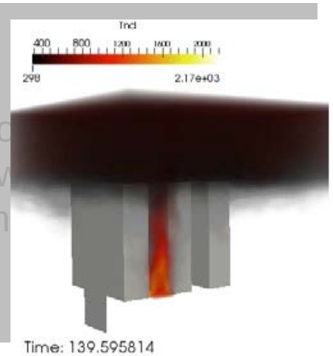

Modeling for understanding and preventing cascading thermal runaway in battery packs

John Hewson, Randy Shurtz
Sandia National Laboratories

2017 Energy Storage Systems Safety & Reliability Workshop
Feb.22-24, 2017, Santa Fe, NM

SAND2017-1843 C

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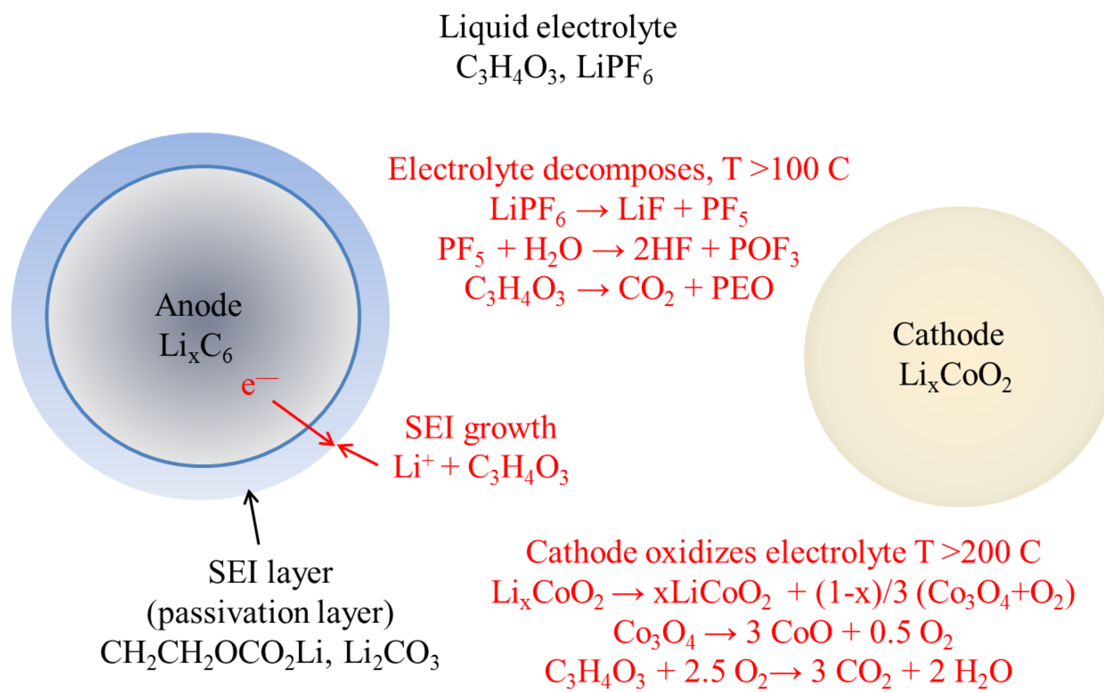
The drive to greater energy density and efficiency

- 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.

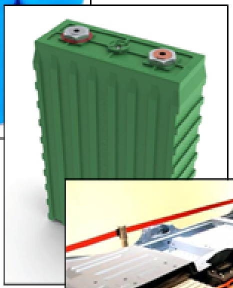


Validated reliability and safety is one of four critical challenges identified in 2013 Grid Energy Storage Strategic Plan

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

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+

- A single cell failure that propagates through the pack could lead to an impact even with very low individual failure rates

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

- How do we decrease the risk?

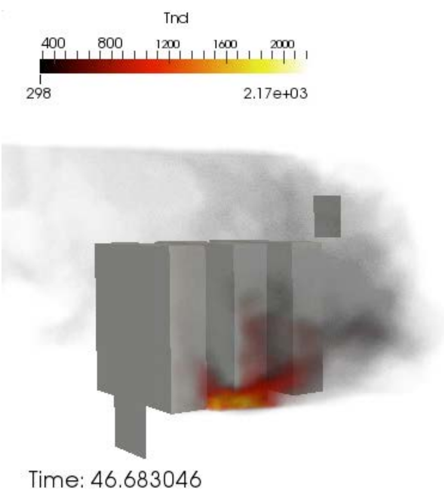
Approaches to designing in safety

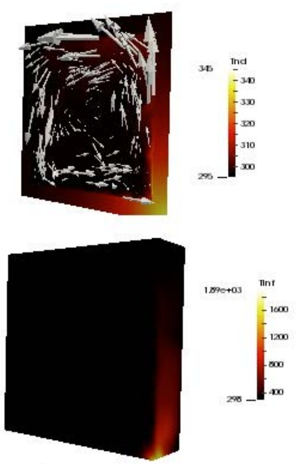
The current approach is to test our way into safety[1]

- 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 testing / validation.



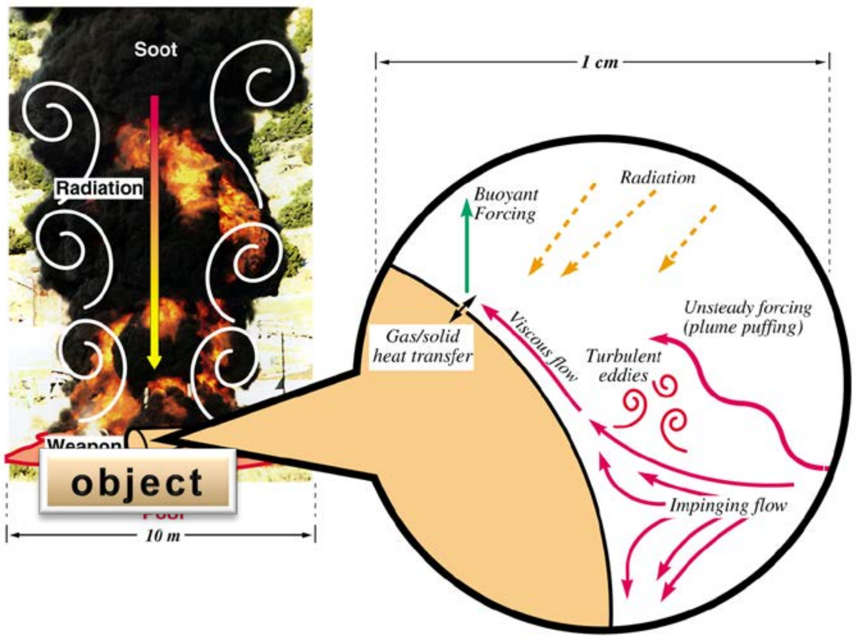


Insight may come from modeling process.

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

How do we evaluate thermal runaway in realistic scenarios?

- 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

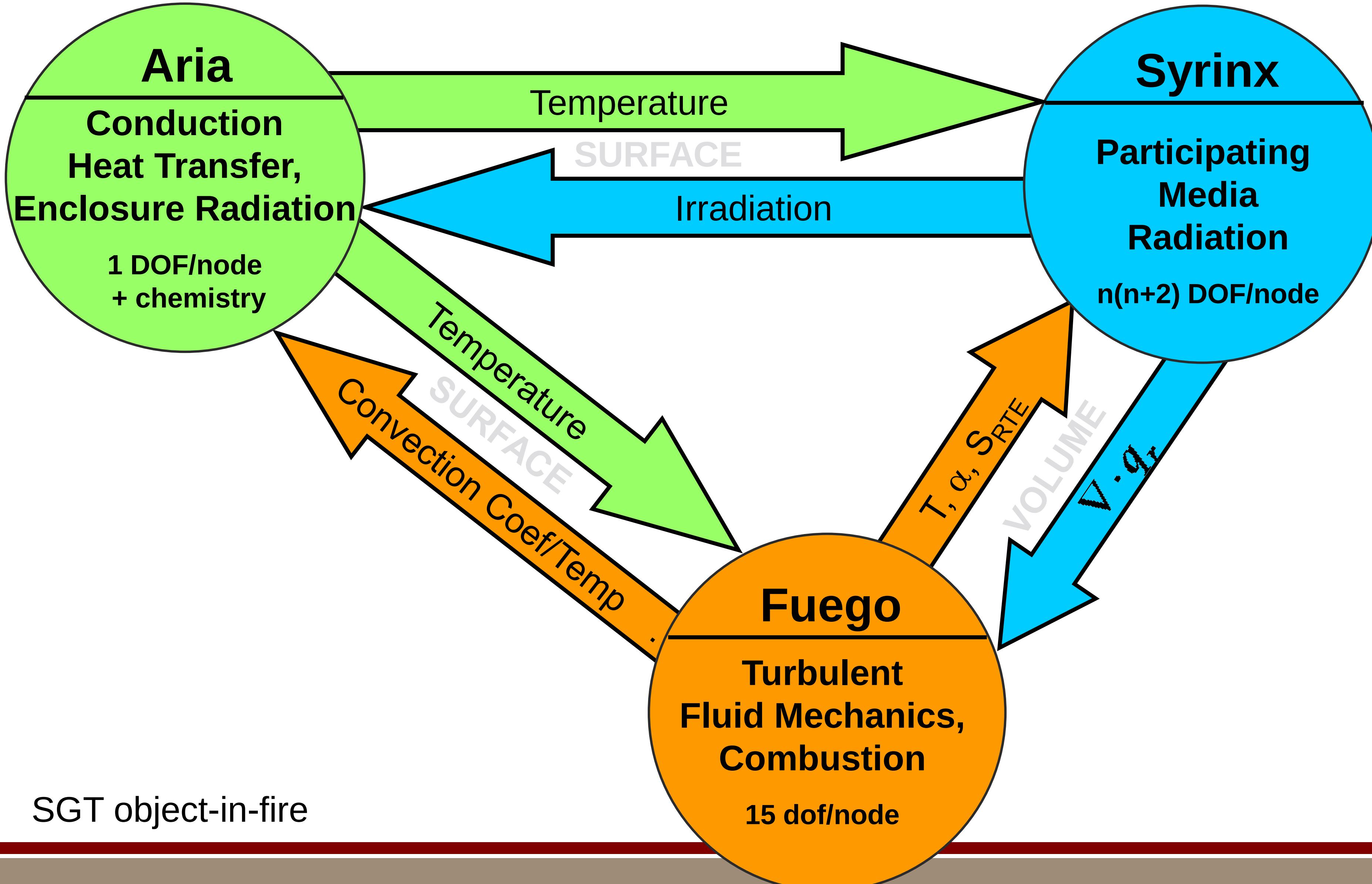


Heat transfer mechanisms in a fire

Physics:

