Title

Are solid-state batteries safer than lithium-ion batteries?

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SUPPLEMENTAL FIGURES

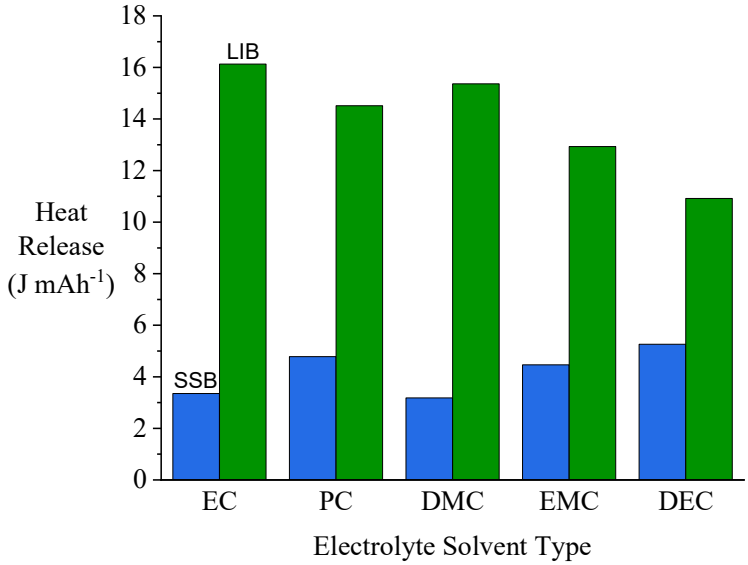

Figure S1. Heat release differences among alkyl carbonate solvents: ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC).

The effect of electrolyte solvent on heat release is shown in Figure S1 for Scenario A. The volume fraction of LE in the cathode of the SSB was 10%, and the volume fraction of the LE in the cathode of the LIB was 30%. The difference in solvent density, molar mass, and stoichiometry can significantly affect heat release. For a LIB, when switching from EC to DEC, the heat release is reduced by 32%. In a SSB, the heat release when switching from EC to DEC increases by 57%. The SSB configuration is LE limited while the LIB is O_2 limited, resulting in an opposite trend in heat release values. With DEC as the solvent, the SSB heat release is 52% less than the LIB, and with EC it is 79% less.

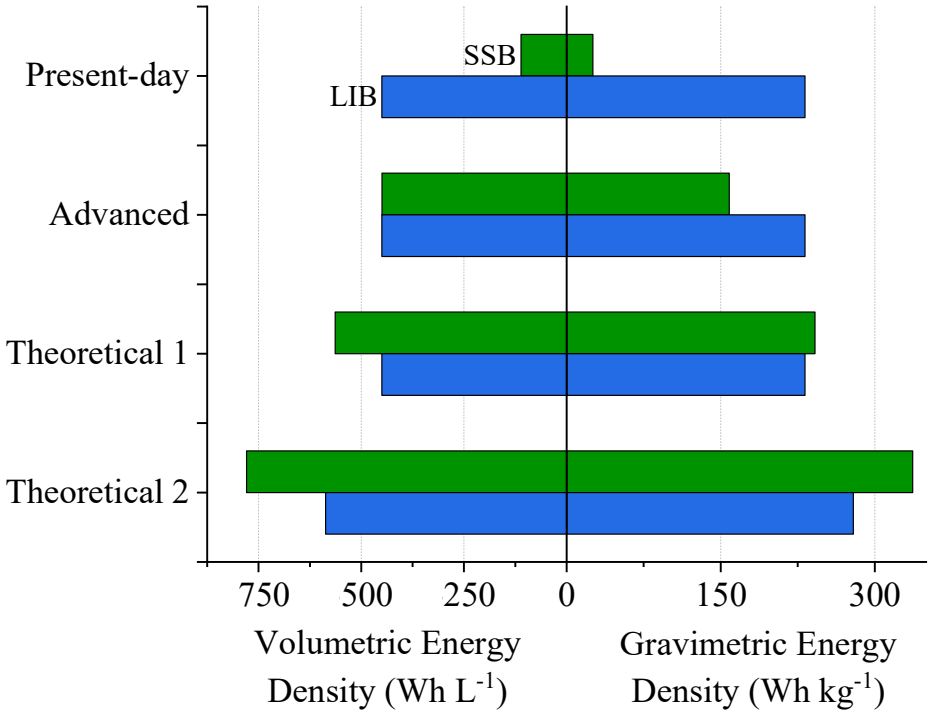

Figure S2. Volumetric and gravimetric energy density of the SSB and LIB configurations for each format. Related to Figure 3.

