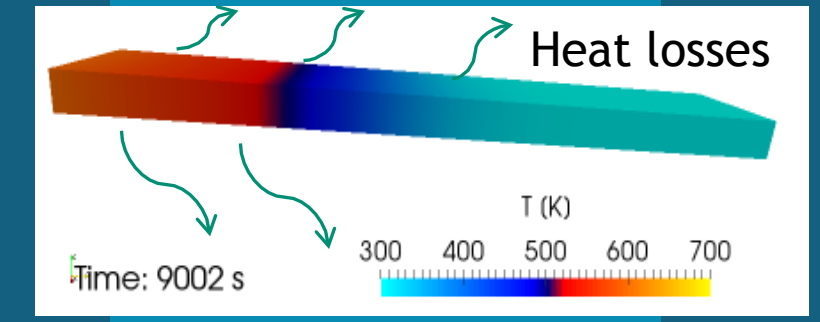
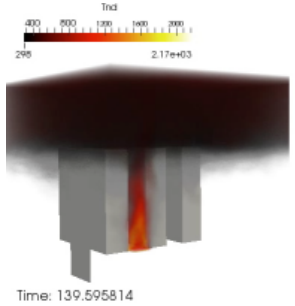
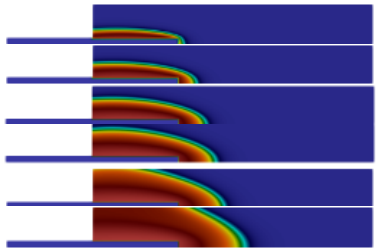
SAND2022-6354C

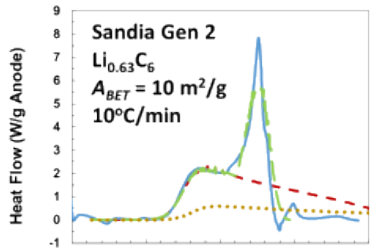
Sandia National Laboratories

Intra-Particle Diffusion-Limited Thermal Runaway Predictions in Lithium-Ion Systems









Presented by

Andrew Kurzawski, Randy Shurtz, Loraine Torres-Castro, and John Hewson

Materials Research Society Spring Meeting and Exhibit, May 5, 2022

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Thermal runaway and cascading failure

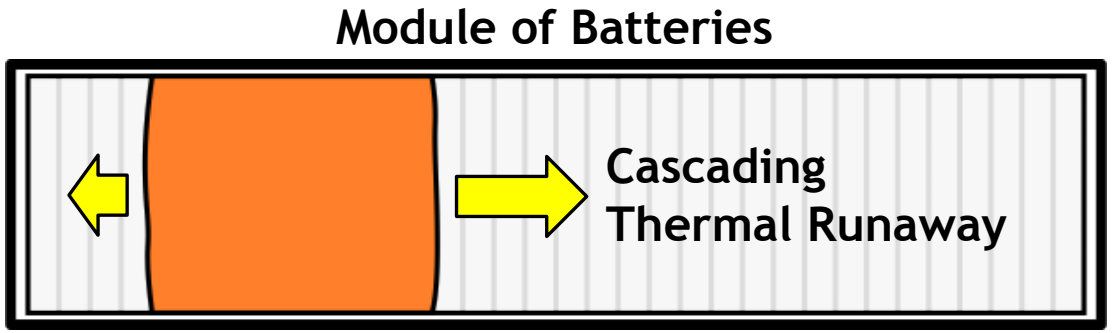
Cascading failure poses a risk to energy storage systems, electric vehicles, and first responders.

The current approach is to test our way into safety.

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

We supplement testing with **predictions** of challenging scenarios and optimization of mitigation.

A key to designing safe systems at larger scales is understanding cascading thermal runaway.



Source: (top) https://cmte.ieee.org/pes-essb/wp-content/uploads/sites/43/2019/06/2019-SM-UL-9540A-IEC-Lithium-Test-Summary.pdf
(bottom) https://www.ul.com/news/ul-9540a-battery-energy-storage-system-ess-test-method

Cascading failure testing with passive mitigation

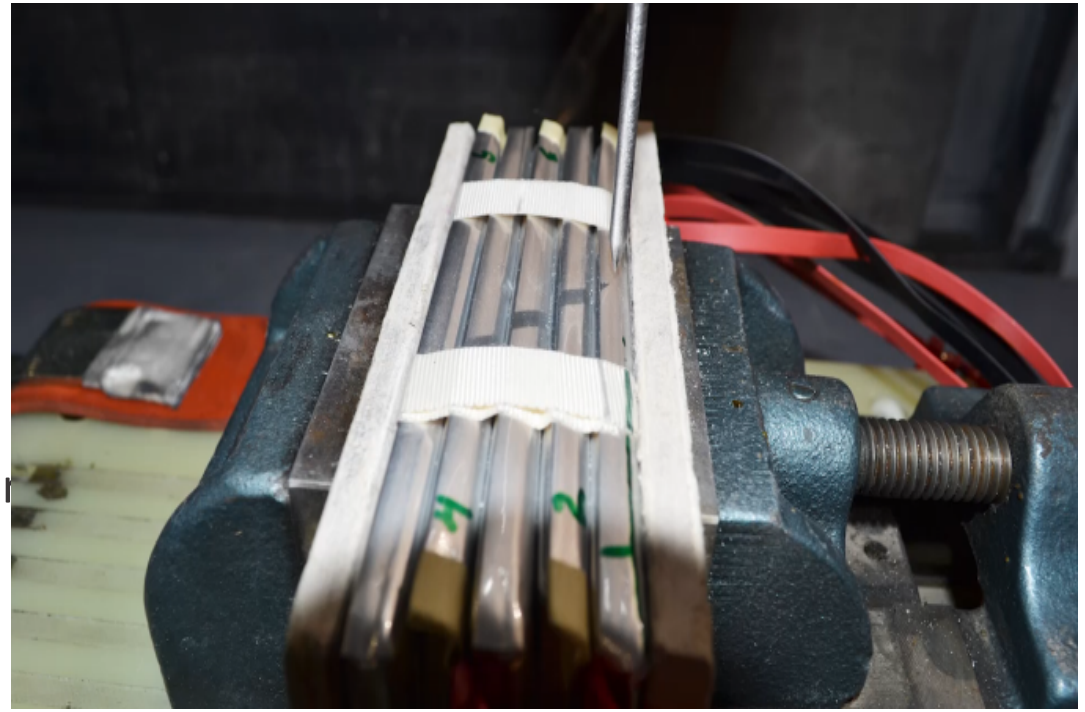
$LiCoO_2$ 3Ah pouch cells

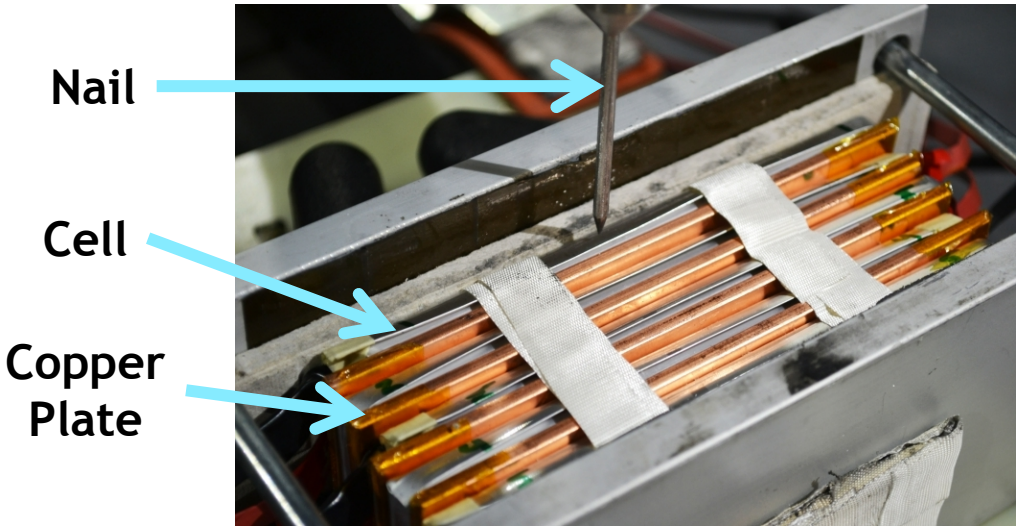
5 closely packed cells with/without aluminum or copper spacer plates

