SAND2022-3892C

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Can a Small Volume of Liquid Electrolyte Bridge the Gap to Commercialization?

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March 30th, 2022, 9:00 AM

39th Annual International Battery Seminar

SAND2021-14837 C

U.S. DEPARTMENT OF ENERGY

NNSA

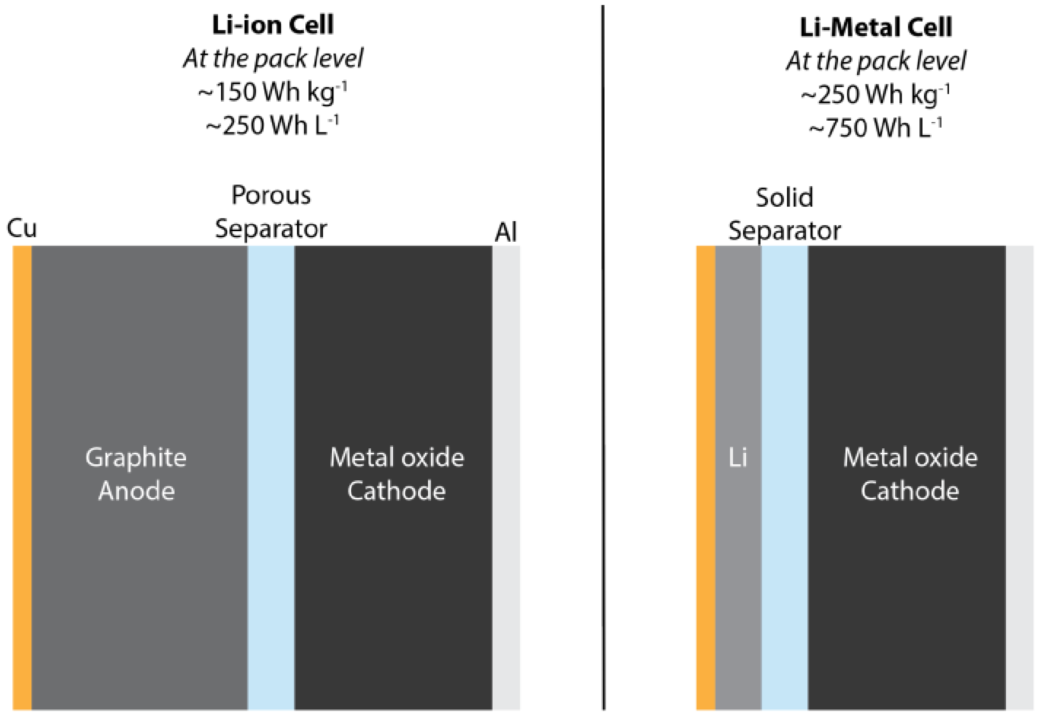
Replacement of Liquid Electrolyte

Liquid Electrolyte (LE)

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

Solid Electrolyte (SE)

- OK ionic conductivity
- Non-flammable (inherently safe?)
- Poor interfacial contact

