



Exceptional service in the national interest

Thermal Stability of Solid-State Battery Components with Liquid Electrolyte

Alex M. Bates, Yuliya Preger, Loraine Torres-Castro, Katharine L. Harrison, Stephen J. Harris, John Hewson

May 9th, 2022
2022 MRS Spring Meeting

SAND2021-14837 C

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.





Solid-State Batteries, Why the Excitement?

Two Primary Advantages

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

LUX SOLID STATE BATTERY TECHNOLOGY LANDSCAPE

1 OXIDE-BASED ELECTROLYTE
From top to bottom: corporates, small-medium enterprises, research institutes,
Panasonic muRata BOSCH dyson
NGK ilika QuantumScope ProLogium University of Colorado Denver
M

2 SULFIDE-BASED ELECTROLYTE
From top to bottom: corporates, small-medium enterprises, research institutes,
TOYOTA FUJIFILM HITEC LG Chem IDEMITSU
SAMSUNG ELECTRONICS LISIEN ZEON
Solid Power POLY PLUS UNIVERSITY OF MARYLAND

3 POLYMER-BASED ELECTROLYTE
From top to bottom: corporates, small-medium enterprises, research institutes,
LG Chem HITACHI Wildcat Discovery Technologies APB Blue Solutions
Hydro Québec SE Rensselaer

4 HYBRID-ELECTROLYTE
From top to bottom: corporates, small-medium enterprises, research institutes,
LG Chem Panasonic GS YUASA BASF Ampere
SARUO ProLogium Ampcera Hydro Québec KGT
Caltech

Shishir Jairam, Lux Research, October 27, 2021



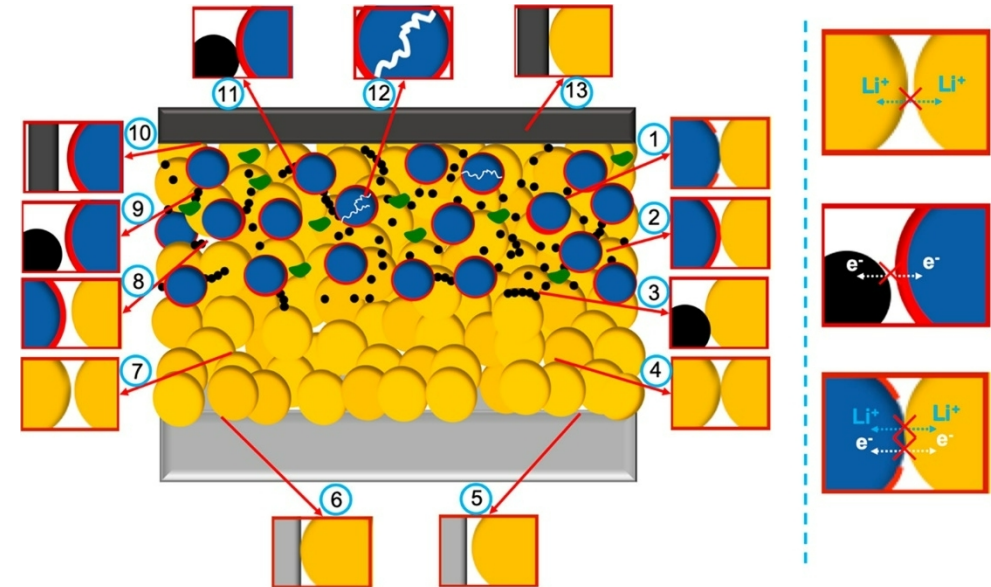
Miller T. Electric bus fires: Bolloré's LMP battery blamed. 247 News Bulletin. 2022 April 30, 2022.