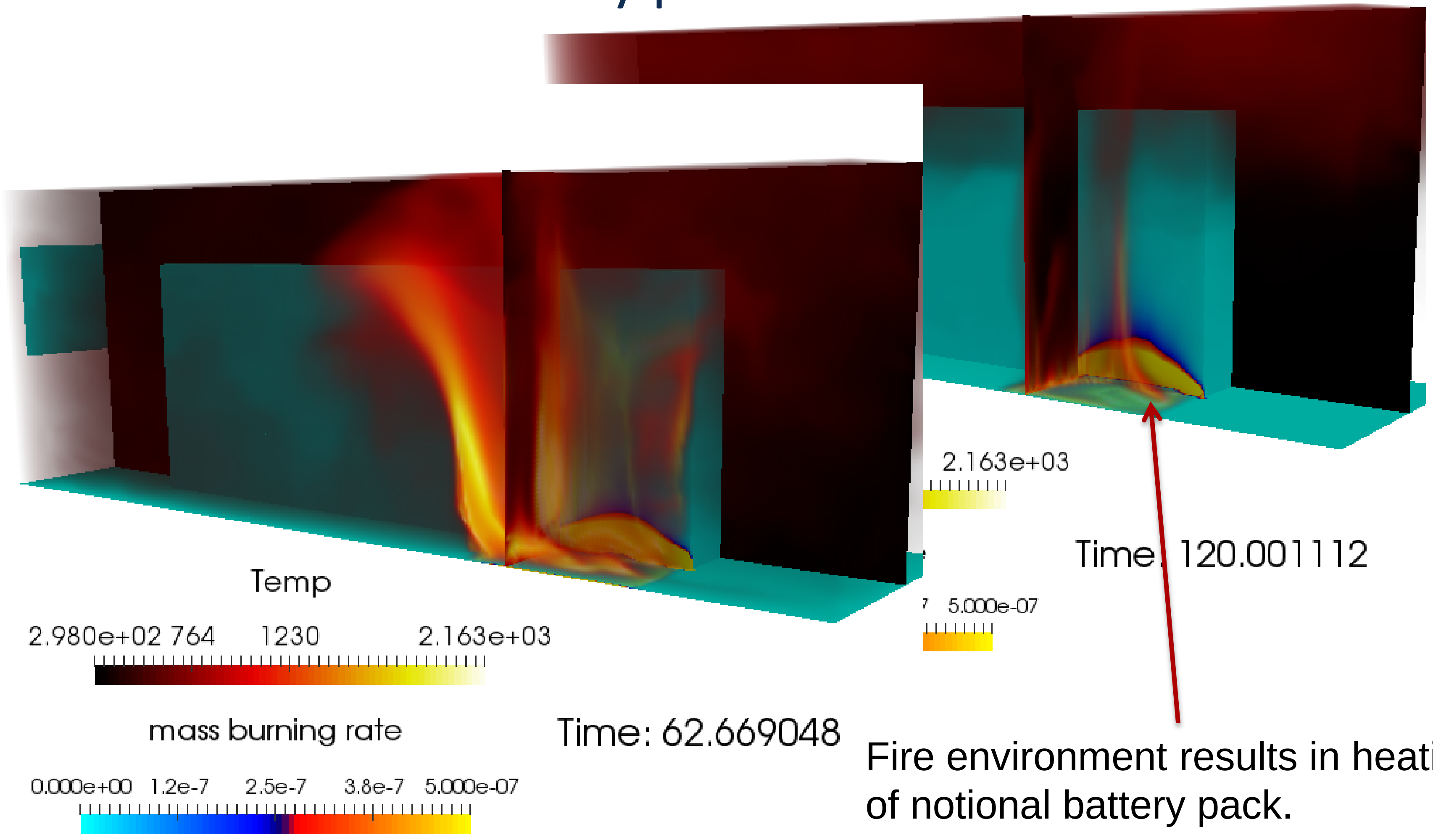
- Turbulent fluid mechanics (buoyant plumes)
- Participating Media Radiation (PMR)
- Reacting flow (hydrocarbon, particles, solids)
- Conjugate Heat Transfer (CHT)
- The simulation tool *predicts* the thermal environment and object response

Multi-physics couplings
Fluids:PMR:Conduction



SGT object-in-fire

From predicting fire environments to predicting heat release in a battery pack

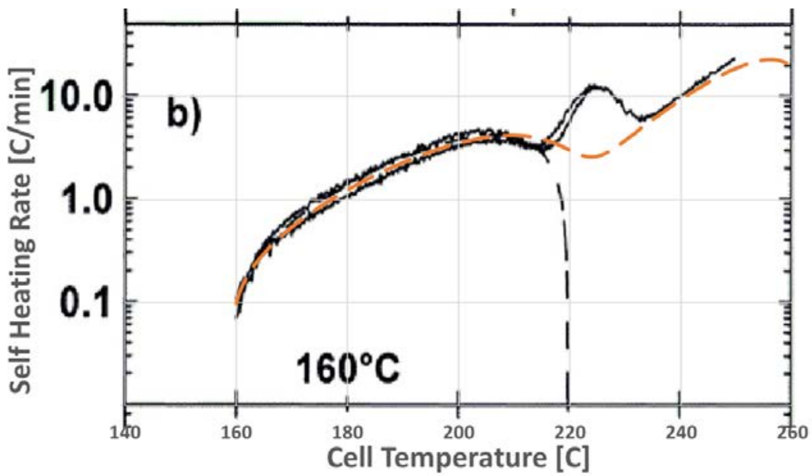


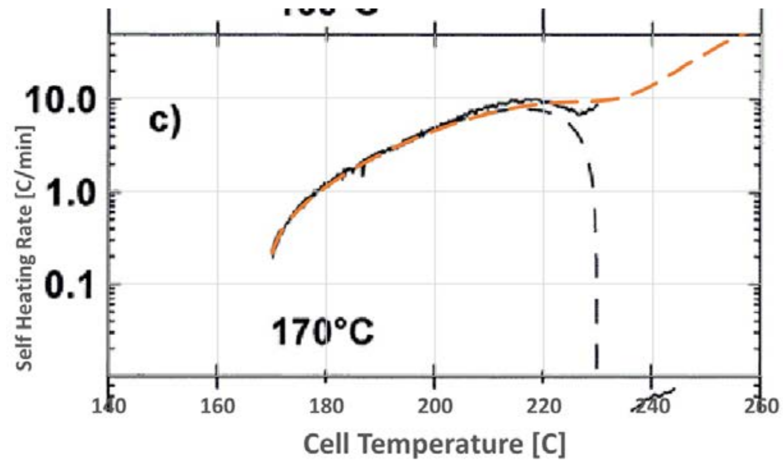
Fire environment results in heating of notional battery pack.

Now focus on what happens to that heated battery pack.

Development of heat release models from calorimetry measurements

- Calorimetry measurements inform and calibrate models for heat release rates.
- Here cathode heat release models are evaluated based on literature measurements.
- These heat release models are in our codes and used in subsequent predictions.





- Measurement from: MacNeil, D. D. and J. R. Dahn (2001). Journal of Physical Chemistry A **105**(18): 4430-4439.
- Models based on Spotnitz, R. and J. Franklin (2003). Journal of Power Sources **113**(1): 81-100.

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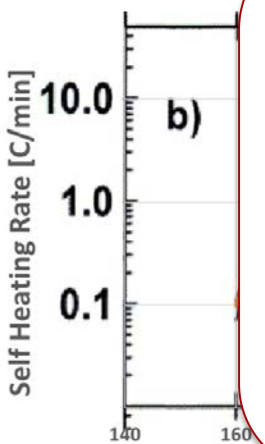

- SEI decomposition $$2\,ROCO_2Li \rightarrow Li_2CO_3 + prod$$
- Cathode-electrolyte $$CoO_2 + C_3H_4O_3 \rightarrow \frac{1}{3}Co_3O_4 + prod$$
- Electrolyte-salt $$C_3H_4O_3 + LiPF_6 \rightarrow prod$$
- Anode-electrolyte $$C_6Li + C_3H_4O_3 \rightarrow Li_2CO_3 + prod$$

- Measurement from: MacNeil, D. D. and J. R. Dahn (2001). Journal of Physical Chemistry A **105**(18): 4430-4439.
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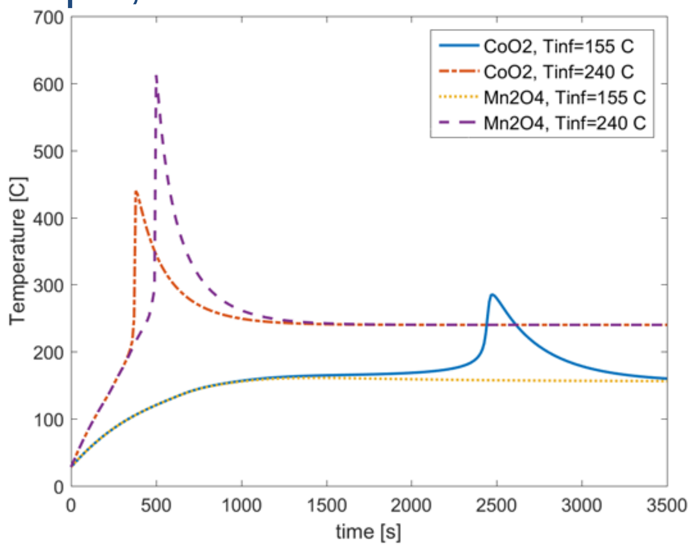
Modeling thermal runaway in lithium ion cells

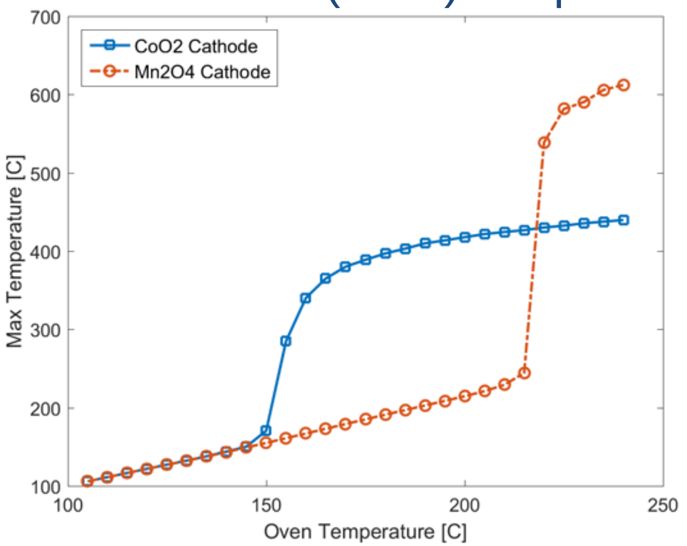
- Evolution simulated using calorimetry-derived heating rates and lumped thermal mass.
- Consider SEI decomposition, cathode-electrolyte reaction, electrolyte

- If you have good low-temperature calorimetry for your ***specific chemistry*** and can adequately model the heat transfer, predictions of initial runaway are achievable.