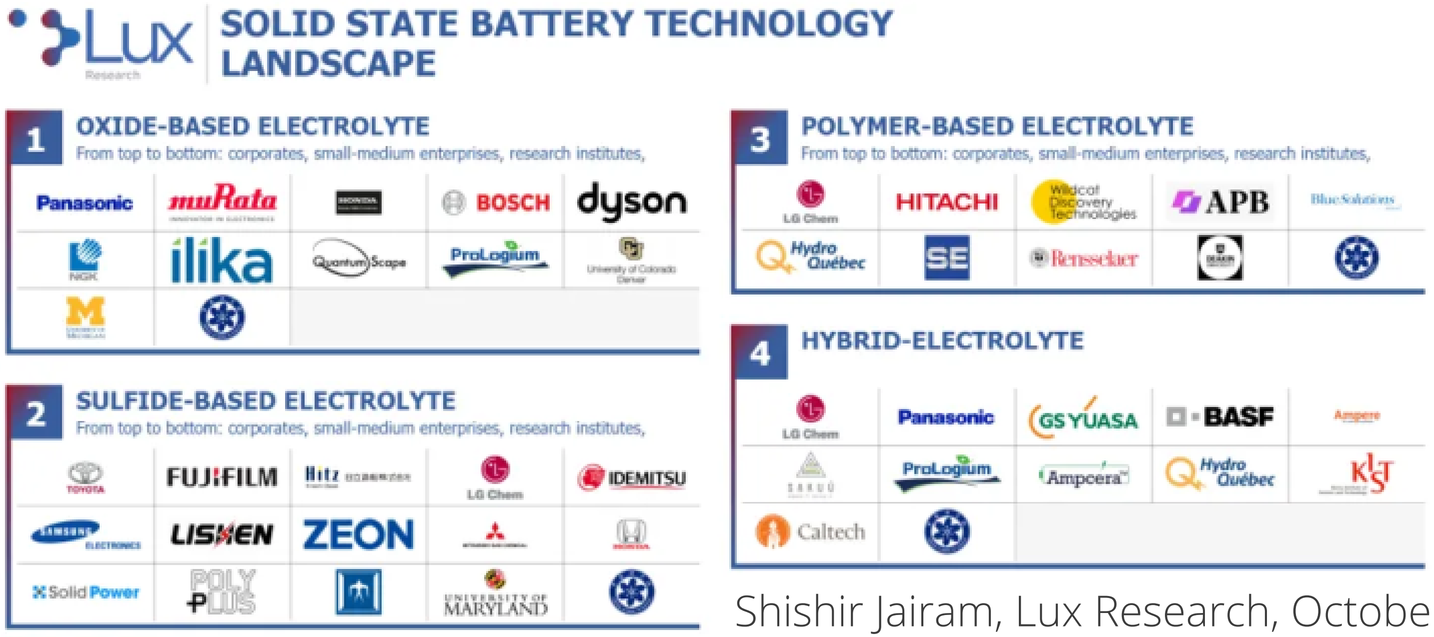


Albertus, P., Babinec, S., Litzelman, S. et al. Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries.

Solid-State Batteries, Why the Excitement?