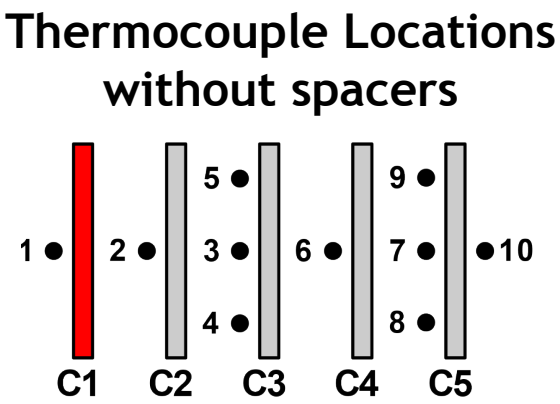
- Spacer thicknesses between 0.8 mm and 3.2 mm
- State of charge (SOC) between 50% and 100%

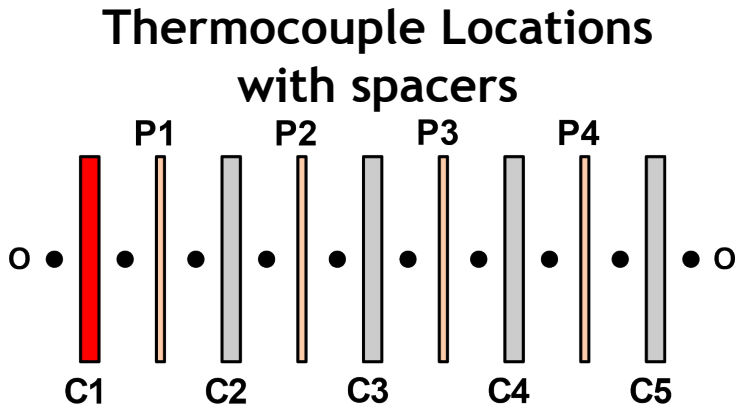
Failure initiated by a mechanical nail penetration in the outer cell (cell 1)

Thermocouples (TC) between cells and spacers (if present)









Torres-Castro, L., Kurzawski, A., Hewson, J., & Lamb, J. (2020). *Journal of The Electrochemical Society*, *167*(9), 090515.

Finite element model for Li-ion cells in thermal runaway

Model: SIERRA/Aria

Discretization in one direction (x)

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

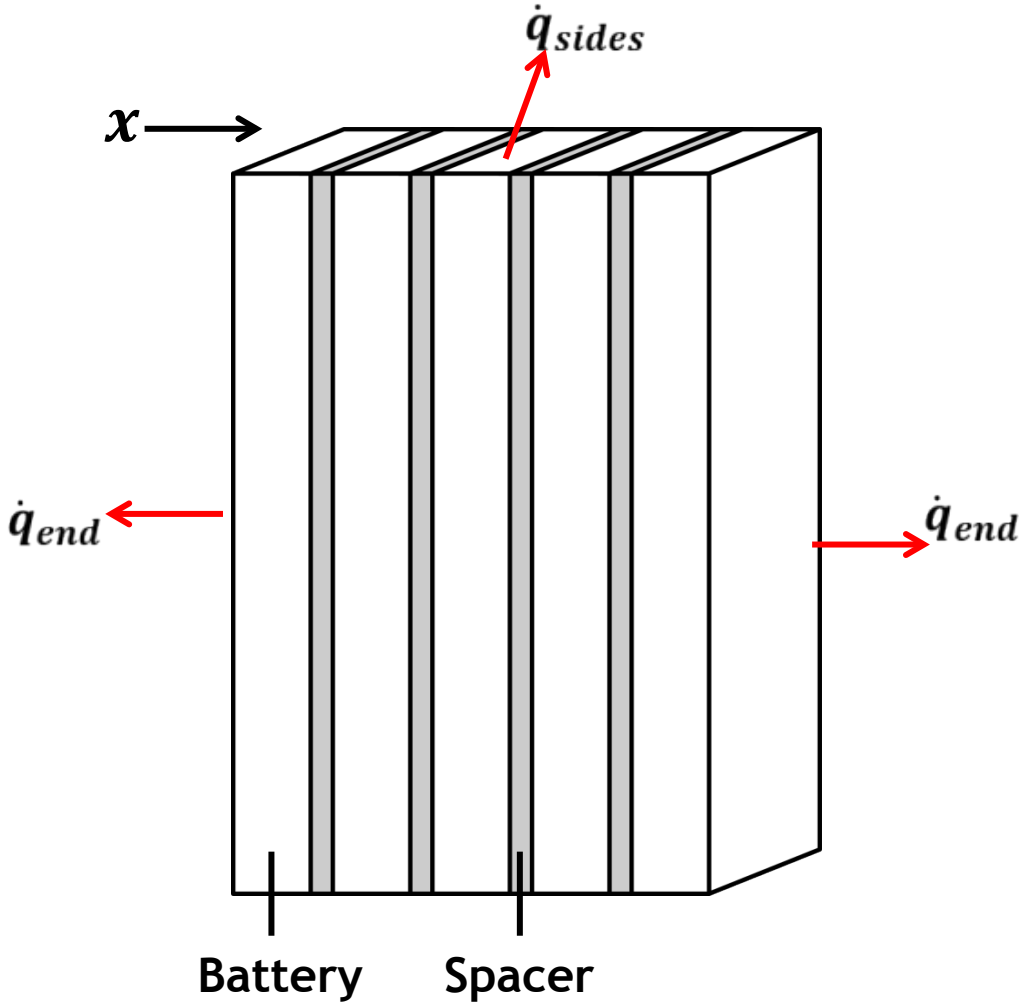
- $k_x \ll k_{yz}$

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:

$$\frac{\partial \rho_i}{\partial t} = \sum_{j=1}^{N_r} \left(\nu_{ij}'' - \nu_{ij}'\right) r_j$$

Energy source:

$$\dot{q}''' = -\sum_{j=1}^{N_r} \Delta H_j r_j$$

Chemical source terms for thermal runaway

Li-ion batteries contain a metal and oxidizer that can react with each other or alkyl carbonate electrolyte to release energy

These reactions occur at sub-grid scales and can be approximated as pre-mixed

Empirical chemical reactions:

- Short-circuit

$$C_6Li + CoO_2 \rightarrow C_6 + LiCoO_2$$

Metal and Oxidizer

- SEI decomposition (Richard 1999)

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + \frac{1}{2}O_2$$

- Anode-electrolyte (Shurtz 2018)

$$2C_6Li + C_3H_4O_3 \rightarrow 2C_6 + Li_2CO_3 + C_2H_4$$

Metal and Electrolyte

- Cathode-electrolyte (Hatchard 2001, Shurtz 2020)

