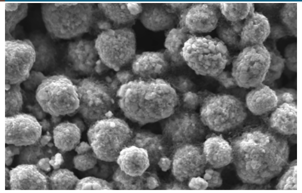
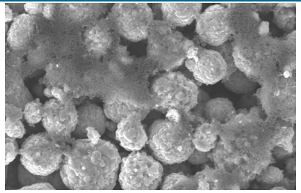
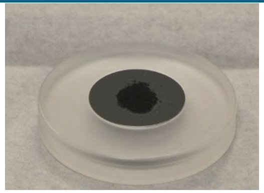
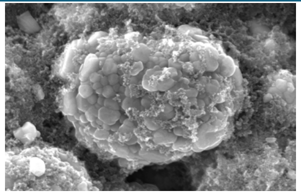
Sandia National Laboratories

Improving Solid State Battery Safety Understanding through Calorimetry and Materials Characterization









2023 DOE OE Energy Storage Peer Review
Santa Fe, NM
Presentation ID #305

PRESENTED BY

Megan Diaz on Oct. 24, 2023

U.S. DEPARTMENT OF ENERGY NNSA

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SAND NO. SAND2023-11290C

BACKGROUND AND TERMINOLOGY

Liquid Electrolyte (LE)

- ✓ High ionic conductivity
- ✓ Fills void spaces
- ✗ Low-energy density graphite anode
- ✗ Several heat release pathways
- ✗ Flammable solvent

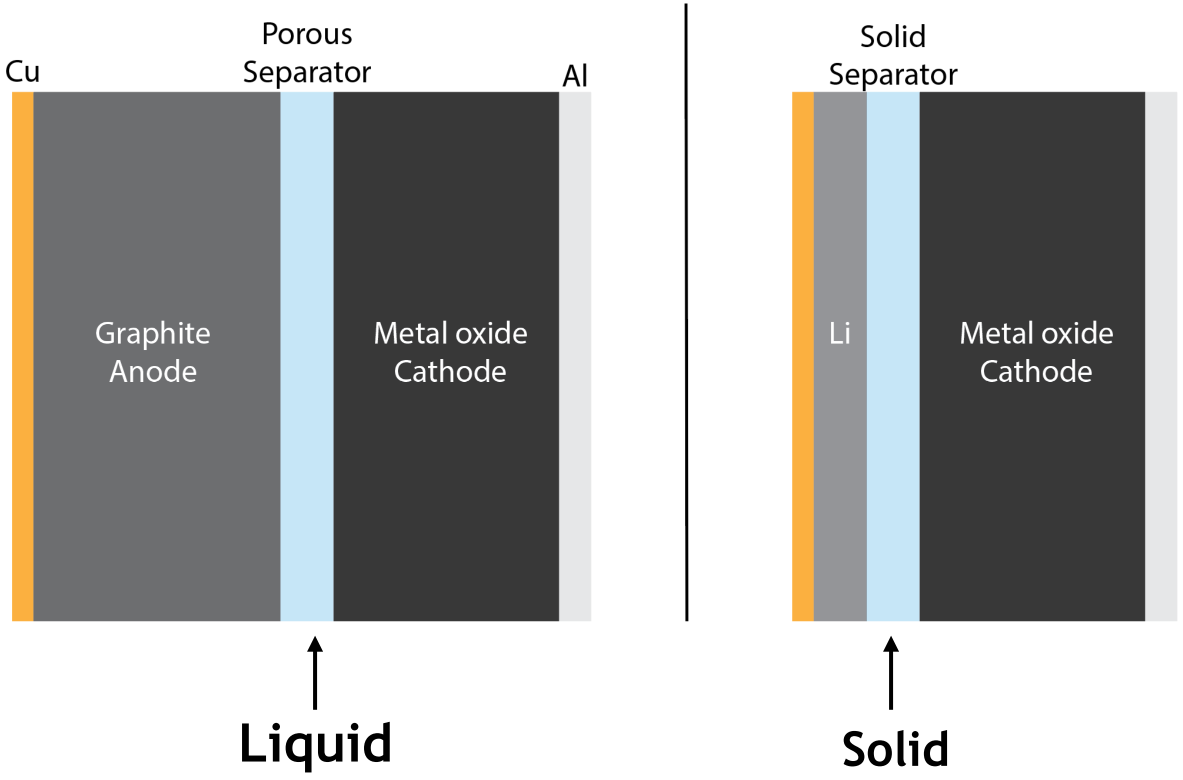
Solid Electrolyte (SE)

- ✓ Sufficient ionic conductivity
- ✓ Non-flammable
- ✓ High Energy Dense Li metal anode
- ✗ Poor interfacial contact

Lithium-Ion Battery (LIB)

Solid-State Battery (SSB) – some LE

All-Solid-State Battery (ASSB) – no LE



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.

PREVIOUS WORK

CellPress Joule

Perspective

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

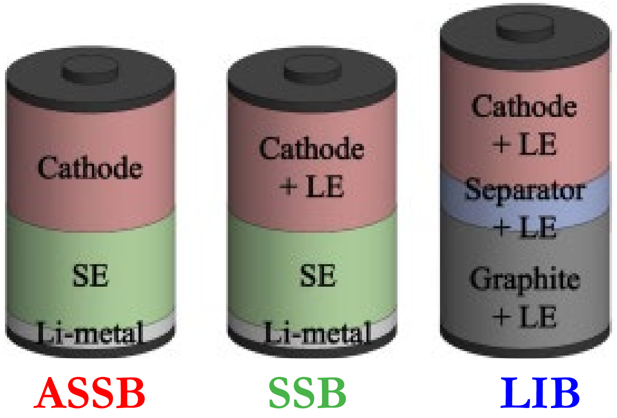
Alex M. Bates,[1,*] Yuliya Preger,[1] Loraine Torres-Castro,[2] Katharine L. Harrison,[3] Stephen J. Harris,[4] and John Hewson[5,*]

SUMMARY

All-solid-state batteries are often assumed to be safer than conventional Li-ion ones. In this work, we present the first thermodynamic models to quantitatively evaluate solid-state and Li-ion battery heat release under several failure scenarios. The solid-state battery anal-

