International Conference on Numerical Combustion
Rome, Italy, October 14-17, 2025
www.icnc2025.com

Bridging Experiment and Simulation: Advancing Thermal Runaway Understanding in Lithium Metal Batteries

Juyoung Oh[1]*, Ming Tang[1]
*lead presenter: jo57@rice.edu
1 Rice University, Department of Materials Science and Nanoengineering, USA

To simulate thermal runaway (TR) in lithium-based batteries, most mathematical models employ Arrhenius-based reaction kinetics and simplify total heat generation as the sum of independent contributions from each component (e.g., solid electrolyte interface (SEI) decomposition, electrodes, electrolyte) [1-3]. However, real systems involve complex interactions, such as anode reactions with both electrolytes and cathodes, which significantly affect heat generation. Thus, the accuracy of TR simulations critically depends on accurate heat modeling, measured heats of reaction, and estimated kinetic parameters. As these are typically derived from calorimetric studies, a thorough understanding of the underlying chemical reactions and precise thermochemical characterization is essential.

Lithium metal batteries (LMBs) are strong candidates for next-generation energy storage systems due to their high theoretical capacity. However, their extreme thermal sensitivity and complex reaction pathways, mainly driven by the high reactivity of Li, pose significant challenges to understanding TR mechanisms. While extensive research has been conducted on the TR behavior of lithium-ion batteries (LIBs), limited data exist on the high-temperature reactivity and TR mechanisms of LMBs, highlighting the need for systematic investigation.

The current study systematically analyzes the chemical reactions between Li metal anodes and two key battery components, carbonate electrolytes and NMC cathodes, under elevated temperatures using differential scanning calorimetry (DSC). For Li-electrolyte systems, the onset of reactions was highly solvent dependent, reflecting variations in the thermal stability of SEI. Following the SEI breakdown, triggered by Li melting at 180℃, a rapid increase in heat flow was shown. The reaction released up to -67.0 kJ/g Li near the stoichiometric Li-to-electrolyte molar ratio of 1:2.5, comparable to that of solid propellants. For Li-cathode systems, thermite-like reactions were evident even in pristine materials, with exothermic reactions initiating around 300-320℃ and releasing around -10 to -15 kJ/g Li. Early-reacted cathode particles acted as local hot spots, allowing heat-driven propagation to adjacent particles. Notably, the heat from Li-electrolyte reaction alone was sufficient to rapidly elevate cathode particle temperatures beyond 300℃, thereby accelerating further reaction propagation.

These results demonstrate that LMBs are susceptible to catastrophic failure under thermal abuse, even in fully discharged states, due to the fuel-like behavior of Li metal and the oxidizing nature of carbonate electrolytes and transition metal oxide cathodes. This emphasizes the necessity of incorporating thermite-like reaction mechanisms and Li phase transitions into TR models. Furthermore, simulating TR from fully discharged states is crucial for accurately understanding state-of-charge (SOC)-dependent TR pathways and ensuring reliable safety assessments.

References

[1] Wang G et al. Advances and challenges in thermal runaway modeling of lithium-ion batteries. The Innovation. 2024; 5(4):100624.
[2] Parhizi M et al. Determination of the core temperature of a Li-ion cell during thermal runaway. The Journal of Power Sources. 2017; 370: 27-35.
[3] Singh BP et al. Improved internal short circuit models for thermal runaway simulations in lithium-ion batteries. APL Energy. 2025; 3(1):016102.