$$5CoO_2 + C_3H_4O_3 \rightarrow 5CoO + 3CO_2 + 2H_2O$$

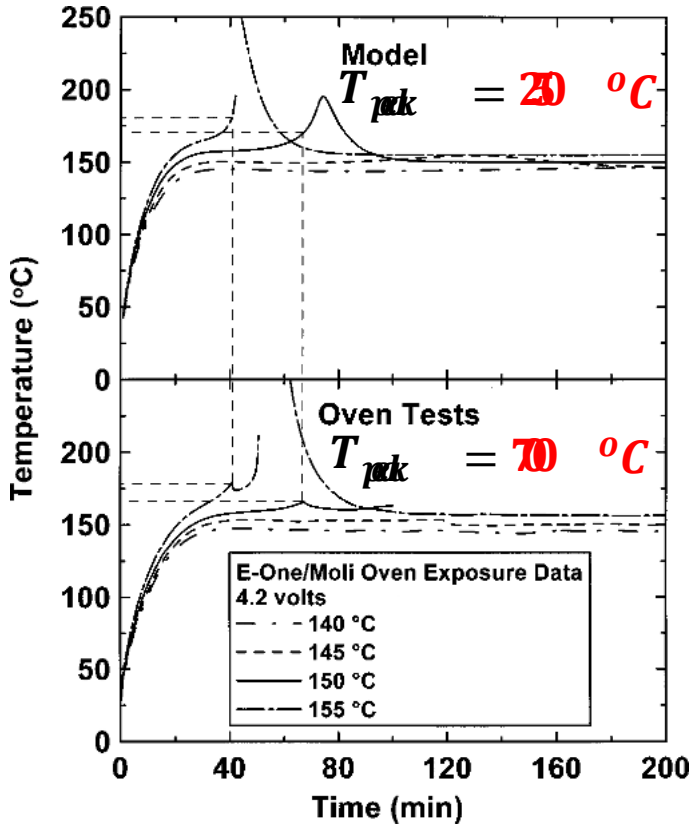
Oxidizer and Electrolyte

Richard, M. N., & Dahn, J. R. (1999). *Journal of The Electrochemical Society*, *146*(6), 2078.
Shurtz, R. C., Engerer, J. D., & Hewson, J. C. (2018). *Journal of the Electrochemical Society*, *165*(16), A3878.
Hatchard, T. D., MacNeil, D. D., Basu, A., & Dahn, J. R. (2001). *Journal of The Electrochemical Society*, *148*(7), A755.
Shurtz, R. C., & Hewson, J. C. (2020). *Journal of The Electrochemical Society*, *167*(9), 090543.

Chemical source terms for thermal runaway

Preliminary chemistry models from literature

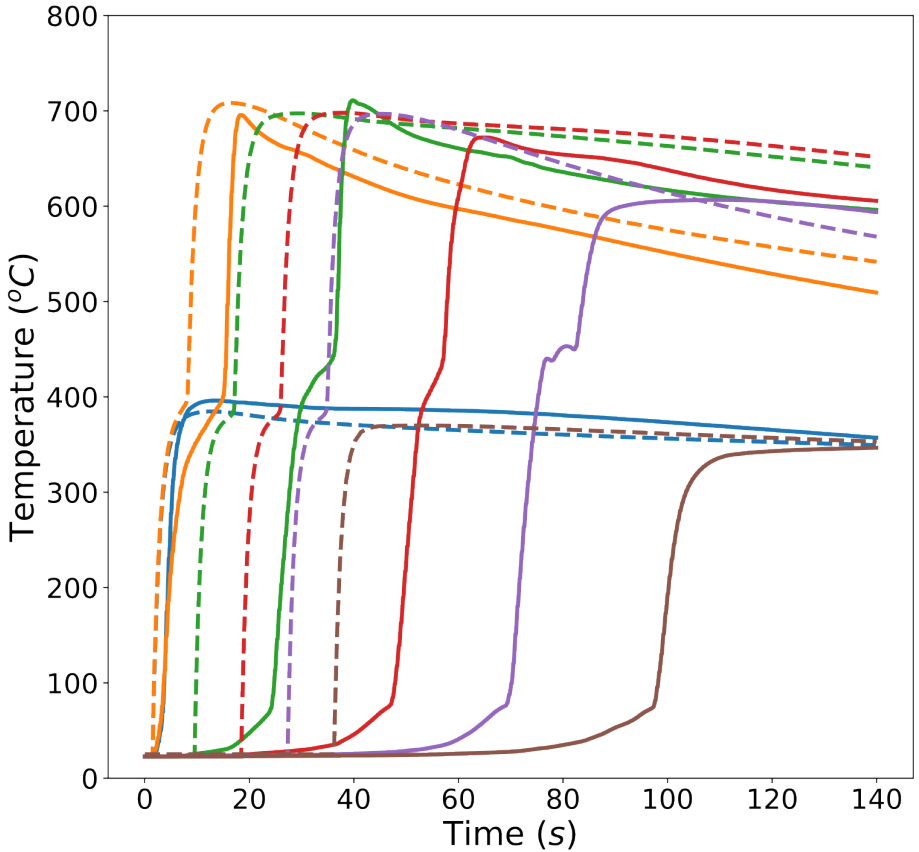
- Based on Dahn group (1999-2001)
- Calibrated for onset, but under-predicts peak temperature due to incomplete thermodynamics



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

Extrapolating literature models to cell-scale with updated thermodynamics

- Reaction rates at propagation temperature (~700°C) are over-predicted
- Velocity of a premixed flame: $v \approx \sqrt{\dot{\omega}\alpha}$



Species transport in electrode particles

Thermal runaway is analogous to very fast degradation

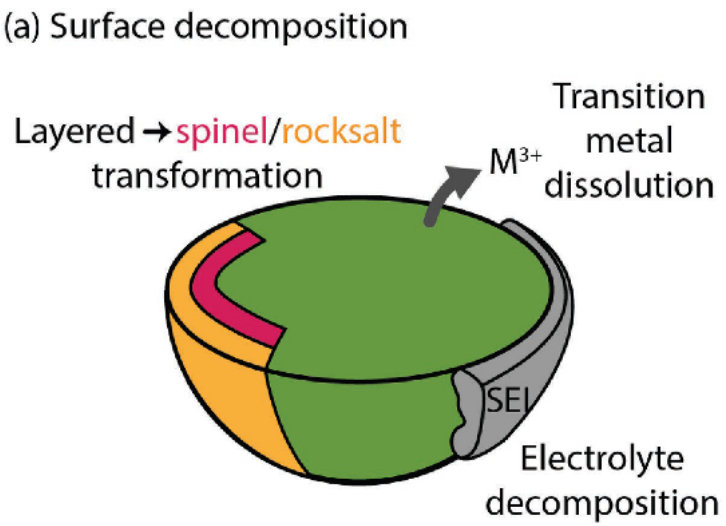
Radin et al. describe three cathode degradation methods that affect transport of Li and O_2 transport

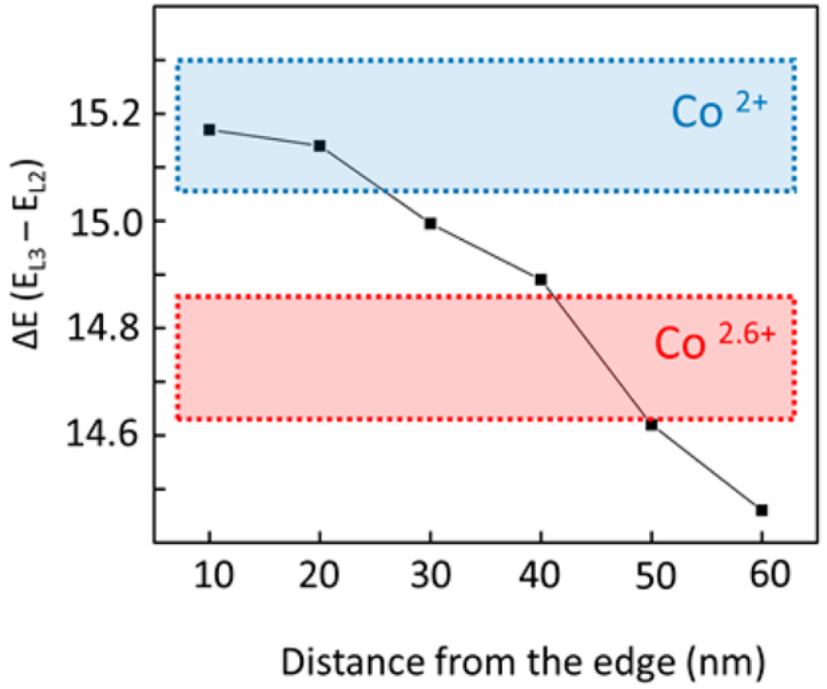
- Surface decomposition, bulk transformations to spinel, mechanical degradation

Sharifi-Asl et al. observed oxygen release occurs at the surface of cathodes where spinel (M_3O_4) and rock salt (MO) begin formation.

The phases grow from the surface towards the core of the particles, leaving O2 behind to diffuse to the surface.

Similarly in the anode, Li must diffuse through the graphite particle to react with electrolyte at the exposed surface.