Context & scale

A string of recent battery fires has sparked conversations on the safety of Li-ion batteries. A possible path to battery safety is a

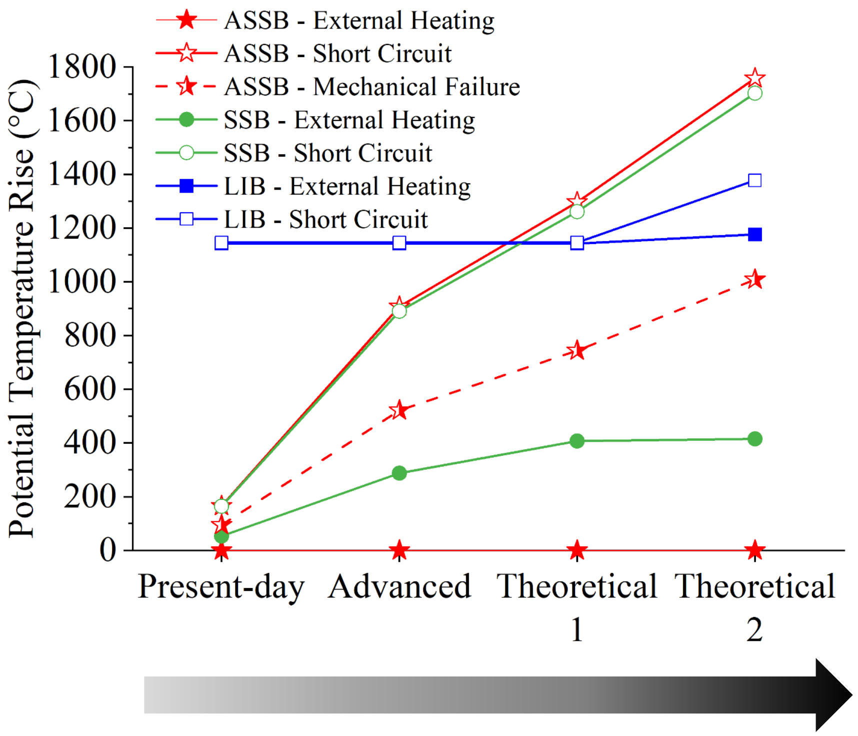


<u>Key Questions of Previous Work</u>

1.) Are solid-state batteries actually safer than LIB?

2.) If a small amount of LE is added to the battery (10%), is there a significant heat release difference compared to the ASSB technology?

-mitigate interfacial resistance



Increasing Energy Density

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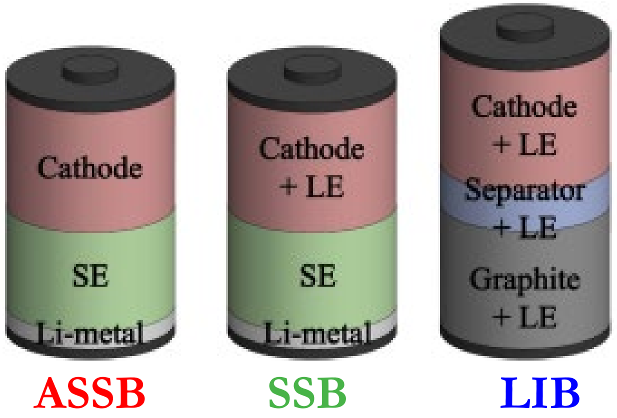

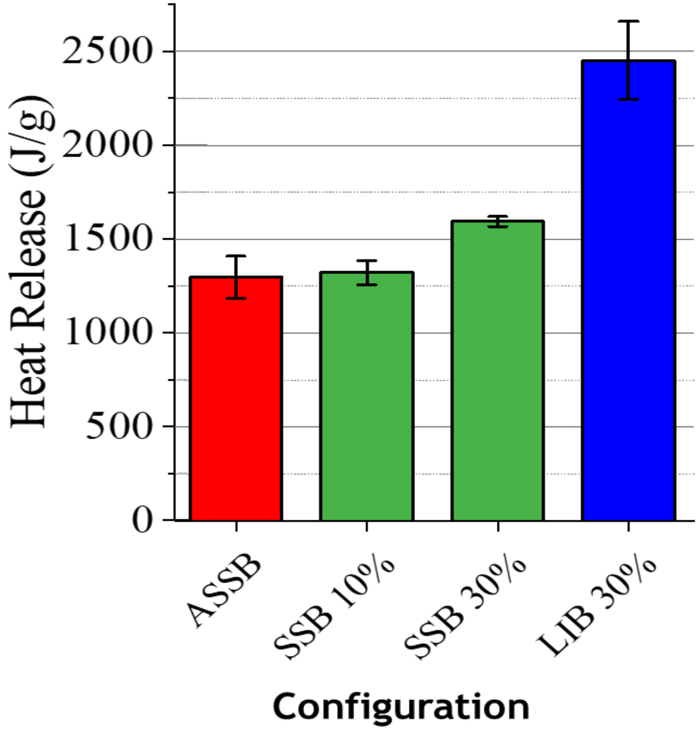

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PROJECT OBJECTIVES

OBJECTIVE: Experimentally validate the key questions from the thermal modeling paper using differential scanning calorimetry and materials characterization techniques.