Two Primary Advantages

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

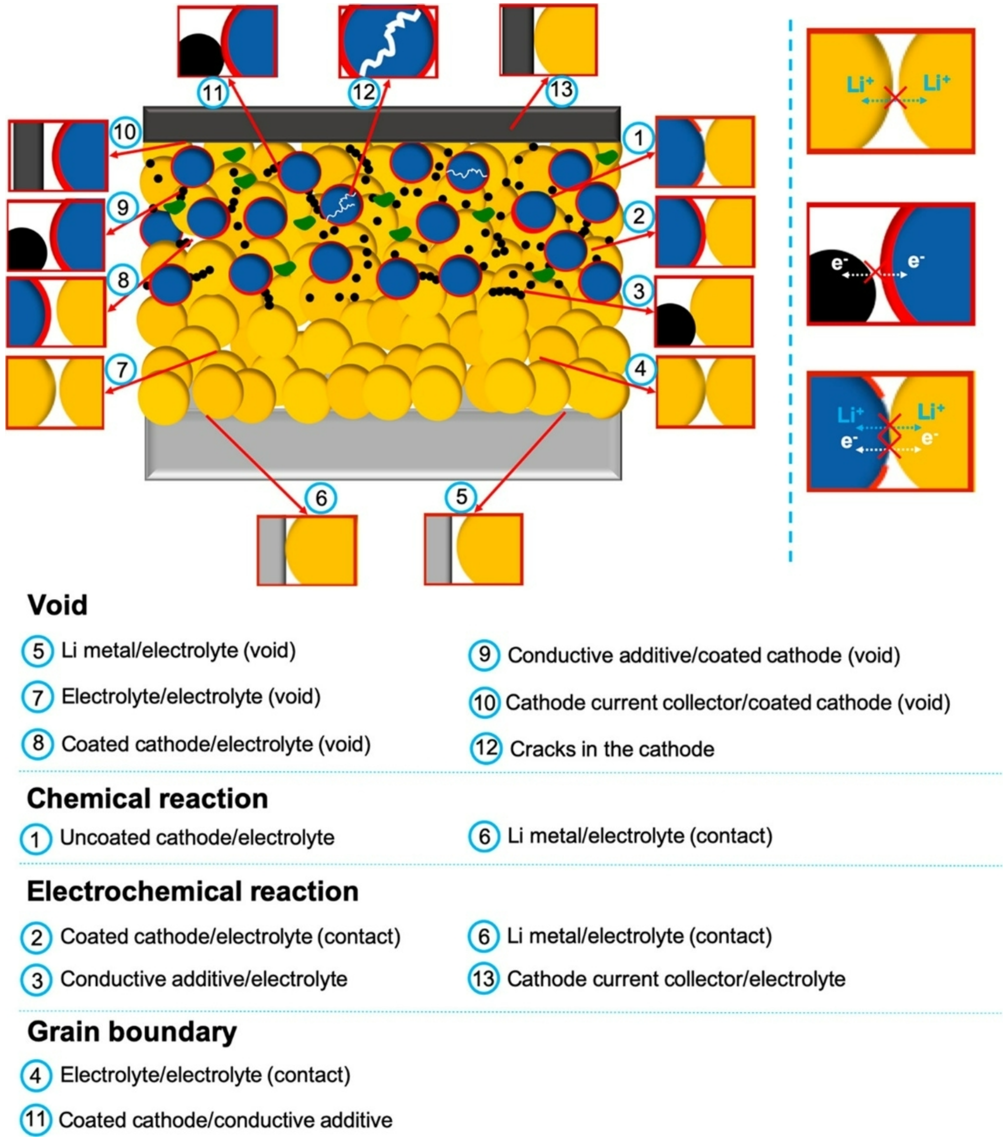


Shishir Jairam, Lux Research, October 27, 2021

Challenges Introduced by Removing Liquid Electrolyte

Interfacial Resistance

- Voids
  - Li-ion transport
  - Li dendrite growth
  - Volumetric energy density



Banerjee, A., Wang, X., Fang, C., Wu, E.A., and Meng, Y.S. (2020). Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes.

Overcoming Interfacial Resistance

Surface Treatment

- Heat, acid, mechanical
  - Improve Li wetting, increase contact area

Interlayers

- Protective coating
  - Increase solid electrolyte stability, enhance mechanical properties

Pressure

- ~10 MPa (100 atm)
  - Decrease void space, maintain contact during volume expansion

Liquid electrolyte/ionic liquids

- Reduce interfacial resistance

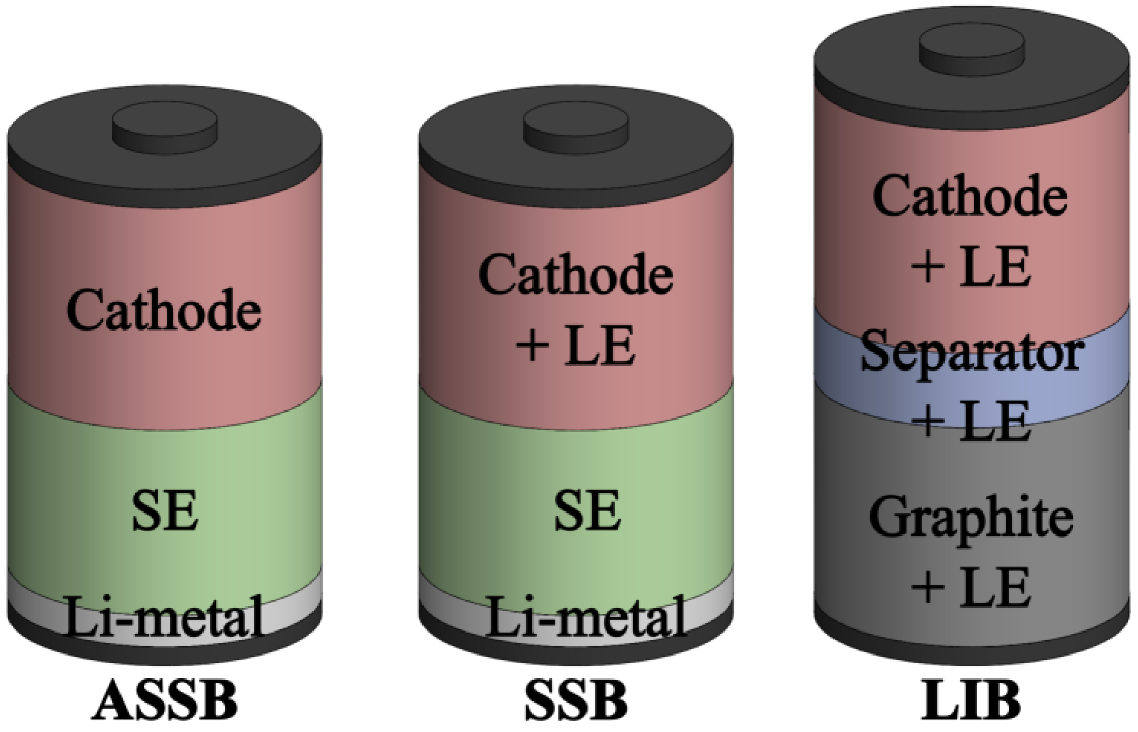
How Safe Are All-Solid-State Batteries?

