Sandia National Laboratories
SNL Energy Storage Technology and Systems – Energy Storage Safety
Funded by Dr. Imre Gyuk
U.S. Department of Energy; Office of Electricity; Energy Storage Systems Program

Modeling Competitive Reactions and Heat Transfer Effects Applicable to Thermal Runaway in Lithium-Ion Batteries

Randy C. Shurtz, John C. Hewson
Fire Science and Technology, Sandia National Laboratories, Albuquerque, NM

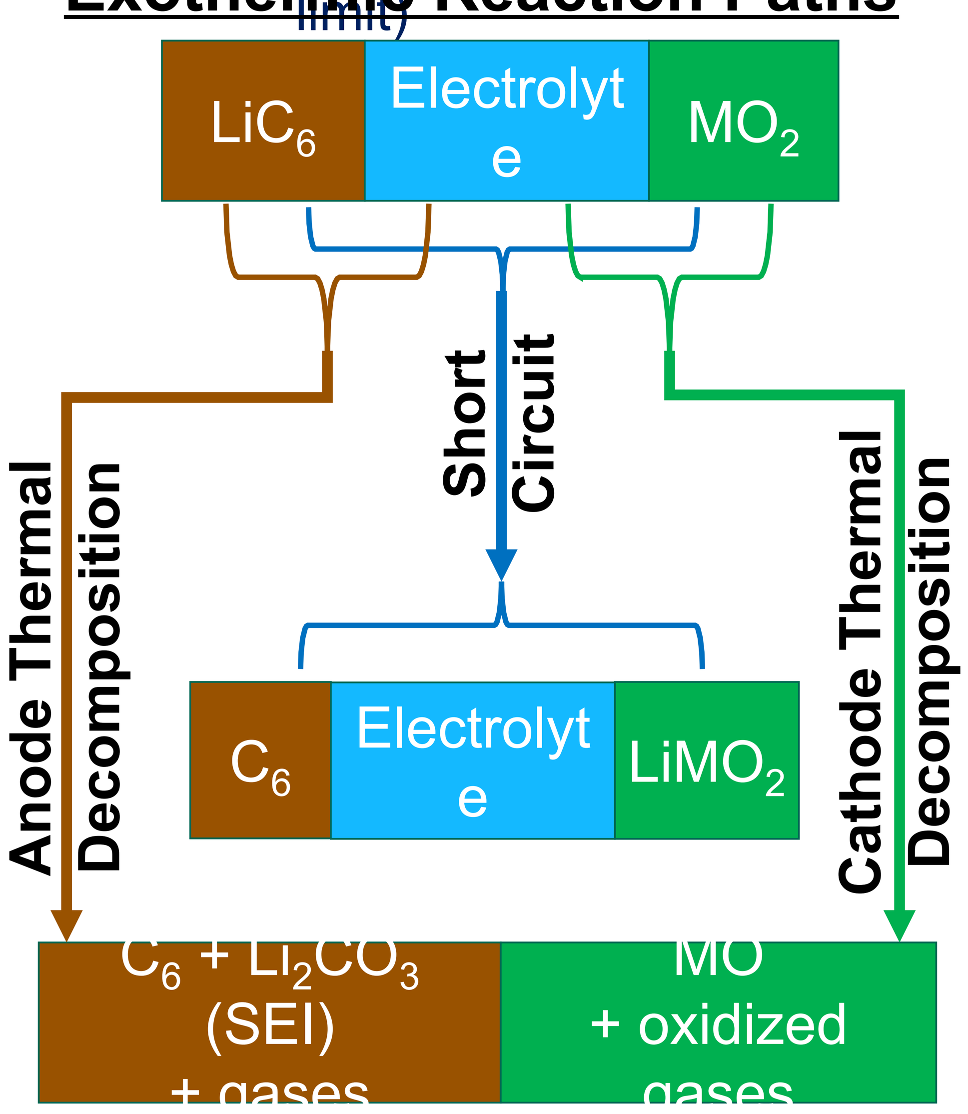
Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Models enable knowledge to be applied to different scenarios and larger scales.
- When thermal runaway models include enough realistic physics, they can be used to:
  - Identify experimentally accessible parameters that strongly influence cascading propagation of thermal runaway through modules of cells.
  - Predict trends in heat transfer and cascading propagation behavior.
  - Identify regions of parameter space of greatest interest for experiments.
  - Evaluate mitigation strategies and explain novel experimental observations.

