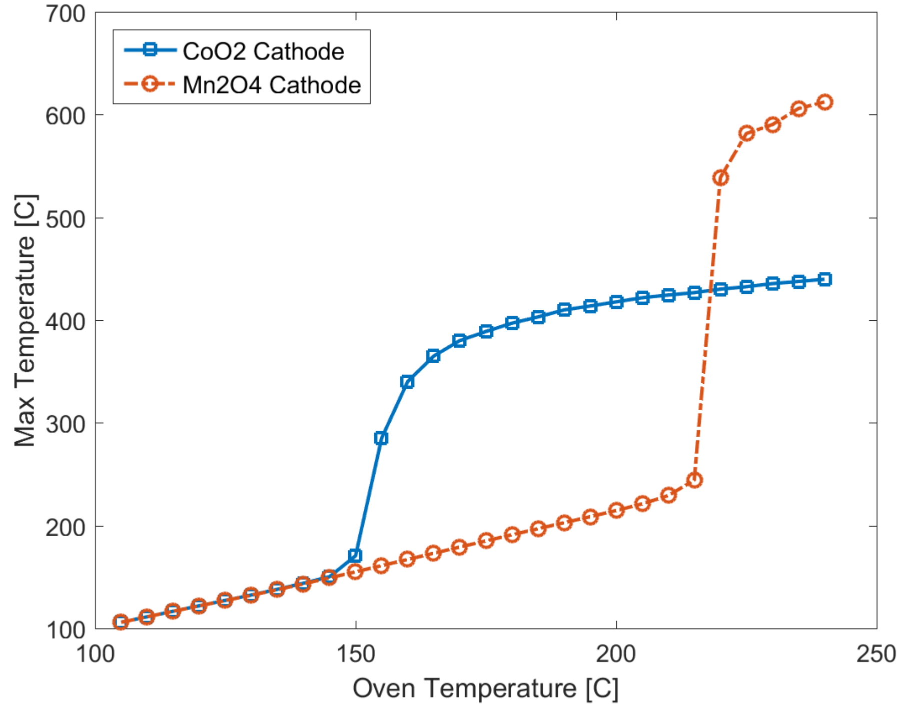
- Increased energy densities and other material advances lead to more reactive systems – greater efficiency / less losses.
  - Charged batteries include a ‘fuel’ and ‘oxidizer’ all internally.
  - Li-Ion electrolyte, packaging, and other materials are often flammable.
  - External heating or internal short circuits can lead to thermal runaway.