Figures:
(top) Radin et al. (2017). *Advanced Energy Materials*, 7, 1602888
(bottom) Sharifi-Asl et al. (2017). *Nano Letters*, *17*, 2165-2171.

Model for solid-state particle diffusion limit

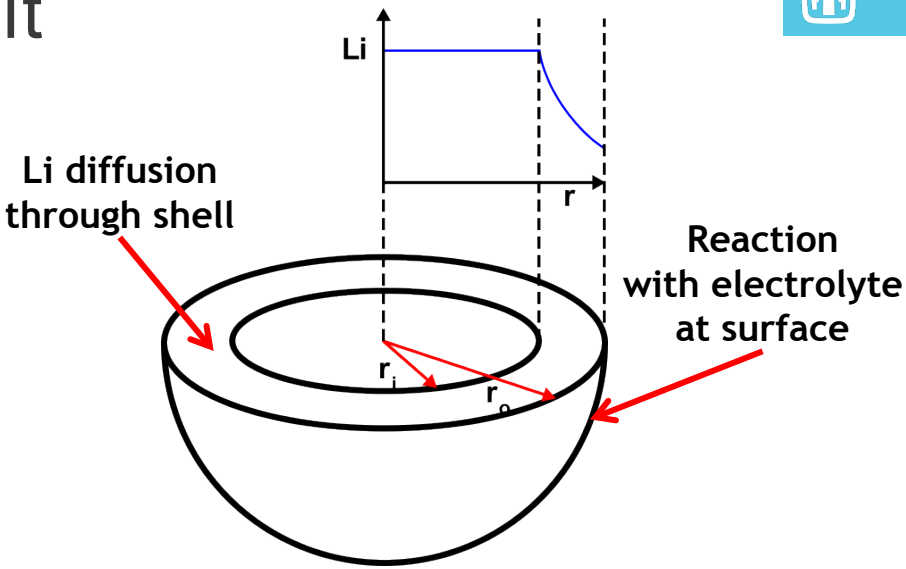
Challenge: Calorimetry measurements only at lower temperatures

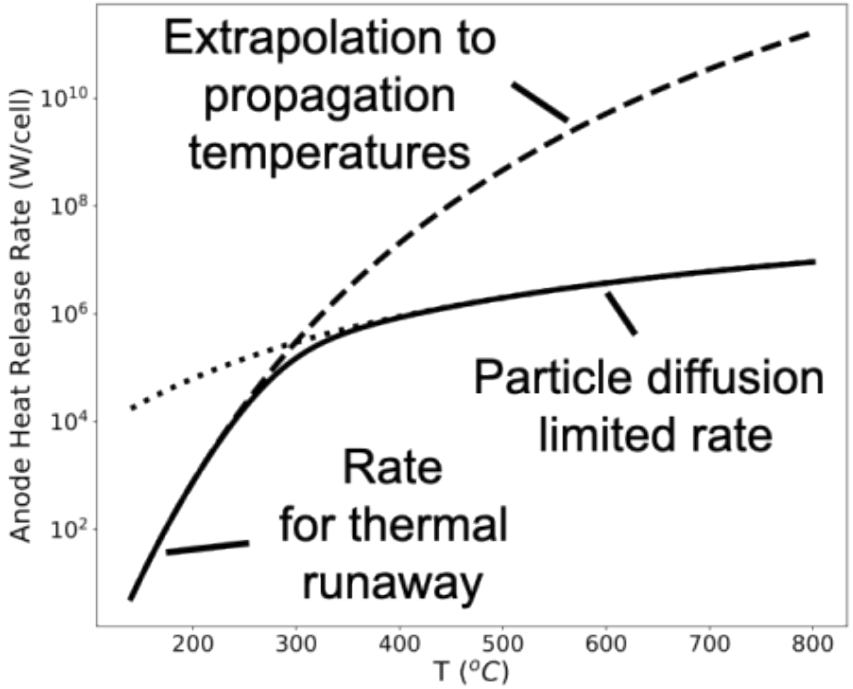
- Lithium and oxygen must diffuse to the particle surface to react with the electrolyte.
- Serial reactions are corrected with the "Damköhler limited" form.

$$k' = \frac{k}{1 + Da}$$

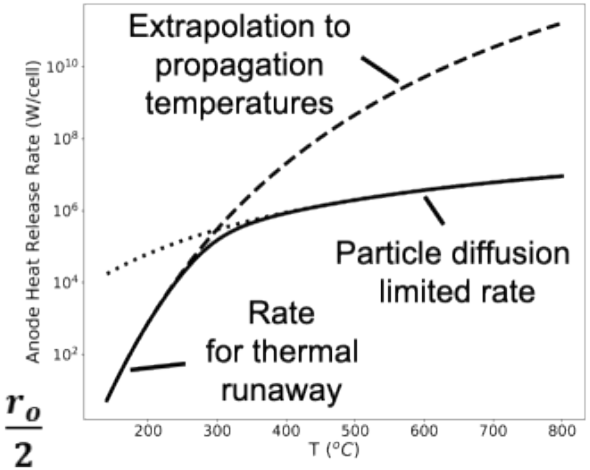
- The Damköhler number is ratio of surface reaction rate to the rate of diffusion between an inner radius (r_i) and outer radius (r_o).

$$Da = \frac{Aexp\left(-\frac{E}{RT}\right)}{a_e \rho D_o \exp\left(-\frac{E_D}{RT}\right)} \frac{(r_o - r_i)r_o}{r_i}$$