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SIGNIFICANCE:

- The failure mechanisms of SSBs and ASSBs are not well understood, leading to an incomplete safety picture.
- SSBs are close to commercialization. Major exothermic failure incidents will risk human life and public perception of SSBs, especially in grid storage near residential areas.
- Lead to early investigation of safer battery chemistries
- Improved modeling predictions of the expected heat release

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ALIGNMENT WITH CORE MISSION OF DOE OE

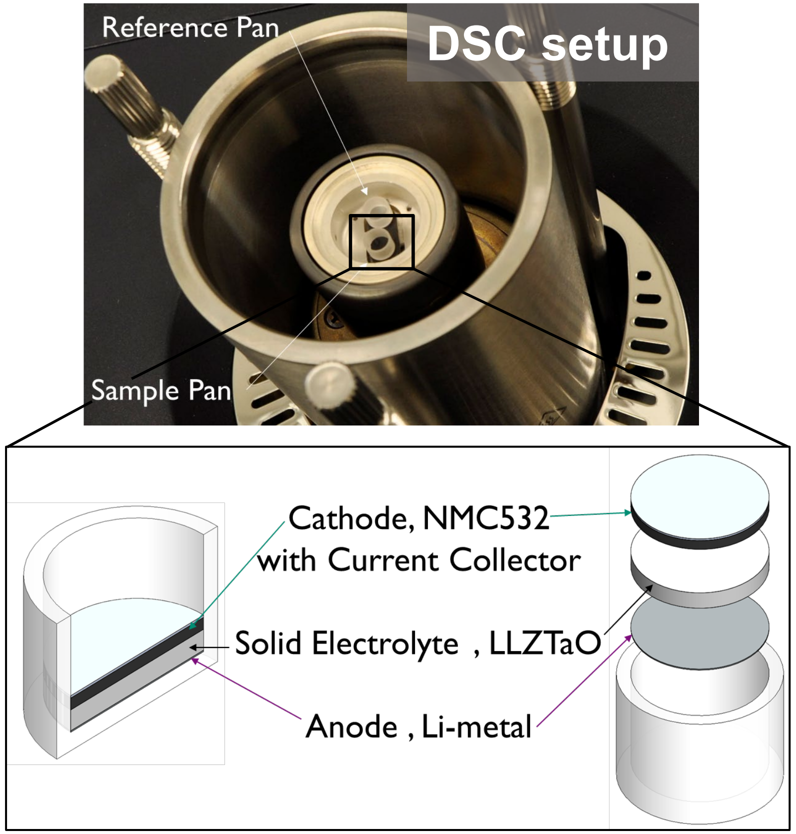
Fundamental understanding of the safety of the materials used in advanced li-ion batteries provides for resiliency, reliability and a confident understanding of the flexibility of new, innovative energy storage technologies used in grid energy storage.

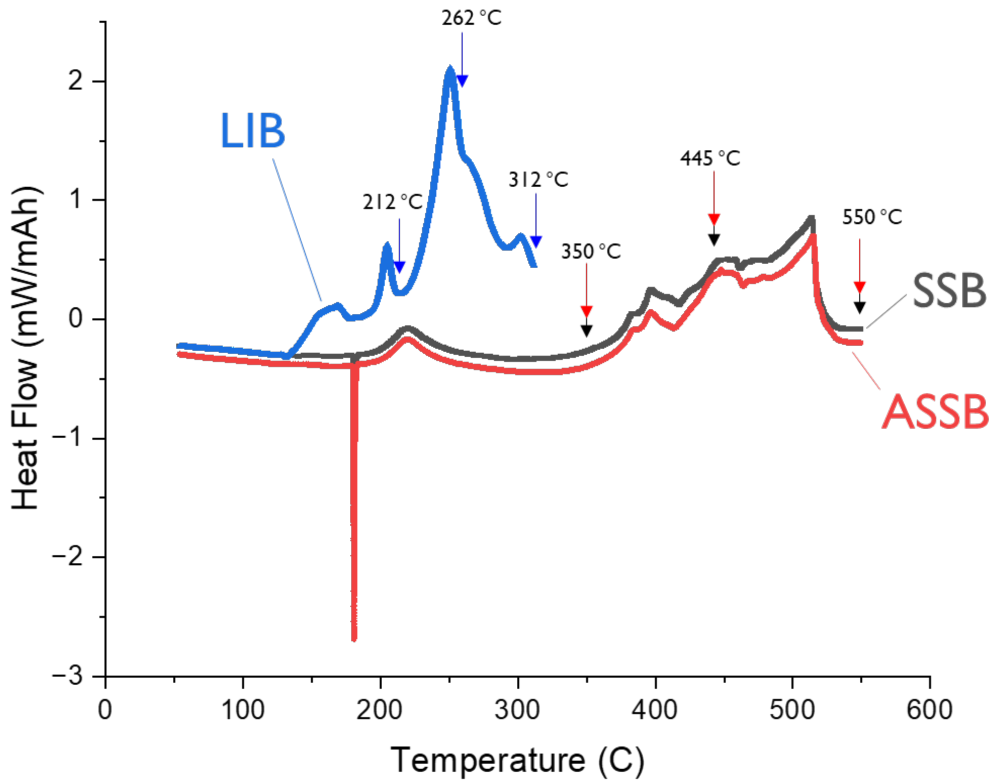
PROJECT METHODOLOGY

Experimental Procedure for Study of Cathode Degradation at Predetermined Temperatures