Motivation

- All-Solid-State Batteries (ASSBs) are assumed to be inherently safe
  - Flammable liquid electrolyte removed
  - Interfacial resistance R_{IF} is a key challenge
- Solid-State Batteries (SSBs) may use liquid electrolyte to reduce cathode R_{IF}
  - Concerns raised on safety impact
  - How important are these concerns?

Scope

- 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



Key Findings

- Liquid electrolyte in SSBs
  - Increase in heat release
    - At low volume per electrode area, manufacturability and performance are more important
    - SSB potential temperature rise below cascading propagation
- Short circuit failure
  - Higher potential temperature rise in ASSBs and SSBs than LIBs
    - Heat release over smaller volume and mass
- Mechanical failure of SE
  - Gases from cathode contact Li-metal
    - Significant heat release

Thermal Model

Relevant Reactions

Rxn#	Reaction Description	Reaction Equation
R1	Cathode decomposition	$2MO_2 \rightarrow 2MO + O_2$
R2	Cathode-electrolyte	$2C_4H_8O_3 + 9O_2 \rightarrow 8CO_2 + 8H_2O$
R3	Anode-electrolyte	$4LiC_6 + 2C_4H_8O_3 \rightarrow 4C_6 + 3C_2H_4 + 2H_2 + 2Li_2CO_3$
R4	Cell discharge	$Li + MO_2 \rightarrow LiMO_2$
R5	Anode-oxygen	$4Li + O_2 \rightarrow 2Li_2O$

Failure Modes

Failure Mode	Reactions Involved
External heating	R1, R2, and R3
Short circuit	R4
Mechanical failure	R1 and R5

Shurtz, R.C. (2020). A Thermodynamic Reassessment of Lithium-Ion Battery Cathode Calorimetry.
Shurtz, R.C., and Hewson, J.C. (2020). Review—Materials Science Predictions of Thermal Runaway in Layered Metal-Oxide Cathodes: A Review of Thermodynamics
Shurtz, R. (2021). Lithium-ion Battery Thermodynamic Web Calculator. https://www.sandia.gov/ess-ssl/thermodynamic-web-calculator/.

Heat Release vs. Liquid Volume Fraction (VF)

All: short circuit heat release equal

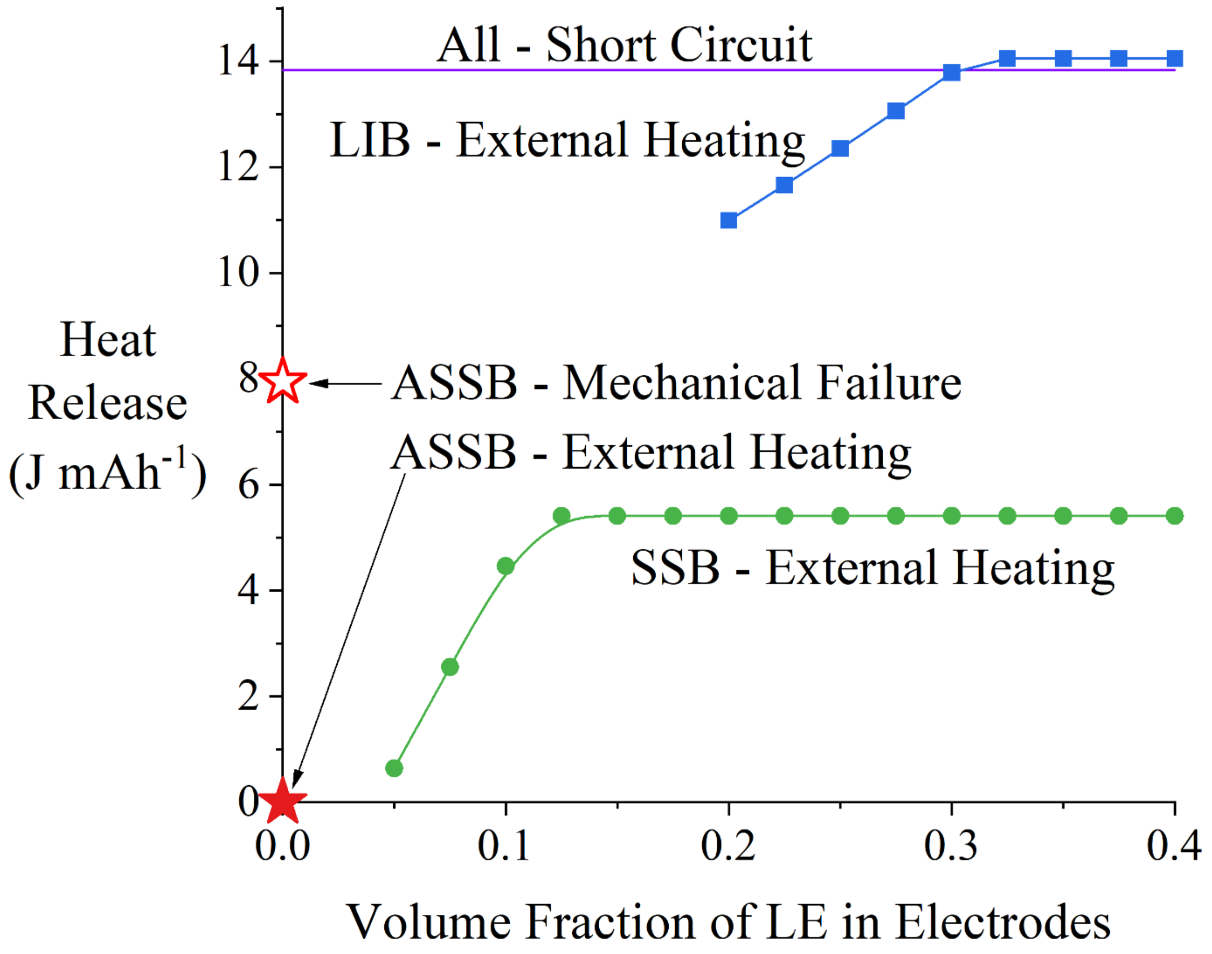
ASSB: no heat release from external heating