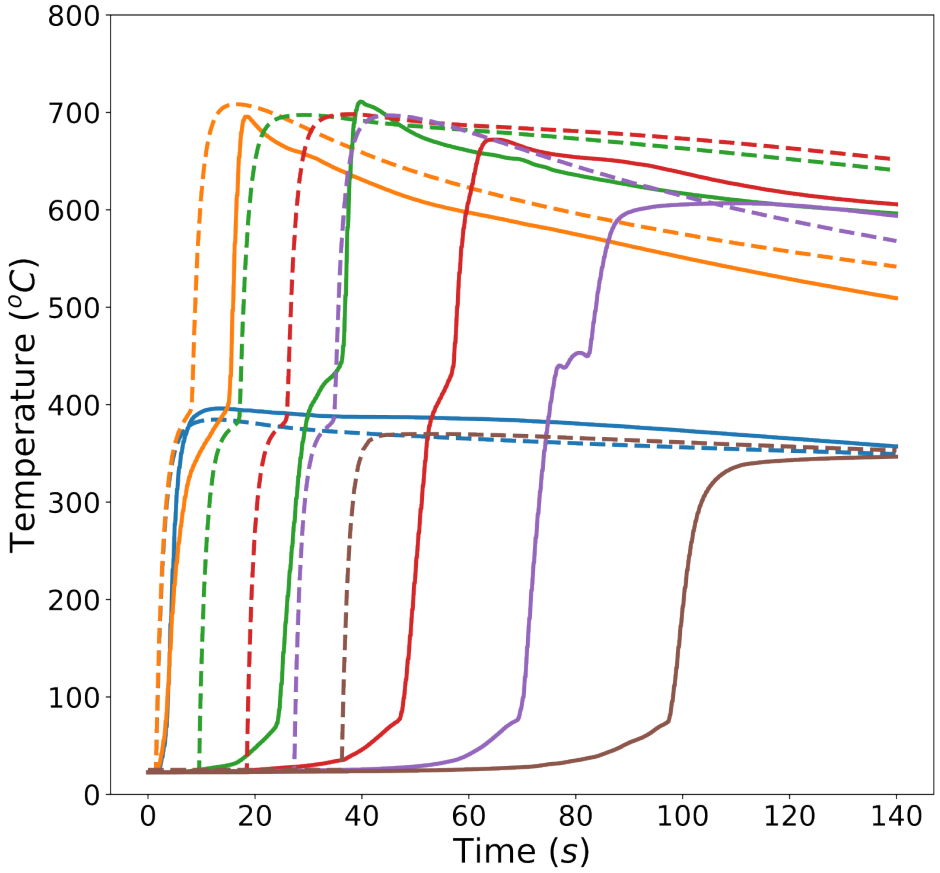




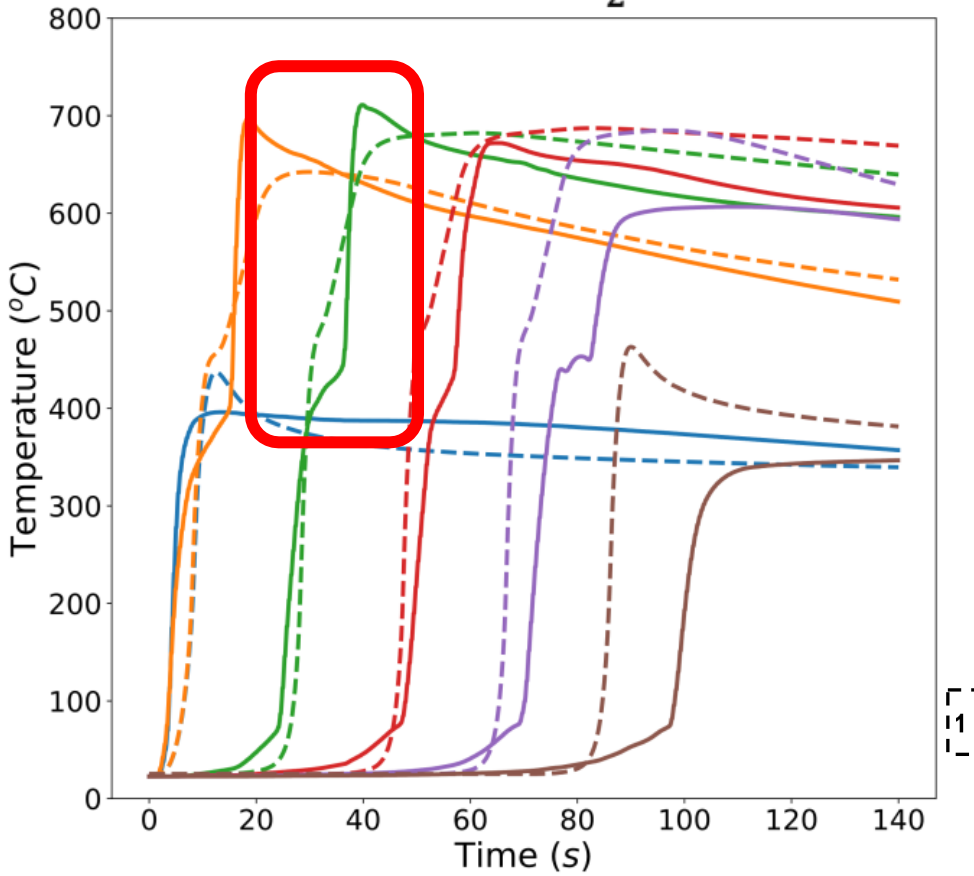
Five cell stack results: 100% SOC

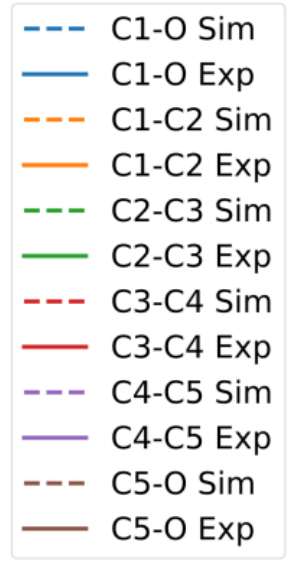


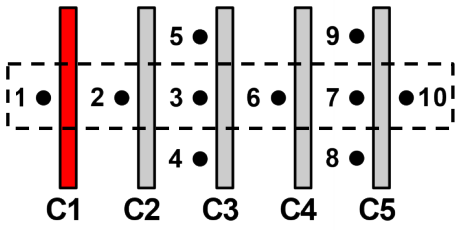
Literature Model



Fixed $r_i = \frac{r_o}{2}$





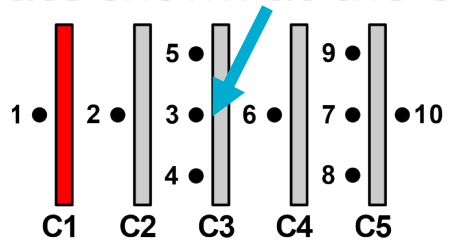


Model for solid-state particle diffusion limit

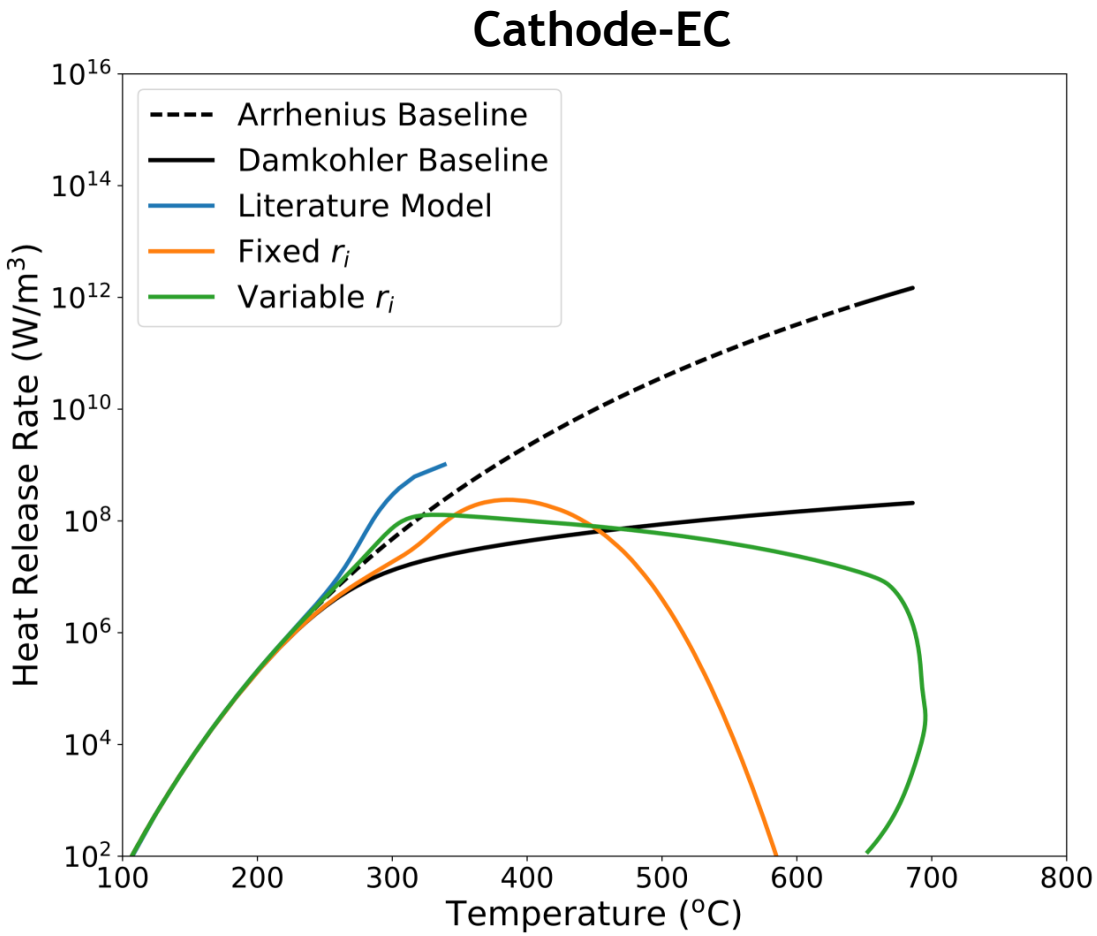
The inner radius as a function of species concentration (ρ_s).