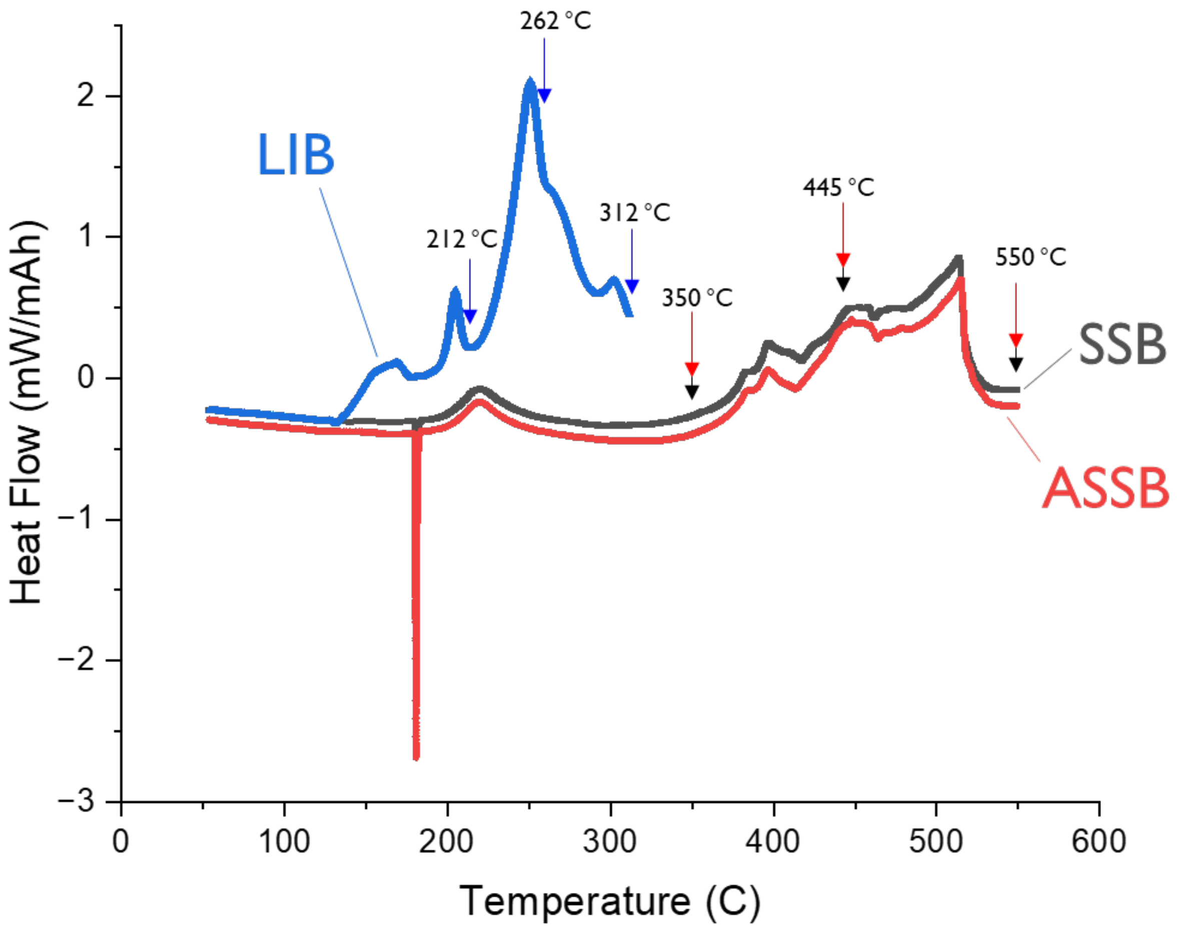
1.) Cathode Degradation: Oxygen Release that has the possibility to lead to exothermic reactions

2.) Completed DSC on microcells up to desired critical temperatures, extracted cathodes, performed XRD and SEM on cathodes





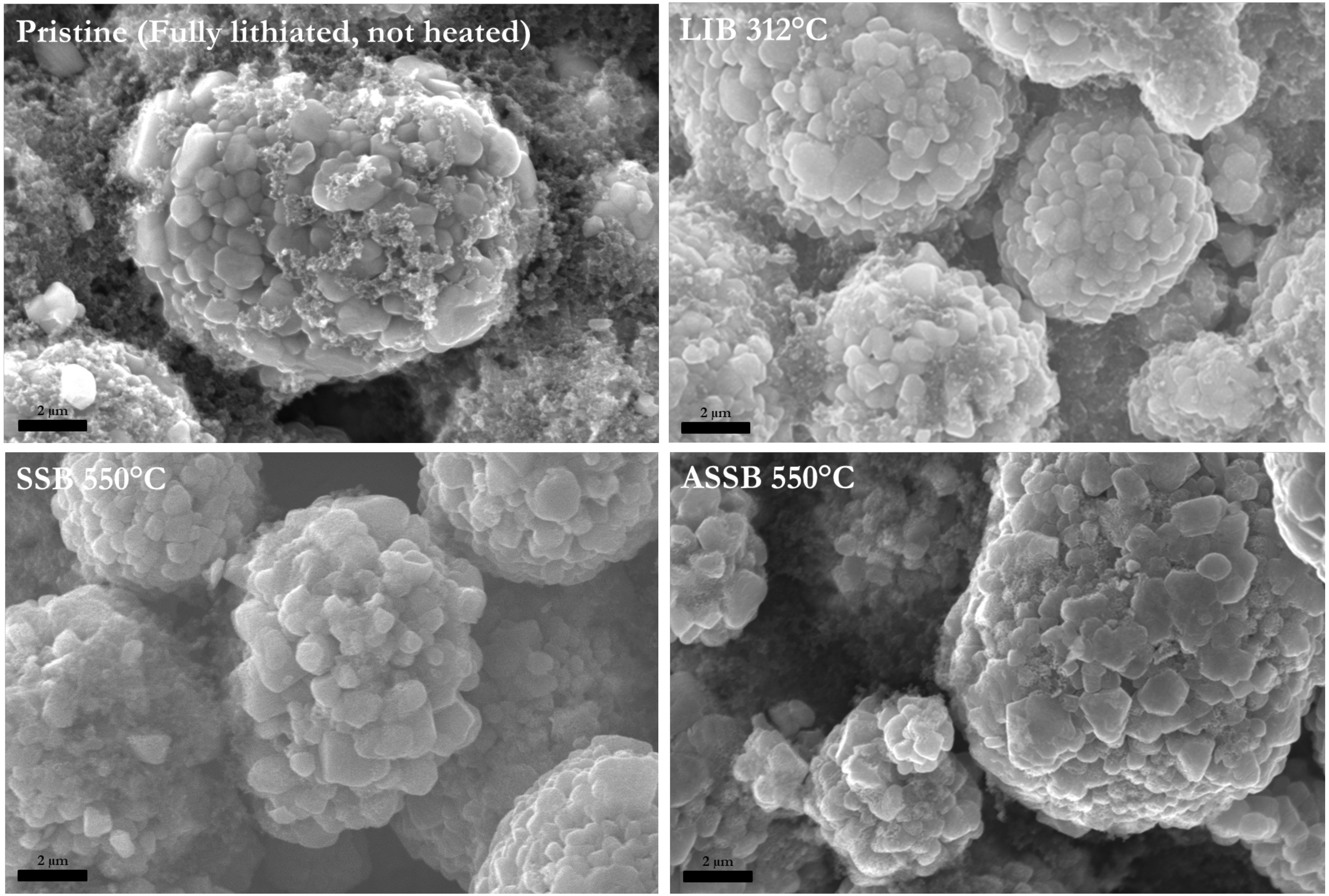
PROJECT RESULTS



-Heat flow for SSB and ASSB cases are extremely similar, with SSB slightly higher.

