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# Are Solid-State Batteries Safe? A Thermodynamic Analysis

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DOE OE Energy Storage Peer Review

10/11/2022 – 3:55 PM

SAND2022-1407 PE

# Project Objective: Safety of Advanced Li-ion Batteries

1. Are All-Solid-State Batteries (ASSBs) inherently safe?
2. Can a small amount of liquid electrolyte be used in a Solid-State Battery (SSB) without significantly impacting its safety?
    - *Interfacial resistance is a major challenge in SSB development*
3. Experimental validation of thermal modeling study.

***Alignment with Core Mission of DOE OE***

*OE leads the Department of Energy's efforts to ensure a resilient, reliable, and flexible electricity system. Advanced Li-ion technologies may offer lower-cost grid energy storage. It is important to understand the safety implications of these technologies to ensure resilience, reliability, and flexibility.*

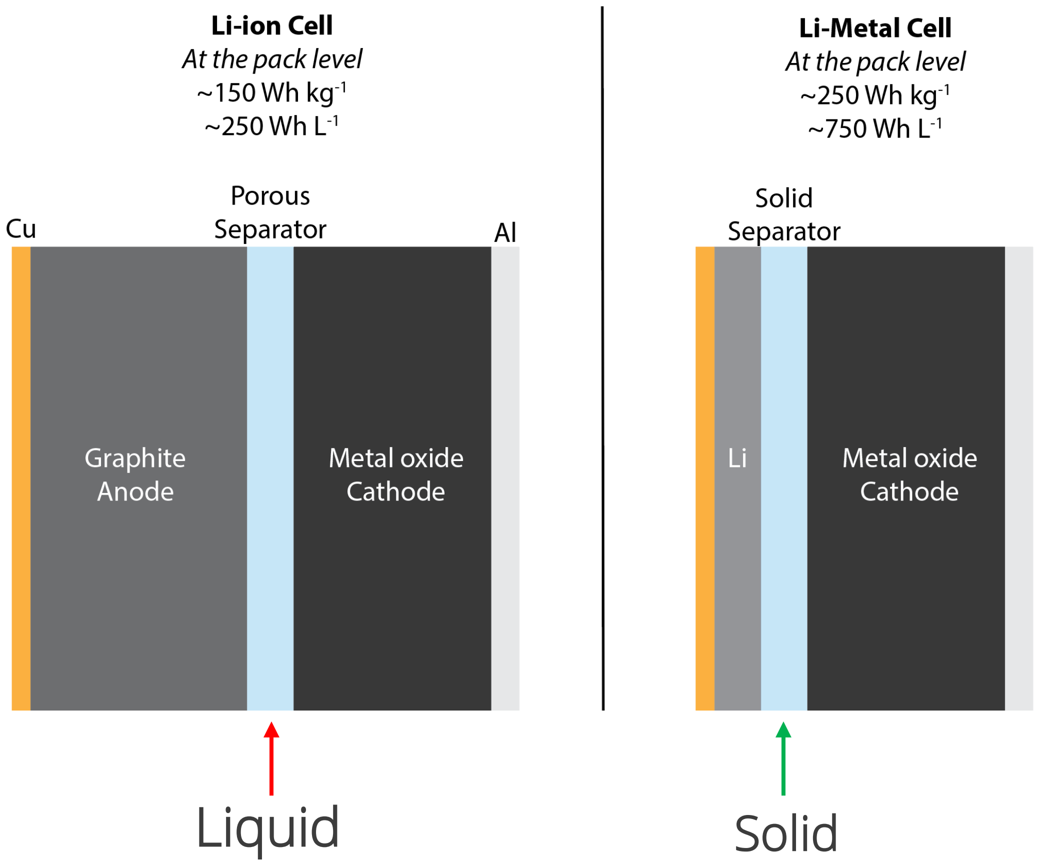
# Background: Solid-State Batteries

## Liquid Electrolyte (LE)

- High ionic conductivity
- Fills void spaces
- Several heat release pathways
- Flammable solvent

## Solid Electrolyte (SE)

- Sufficient ionic conductivity
  - Highly material dependent
- Non-flammable
- Poor interfacial contact