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

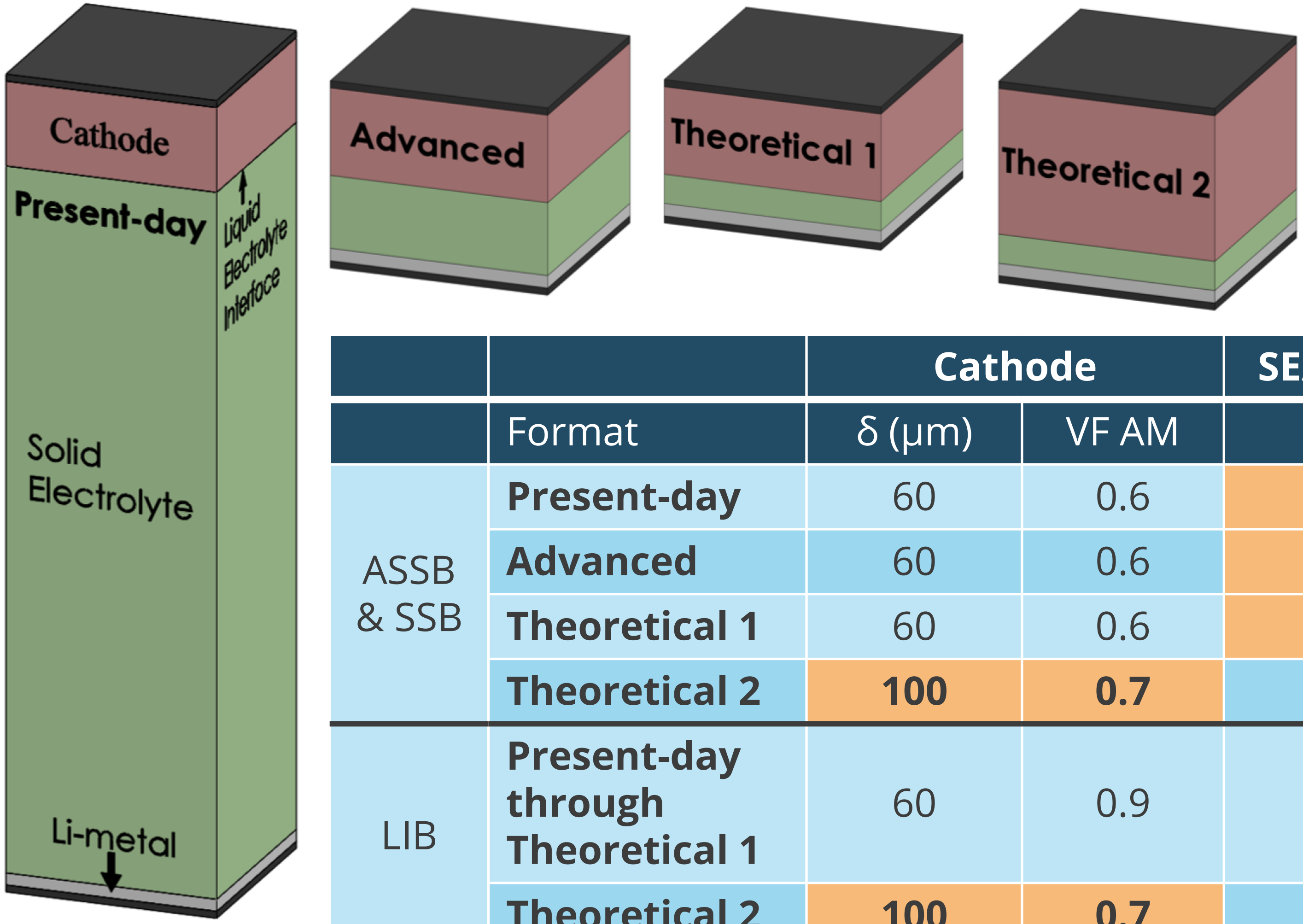
SSB: Heat release negligible <8% VF

- Cathode pores filled with SE

