SAND2020-9994C

High-temperature kinetics of thermal runaway reactions

Andrew Kurzawski, Randy Shurtz, and John Hewson

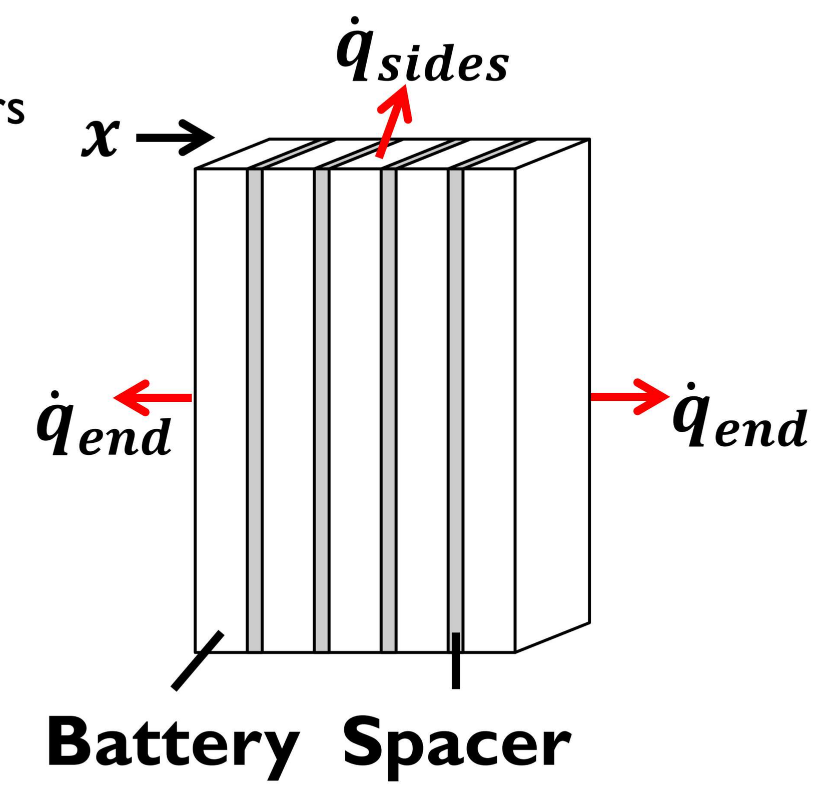
Fire Science and Technology, Sandia National Laboratories, Albuquerque, NM

Introduction

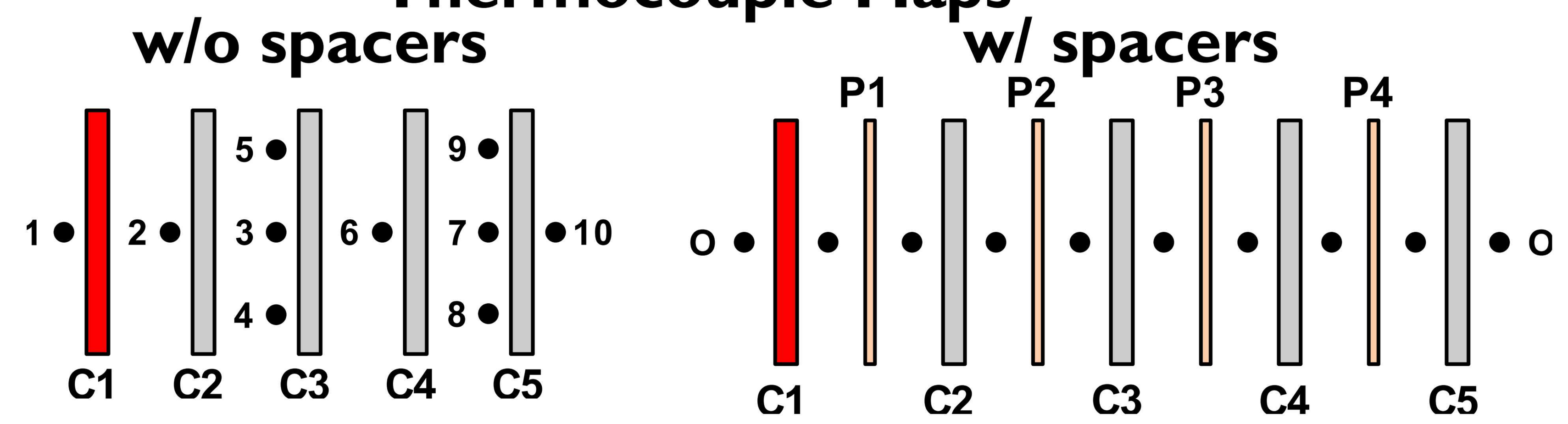
- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Models enable knowledge to be applied different scenarios and larger scales.
- Cascading failure in Li-Ion cells can be related to premixed flame propagation:
  - Negligible reactant diffusion
  - Propagation through stacks of cells is unsteady due to gaps
- Legacy models effectively predict onset of thermal runaway, but they struggle with high-temperature propagation.
- This work investigates applying an intra-particle diffusion limiter to runaway reactions within the cathode and anode materials.