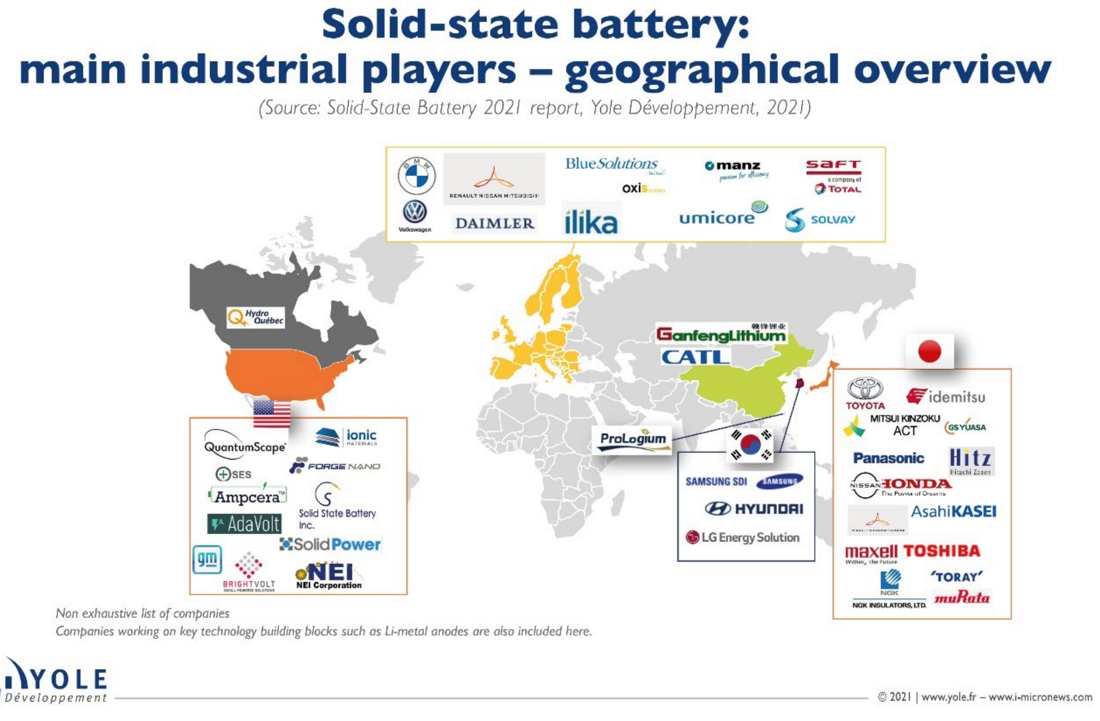



Albertus, P., Babinec, S., Litzelman, S. et al. Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries.

# Why the Excitement?

## Two Primary Advantages

- Energy density
  - Li-metal anode
- Safety
  - Replacement of flammable liquid electrolyte

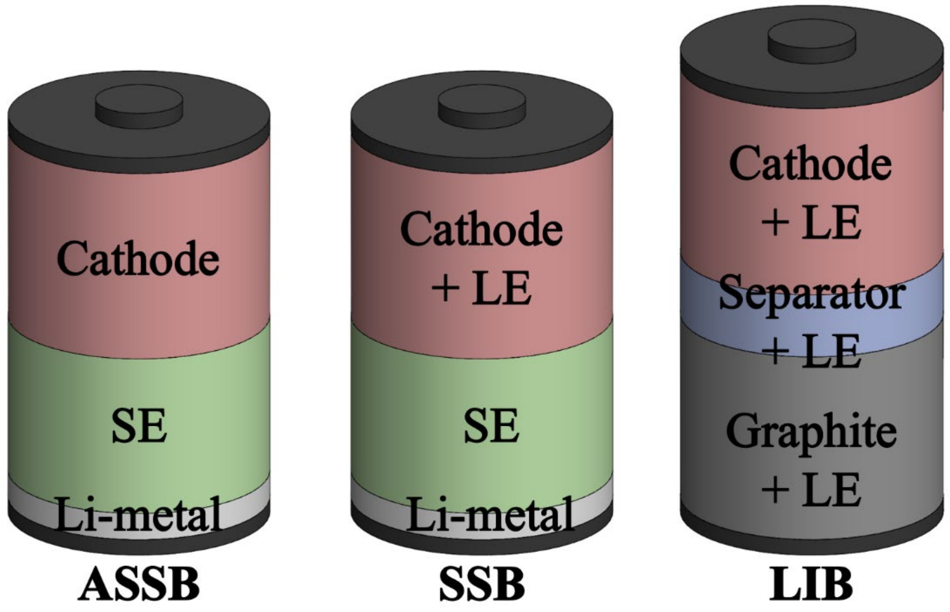



er 27, 2021

Miller T. 247 News Bulletin. 2022 April 30, 2022.