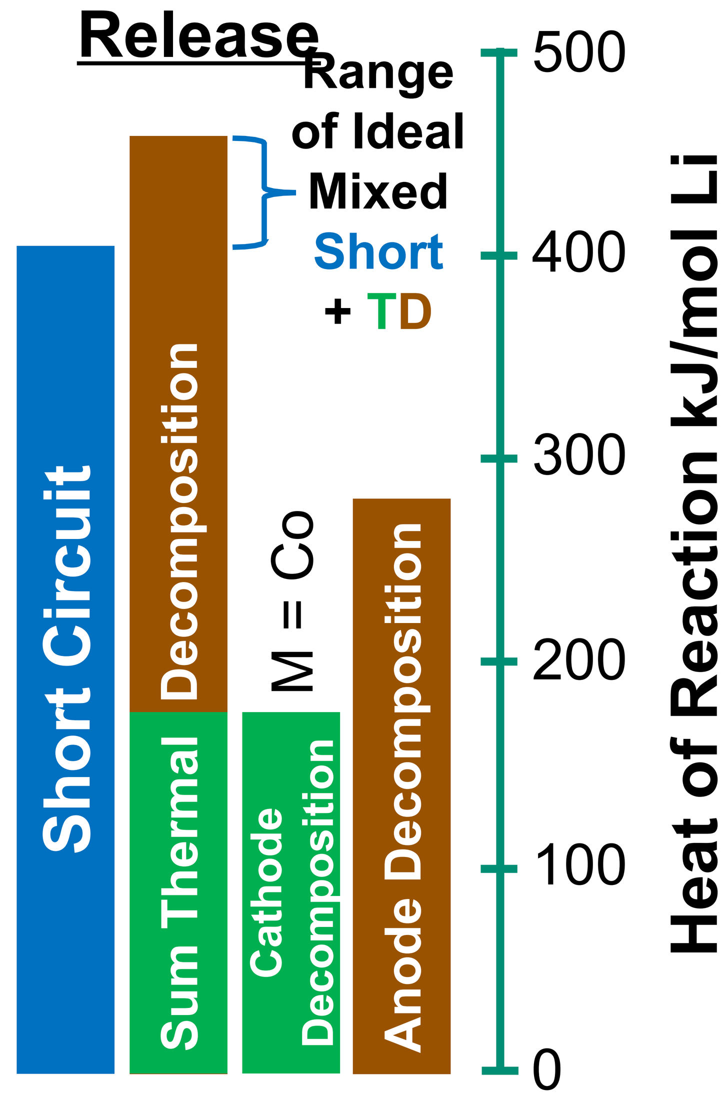
I: Competitive Energy Release Pathways

- Charged electrode species and organic electrolyte are reactive materials
  - Thermodynamically unstable
- Short circuits and thermal decomposition (TD) compete for common reactants
  - Total mixed heat release is not a summation (pure TD is upper limit)

Exothermic Reaction Paths



Energy Release



II: Effective Environment Temperature

- Thermal runaway (TR) occurs when heat sources exceed heat dissipation losses

$$mc_p\frac{dT}{dt} = \dot{Q}_{source} - \dot{Q}_{loss}\text{, where } \dot{Q}_{loss} = hA(T-T_\infty) + \varepsilon\sigma A(T^4 - T_\infty^4)$$

- Energy sources driving thermal decomposition can be external or internal
- For internal source P, linearize losses and assume thermal equilibrium

