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Safety Impacts of Liquid Electrolyte Inclusion in Solid State Batteries

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Summary

Motivation

- Solid-state batteries are believed to enhance safety over conventional Li-ion
  - Interfacial resistance remains a key challenge
- Liquid electrolyte is often added to reduce interfacial resistance
  - This addition raises concerns regarding safety impact

Thermal modeling was utilized to explore the safety impact of liquid electrolyte

Key Findings

- Liquid electrolyte inclusion increases heat release; however, the heat release may be insignificant when considering manufacturability and performance using a volume fractions below 8%
- Solid-state separator failure may lead to significant heat release even in all-solid-state batteries
- Temperature rise during external heating failure may keep temperatures below those at which we typically see cascading propagation
- Short circuit failure can lead to higher peak temperatures in all-solid-state batteries since the same amount of heat is generated over a smaller mass volume

Thermal Model

ASSB = all-solid-state battery
SSB = solid-state battery (with liquid electrolyte)
LIB = conventional Li-ion battery

Scenarios

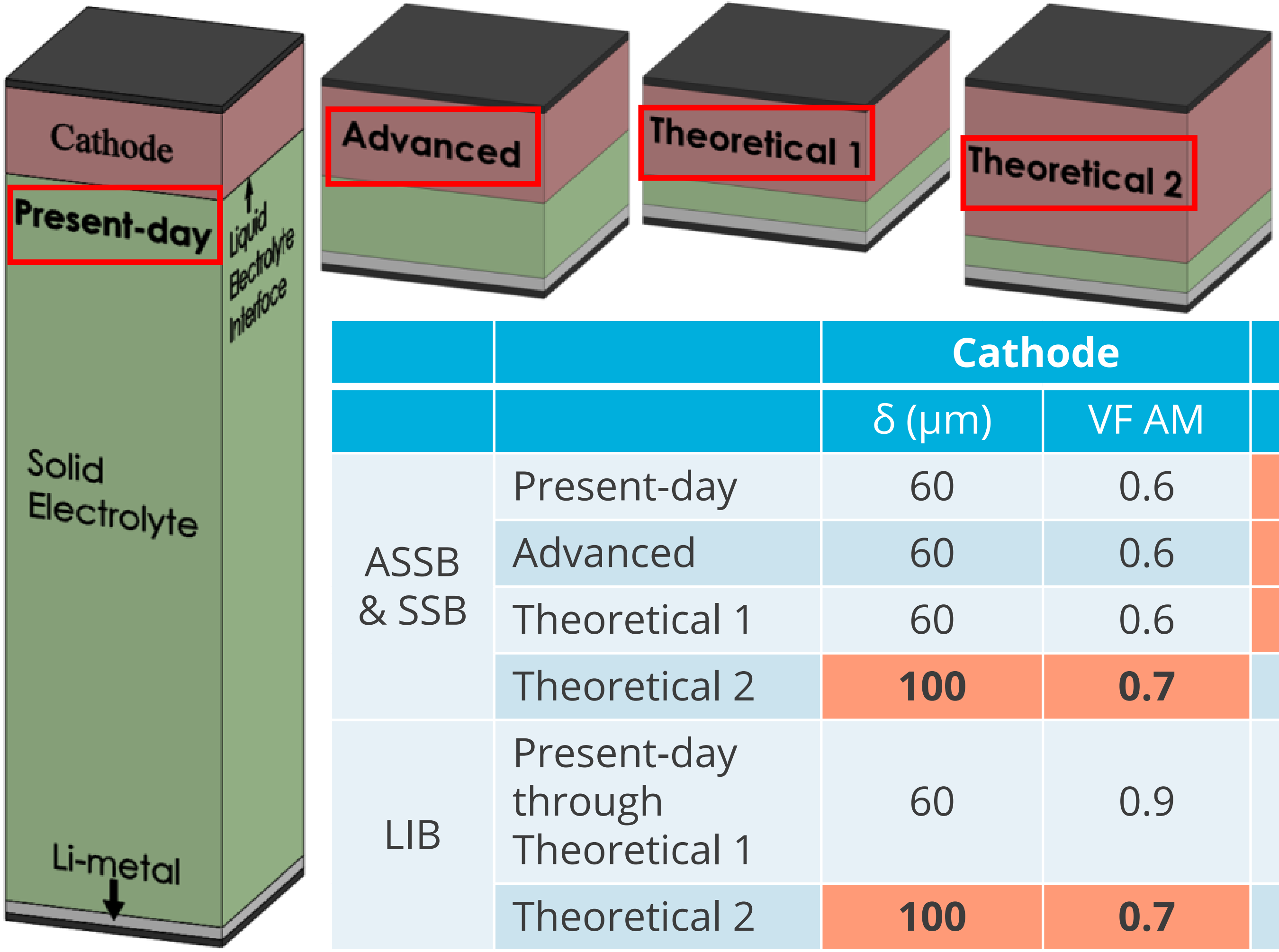
Scenario	Failure Mode	Reactions	Key Assumptions
A	**External heating**	R1, R2, and R3	No SE/separator failure, SE is non-permeable
B	**Short circuit**	R4	Other forms of heat release are zero
C	**Mechanical failure**	R1 and R5	Only applied to ASSB