# Project Scope: Thermodynamic Model

- Safety quantified through thermodynamic calculations of heat release
  - ASSB vs. SSB vs. LIB (Li-ion battery)
    - Cathode – NMC111
    - Solid electrolyte - LLZO
    - Liquid electrolyte – $LiPF_6$ in EMC
    - Anode – Graphite or Li-metal
  - Different failure conditions
    - External heating
    - Short circuit
    - Mechanical failure of the solid electrolyte (SE)
  - Ignore details of geometry and casing



# Project Results:
# Heat Release vs. Liquid Volume Fraction (VF)

All: short circuit heat release equal

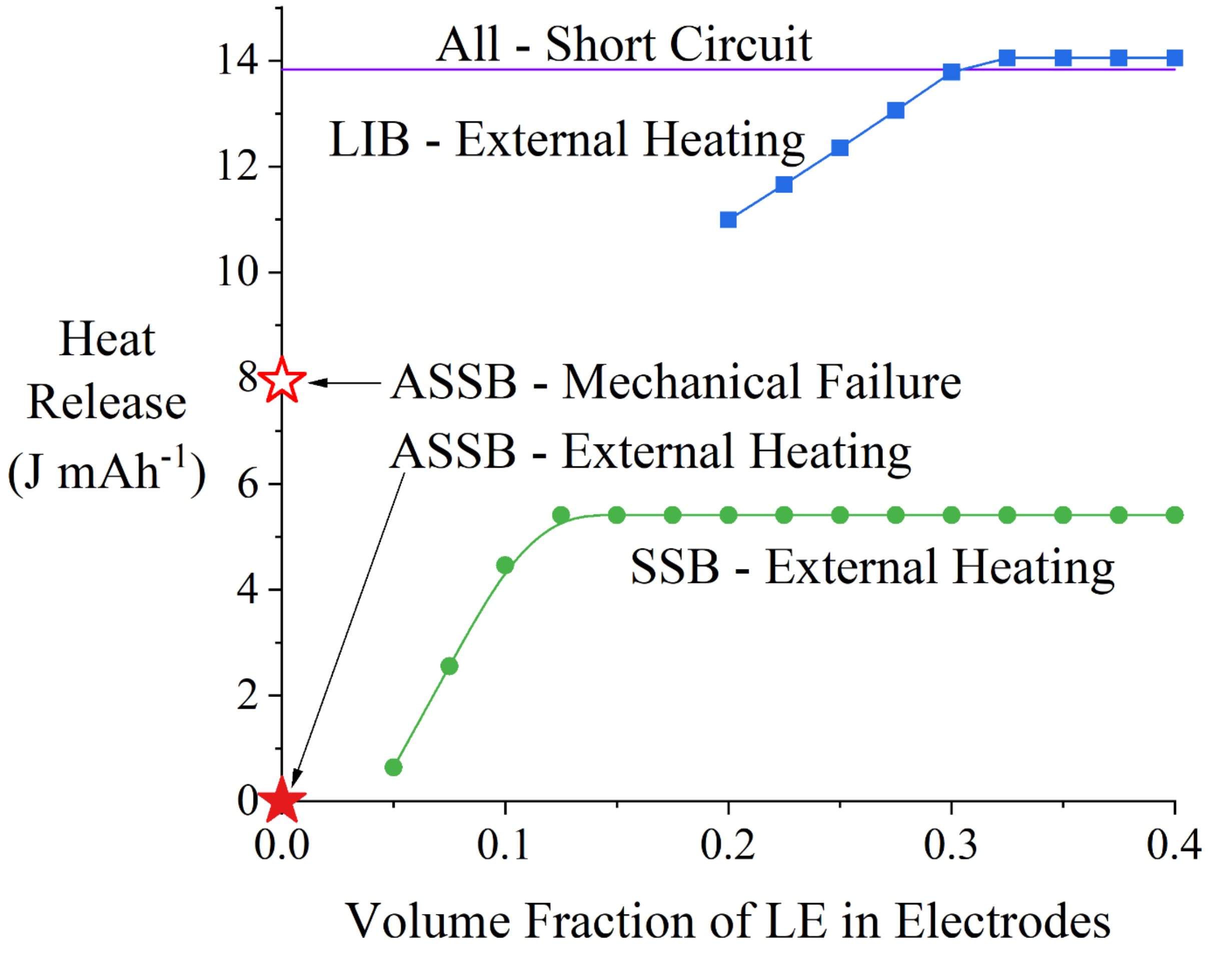
ASSB: no heat release from external heating