-Major exothermic peak for LIB at a significantly lower temperature.
-More heat release than SSB & ASSB

Project Results

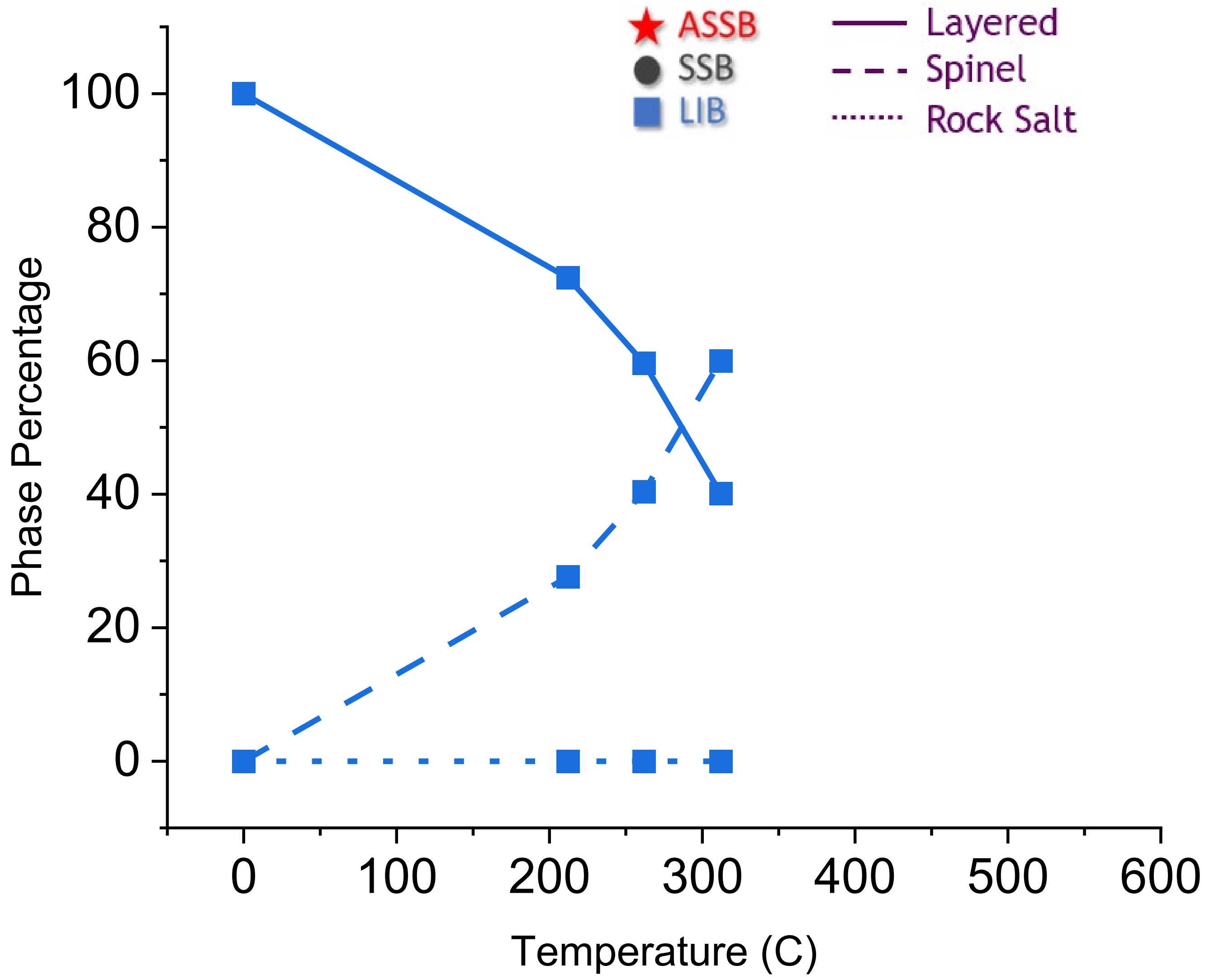


-SSB & ASSB exhibit degradation compared to pristine sample

-More binder in pristine image

-Next Steps: LIB at 550°C

PROJECT RESULTS



Layered → Rock Salt

$$MO_2 \rightarrow MO + O_2$$

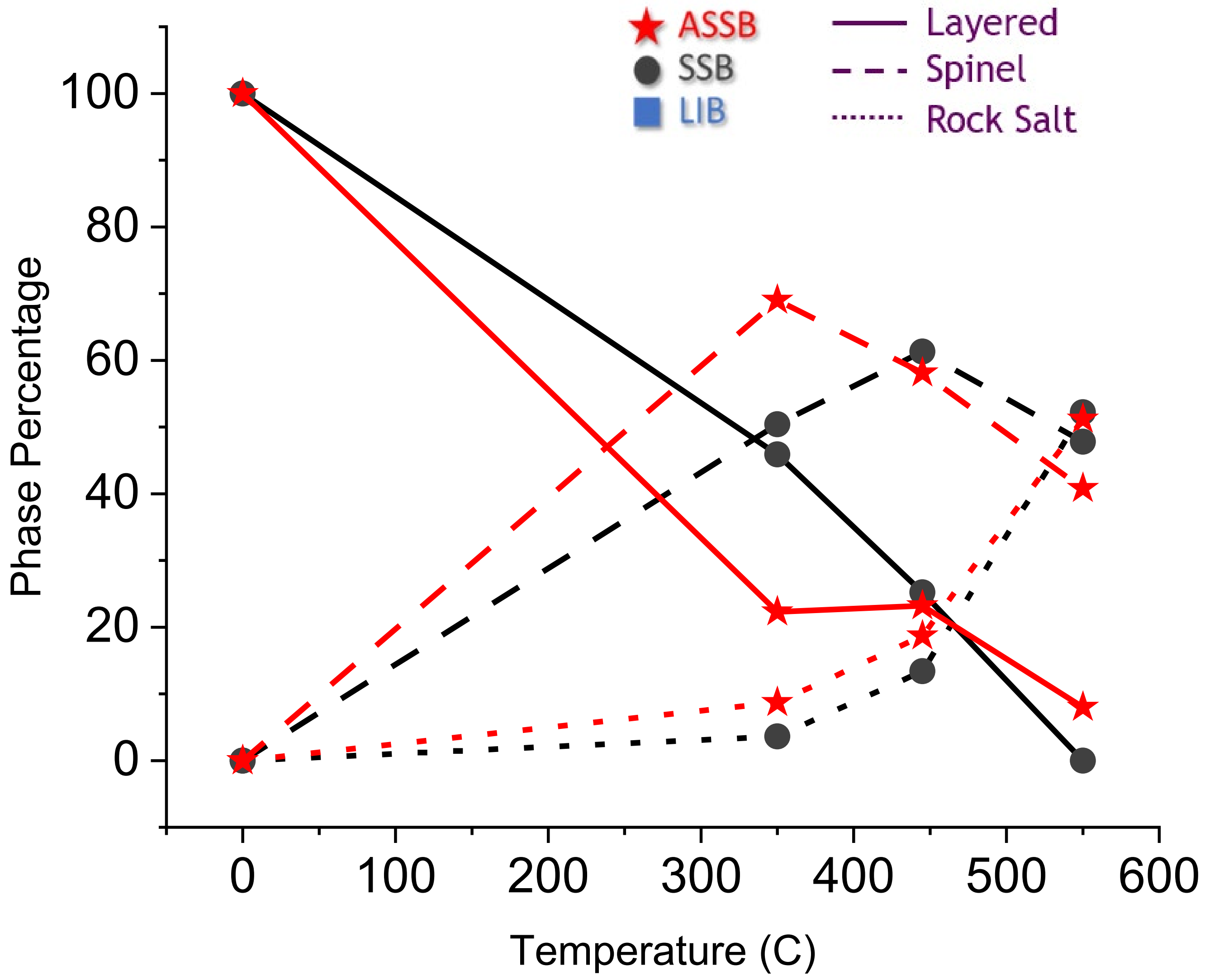
Spinel Intermediates

$$LiM_2O_4 \; and \; M_3O_4$$

Post-Major Exotherm

-LIB has started to degrade (60% spinel), but further release of oxygen is possible. If unreacted LE is still present, then an additional exothermic event is still possible.

PROJECT RESULTS



Layered → Rock Salt

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Post-Major Exotherm

-SSB and ASSB: Very similar extent of degradation, with over 50% rock salt phase after peak heat flow. (Oxygen release)

SUMMARY

- **SSB and ASSBs safer than LIB in some regards** – exothermic failure occurs at lower temperature for LIB : potentially lower onset temperature to thermal runaway
  but SSB and ASSBs are not inherently safe – oxygen release from cathode degradation provides opportunity for exothermic events (DSC, XRD)

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- Degradation of SSB and ASSB very similar – suggests similar failure modes, and confirms an acceptable trade-off in performance and safety by adding liquid electrolyte (DSC, XRD, SEM)
  Presence of a small amount of liquid electrolyte does not significantly change thermal failure mechanisms in SSB.
    - **Increased design options → Quicker Commercialization**

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    - **Increased design options → Quicker Commercialization**

