Are Solid-State Batteries Safe? A Thermodynamic Analysis

Alex M. Bates

DOE OE Energy Storage Peer Review
10/11/2022 – 3:55 PM
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

Solid-state battery: main industrial players – geographical overview


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

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)
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.
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

Alex Bates  
Power Sources R&D

Lorraine Torres-Castro  
Power Sources R&D

Yuliya Preger  
Energy Storage Tech & Systems

Katharine Harrison  
Nanoscale Sciences Department

Stephen Harris  
Lawrence Berkeley National Laboratory

Randy Shurtz  
Fire Sciences and Technology

John Hewson  
Fire Sciences and Technology
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.

Previous Work

Project Contacts

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


Name of presenter: Alex Bates
Corresponding email: ambates@sandia.gov

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

<table>
<thead>
<tr>
<th>Format</th>
<th>Cathode</th>
<th>SE/Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Present-day</strong></td>
<td>60 0.6</td>
<td>500</td>
</tr>
<tr>
<td><strong>Advanced</strong></td>
<td>60 0.6</td>
<td>50</td>
</tr>
<tr>
<td><strong>Theoretical 1</strong></td>
<td>60 0.6</td>
<td>20</td>
</tr>
<tr>
<td><strong>Theoretical 2</strong></td>
<td>100 0.7</td>
<td>20</td>
</tr>
</tbody>
</table>

**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

- Present-day
- Advanced
- Theoretical 1
- Theoretical 2

Legend:
- SSB – external heating
- ASSB/SSB – short circuit
- ASSB – mechanical failure
- LIB – external heating
- LIB – short circuit

Heat Release
(kJ L⁻¹)
Heat Release
(kJ kg⁻¹)