Reactions

Rxn#	Name	Reaction
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	$4Li + O_2 \rightarrow 2Li_2O$

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/.

Thermal Model



		Cathode		SE/Separator
		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

Cathode
- NMC111

SE
- LLZO

Liquid Electrolyte
- $LiPF_6$ in EMC

Anode
- Graphite
- Li-metal

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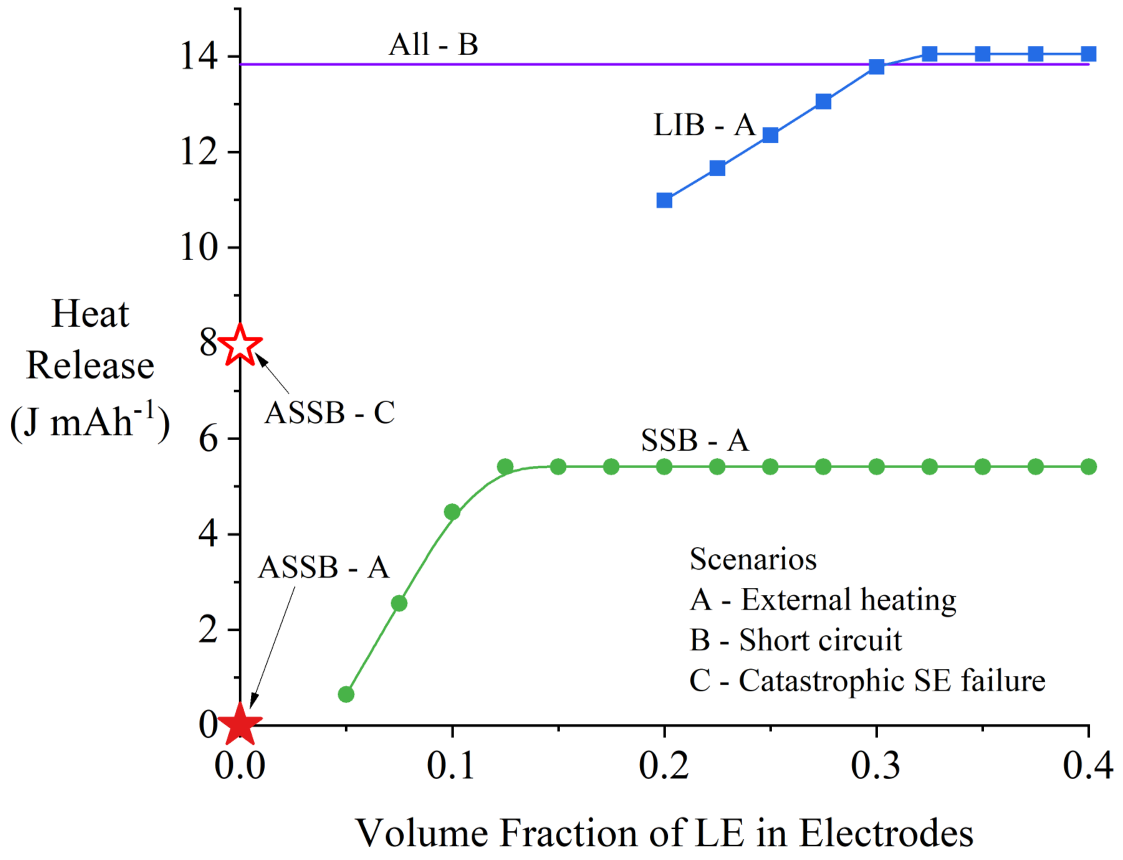
Heat Release as a Function of Liquid Volume Fraction