Omit title from source and indicate it is a SSB fire

Challenges Introduced by Removing Liquid Electrolyte

Interfacial Resistance

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



Void

- ⑤ Li metal/electrolyte (void)
- ⑦ Electrolyte/electrolyte (void)
- ⑧ Coated cathode/electrolyte (void)
- ⑨ Conductive additive/coated cathode (void)
- ⑩ Cathode current collector/coated cathode (void)
- ⑫ Cracks in the cathode

Chemical reaction

- ① Uncoated cathode/electrolyte
- ⑥ Li metal/electrolyte (contact)

Electrochemical reaction

- ② Coated cathode/electrolyte (contact)
- ③ Conductive additive/electrolyte
- ④ Electrolyte/electrolyte (contact)
- ⑥ Li metal/electrolyte (contact)
- ⑬ Cathode current collector/electrolyte

Grain boundary

- ④ Electrolyte/electrolyte (contact)
- ⑪ Coated cathode/conductive additive



Heat Release vs. Liquid Volume Fraction (VF)

All: short circuit heat release equal

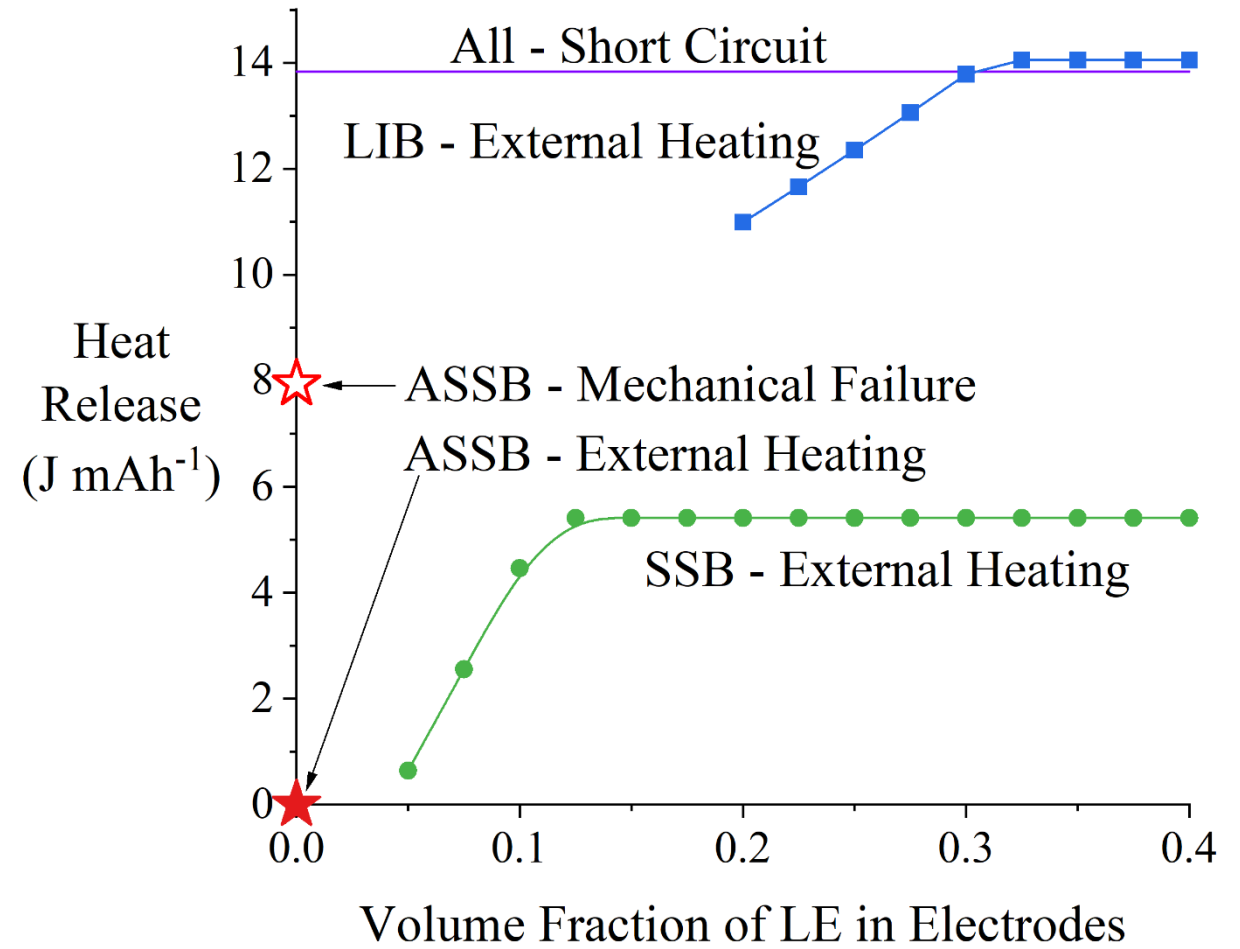
ASSB: no heat release from external heating