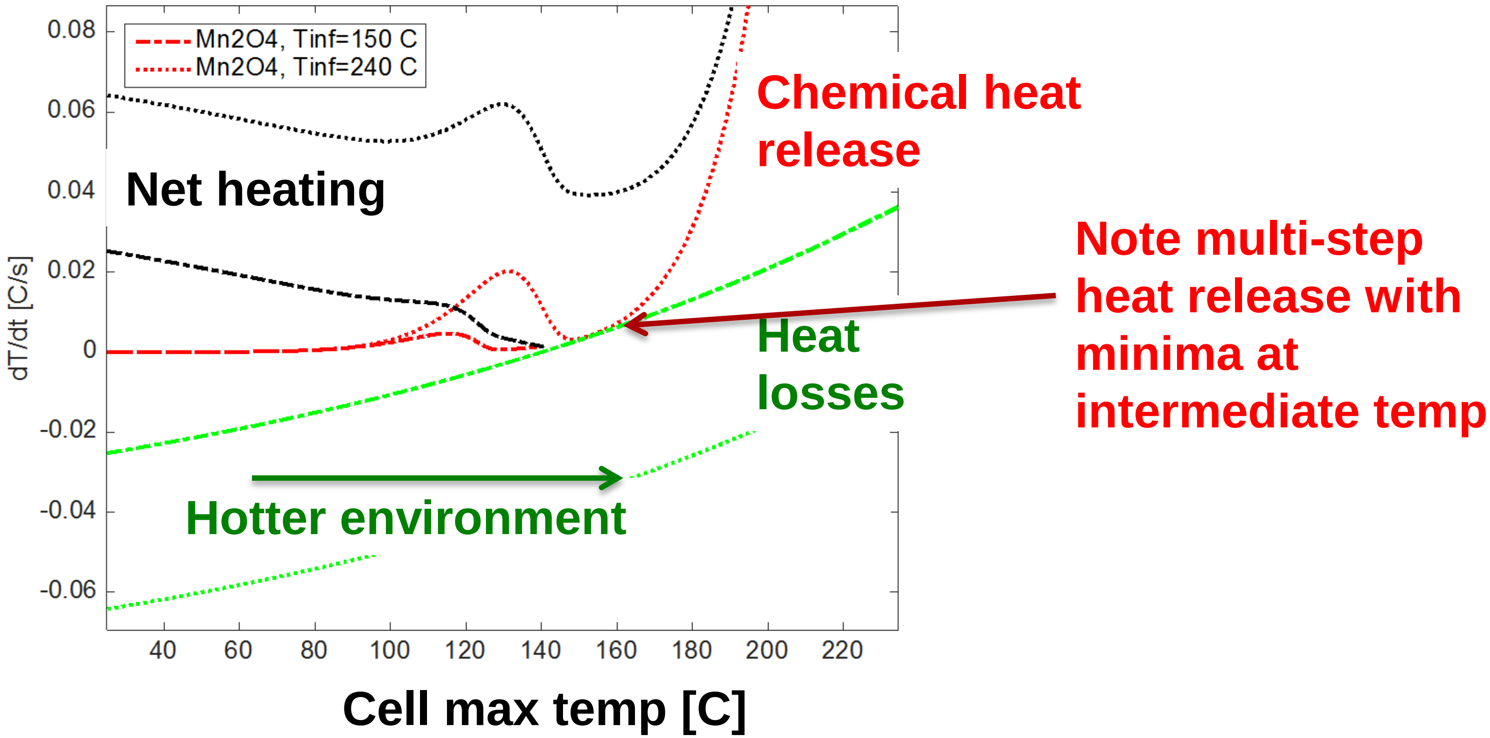
Temp. evolution two environ. temps., two cathode materials



Max temp. predicted versus environment (oven) temp.

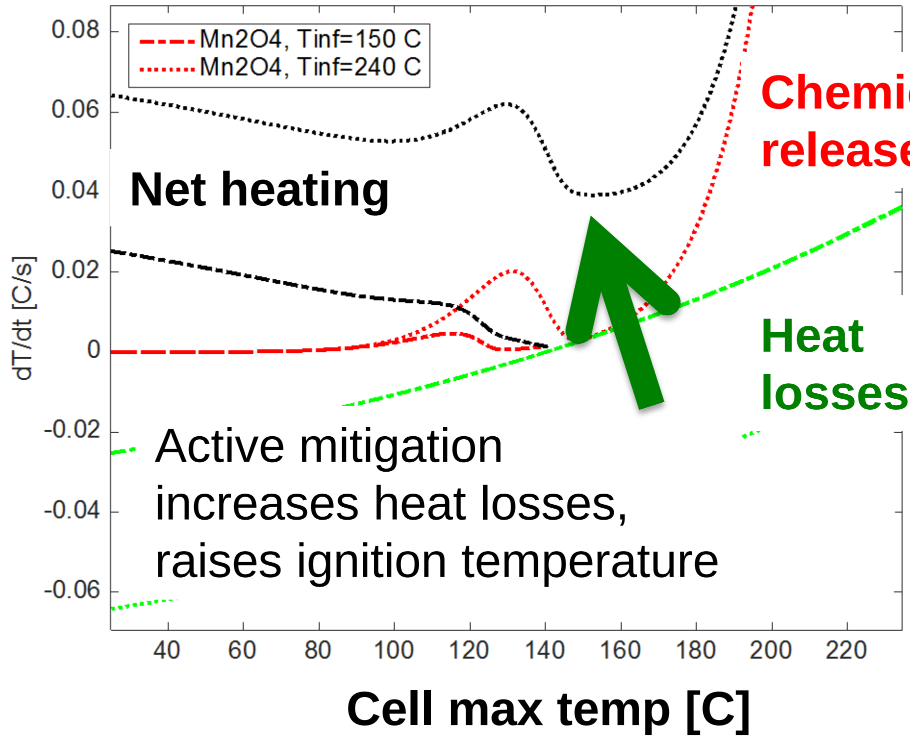


Thermal runaway occurs if heat release exceeds heat losses



- Predicted heating rates based on ARC measurements.
- If heat losses exceed heat generation, runaway can be arrested.

Thermal runaway occurs if heat release exceeds heat losses



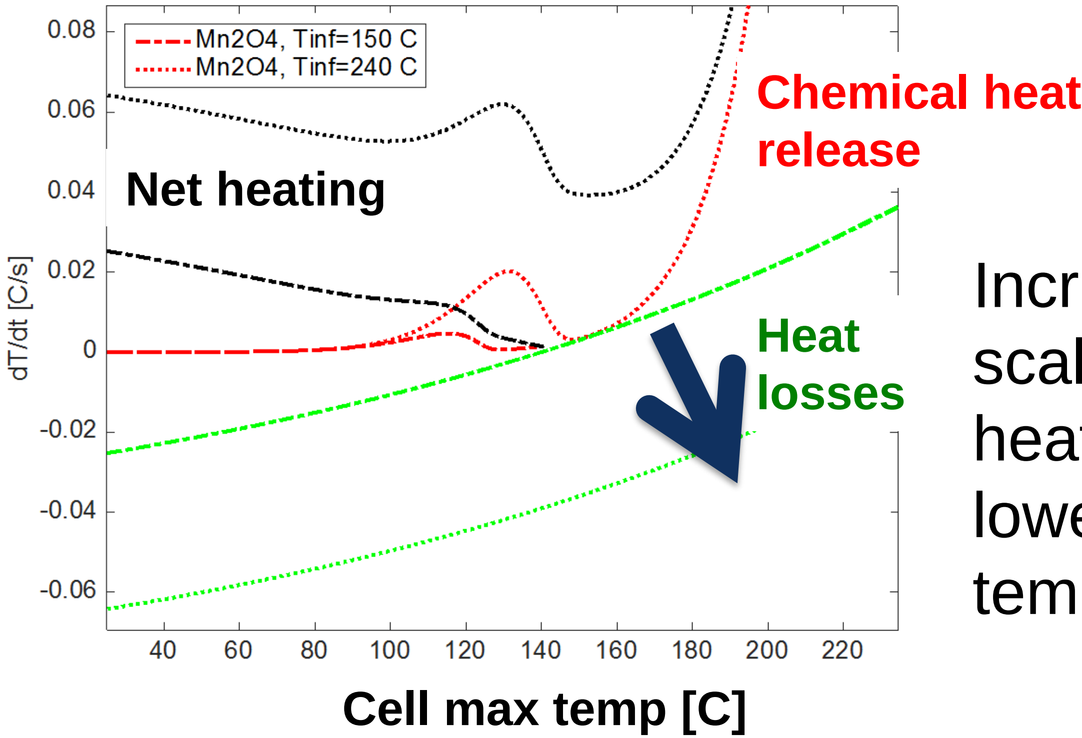
But, if the temperature dependence is strong, sensitivity to scale and heat losses is small.

Focus mitigation on shallow-sloped regions!