Finite Element Model of Pouch Cells

- Discretization in one direction (***x***)
- Multi-layered system of batteries and spacers
- System of 5 LiCoO2 3 Ah pouch cells
- Empirical chemical reactions
  - SEI decomposition
  - Anode-electrolyte (Shurtz)
  - Cathode-electrolyte
  - Short circuit
- Experimental data
  - Nail penetration in first cell (C1)
  - State of charge (SOC) 50-100%
  - No electrical connections
  - Copper and aluminum spacers
  - Measured skin temperature with thermocouples between cells



Thermocouple Maps



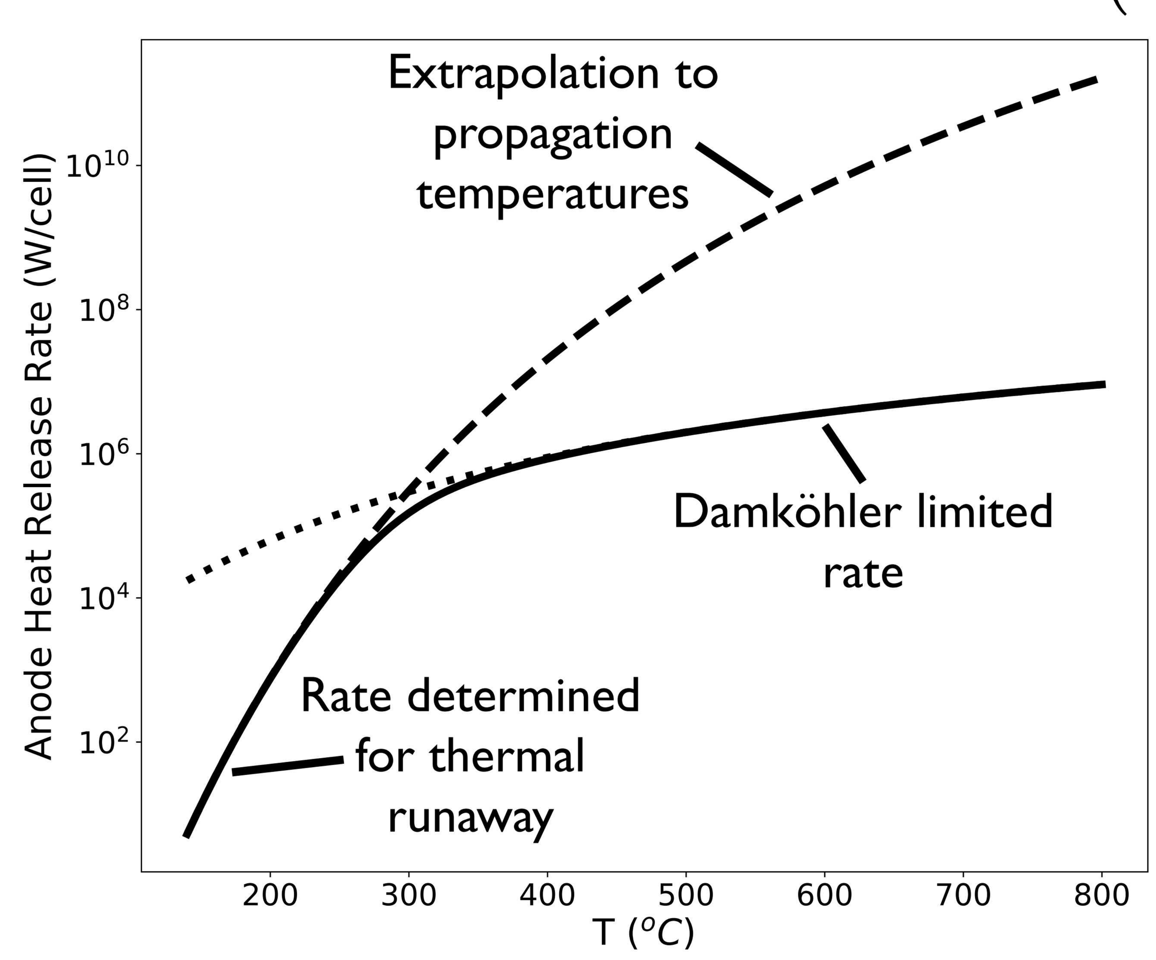
Limiting High-Temperature Rates

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

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