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

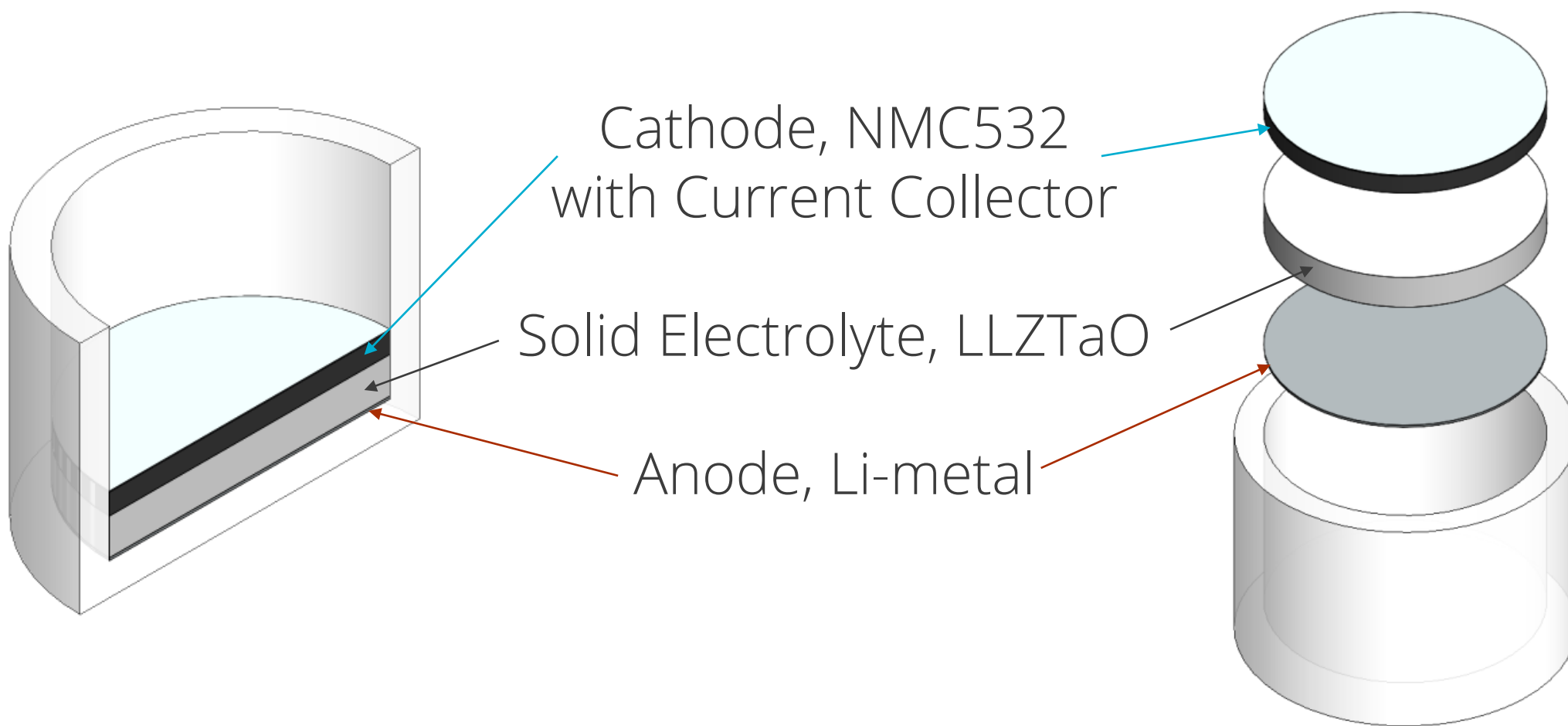




Key Findings