- Criterion for self heating:

$$QAe^{-E/RT} + \left(V^2 / R\right)_{internal} > h_{eff}A\left(T - T_\infty\right)$$

Increasing scale increases temperature inhomogeneities

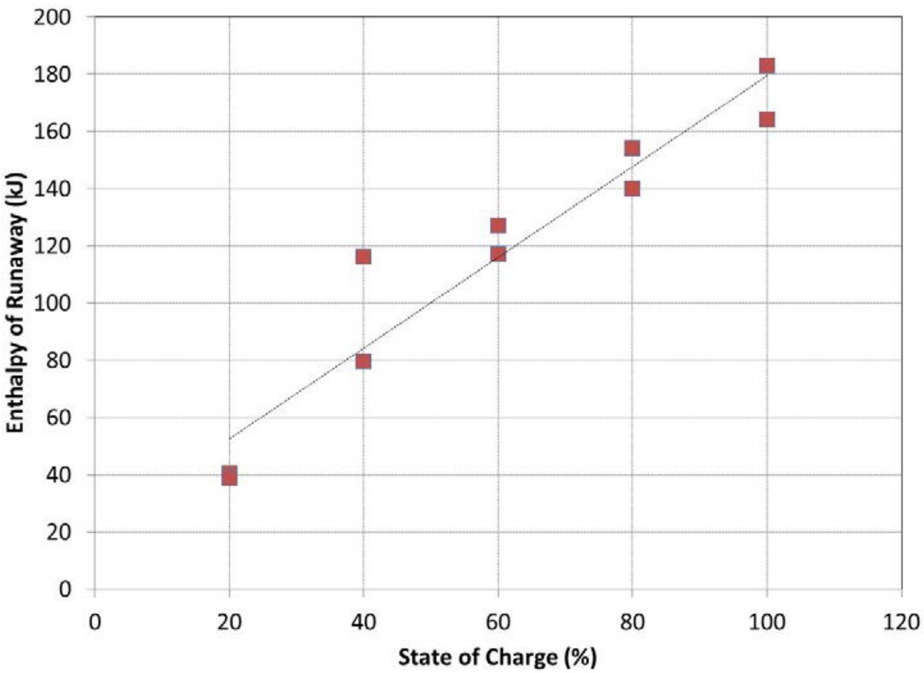


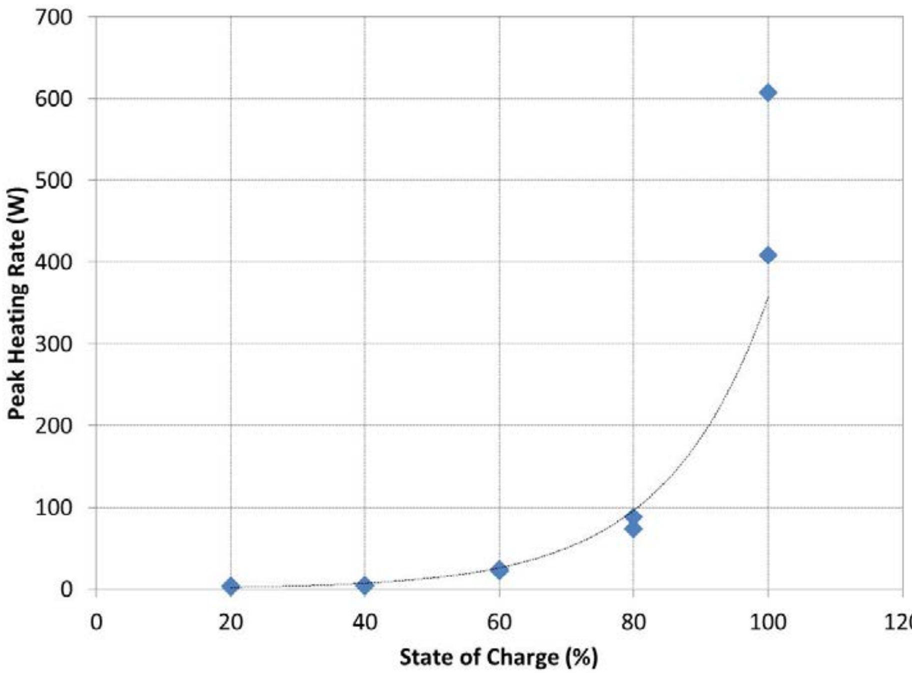
Increasing battery scale reduced heat losses, lowers ignition temperature

Depends on thermal diffusivity:
Can be important at 10+ cm.

$$\left(T_{\max} - T_{\infty}\right) \approx \frac{L^2}{\alpha}\frac{dT}{dt}$$

Impact of SOC on Runaway – Josh Lamb Expts.

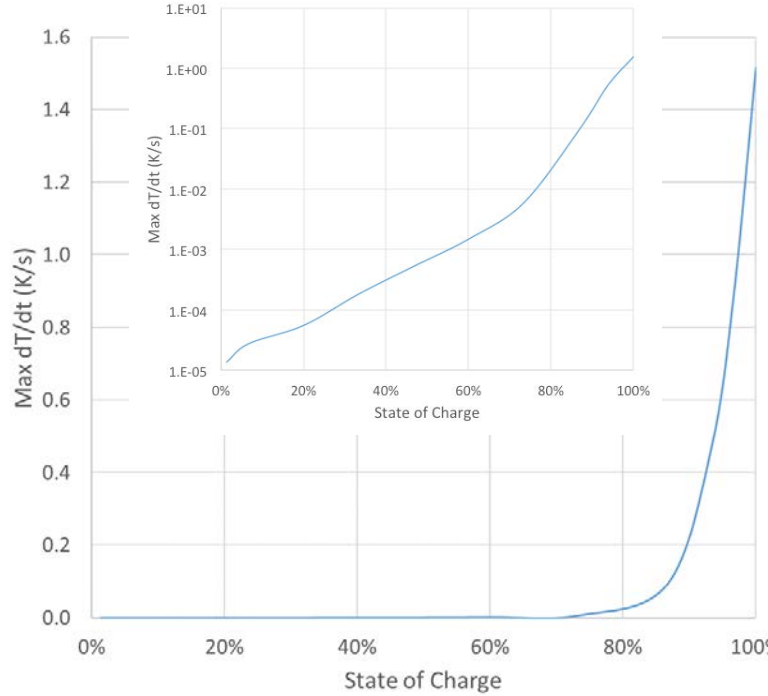


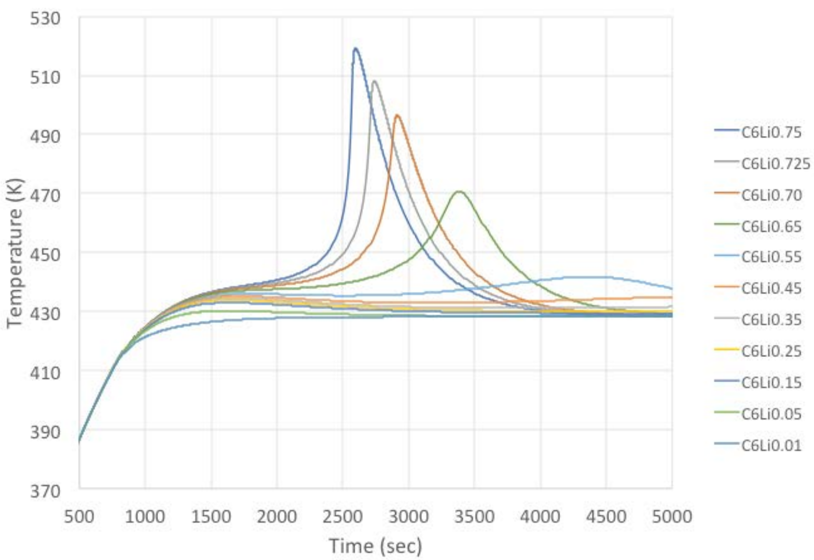


- **Results show a nearly linear relationship between total heat release (kJ) and cell SOC – similar to data for cell size this suggests that failure enthalpy is based largely on the stored energy available**
- **Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship 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.

Relating short circuits to the oven test

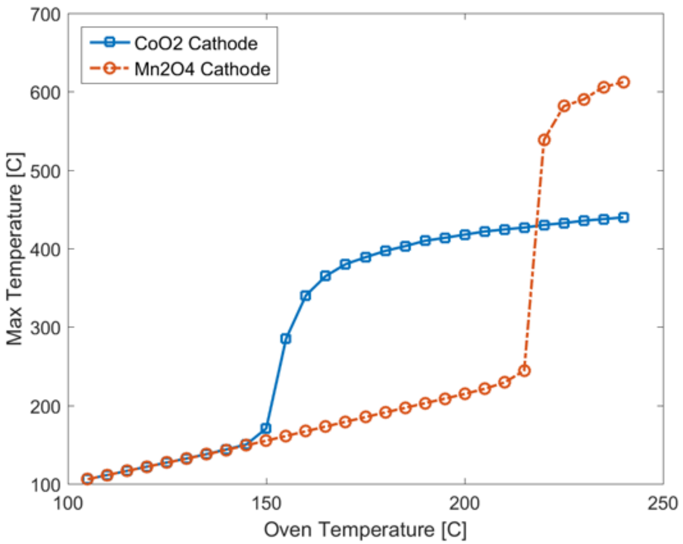
- Criterion for self heating:

$$\underline{QAe^{-E/RT} + \left(V^2 / R\right)}_{internal} > \underline{h_{eff} A\left(T - T_\infty\right)}$$

- Oven test: Determine the transition to thermal runaway based on an environment temperature.
- Heat release from short circuit has a mild temperature dependence and can be related to environment temperature:

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

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

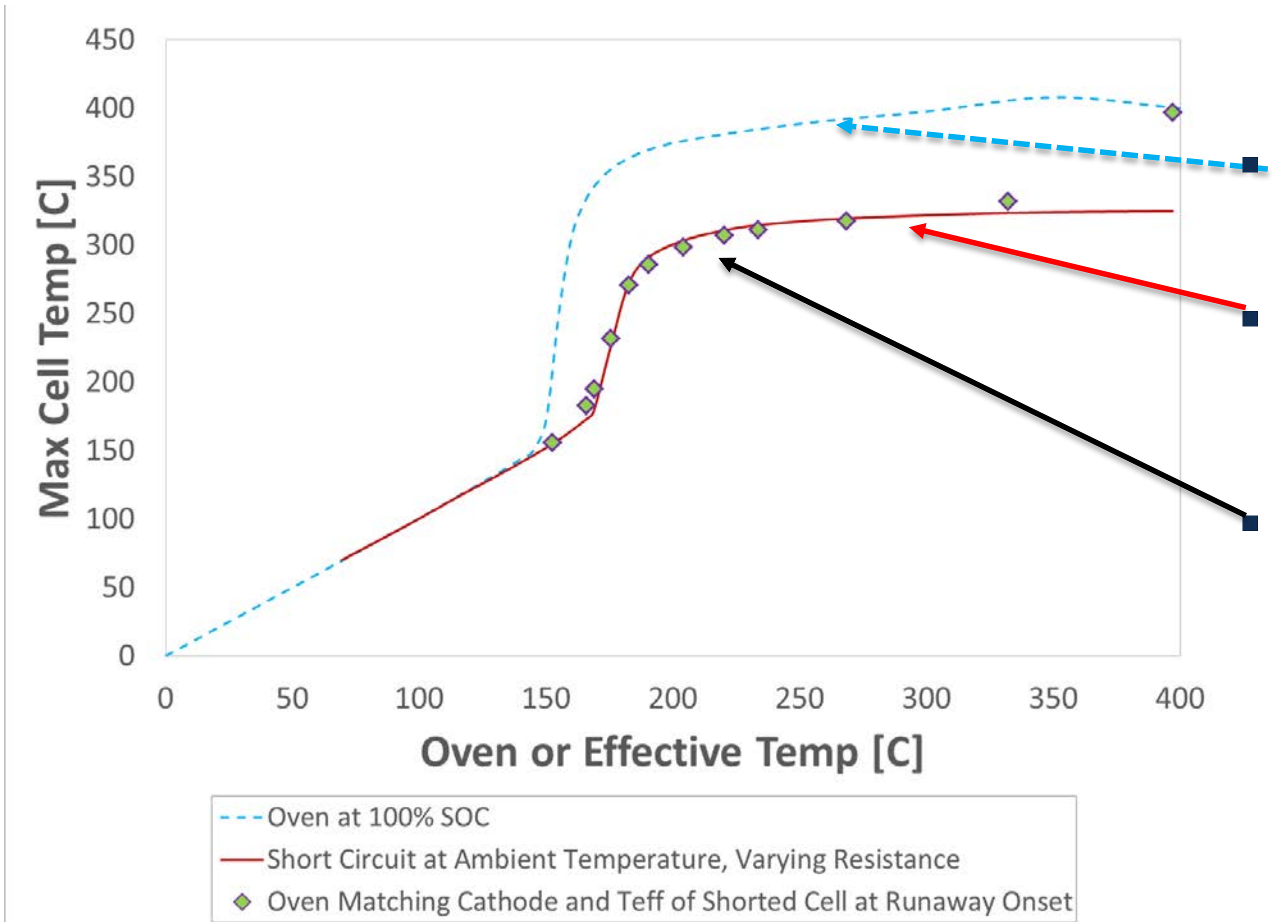


Max temp. predicted versus environment (oven) temp.

Relating short circuits to the oven test-2

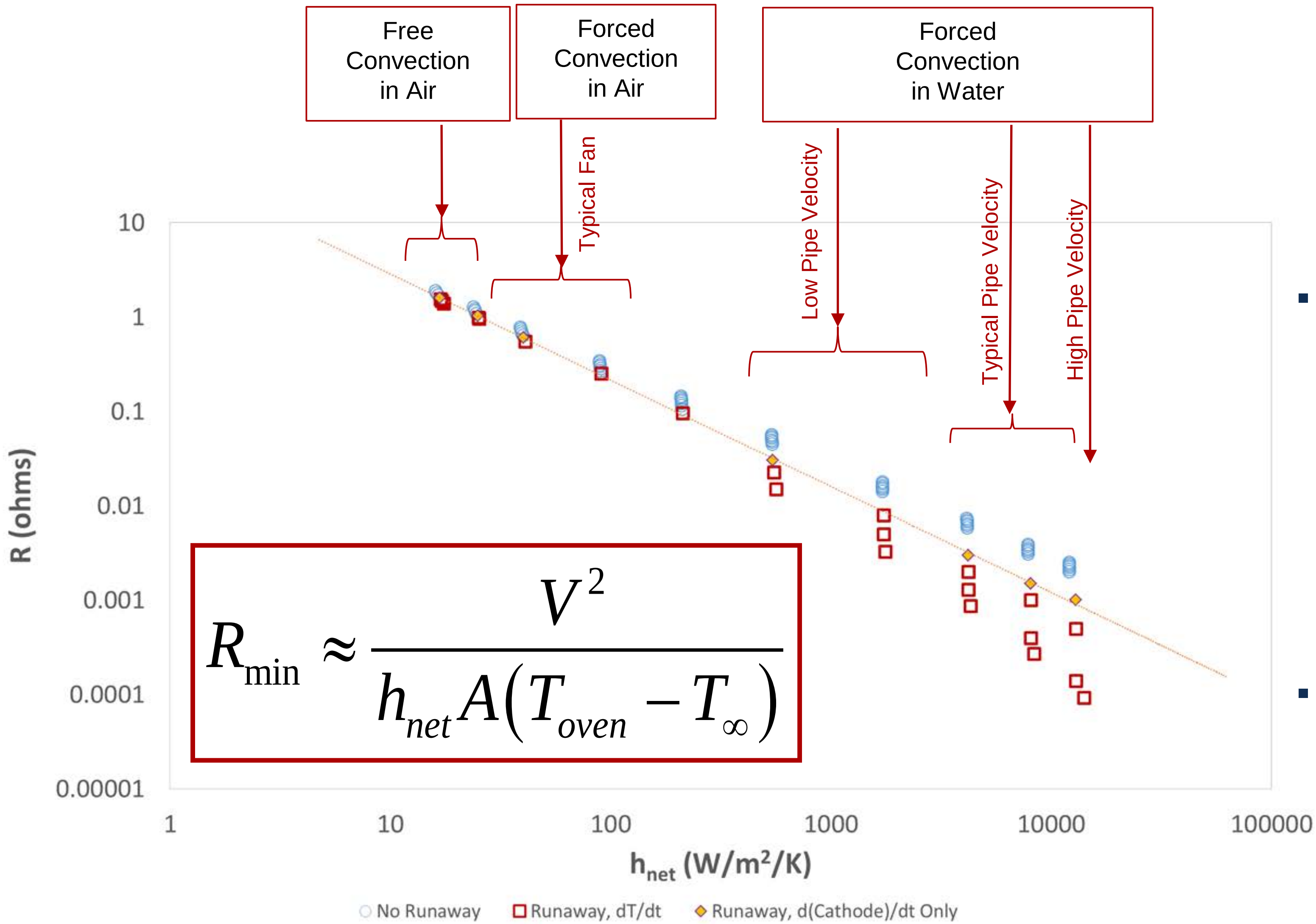
$$\boxed{T_{eff} = T_{\infty} + P / h_{net} A}$$

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



- Oven test, 100% SOC.
- Short circuits and thermal runaway, varying resistance.
- Equivalent oven tests need reduced SOC because energy is discharged to heat cells.

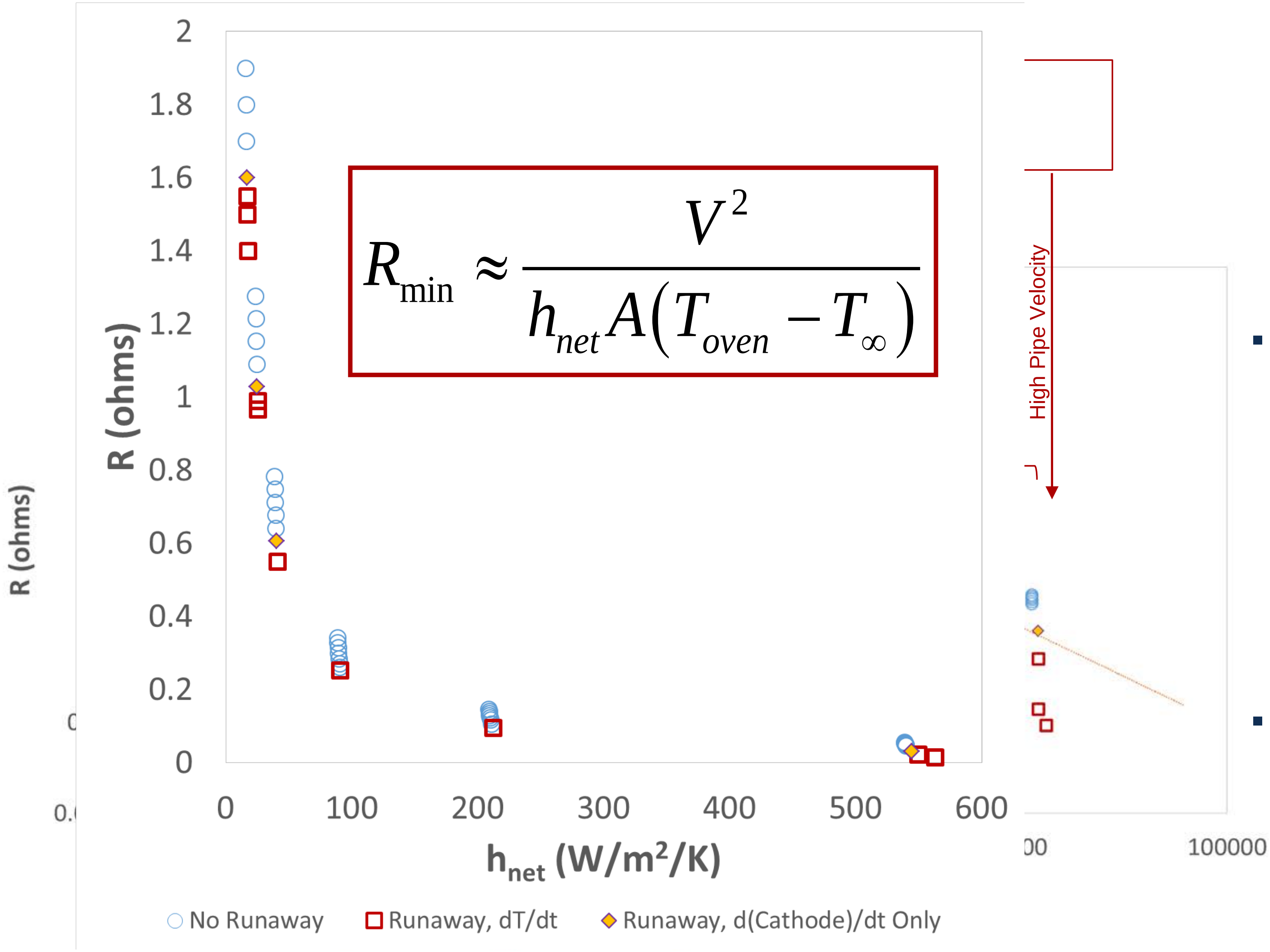
Required cooling for a given short circuit



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

- 18650 cells, homogeneous heating: internal temperature fluctuations will be worse for large format systems and localized shorts.
- 100% SOC, but energy required for heating is unavailable for runaway.