- Where the Damköhler number is defined as the ratio of the reaction rate at the surface of a characteristic particle to the rate of diffusion between an inner radius (r_i) and outer radius (r_o).

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



- The limiter is applied to lithium diffusion in the anode and oxygen diffusion in the cathode.
- Extrapolation of legacy reaction models to propagation temperatures results in over-prediction of propagation speed.
- Without the limiter, thermal runaway simulation propagates through all five cells over 2x faster than experiments.
- With the limiter, the propagation speed is comparable to experiments.

Damköhler Limiter Validation

100% SOC

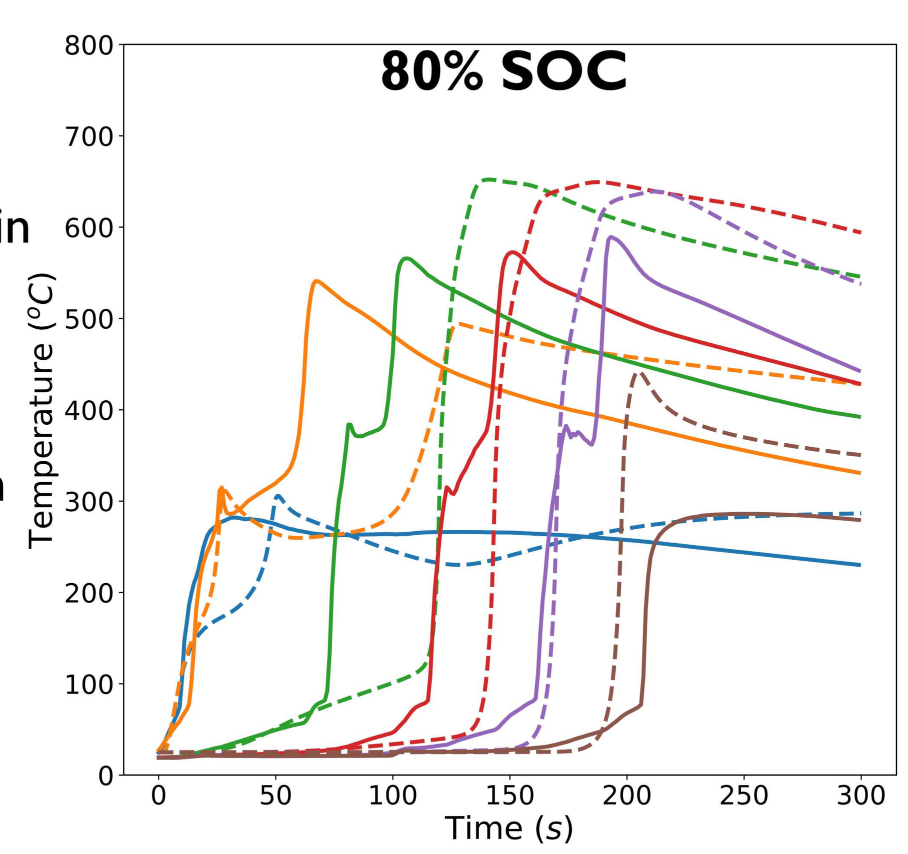
- Propagation speed is slightly over-predicted.
- Initiation of thermal runaway in each cell is slower in simulations.