ASSB: large heat release on SE mechanical failure



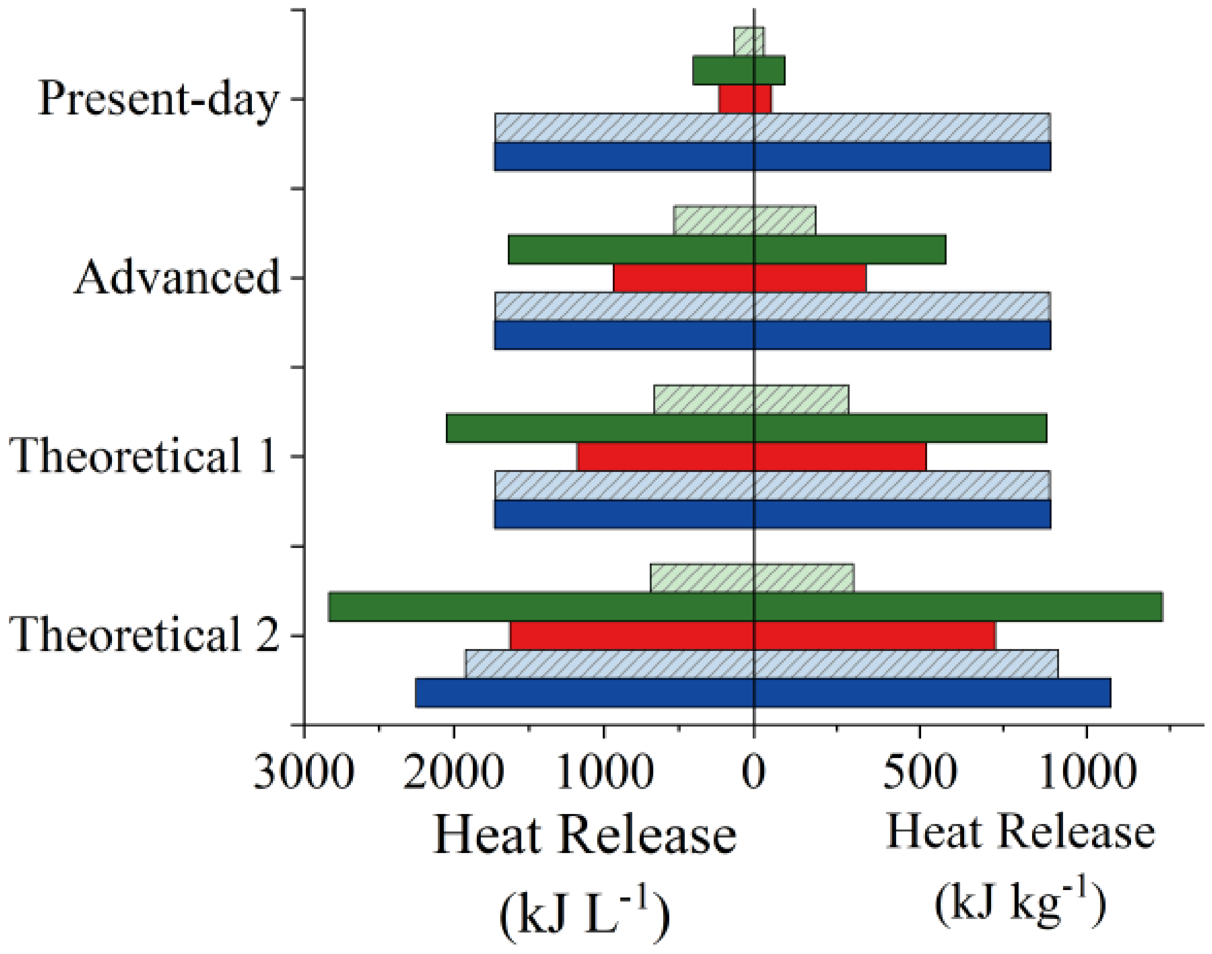
Thermal Model



		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	0.9	20
	Theoretical 2	**100**	**0.7**	20