Grid Energy Storage will benefit from a larger safe operating temperature window of SSBs, and the ability to predict with confidence the safety of next-generation energy storage battery chemistries.

Project Team

Megan Diaz
Energy Storage Tech & Systems

Yuliya Preger
Energy Storage Tech & Systems

Alex Bates
Power Sources R&D

Loraine Torres-Castro
Power Sources R&D

Nathan B. Johnson
Power Sources R&D

PROJECT IMPACT: Publications and Presentations

Presentations

- A. Bates, J. Langendorf, J. Lamb, Y. Preger, L. Torres-Castro, M. Diaz "How Safe Are Solid-State Batteries? An Exploration of Heat Release" The Minerals, Metals & Materials Society (TMS) Annual Meeting & Exhibition, San Diego, CA, March 19-23, 2023.
- M. Diaz, A. Bates, Y. Preger, L. Torres-Castro, R. Shurtz "Investigation of Exothermic Reaction Pathways in Solid-State Batteries: Implications for Safety" Materials Research Society (MRS), San Francisco, CA, April 10-14, 2023.
- M. Diaz, A. Bates, Y. Preger, L. Torres-Castro, K. Harrison, S. Harris, J. Hewson "Are Solid-State Batteries Safer Than Lithium-ion Batteries?" DOE ESS Safety & Reliability Forum, Santa Fe, NM, June 6-8, 2023. (Poster)
- M. Diaz, A. Bates, Y. Preger, L. Torres-Castro, N. B. Johnson "Characterizing the Cathode Degradation Process from Thermal Abuse in Solid State Batteries" The Electrochemical Society (ECS), Gotenborg, Sweden, October 8-12, 2023 (Poster)

Publications

- "Characterizing the Cathode Degradation Process from Thermal Abuse in Solid State Batteries" (In preparation)
- "Consistency in Differential Scanning Calorimetry Testing of Li-ion Battery Materials Across Instruments and Institutions" (In preparation)

Previous Work

- 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
- 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 ACKNOWLEDGMENTS