LIB: heat release dependent on VF (20 to 40%)

SSB: Heat release negligible <8% VF

- Cathode pores filled with SE

ASSB: large heat release on SE mechanical failure



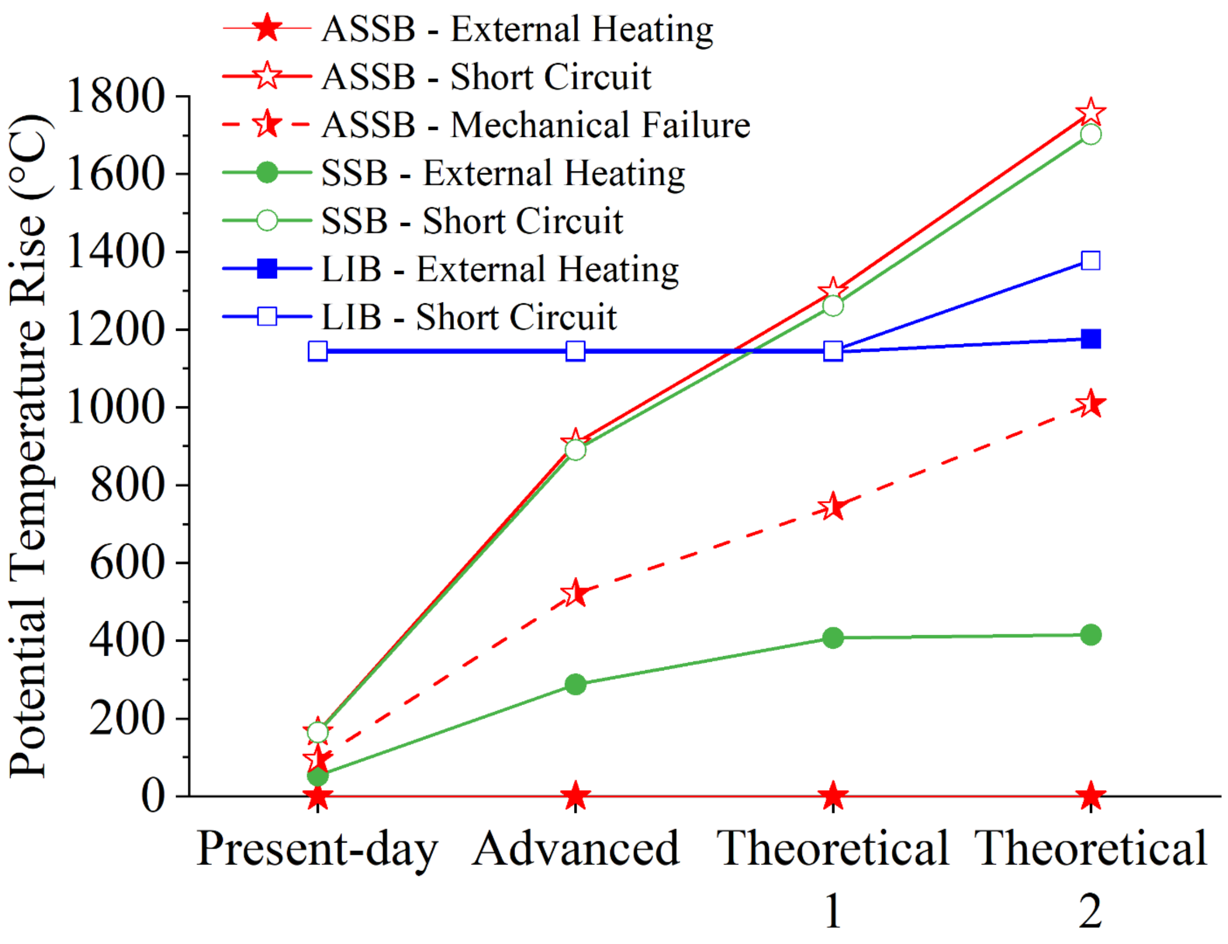
# Project Results:
# Potential Temperature Rise