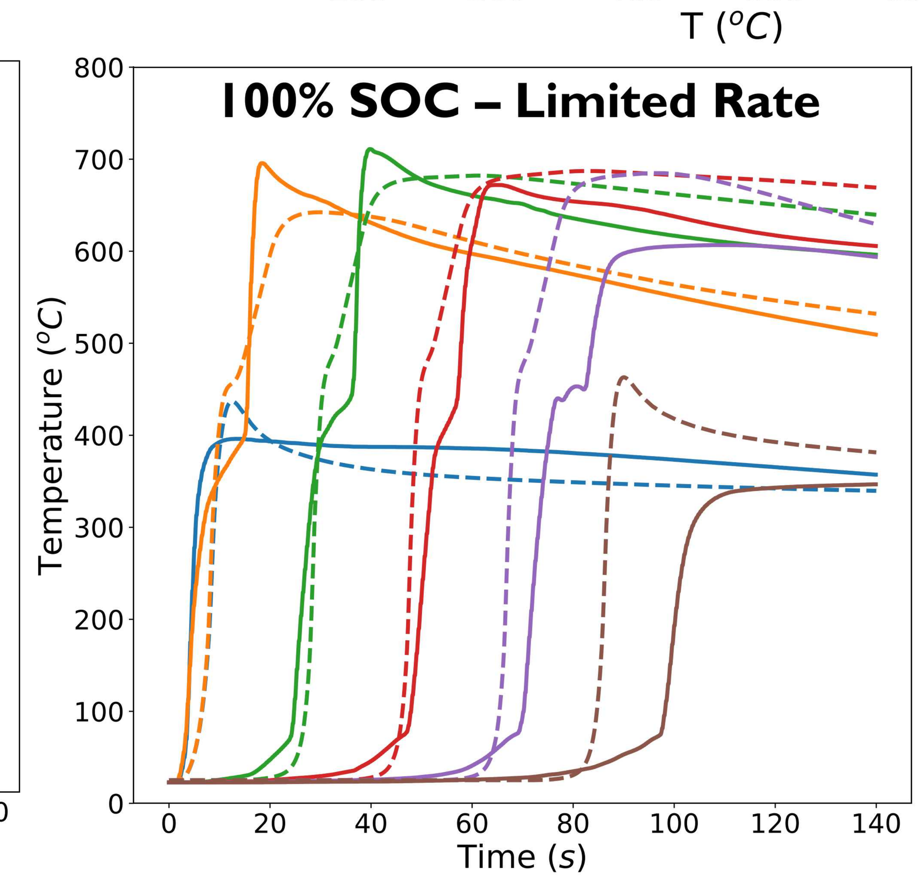
80% SOC

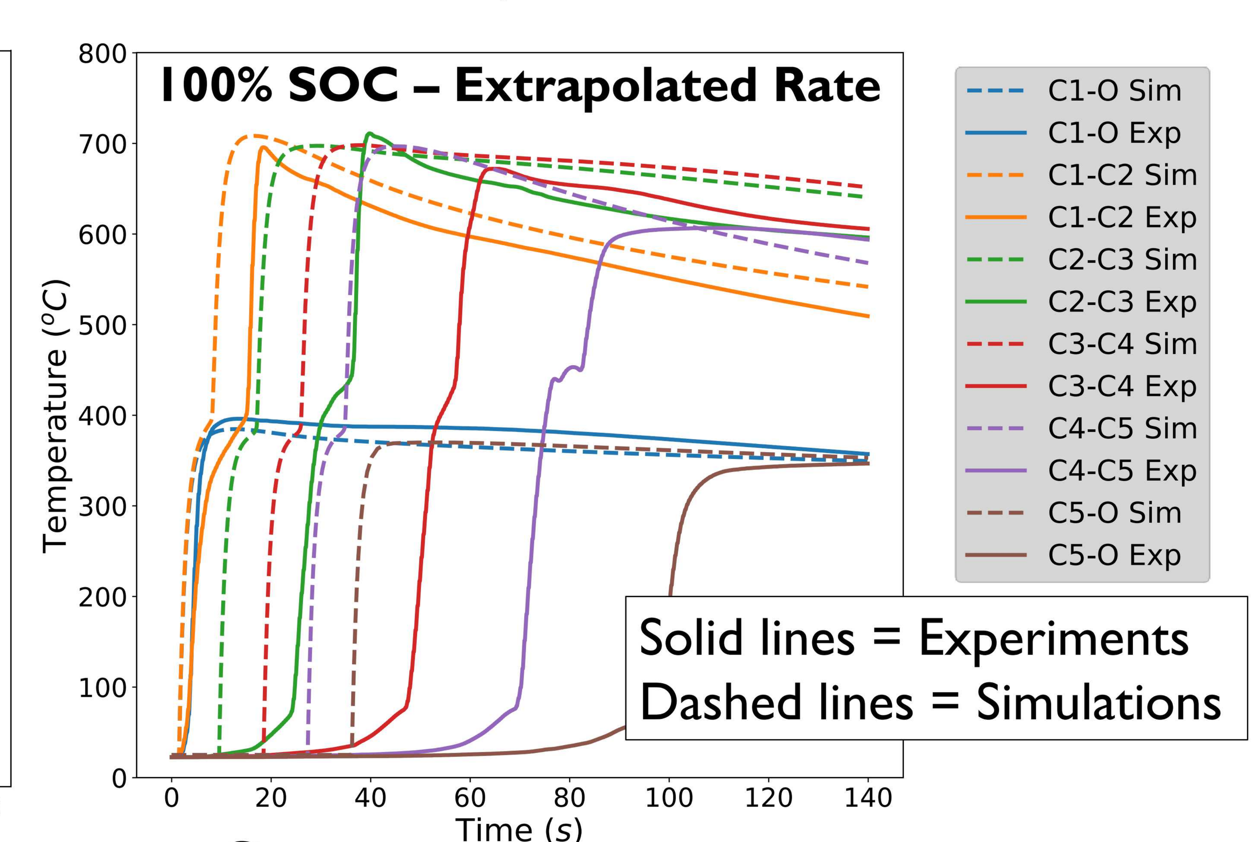
- Energy density decreases with a lower state of charge.
- Total propagation time is comparable between the simulation and experiment.
- Temperatures in cells 2-5 are over-predicted, suggesting uncaptured physics.