Figure S2 shows volumetric and gravimetric energy densities for each format. These energy density calculations include estimates for ancillary materials (i.e. current collectors, packaging, binders, etc.). This was done by setting LIB energy densities to 235 Wh kg^{-1} and 450 Wh L^{-1}, and backing out the required packaging weight, 6.3% of the LIB cell by weight. These energy densities are based on values shown in the ARPA-E RANGE program and a technology transition case study by the USABC.[1,2] The same weight and volume of ancillary components is applied to the SSB and ASSB, as true values are unknown at this time.

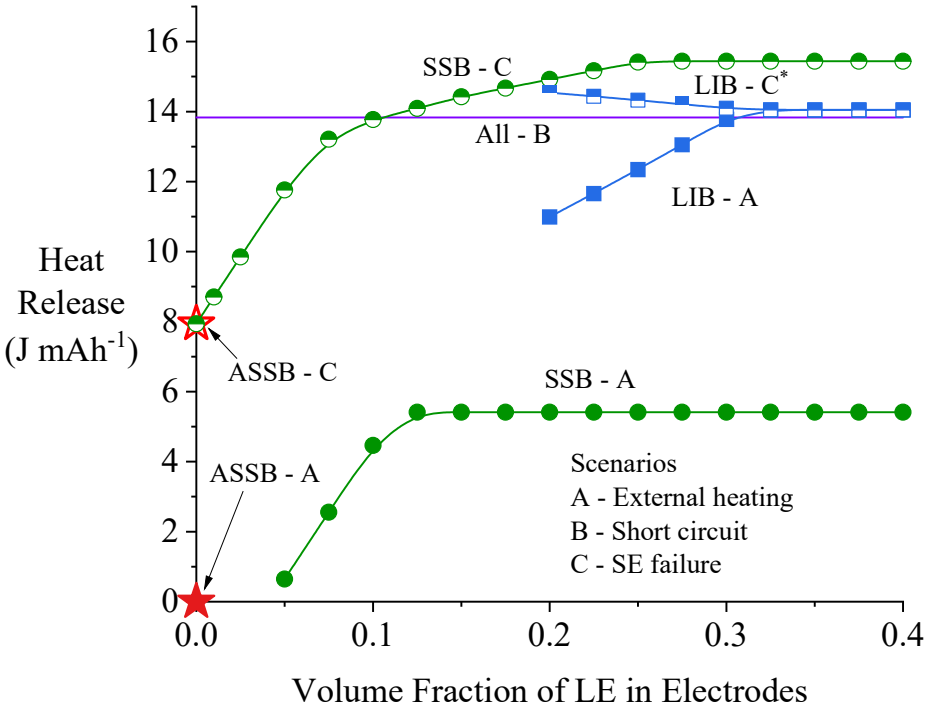

Figure S3. Heat release dependence on volume fraction of LE when Scenario C is extended to the SSB configuration and CO_2 and H_2O can react with lithiated anode for the LIB configuration, labeled LIB – C*. Related to Figure 2.