Required cooling for a given short circuit



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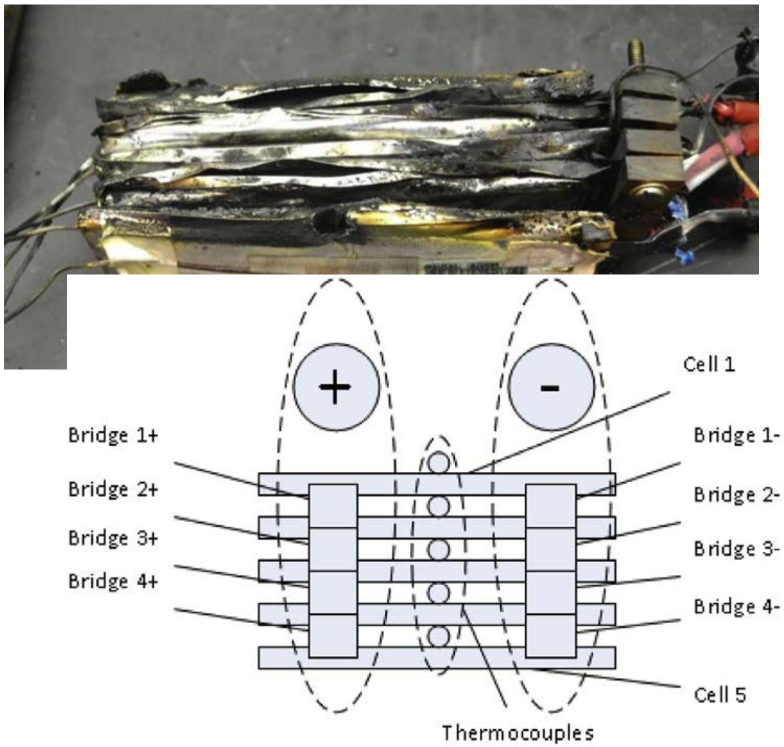
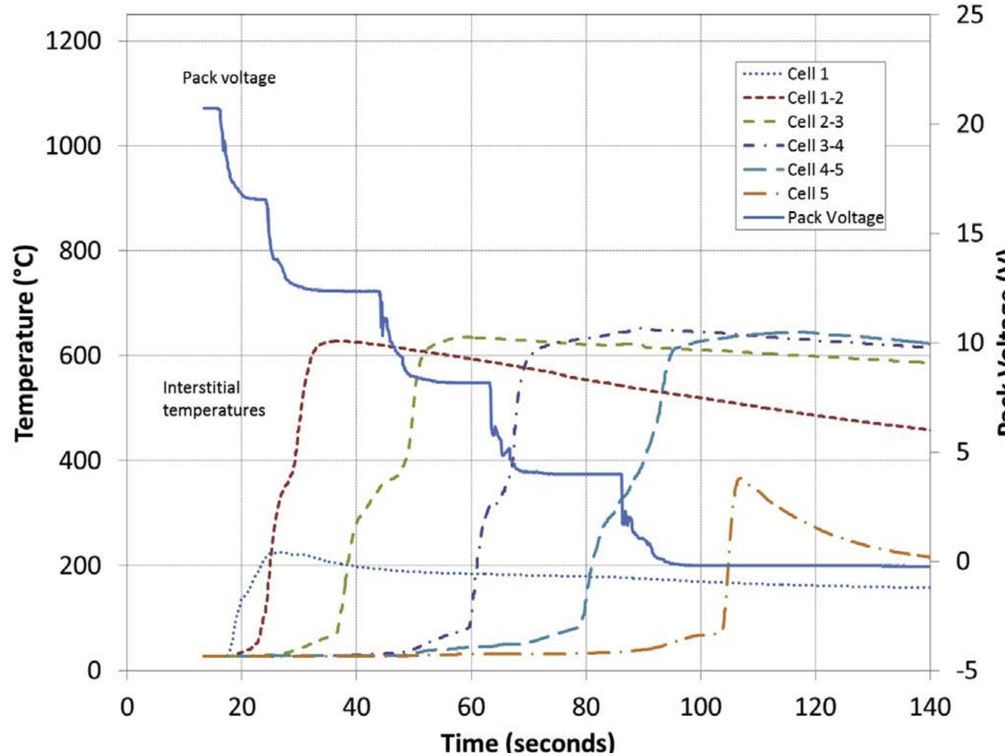
- 18650 cells, homogeneous heating: internal temperature fluctuations will be worse for large format systems and localized shorts.
- 100% SOC, but energy required for heating is unavailable for runaway.

Failure of a single cell can propagate to rest of pack

Experimental propagation in 5 stacked pouch cells

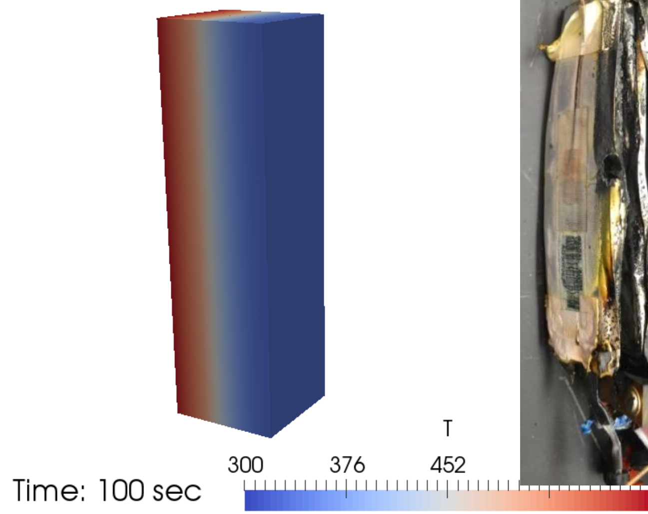


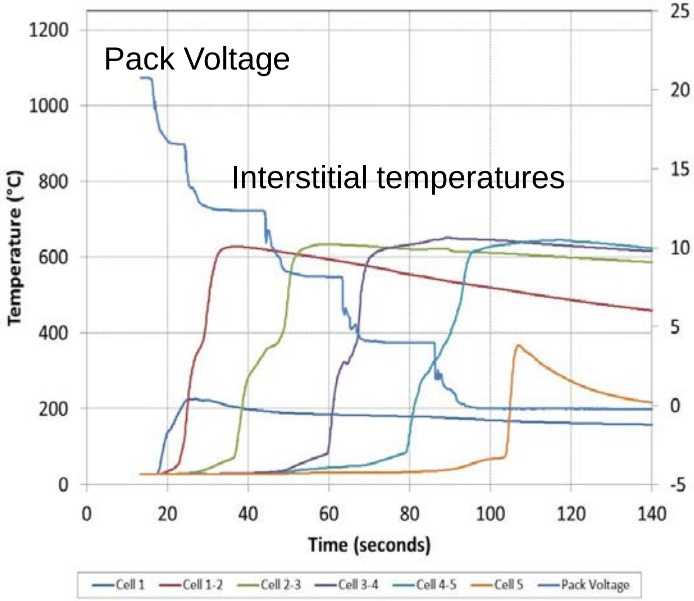


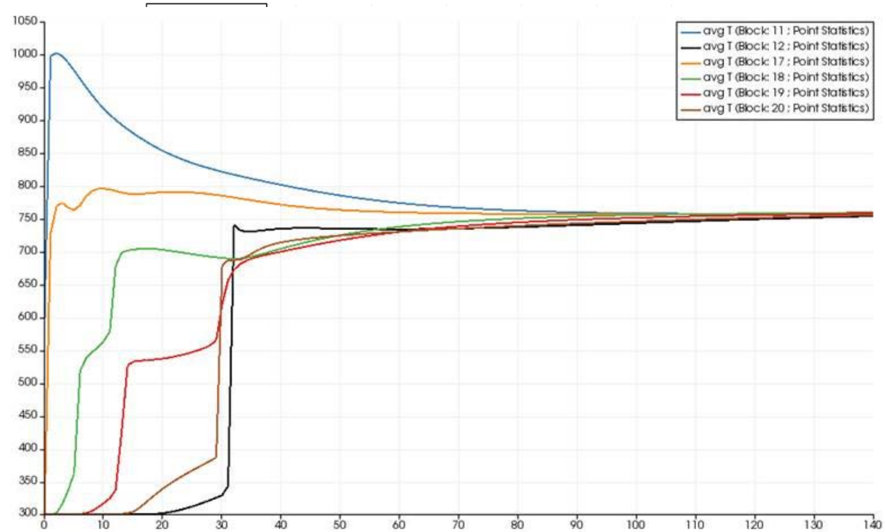
Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

Cascading propagation across multiple (5) cells

- Prediction and mitigation of cell-to-cell propagation is key to addressing risk.
- Here simulating propagation across series of pouch cells.
- Accurate measurements of highest temperature kinetics unavailable and need to be calibrated to get agreement.