Cathode Chemistry Drives Cell Failure

Simulated oven tests for 18650 cells
2 cathode materials, 2 temperatures





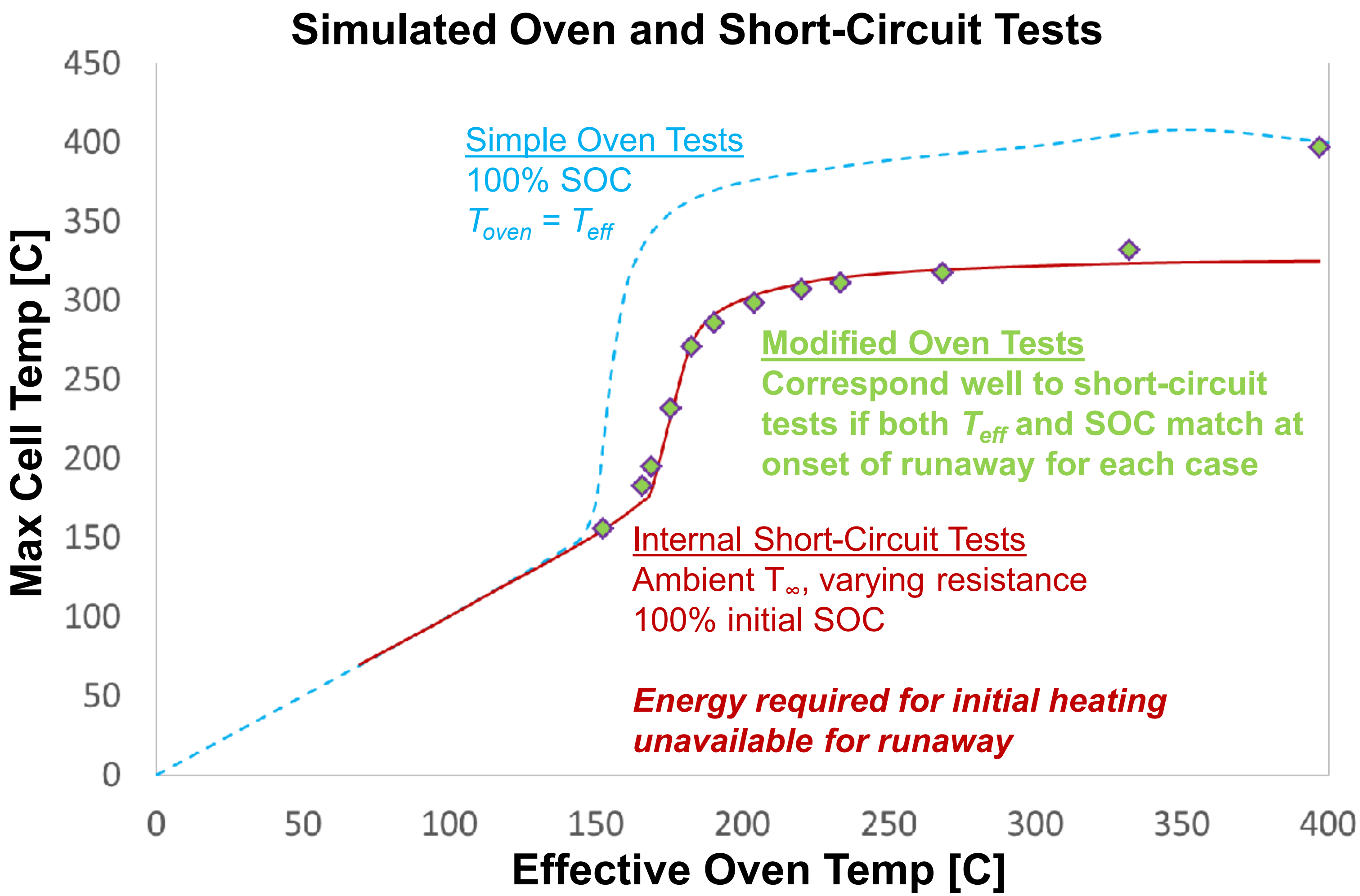
- Differences in cathode chemistry must be understood and quantified to predict thermal runaway of single cells

$LiCoO_2$ model from Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society 148(7): A755-A761.
$LiMn_2O_4$ model from Spotnitz, R. and J. Franklin (2003). Journal of Power Sources **113**(1): 81-100.

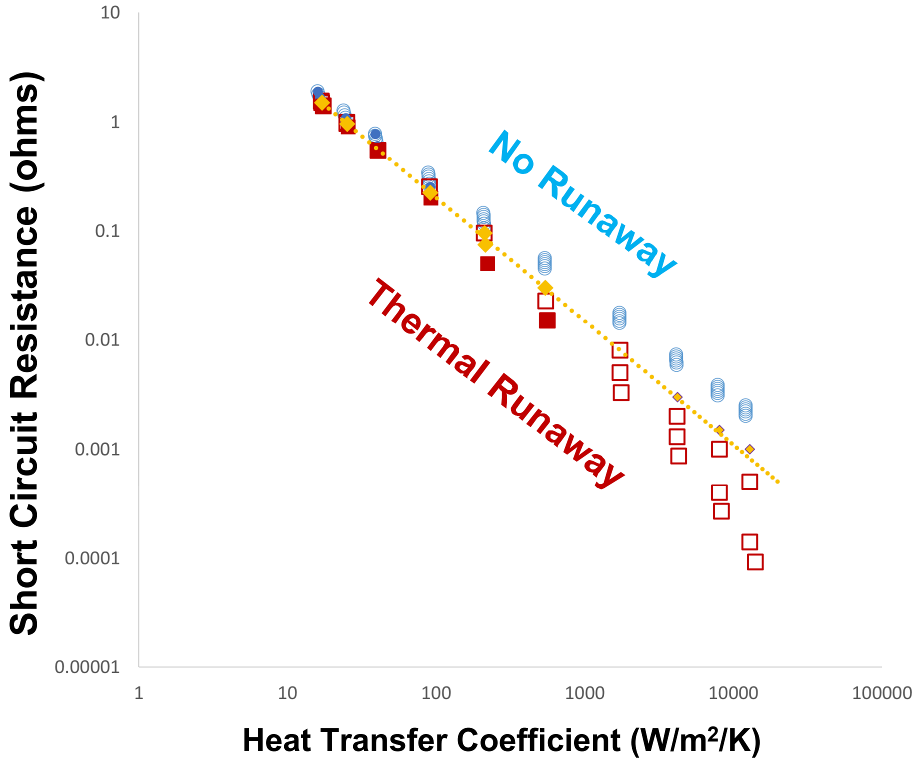
How are Different Heat Sources Analogous?