Increasing Energy Density

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

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

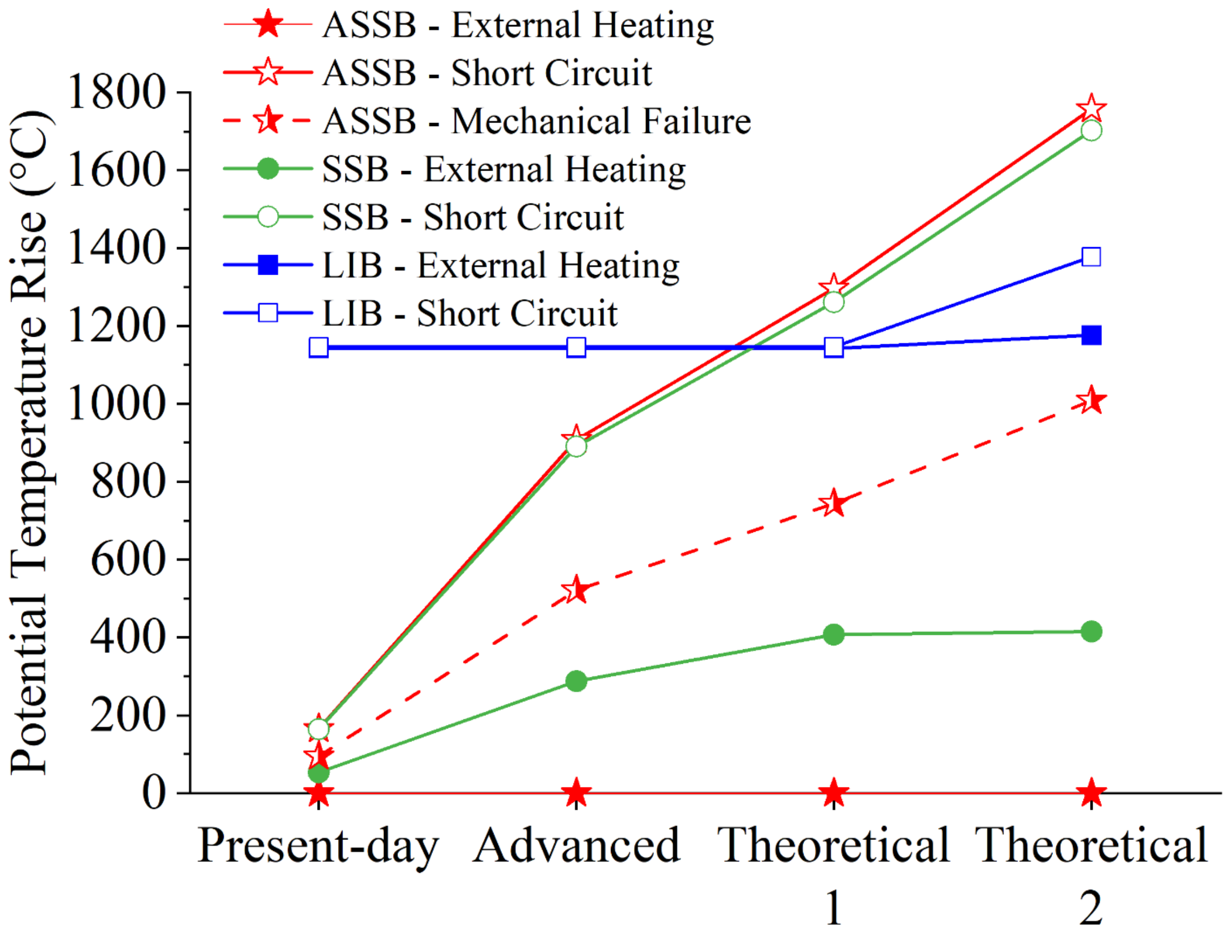
Potential Temperature Rise

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.

Conclusions

- We consider thermodynamic heat release as our safety measure
  - SSBs are not ALWAYS inherently safer than LIBs
- Potential temperature rise increases significantly with energy density
  - Critical consideration for future ASSBs/SSBs
- High heat release from SE mechanical failure
  - O_2 reaction with Li-metal
- SSBs with <8% liquid electrolyte by cathode volume
  - Heat release small enough that cost, manufacturability, and performance enhancements may allow for commercialization

Request

Can I abuse your batteries?