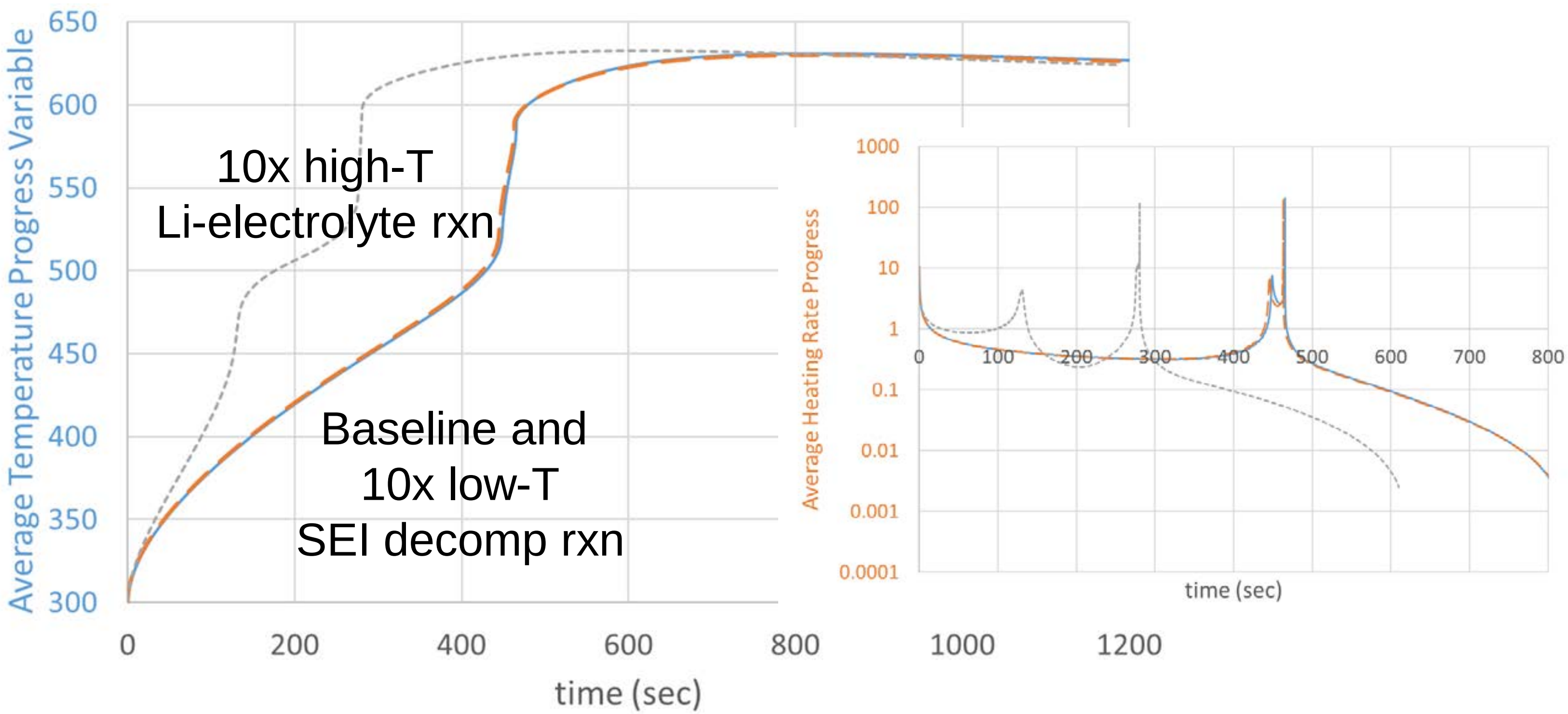




Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

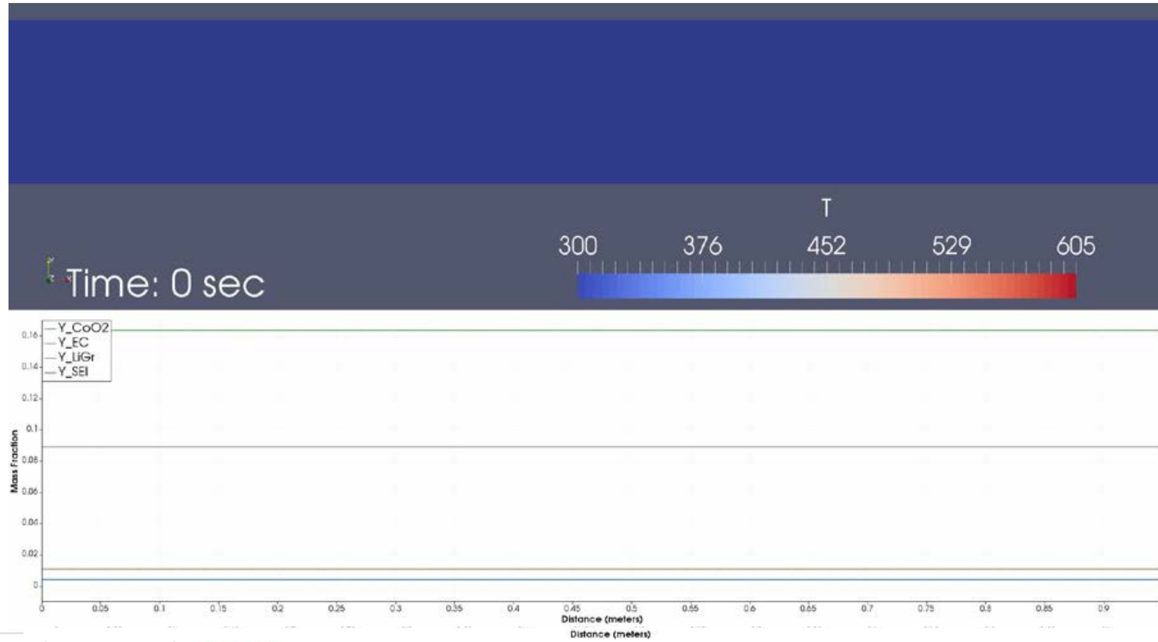
Sensitivity of propagation rate to high-T kinetics

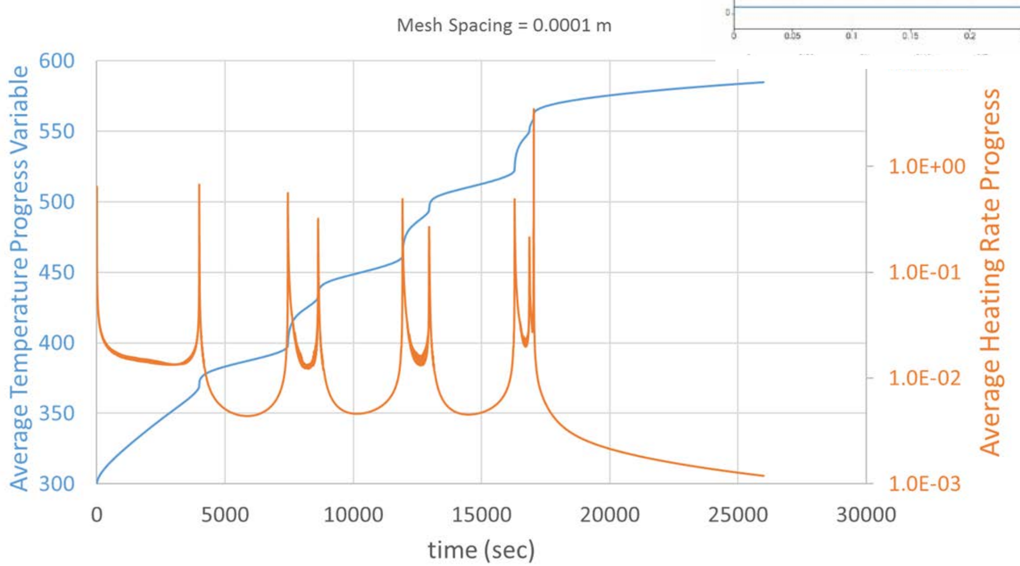
- Multiply low and high temperature rates by 10x.
  - Accelerated low-T rates has negligible effect.
  - Accelerated high-T rates has first-order effect (anode Li-electrolyte reaction).



Pulsating Propagation at large scales

- Extend modeling to large scales at small cost relative to measurements.
- Here predictions include multi-step mechanism involving anode, cathode, electrolyte reactants.
- Pulsating front speed observed.





- Propagation across a large pack (128 cells here) exhibits pulsating instabilities.
- Note heating rate varies by 100x (log scale).

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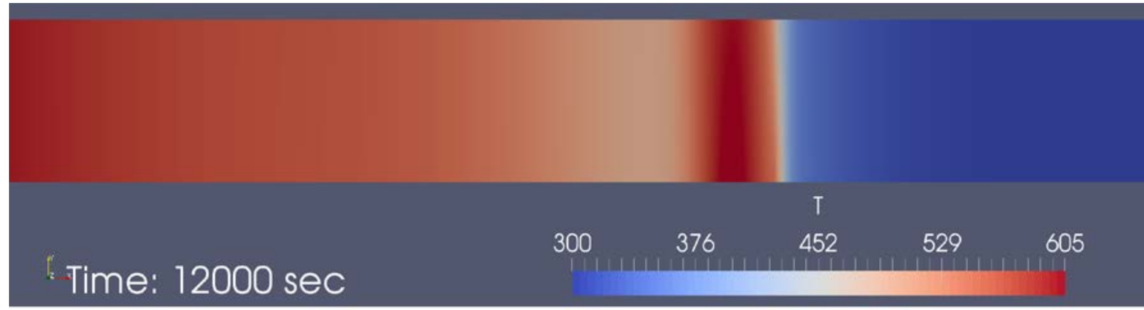
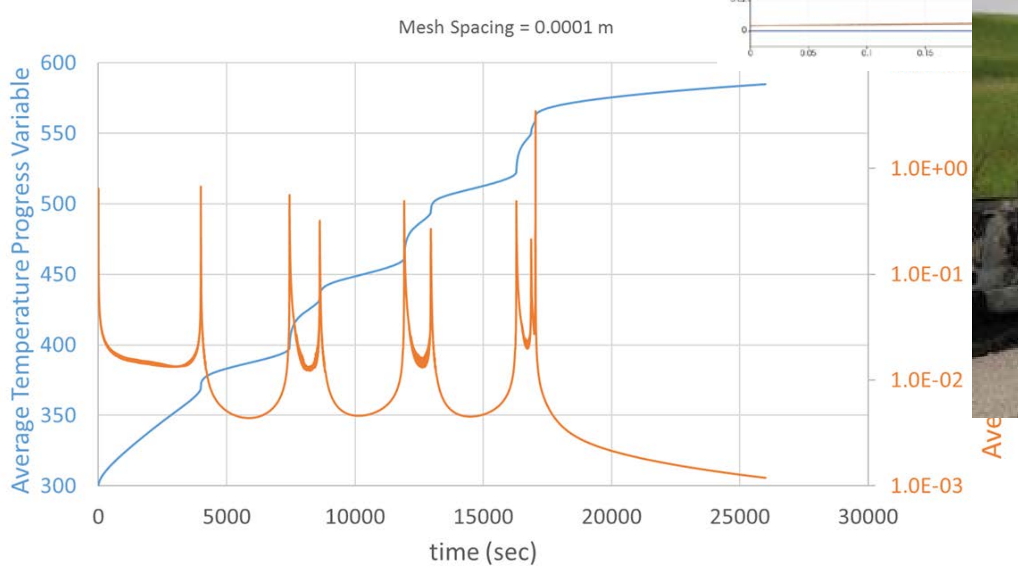