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

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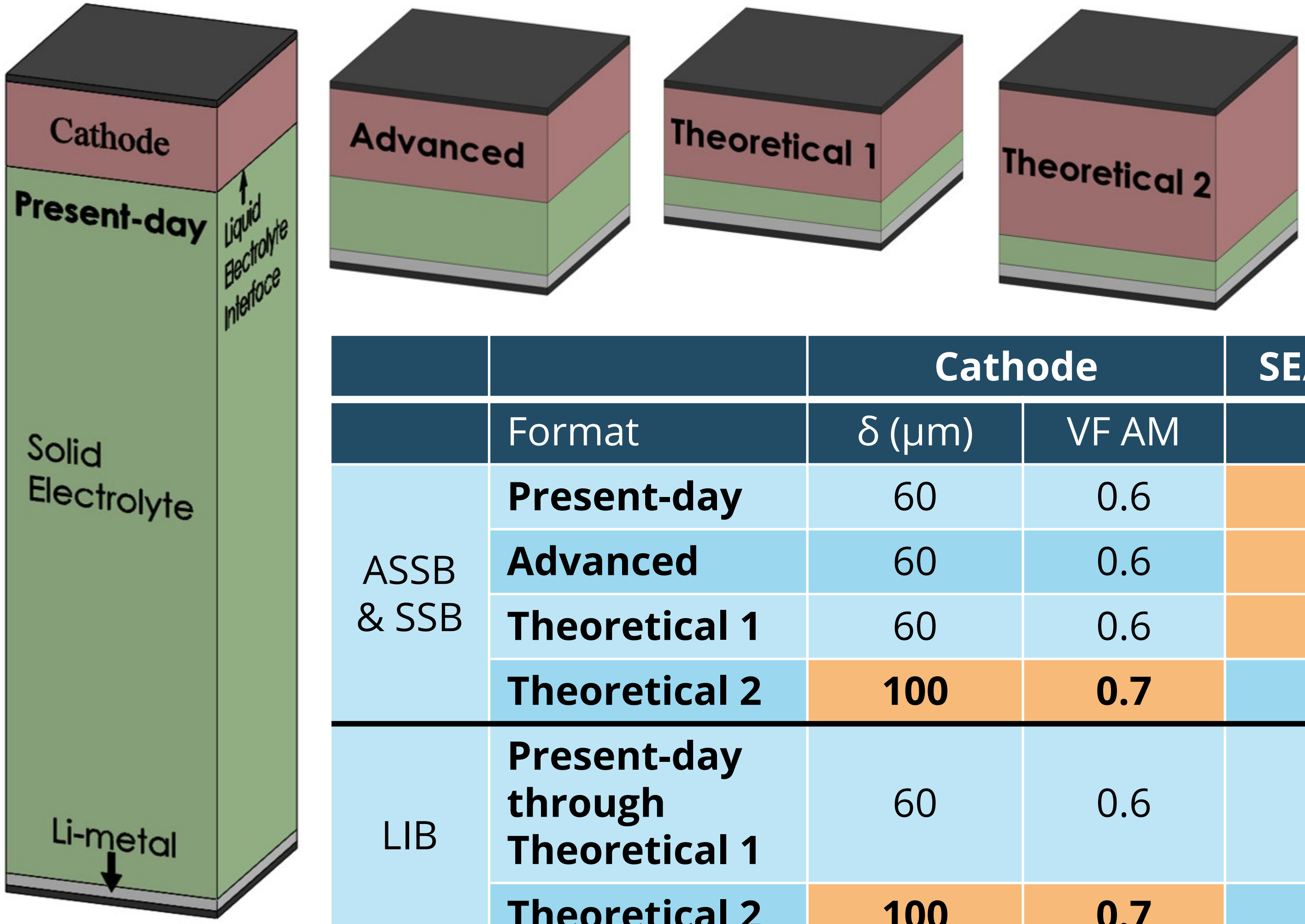
For questions about this presentation: **Megan Diaz**
Corresponding email: mmdiaz@sandia.gov

For further details on modeling and initial experiments, visit the poster "*Are Solid-State Batteries Safer Than Lithium-ion Batteries?*"- Alex Bates