- LIB heat release is nearly double that of SSB at a VF of 0.2
- SE failure in the ASSB allows O_2 to react with Li, releasing substantial heat (open red star)
- A small enough amount of liquid electrolyte (VF < 0.08) has little effect on heat release
- Short circuit failure can release the same amount of heat for each configuration



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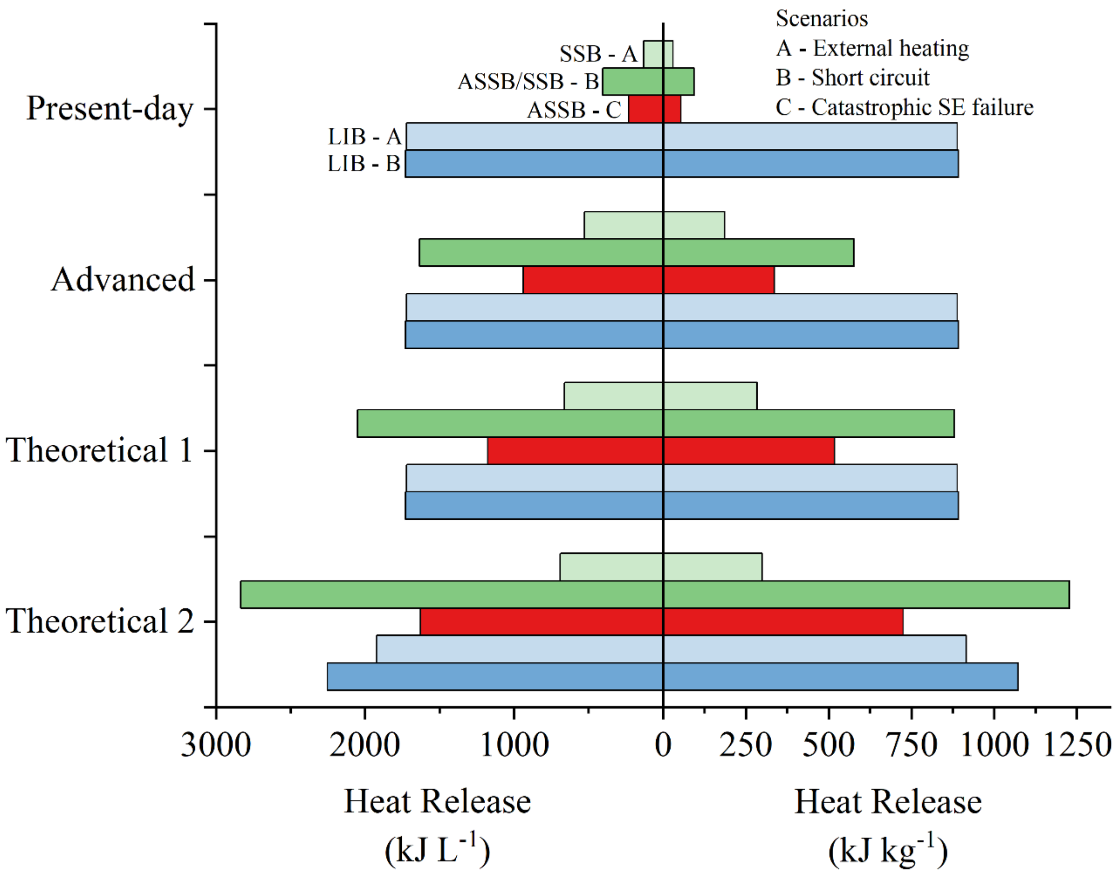
Heat Release Dependence on Cell Format