In Scenario C, catastrophic SE failure allows chemical species produced at the cathode to react with Li in the anode. In this scenario, due to CO_2 and H_2O produced in R2, two additional reaction pathways exist

$$2Li + 2CO_2 \rightarrow Li_2CO_3 + CO \qquad \text{R6}$$

$$2Li + 2H_2O \rightarrow 2LiOH + H_2 \qquad \text{R7}$$

Generally, these reactions are not considered in thermodynamic models of LIBs as they result in heat release higher than experienced experimentally. Venting in LIB removes some gases from the electrodes prior to reaction, but it is not clear what venting might occur or be possible in SSB scenarios, because the overall porosity of the cathode is significantly reduced. In the main text of this work, we assume the SE prevents chemical species transfer between the cathode and anode in Scenario A. Consistent with Scenario C of the main text, and here labeled Scenario C*, all possible intermediate gases are assumed retained within the cell and transfer across the electrolyte is allowed. As such, R6 and R7 are considered in the ASSB, SSB, and LIB configurations. In this case, we see heat release for the SSB, Scenario C*, comparable to and slightly exceeding the LIB case from Scenario A. This is due to the high heat release of R6 and R7 shown in Table S3. In the LIB case, LE reaction with the lithiated anode, R3, is assumed to occur before anode reaction with CO_2 and H_2O, R6 and R7. For the LIB and SSB plateau regions, all the anode lithium has reacted exothermically. The assumptions for heat release reaction sequencing leads to slightly more heat release in the SSB case than the LIB case, but there is a lack of relevant measurements. Scenario C* applied to the SSB and LIB configurations further identifies the severity of potential SE failure.

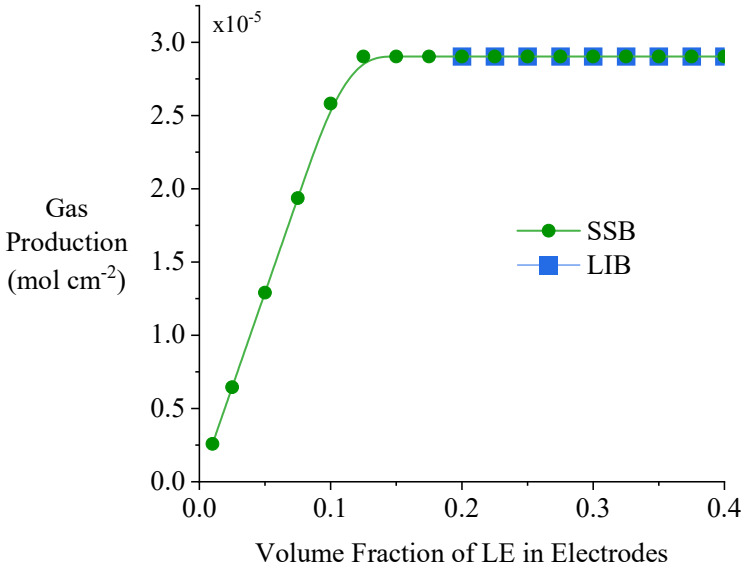

Figure S4. Amount of CO_2 and H_2O produced by cathode-released oxygen reacting with LE (reaction R2) as a function of LE (EMC) amount for Scenario A.

The EMC reaction produces equimolar amounts of CO_2 and H_2O. At higher volume fractions of LE in the cathode, the amount of gas produced reaches a plateau because there is no more O_2 to react. At a volume fraction of 10% in the SSB, the gas production is reduced by one third relative to 30% volume fraction LE in the LIB. A reduction to 0.05 volume fraction of LE in the SSB reduces gas production by over half relative to the LIB. In addition to CO_2 and H_2O, the LIB can produce C_2H_4 and H_2 through the reaction of LE and Li in the anode. Both produced gases are combustible and may further increase the internal pressure of the cell and heat produced.