External Heating: LIB highest

SSB below typical propagation

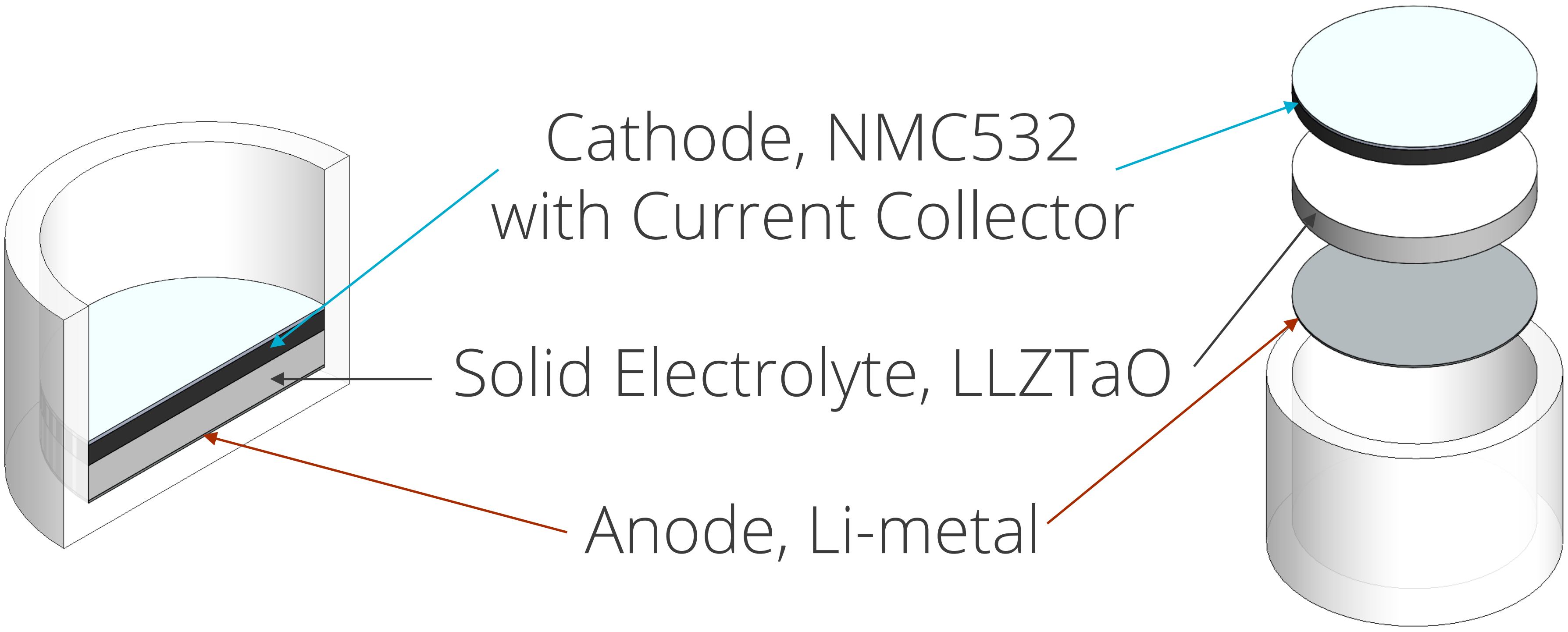
Short Circuit: ASSB/SSB exceeds LIB at Theoretical 1

Mechanical Failure: ASSB approaches LIB



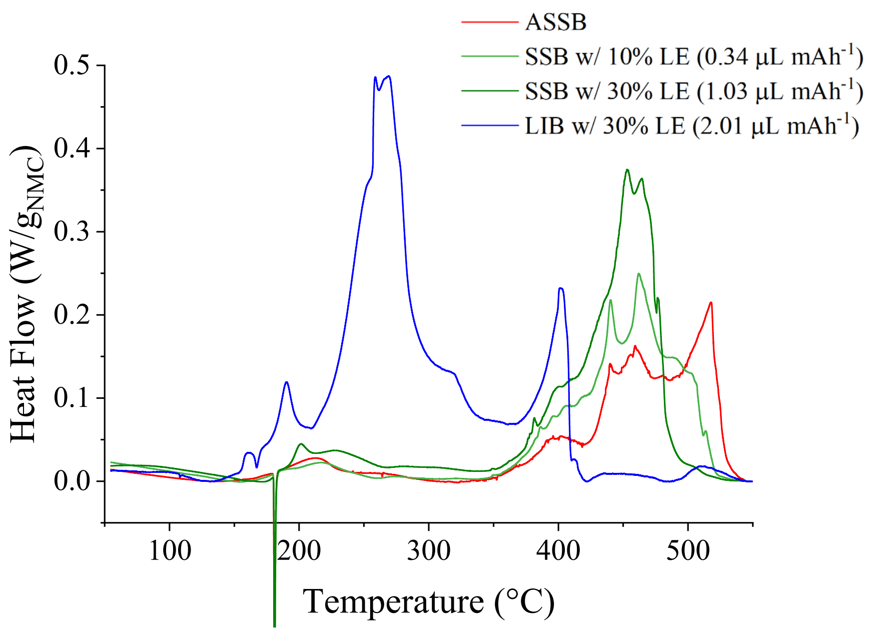

Torres-Castro, L., Kurzawski, A., Hewson, J., and Lamb, J. (2020). Passive Mitigation of Cascading Propagation in Multi-Cell Lithium Ion Batteries.