- External heating and short circuit failure heat releases are similar for LIB and dramatically different for SSB
- SSB heat release due to short circuit surpasses LIB when the SE is 20 µm thick
- Separator failure is more consequential than the addition of liquid electrolyte
- Specific heat release will become an important issue as energy densities improve

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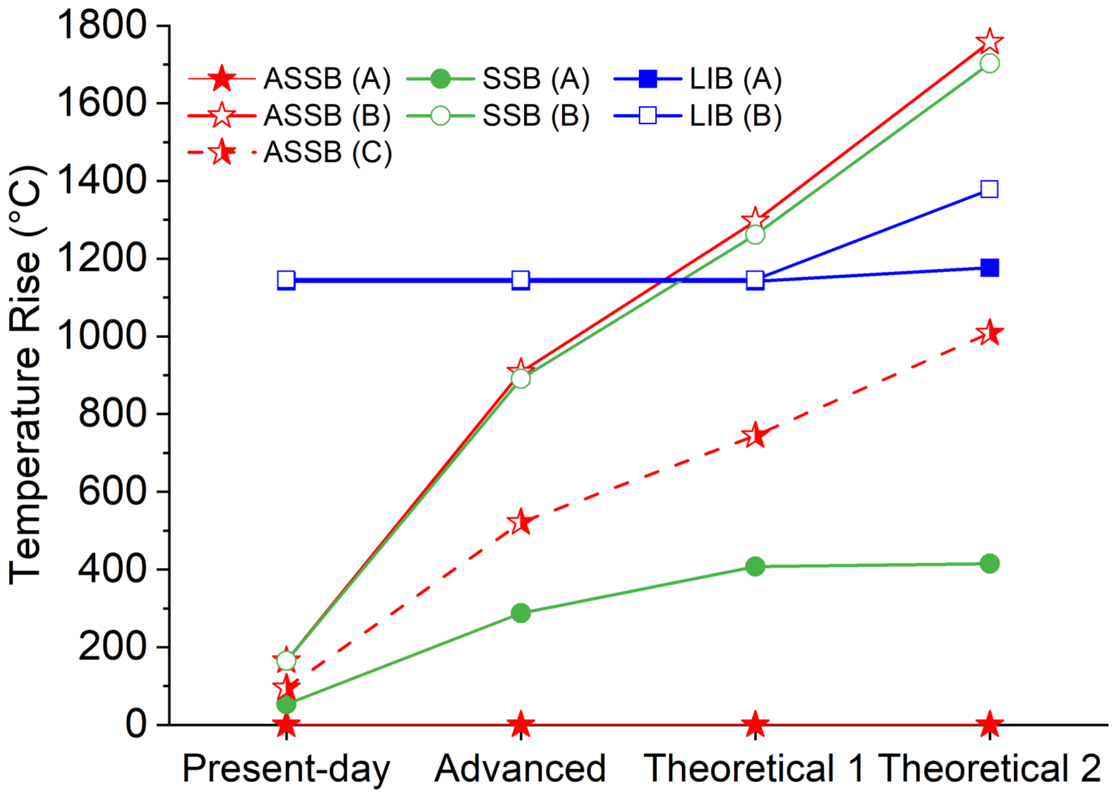
Potential Temperature Rise

- Specific heat release has a significant impact on potential temperature rise
- ASSB and SSB potential temperature rise due to short circuit surpasses LIB (open shapes)
- SE failure in the ASSB results in potential temperature rise rivaling the LIB (half filled star)
- External heating failure stays below what typically results in propagation (filled green circle)