$$\frac{r_i}{r_o} = \left(\frac{\rho_s}{\rho_{s,o}}\right)^{1/3}$$

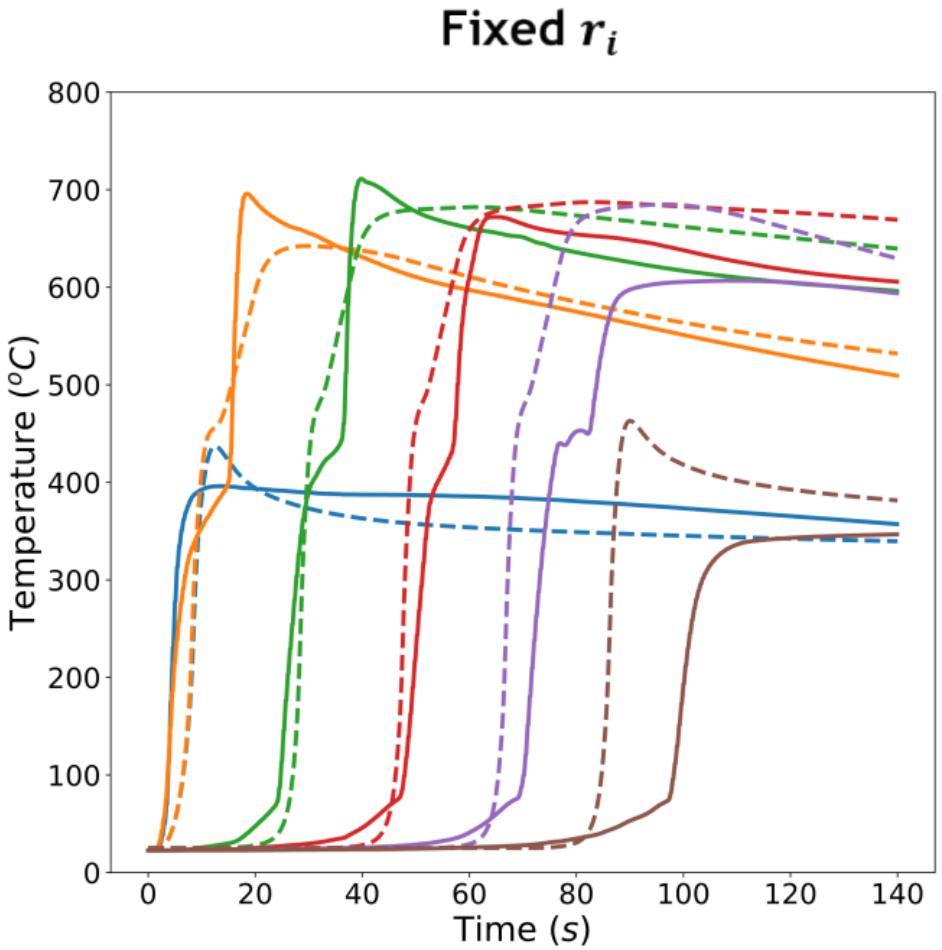
Ex: heat release rate shown at the edge of Cell 3 closest to Cell 2.

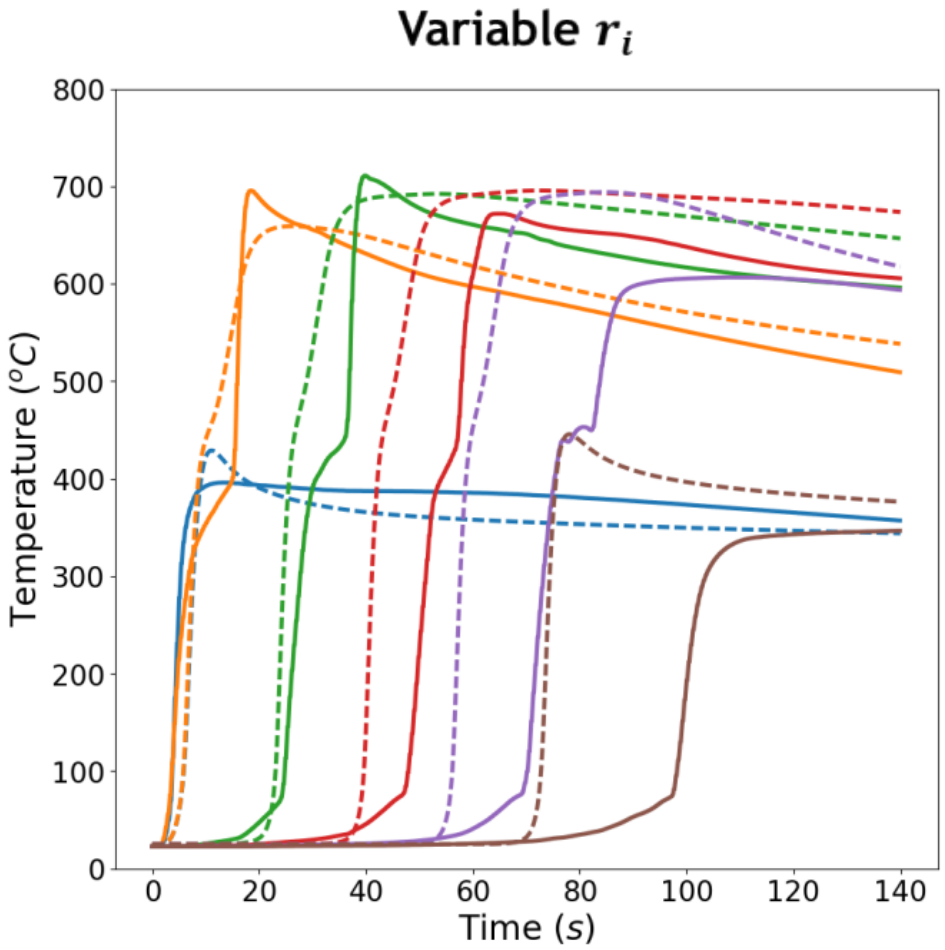


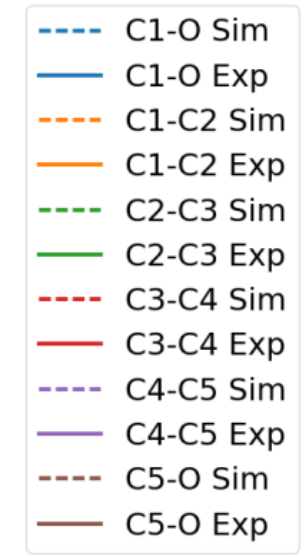
- Baseline rates exclude concentration dependence.
- Literature models propagate too fast.
- Fixed $r_i = 0.5r_o$ resulted in good bulk propagation predictions, but the initial rate is slow relative to experiments.
- Variable r_i model include concentration dependence for anode and cathode particles, r_o values from Guo 2002.