When $\frac{dT}{dt} = 0$, $\dot{Q}_{source} = \dot{Q}_{loss}$

If $\dot{Q}_{source} = P$ and $\dot{Q}_{loss}$ is linearized as $\dot{Q}_{loss} = h_{eff}A(T - T_\infty)$,

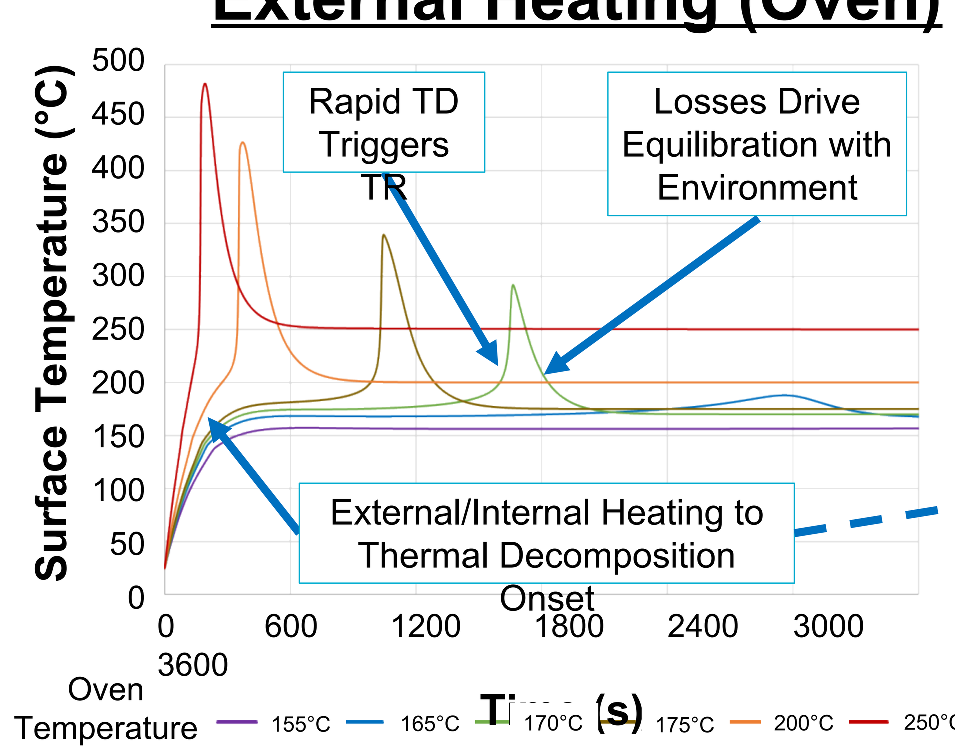
$$T_{eff} = T_\infty + P/h_{eff}A$$

Effective Environment Temperature Derived

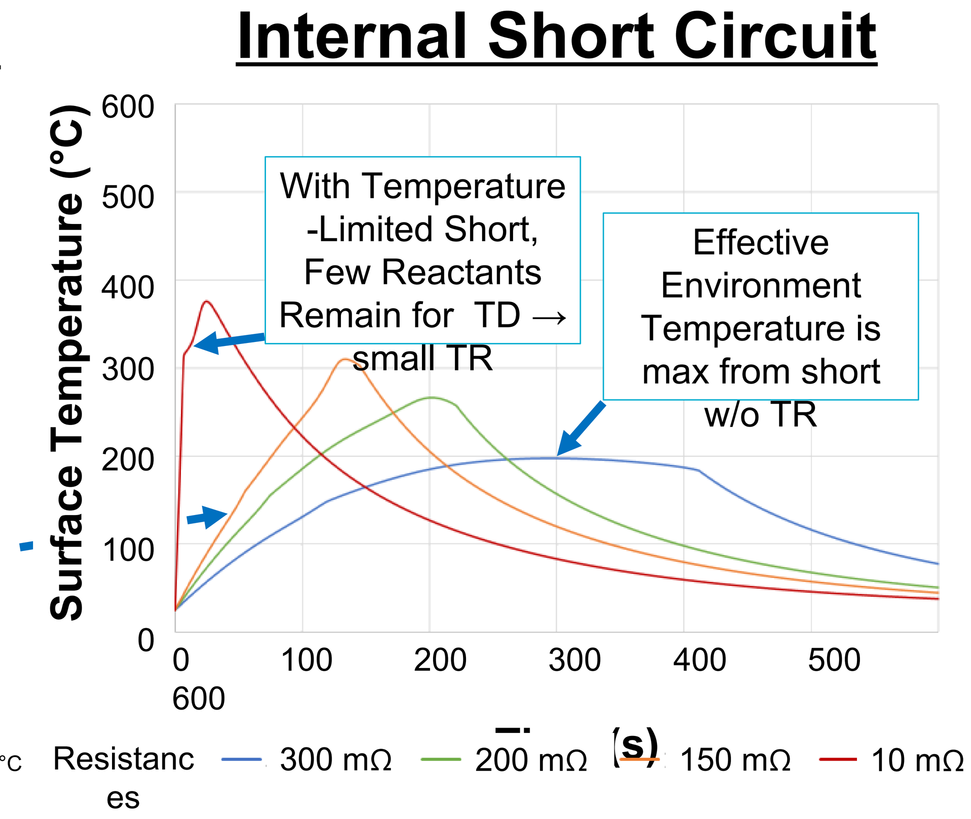
- Effective environment temperature is basis to compare internal/external sources

Examples modeled as 0D for $h_{eff} = 18\ \frac{W}{m^2K}$ with $P = \frac{V^2}{R}$, V = 4.2V, 1.5 Ah 18650

External Heating (Oven)