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

Conclusions

- ASSBs are safer than LIBs during external heating failure
  - However, this is not necessarily true during short circuit failure or if the SE does not act as a barrier to gas and liquid
- Solid electrolyte existing as a barrier to gas and/or liquid transfer is critical to thermal runaway prevention in several abuse modes
- As energy density is improved, specific heat release becomes more consequential
  - The potential temperature rise of an ASSB is expected to be higher than a LIB due to heat generation over a smaller mass and volume
  - Short circuit failure in high energy density ASSBs is of critical concern regarding cascading propagation, due to high potential temperature rise
- A compromise may be possible between cost, manufacturability, performance, and safety by varying the amount of liquid electrolyte in a SSB

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Questions?

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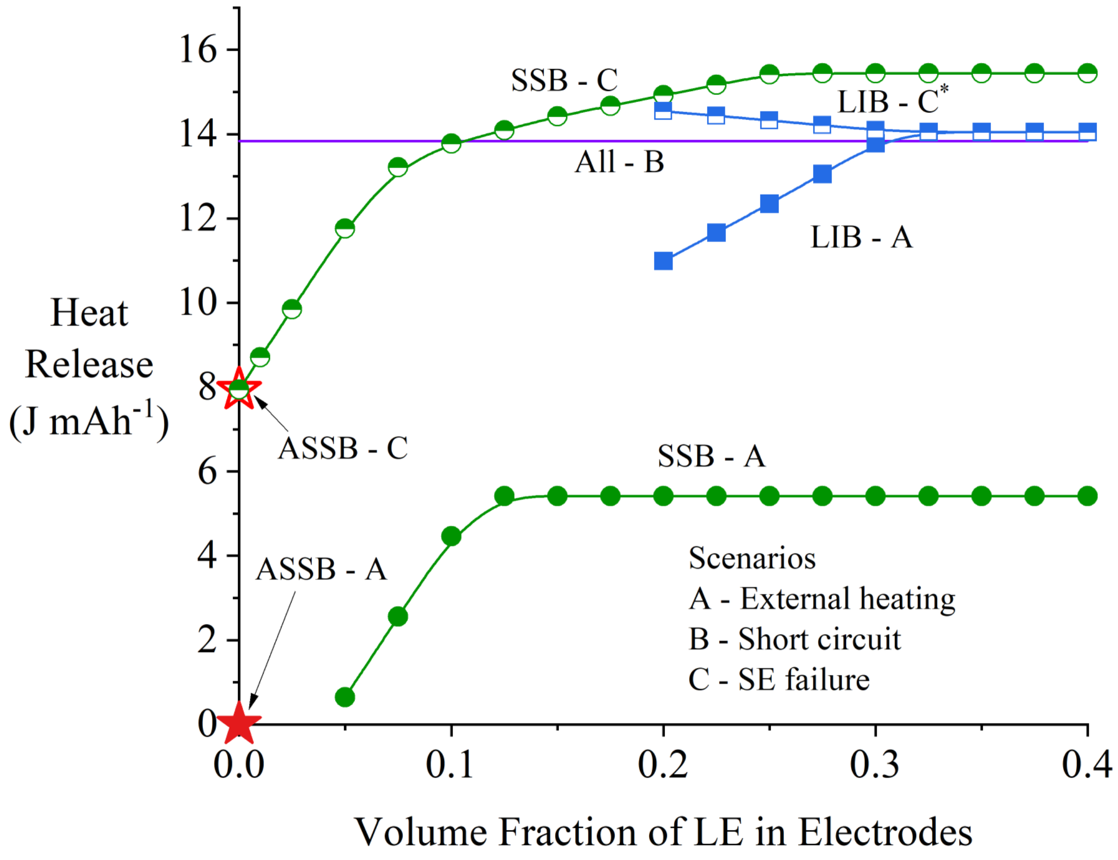
Extending Scenario C to SSB and LIB

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