Supplementary Slides

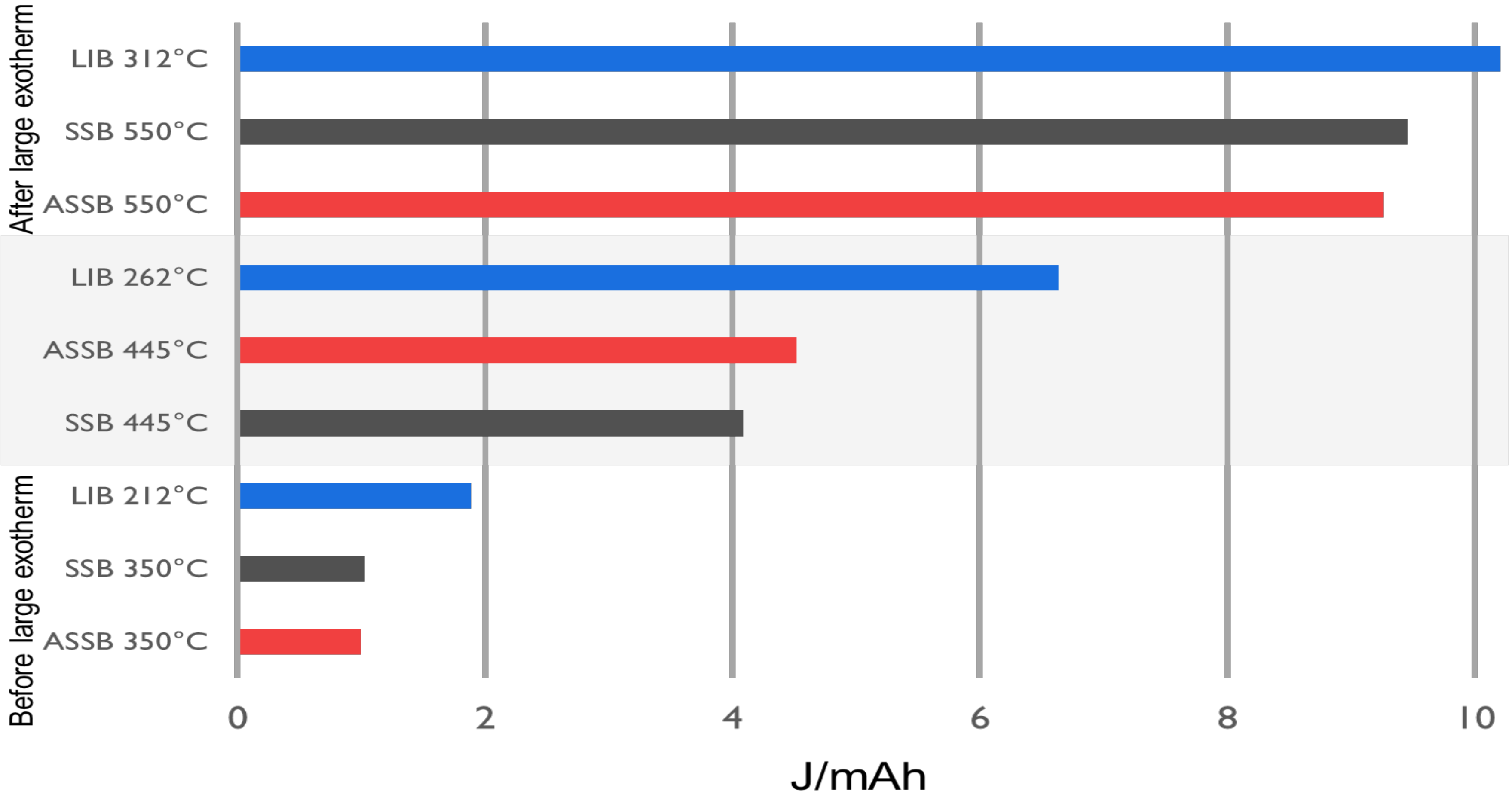
Thermal Modeling Cell Formats



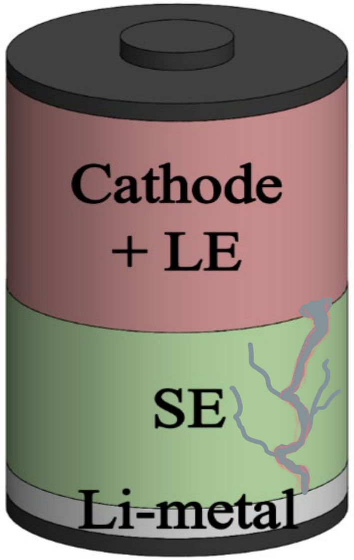
		Cathode		SE/Separator
	Format	δ (μm)	VF AM	δ (μm)
ASSB & SSB	**Present-day**	60	0.6	**500**
	Advanced	60	0.6	**50**
	Theoretical 1	60	0.6	**20**
	Theoretical 2	**100**	**0.7**	20
LIB	**Present-day through Theoretical 1**	60	0.6	20
	Theoretical 2	**100**	**0.7**	20

Increasing Energy Density

Heat Flow from each Temperature Stopping Point



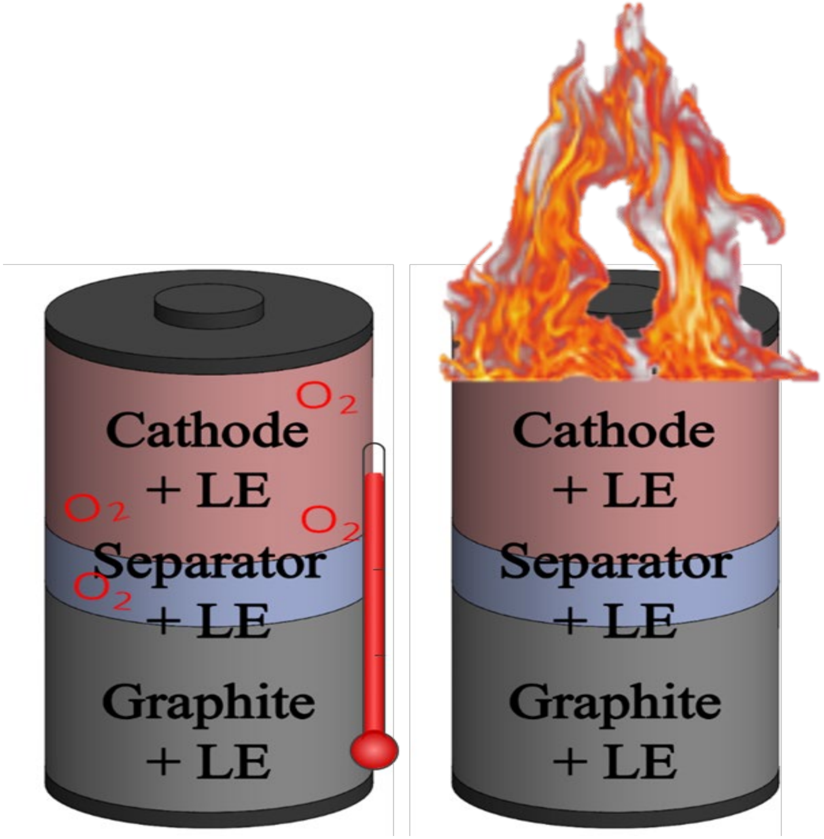
Heat Release Failure Modes



<u>Short Circuit (ASSB,SSB,LIB)</u>

Dendritic hard short, nail penetration test

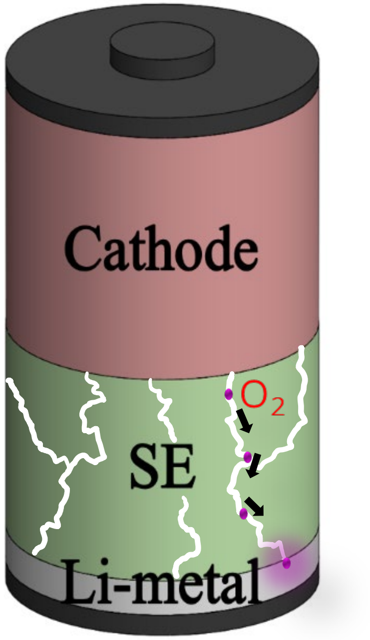
Hard short causes heat release



<u>External Heating (ASSB,SSB,LIB)</u>

Thermal Runaway of adjacent battery

Oxygen generated from breakdown of cathode reacts with LE (& anode for LIB)



<u>SE Mechanical Failure (ASSB)</u>

Cracking of SE: ie. Car accident, SE too thin

SE integrity failure allows for oxygen from cathode to mix with Li-metal