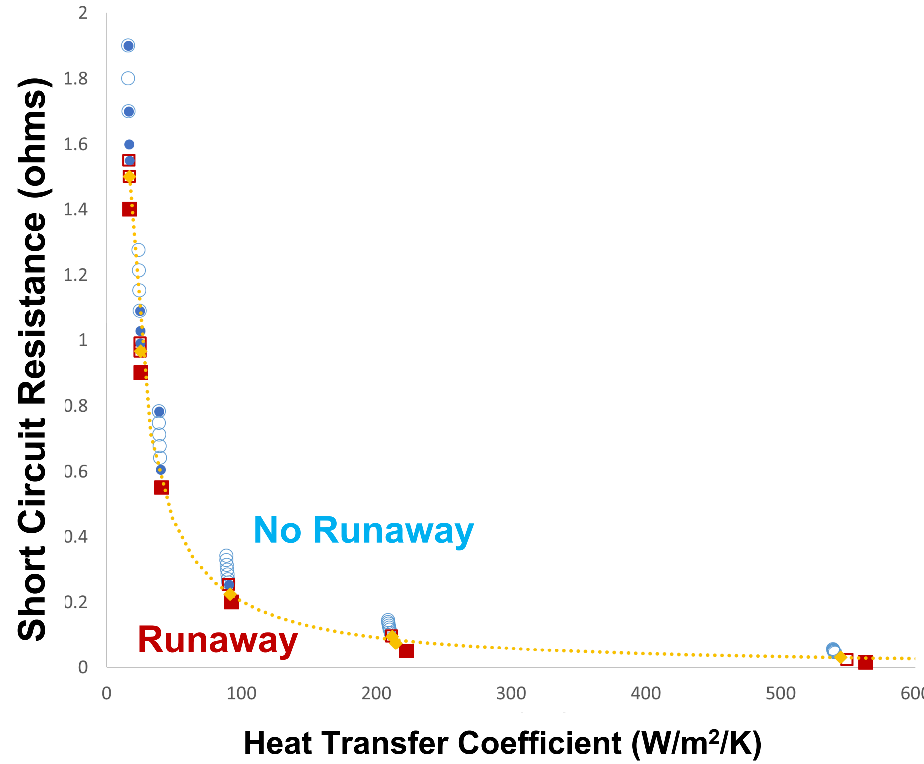
Energy balance on a cell yields:

$$T_{eff} = T_\infty + P / h_{net} A \qquad P = \frac{V^2}{R} \qquad h_{net} = h + h_{rad} = h + \varepsilon\sigma\left(T_w^2 + T_\infty^2\right)\left(T_w + T_\infty\right)$$



R vs h Relationship Holds for Localized Short





Lumped Cell ○ No Runaway □ Runaway, dT/dt ◇ Transition Runaway

Meshed Cell ● Meshed no Runaway ■ Meshed Runaway ◆ Meshed Transition

- Lumped capacitance previously reported as good approximation for this battery
- Transition region becomes more gradual due to inhomogeneous competition for reactants