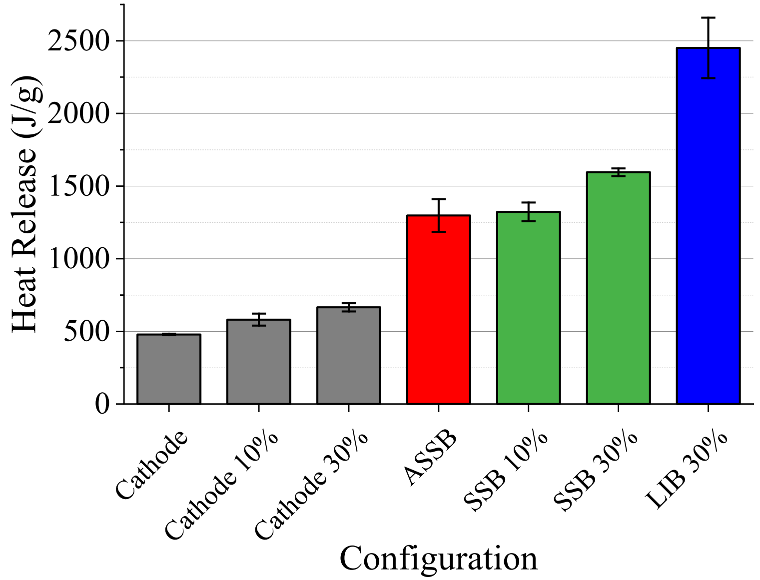
# Project Scope:
# Experimental Validation: DSC Microcell Setup




- Sample pan inner diameter ~5.5 mm
- SE thickness 0.5-0.7 mm (comparable to Present Day format)
- Cathode at 100% SOC (identical to previous work)
- N-to-P ratio 1-to-1 (identical to previous work)

# Project Results: Solid-State Battery Heat Release




- Onset to large exothermic events occurs at a much lower temperature for LIB than for SSB with or without liquid electrolyte

- 10% VF of liquid electrolyte has little to no effect on overall heat release compared to the ASSB
- At some VF, increasing liquid electrolyte does increase overall heat release
- The overall heat release of the LIB is much higher than the SSB

# Project Results:
# Summary of Key Findings

- SSBs are not ALWAYS inherently safer than LIBs
- High energy density and specific heat release are important to safety
- SE mechanical failure can lead to high heat release
- Acceptable trade off in performance and safety with liquid electrolyte
- Onset to large exothermic events occurs at higher temperatures for SSBs compared to LIBs
  - Liquid electrolyte inclusion in SSB pushes peak heat release to lower temperatures
  - Cycle dependent Li-metal morphology changes may significantly impact onset

# Project Team

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# Project Impact: Publications and Presentations

First thermodynamic analysis of solid-state battery heat release.

Presentations

- **Thermal Modeling of Liquid Electrolyte in Solid-State Batteries,** Solid-State Battery Summit, Virtual, August 2021
- **How Safe Are All-Solid-State Batteries?,** MRS Fall Meeting, Boston, MA, December 2021
- **Are Solid-State Batteries Always Safer Than Lithium-ion Batteries? Establishing a Basic Thermodynamic Approach for Evaluation,** IAPG Chemical Working Group, Virtual, February 2022
- **Are Solid-State Batteries Safer than Lithium-ion Batteries?,** International Battery Seminar, Orlando, FL, March 2022
- **Thermal Stability of Solid-State Battery Components with Liquid Electrolyte,** MRS Spring Meeting, Honolulu, HI, May 2022
- **Are Solid-State Batteries Always Safer Than Lithium-ion Batteries? Establishing a Basic Thermodynamic Approach for Evaluation,** Soteria Webinar Series, Virtual, May 2022
- **Are Solid-State Batteries Safer Than Lithium-ion Batteries?,** Gordon Research Conference, Ventura, CA, June 2022
- **Are Solid-State Batteries Safe? A Thermodynamic Analysis,** TechConnect World, National Harbor, MD, June 2022
- **Are Solid-State Batteries Inherently Safe? A Dive into Heat Release Through Calorimetry,** Solid-State Battery Summit, Chicago, IL, August 2022

