High-temperature kinetics of thermal runaway reactions

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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.

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

- w/o spacers
- w/ spacers

Battery Spacer

1/16” Copper Spacers 100% SOC

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 unencapsulated 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).

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.
  \[ k' = \frac{k}{1 + Da} \]
  \[ Da = \frac{Ae}{a_0 D_o \exp{\left(-\frac{E_o}{RT}\right)}} \frac{(r_o - r_i) r_i}{T_i} \]

- 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.

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.

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