Internal Short Circuit

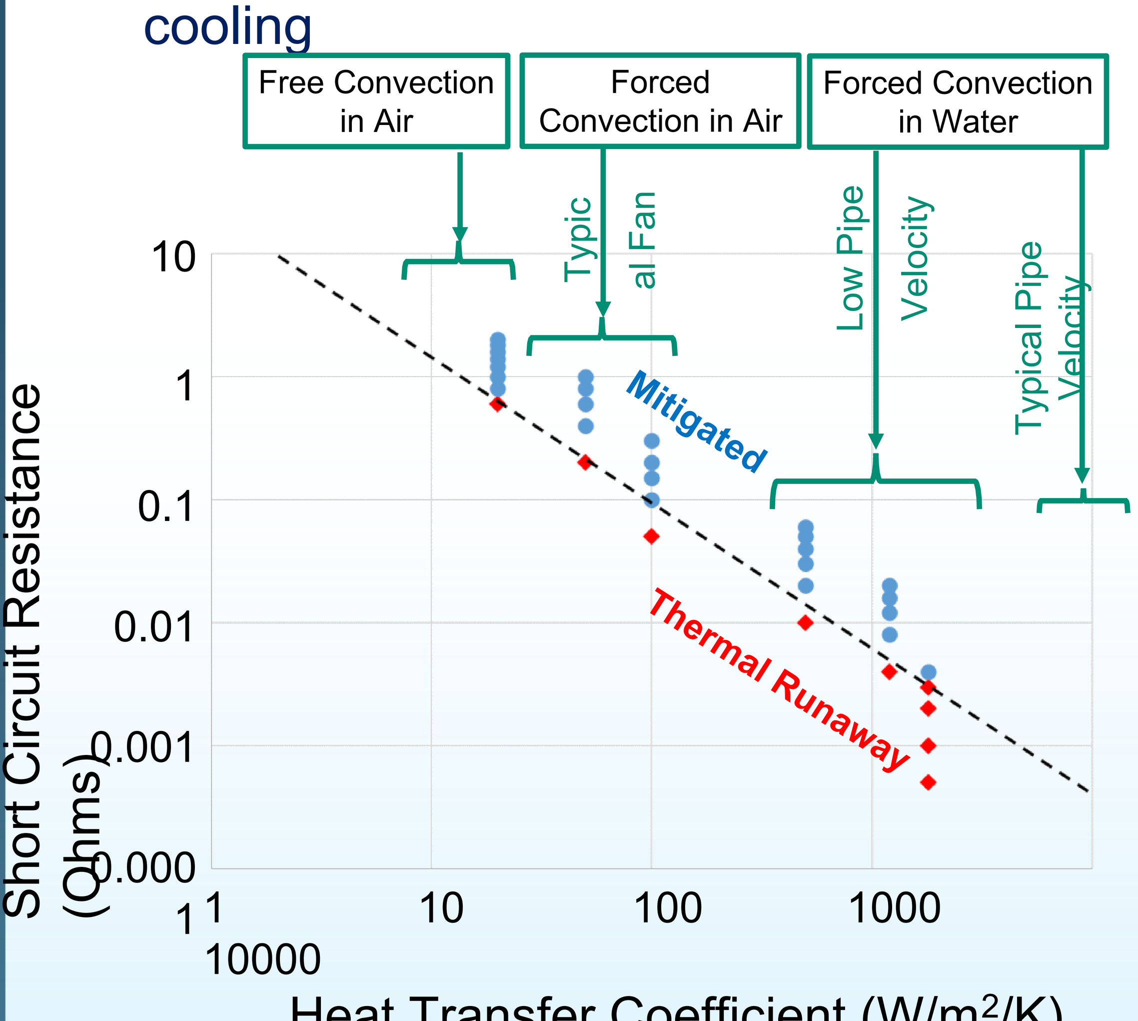


III: Cooling Requirements for Short Circuits

- Models can be used to estimate cooling requirements to mitigate TR
  - Homogeneous (0D) heating of 1.5 Ah 18650 shown at lower far left
  - Inhomogeneous deviations from 0D case shown at lower center + right