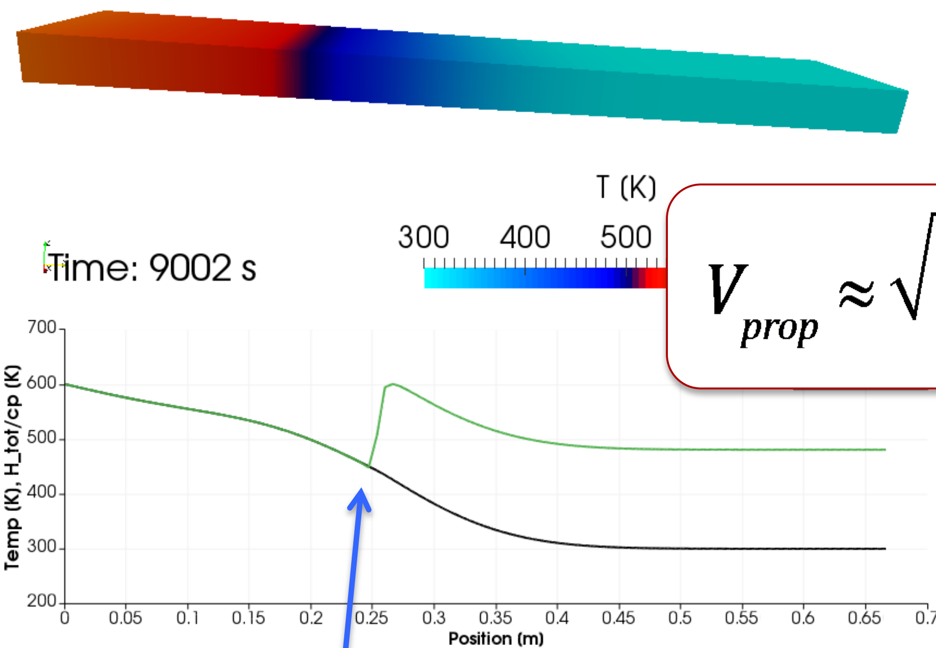
2011 Chevy Volt Latent Battery Fire at DOT/NHTSA Test Facility



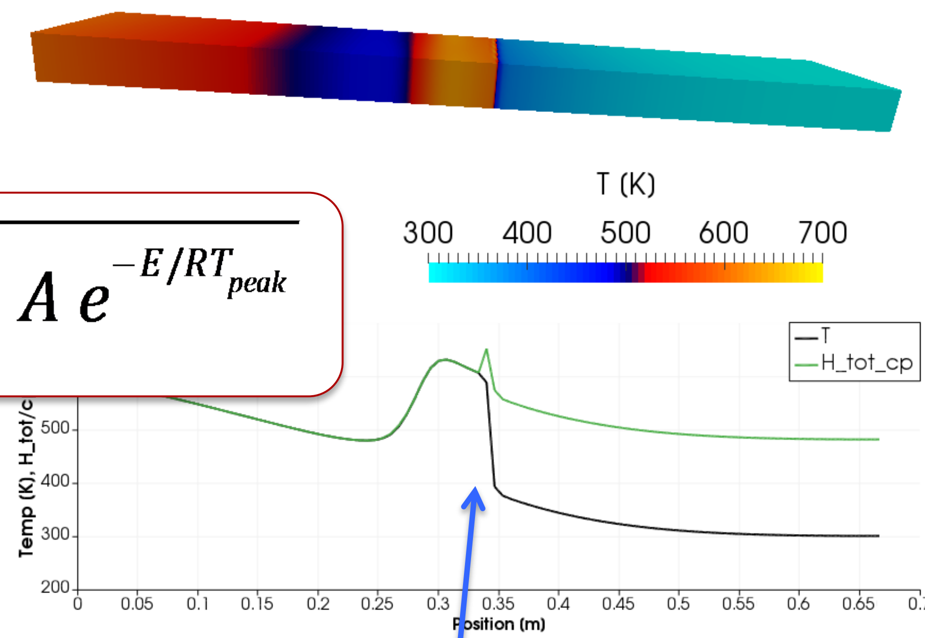
- Note heating rate varies by 100x (log scale).

The mechanism of pulsating propagation

- Heat released is conducted upstream of reaction front, increasing the total enthalpy (sum of sensible and chemical enthalpy) $H_{TOT} = c_p T + Y_r \Delta H_r$
- Front propagates rapidly through preheated region with larger H_{TOT}.

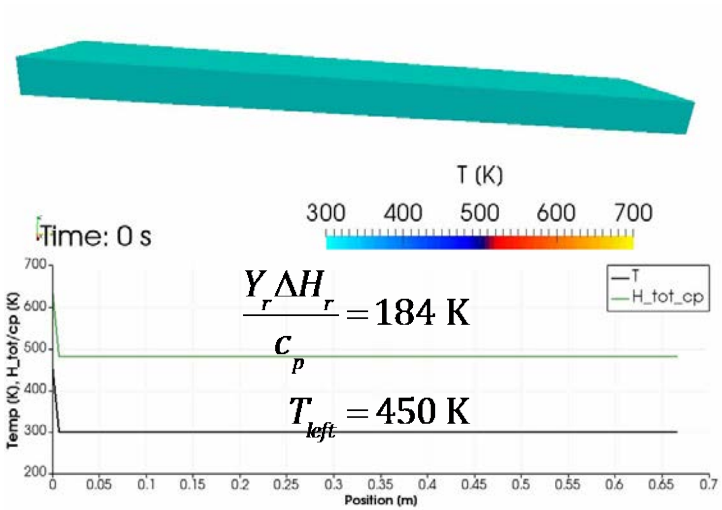


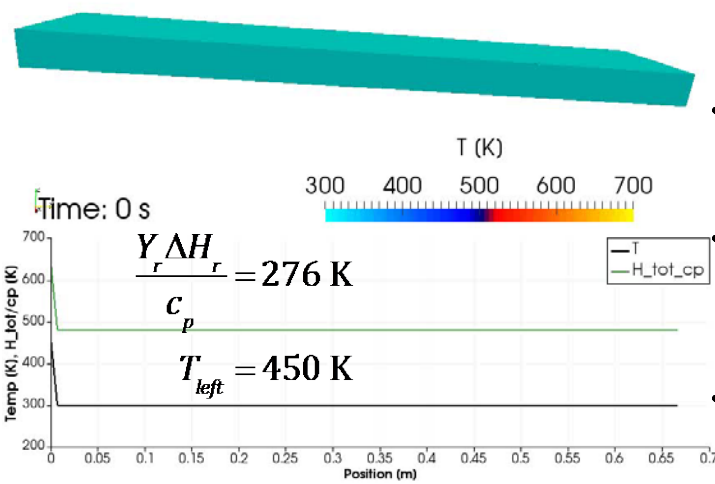
$$V_{prop} \approx \sqrt{\alpha \, A \, e^{-E/RT_{peak}}}$$



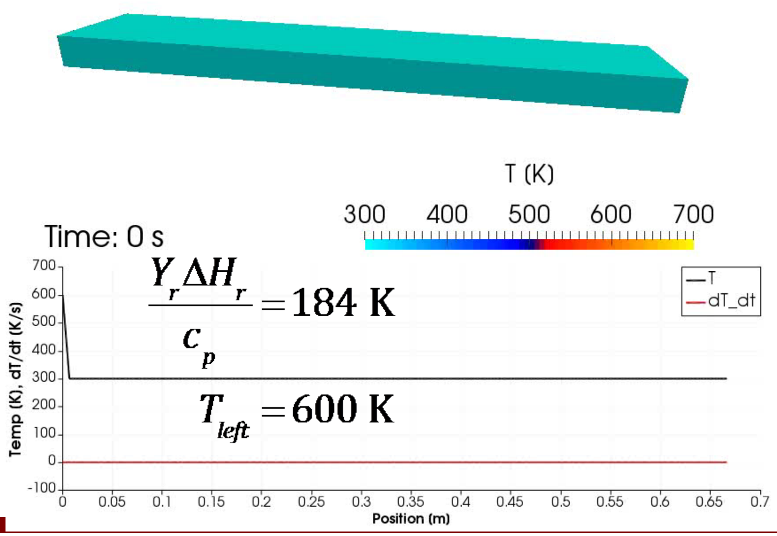
- Slow propagation (low Temp), but preheating mixture ahead of reaction front.
- Rapid propagation (high Temp), into preheated mixture.

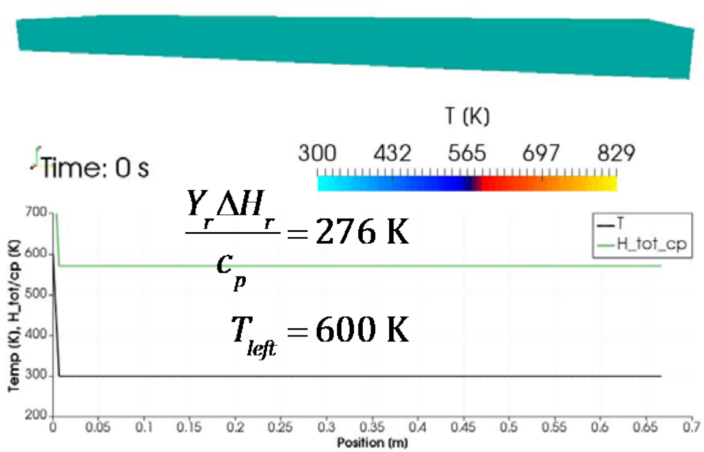
Parameter studies of propagation at large scales are possible with models





- Prediction and mitigation of cell-to-cell propagation is key to addressing risk.
- Single-step heat-release predictions with a range of heat release and boundary temps.
- Propagation across a large pack (80 cells here) exhibits pulsating instabilities.





In closing

- Thermal runaway is a risk and potential barrier to development and acceptance.
- Heat release rates are moderate relative to potential dissipation.
- Heat release rates scale exponentially with SOC – net heat release.
- Identification of thermal ignition criterion and sensitivity to low temperature rates.
- Identified relationship between short-circuit failure and required heat dissipation.
- Cell-to-cell propagation along homogenized pack structures exhibits pulsating behavior, depending on total enthalpy transport.
- Quality measurements are key to parameter identification.

Acknowledgements

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

http://www.sandia.gov/ess/

- Collaborative discussions with Josh Lamb, Summer Ferreira, Chris Orendorff, Babu Chalamala Dave Ingersoll, Harry Moffat and Stefan Domino from Sandia and Forman Williams from UCSD have provided insight and guidance.