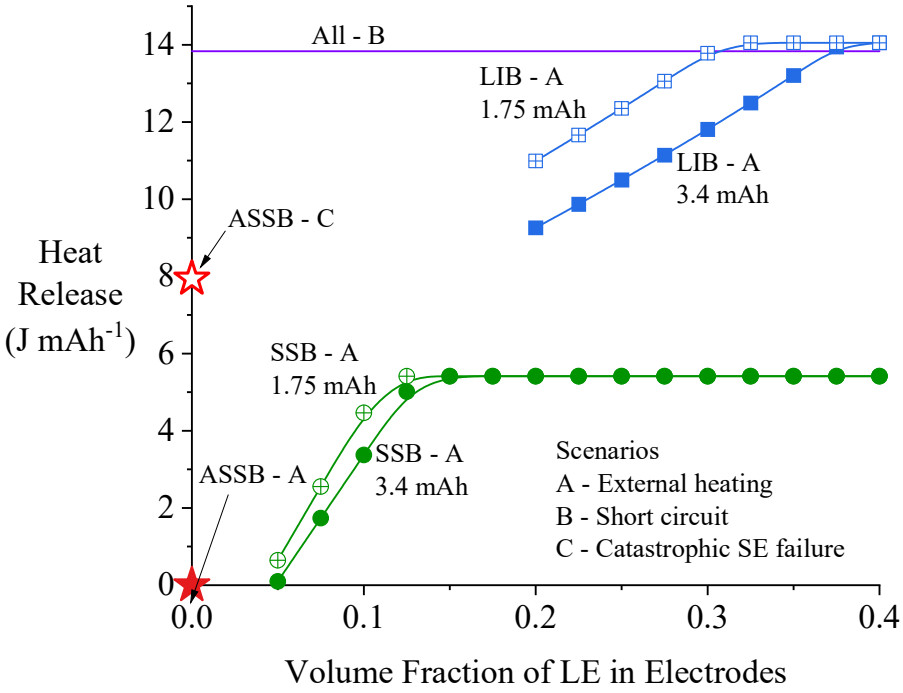

Figure S5. Heat release dependence on LE volume fraction when the cell capacity is changed from 1.75 mAh cm^{-2} (Present-day through Theoretical 1 formats) to 3.4 mAh cm^{-2} (Theoretical 2 format). Related to Figure 2.

Figure S5 shows heat release as a function of LE content for the Theoretical 2 format, representing a capacity change from 1.75 mAh cm^{-2} to 3.4 mAh cm^{-2}. This figure indicates the heat release sensitivity to increasing cathode loading. Here, the VF required to reach maximum heat release is shifted to a higher value. This shift is more significant in the LIB due to an increase in LE volume corresponding with an increased anode thickness.

SUPPLEMENTAL TABLES

Table S1. Material densities.

	Density (g cm^{-3})
Cathode	2.50
ASSB & SSB anode	0.53
LIB anode	1.54
ASSB & SSB SE	4.84
LIB separator	0.85
Liquid electrolyte (EMC)	1.12

Table S1 gives the density of each material utilized for gravimetric calculations. The density of the SE is a result of considering 95% relative density for cubic phase LLZO. The LIB anode density is based on the theoretical density of LiC_6, 2.203 g cm^{-3}, and multiplied by one minus the porosity of the anode.

Table S2. Representative electrolyte volumes in terms of µL if 2032 coin cells were used.

		Cathode (µL)	**Anode (µL)**	**SE/Separator (µL)**	**Total (µL)**
SSB	**Present-day**	1.35	0	0	1.35
	Theoretical 2	2.24	0	0	2.24
LIB	**Present-day**	4.04	2.05	1.35	7.44
	Theoretical 2	6.73	3.99	1.35	12.07

The liquid electrolyte (LE) volumes utilized in the main text are on a per area basis. Table S2 provides the actual volume of electrolyte needed, and is only to provide a tangible volume for comparison, if a 2032 coin cell were used with the listed configurations and formats.

Table S3. Summary of reactions and representative heat releases.

Rxn #	**Reaction name**	**Reaction**	**ΔH [J mAh^{-1}]**	**Ref.**
R6	Anode-carbon dioxide	$2\mathrm{Li} + 2\mathrm{CO_2} \rightarrow \mathrm{Li_2CO_3} + \mathrm{CO}$	-3.96[b]	[3]
R7	Anode-water	$2\mathrm{Li} + 2\mathrm{H_2O} \rightarrow 2\mathrm{LiOH} + \mathrm{H_2}$	-2.98[b]	[4]

Tables S3 gives the heat release per capacity for reactions occurring in Scenario C* of the SI.

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1. Arpa-E (2012). RANGE Program Overview. In D.o. Energy, ed.
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