Publications

- A.M. Bates, Y. Preger, L. Torres-Castro, K.L. Harrison, S.J. Harris, J.C. Hewson, **"Are solid-state batteries safer than lithium-ion batteries?"**, Joule, 6, 1-14, April 2022.
- A.M. Bates, R.C. Shurtz, Y. Preger, L. Torres-Castro, K.L. Harrison, S.J. Harris, J.C. Hewson, **"Calorimetric study of solid-state battery heat release",** (in preparation).

Previous Work

- J. Lamb, L. Torres-Castro, J.C. Hewson, R.C. Shurtz, Y. Preger, **"Investigating the role of energy density in thermal runaway of lithium-ion batteries with accelerating rate calorimetry",** Journal of the Electrochemical Society, 168, 2021.
- R.C. Shurtz, **"Lithium-ion battery thermodynamic we calculator",** https://www.sandia.gov/ess-ssl/thermodynamic-webcalculator/, 2021.
- R.C. Shurtz, J.C. Hewson, **"Review—materials science predictions of thermal runaway in layered metal-oxide cathodes: a review of thermodynamics",** Journal of the Electrochemical Society, 167, 2020.
- R.C. Shurtz, **"A thermodynamic reassessment of lithium-ion battery cathode calorimetry",** Journal of the Electrochemical Society, 167, 2020.

# Project Contacts

- Funded by the U.S. Department of Energy, Office of Electricity, Energy Storage program. Dr. Imre Gyuk, Program Director.

- Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

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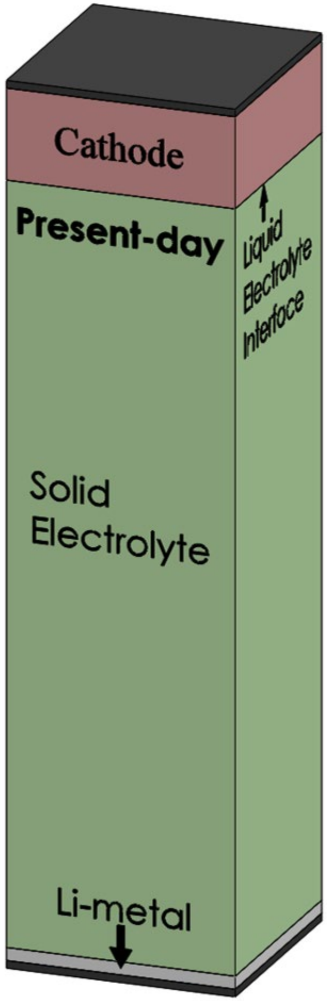
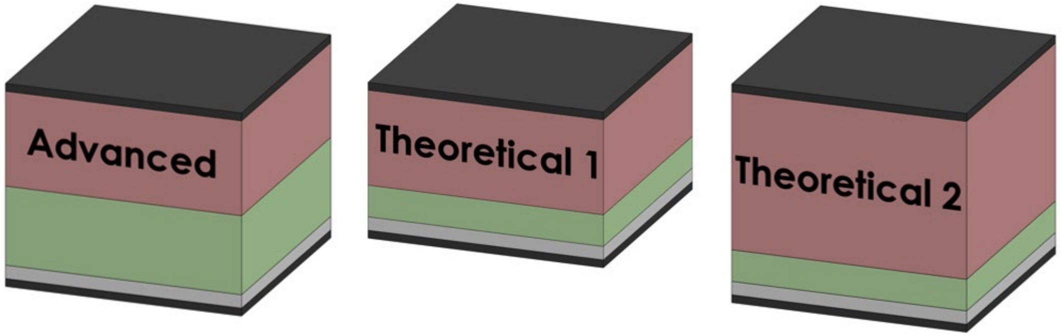
For further details on experimental work, see the following poster:
"Are Solid-State Batteries Safer Than Lithium-ion Batteries?" – Megan Diaz