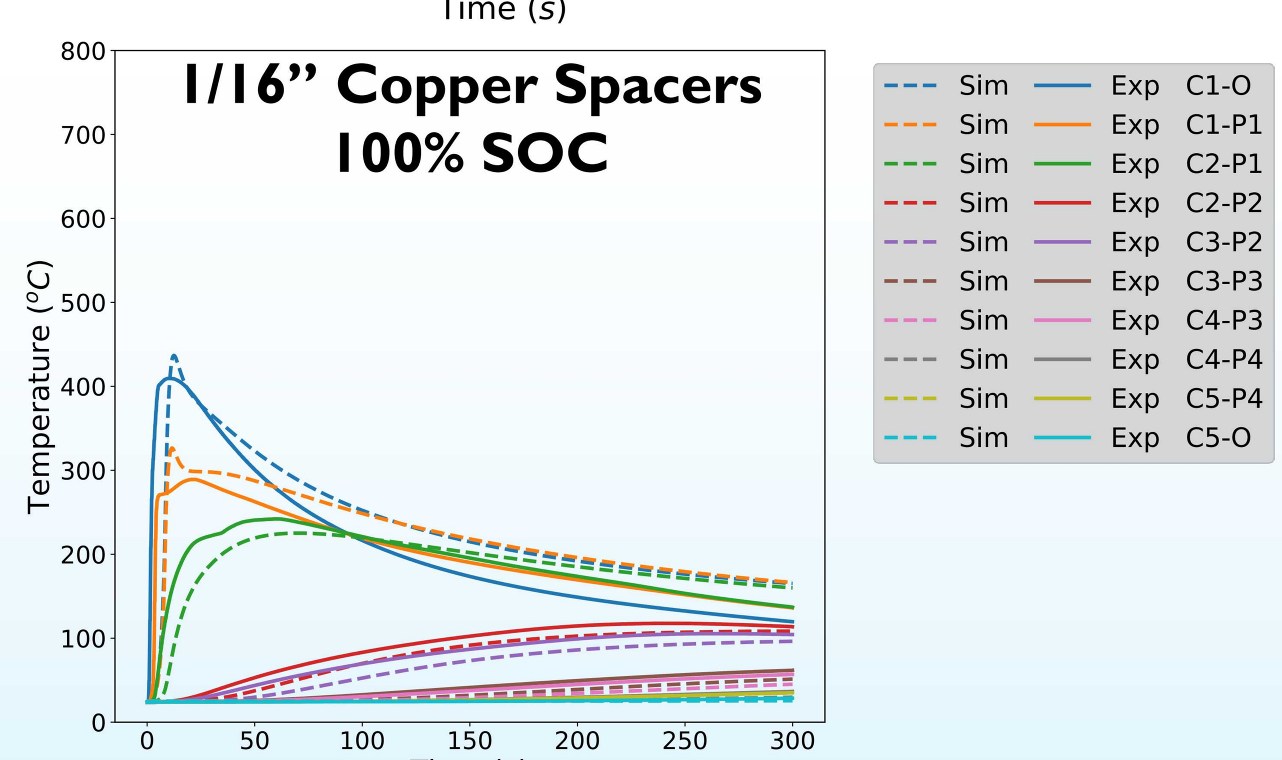
Aluminum and Copper Spacers

- Energy density decreases with the addition of spacers.
- Good prediction of propagation times.
- Decrease in energy density quenches propagation in both simulations and experiments (see 1/16" Cu Spacer plot).









Summary

- An intra-particle diffusion rate limiting model for the rate of thermal runaway in Li-ion batteries was proposed, characterized by the Damköhler number at the particle scale.
- The Damköhler limiter model correctly predicts the boundary of propagating thermal runaway with decreasing energy density due to reducing state of charge and the addition of inert spacer materials.
- This model offers an improvement over extrapolating legacy models to high temperatures as the onset behavior is preserved while the high temperature rates are reduced.
- Potential areas of improvement include the reaction rate at the onset of thermal runaway and the dependence of heat release on the SOC.

Acknowledgements:

- Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity
- Special thanks to the following people for providing experimental data, thoughtful discussions, and advice
- Loraine Torres-Castro, Joshua Lamb, Yuliya Preger, Jacob Mueller, and Alex Headley