- Define power of short in effective environment temperature to correlate minimum internal short resistance that can be mitigated with degree of cooling

From $T_{eff} = T_\infty + P/h_{eff}A$ and $P = \frac{V^2}{R}$:

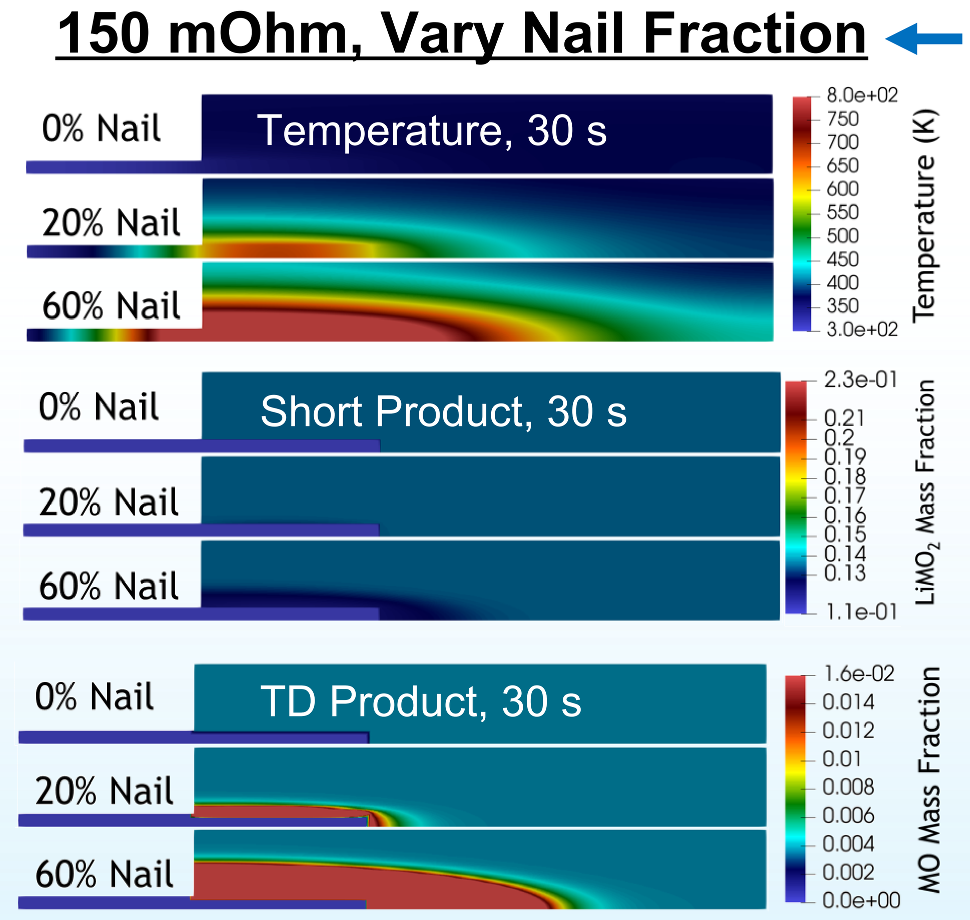
$$R_{min} = \frac{V^2}{h_{eff}A(T_{eff} - T_\infty)}$$