Conclusions

- We consider thermodynamic heat release as our safety measure
  - Fire safety depends on geometry and environment (future work)
- Potential temperature rise increases significantly with energy density
  - Critical consideration for future ASSBs/SSBs
- High heat release from SE mechanical failure
  - O_2 reaction with Li-metal
- SSBs with <8% liquid electrolyte by cathode volume
  - Heat release small enough that cost, manufacturability, and performance enhancements may allow for commercialization

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Acknowledgements

Funded by the U.S. Department of Energy, Office of Electricity, Energy Storage program. Dr. Imre Gyuk, Program Director. S.J.H. was supported by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the US Department of Energy under the Advanced Battery Materials Research program.

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Questions?

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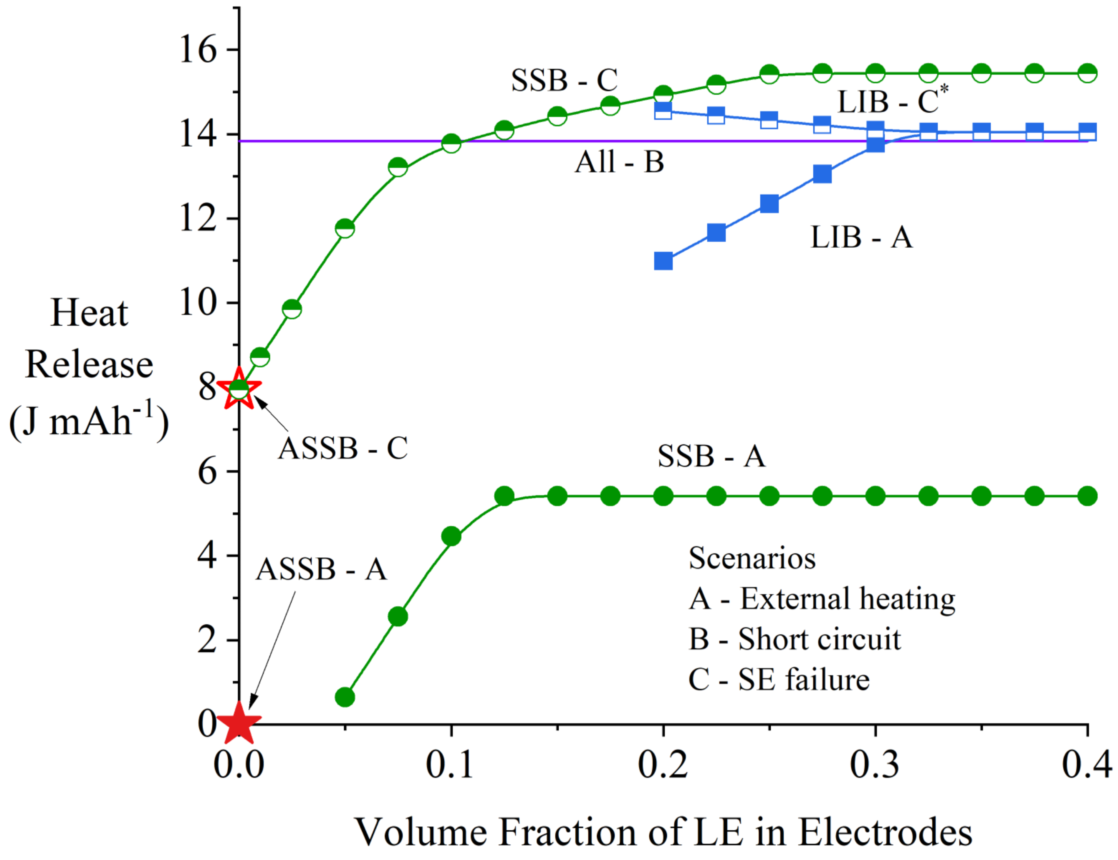
Extending Scenario C to SSB and LIB

Amount of liquid electrolyte per unit area, for reference

- SSB contains 0.6 μL cm^{-2} (@0.1 VF of LE)
- LIB contains 3.62 μL cm^{-2} (@0.3 VF of LE)



Rxn#	Name	Reaction
R6	Anode-carbon dioxide	$2Li + 2CO_2 \rightarrow Li_2CO_3 + CO$
R7	Anode-water	$2Li + 2H_2O \rightarrow 2LiOH + H_2$

Heat Release Dependence on Solvent and Energy Densities