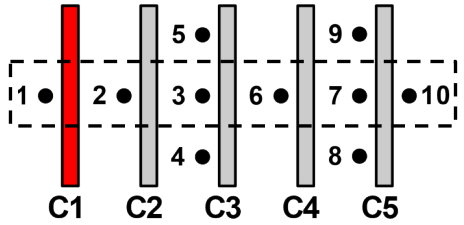


Five cell stack results: 100% SOC, no spacers

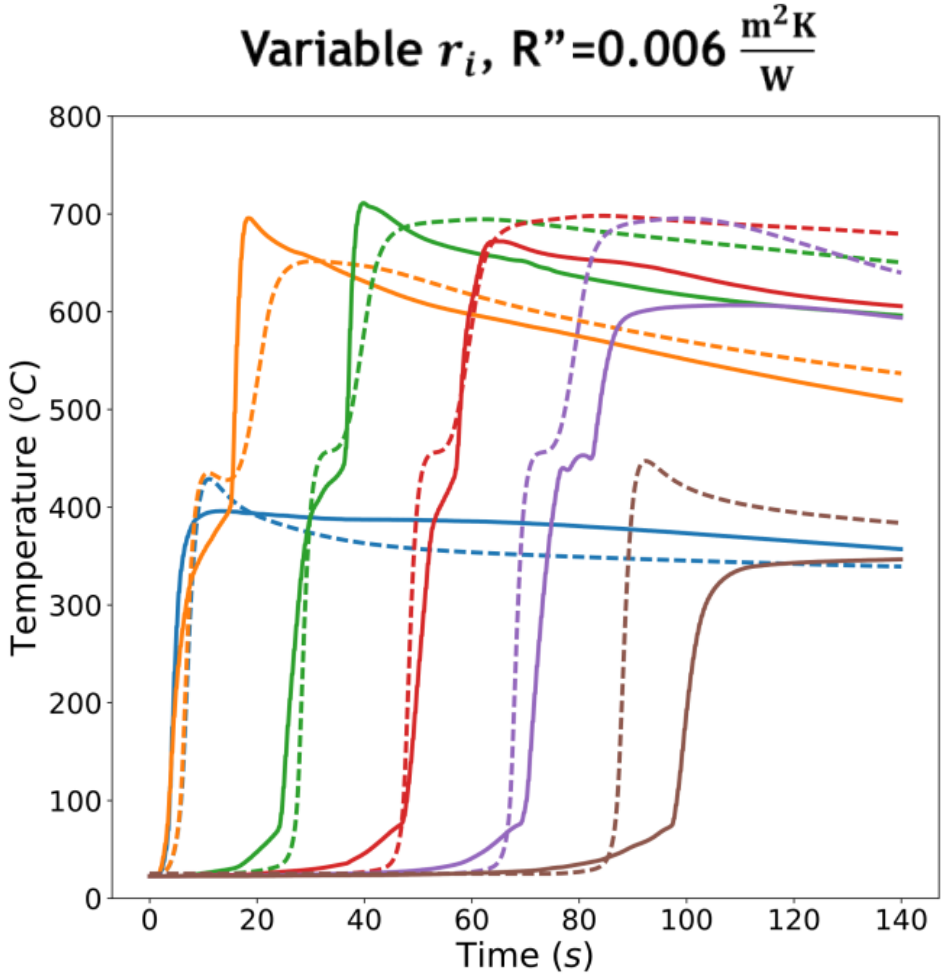


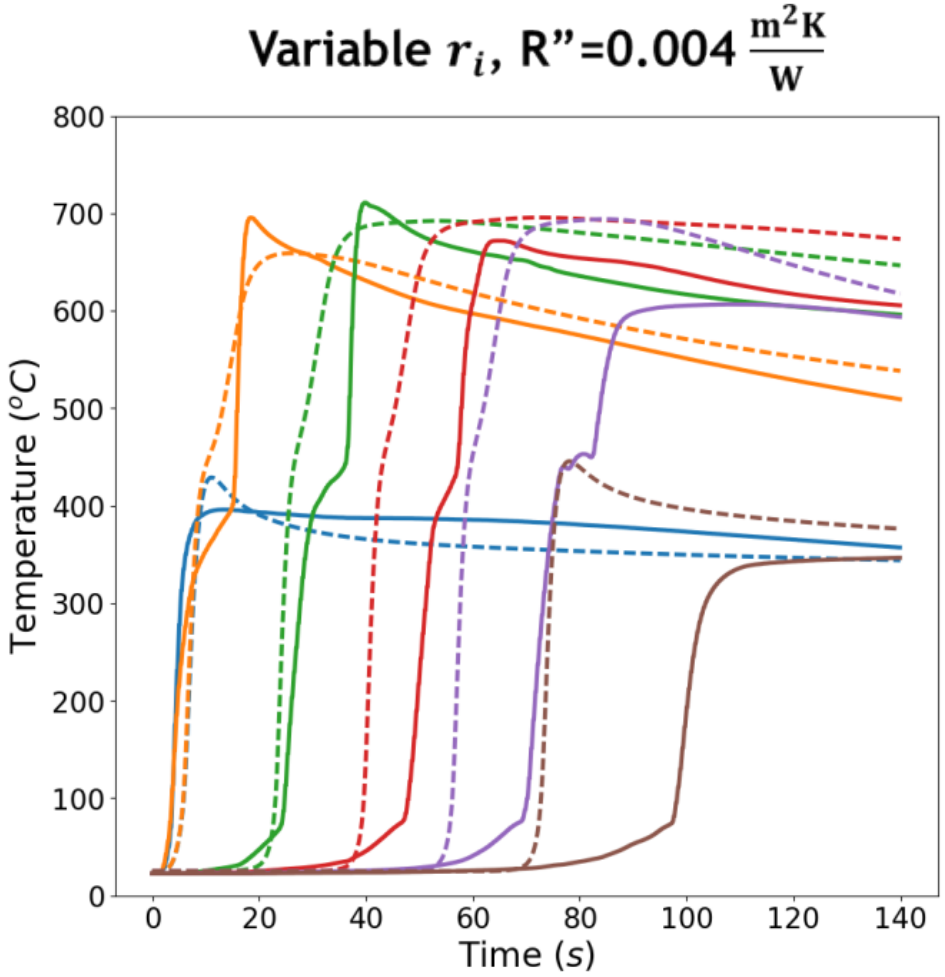


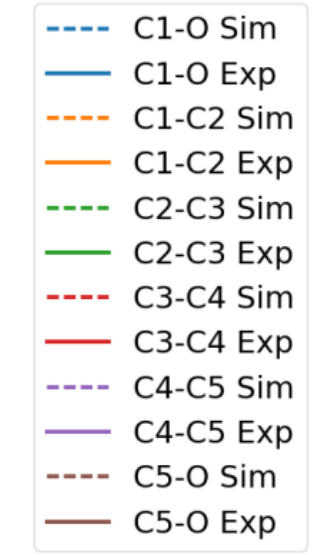


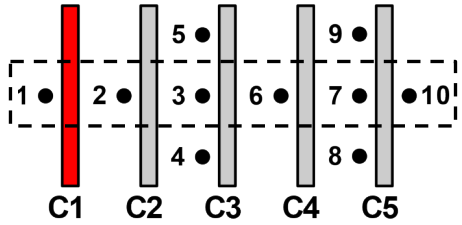


Five cell stack results: 100% SOC, no spacers

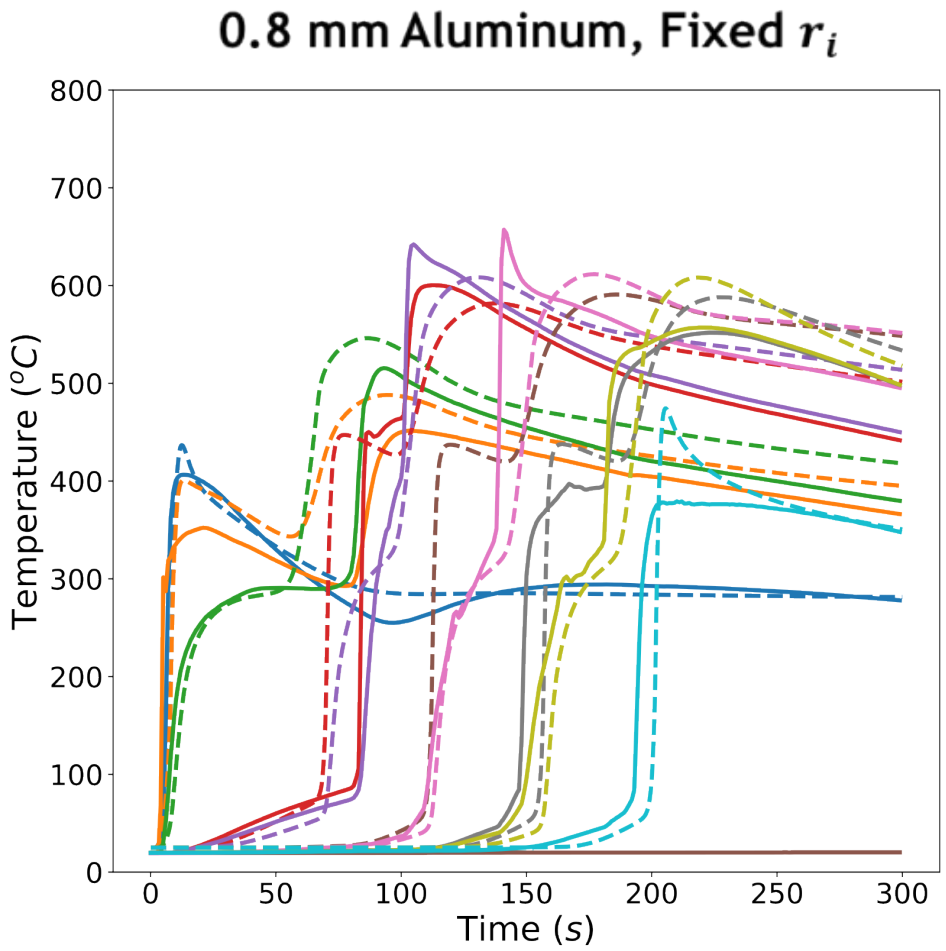


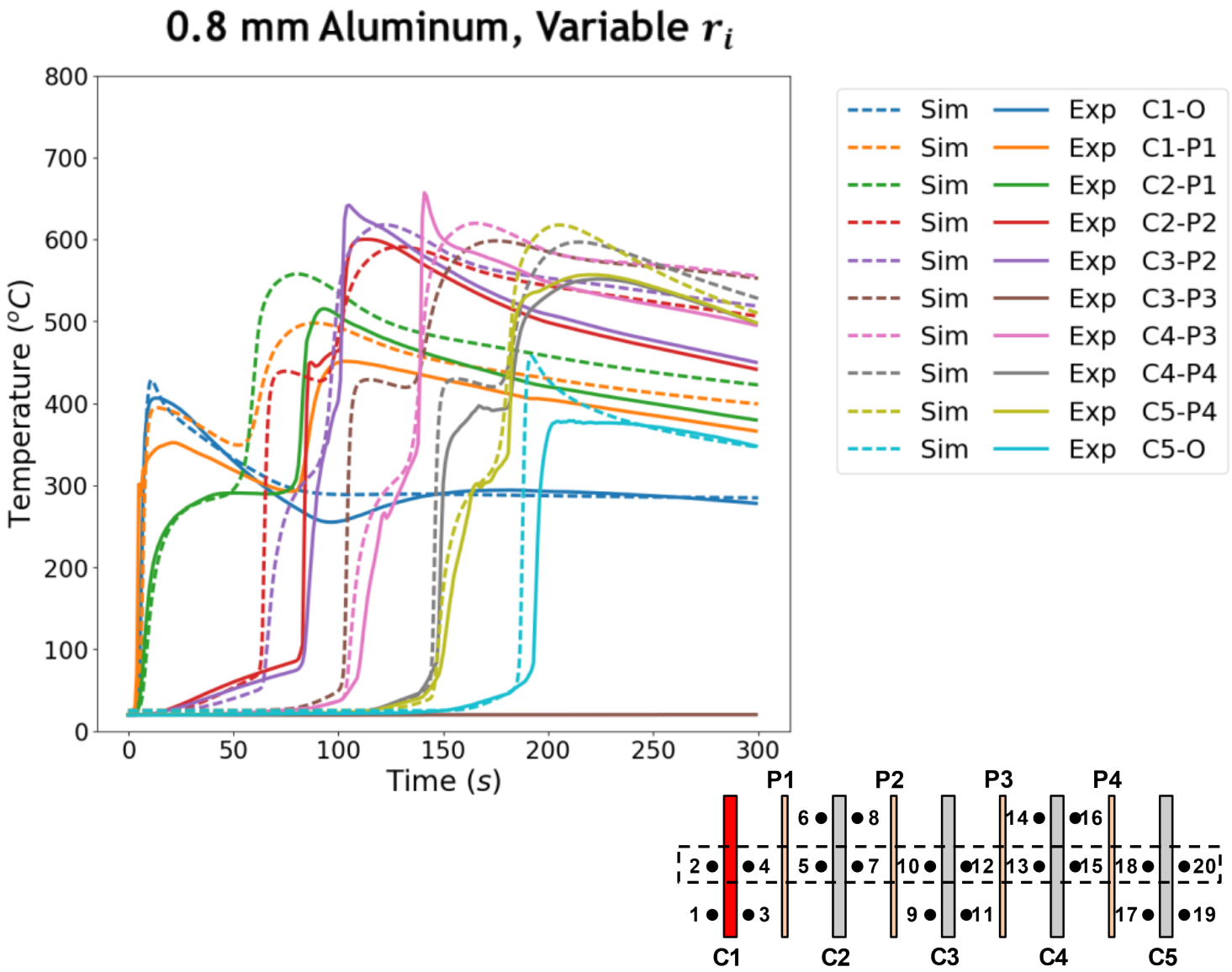






Results: 100% SOC, metallic spacers





Summary

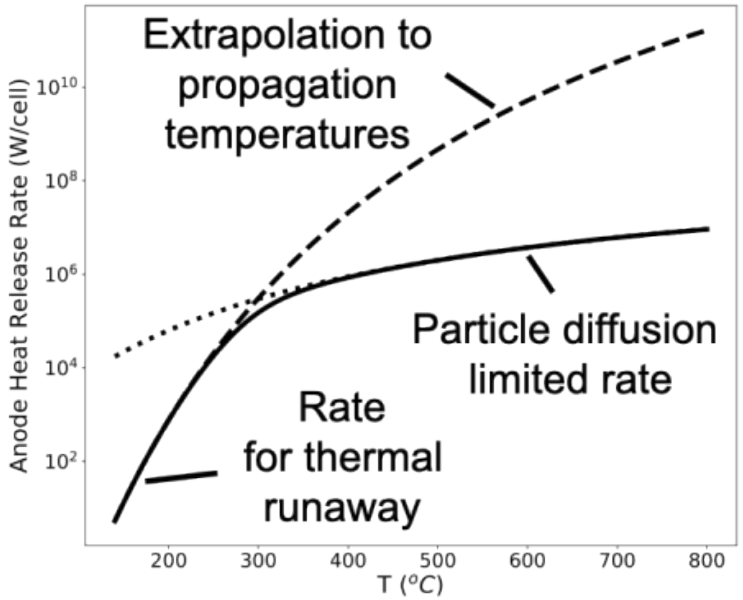
Using legacy chemistry source terms predicts onset of thermal runaway, but extrapolating this to higher temperature over-predicts cell-scale propagation speeds.

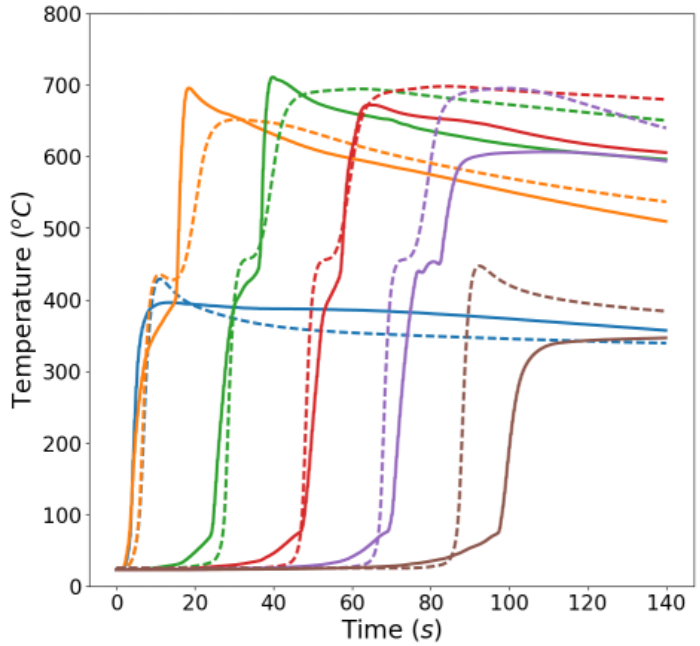
Results suggest that inclusion of intra-particle diffusion limits (or a similar change in the kinetics) becomes important for higher temperature cell-scale propagation.

Predictions of fixed and variable internal particle radius formulations were tested on a range of conditions with variable state-of-charge and passive mitigation spacers.

These results represent an extension of prediction capabilities to predict propagation and its limits over a range of thermal “dilution” conditions.

Understanding mitigation boundaries is important for designing safe energy storage systems.





Acknowledgements

This work is supported by US Department of Energy, Office of Electricity Energy Storage Program. We thank Dr. Imre Gyuk, Manager of the Energy Storage Program.