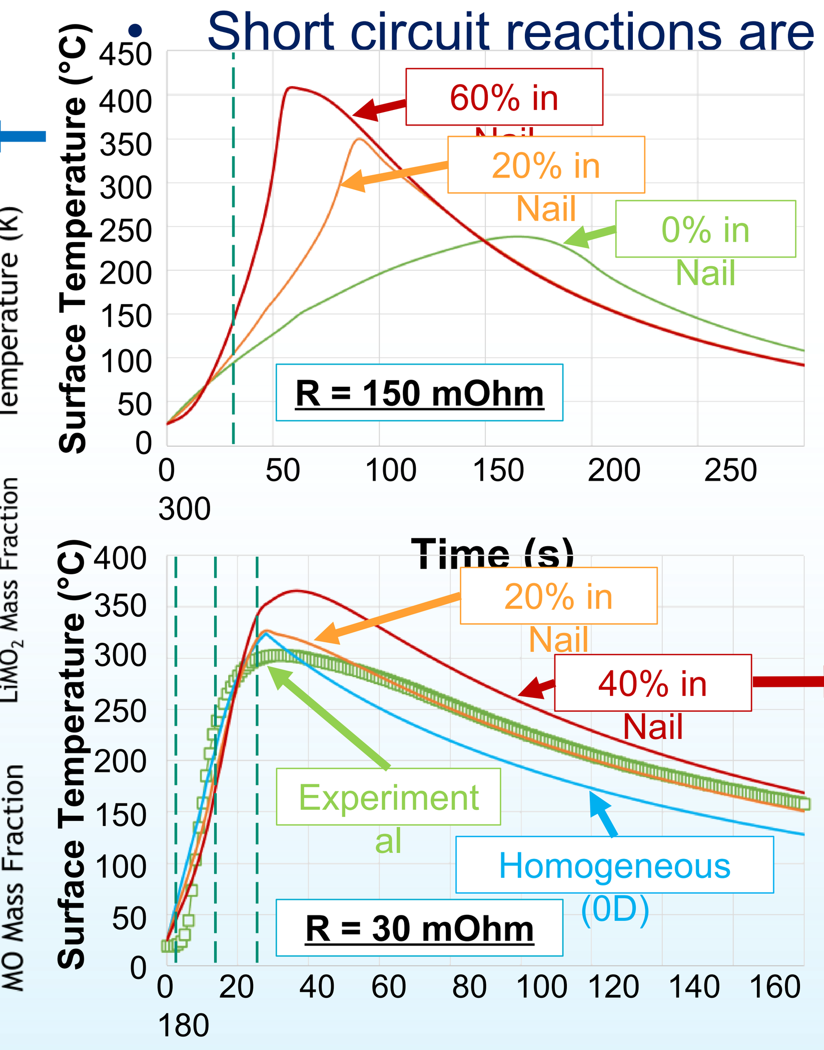


IV: Thermal and Chemical Inhomogeneities

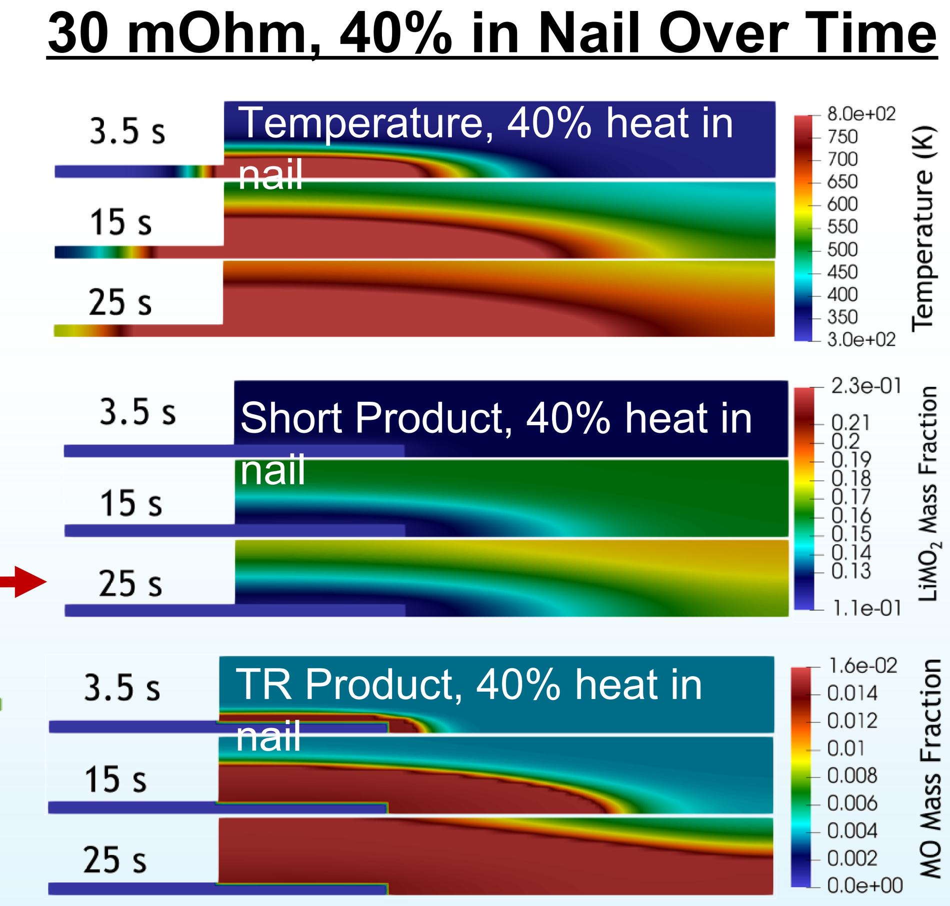
- 2-D axisymmetric simulations of 18650, vary % of total resistance (heat) in nail
  - Nail is hot because heat release is concentrated in small volume
  - Thermal degradation reactions dominate near hot nail
  - Short circuit reactions are more common near cooler periphery

150 mOhm, Vary Nail Fraction





30 mOhm, 40% in Nail Over Time



Nail penetration data (1.5 Ah 18650) courtesy of Loraine Torres-Castro at Sandia National Laboratories

For related work, see also:

R. C. Shurtz, J. D. Engerer, and J. C. Hewson, *J. Electrochem. Soc.*, vol. 165, no. 16, pp. A3878-A3890, (2018), https://dx.doi.org/10.1149/2.0541816jes
R. C. Shurtz, *J. Electrochem. Soc.*, vol. 167, no. 14, p. 140544, (2020), https://doi.org/10.1149/1945-7111/abc7b4
R. C. Shurtz and J. C. Hewson, J. Electrochem. Soc., vol. 167, no. 9, p. 090543, (2020), https://doi.org/10.1149/1945-7111/ab8fd9
A. M. Bates, Y. Preger, L. Torres-Castro, K. L. Harrison, S. J. Harris, and J. Hewson, Joule, (2022), https://doi.org/10.1016/j.joule.2022.02.007