# Project Scope: Extension to Real Battery Parameters

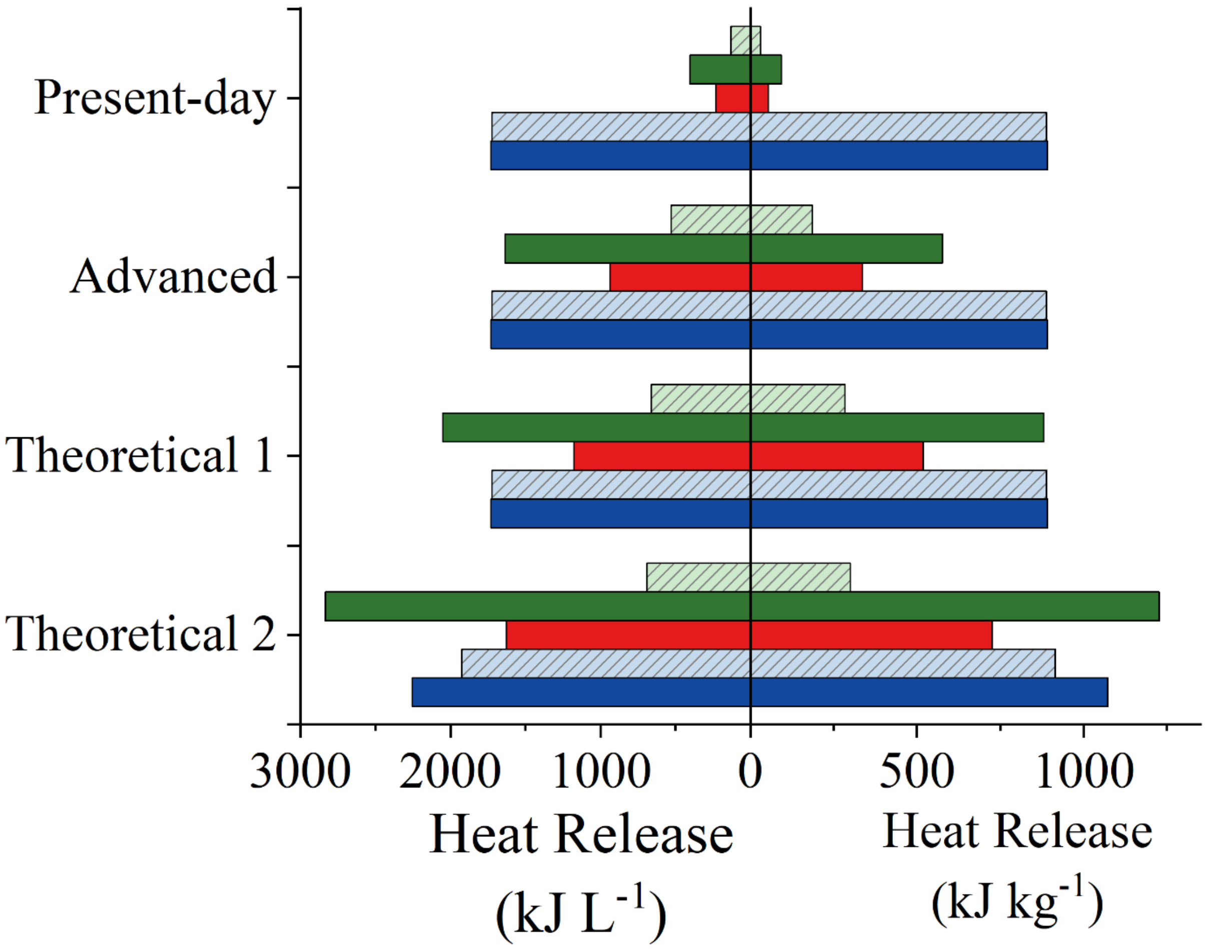



| | | Cathode | | SE/Separator |
|---|---|---|---|---|
| | Format | δ (μm) | VF AM | δ (μm) |
| ASSB & SSB | **Present-day** | 60 | 0.6 | **500** |
| | **Advanced** | 60 | 0.6 | **50** |
| | **Theoretical 1** | 60 | 0.6 | **20** |
| | **Theoretical 2** | **100** | **0.7** | 20 |
| LIB | **Present-day through Theoretical 1** | 60 | 0.6 | 20 |
| | **Theoretical 2** | **100** | **0.7** | 20 |

Increasing Energy Density

# Project Results: Heat Release Dependence on Cell Format




Present day: SSB heat release similar to ASSB

Advanced: Significant jump in ASSB/SSB heat release
ASSB/SSB short circuit approaching LIB

Theoretical 1: ASSB/SSB short circuit exceeds LIB

Theoretical 2: Jump in ASSB/SSB worse than LIB