- 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

DSC Microcell Setup

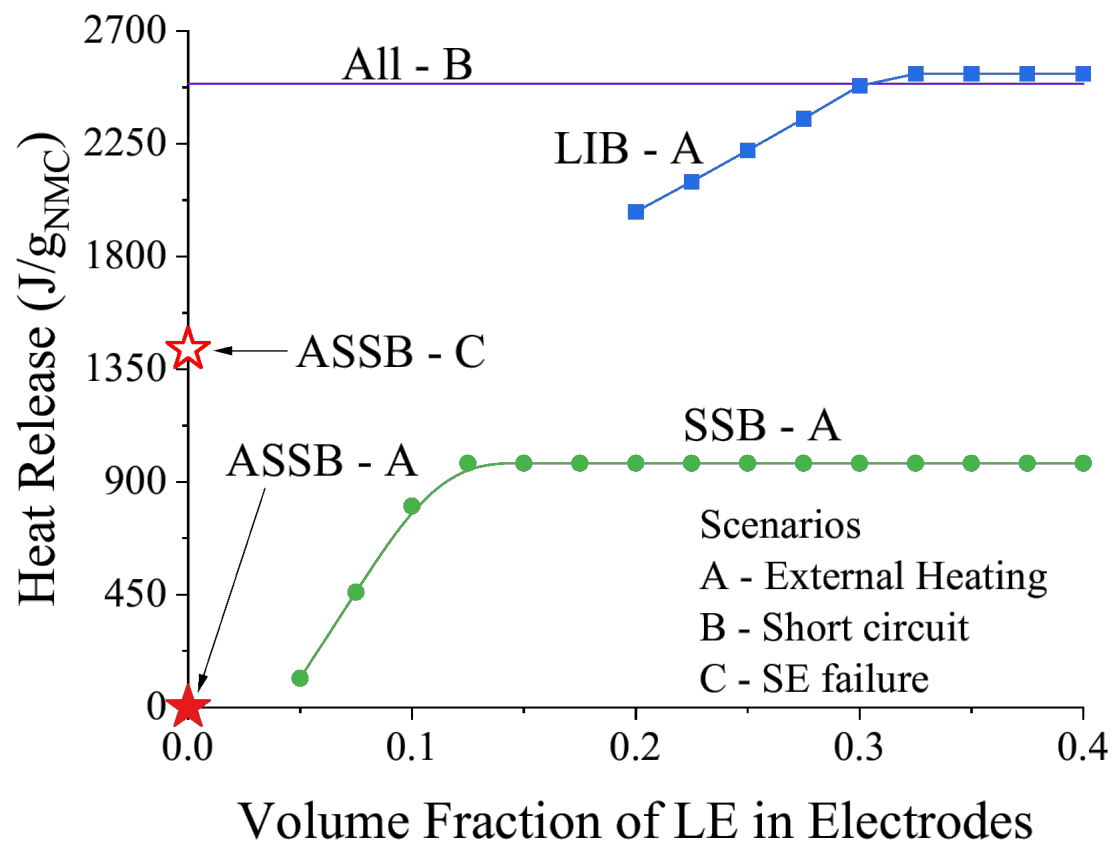




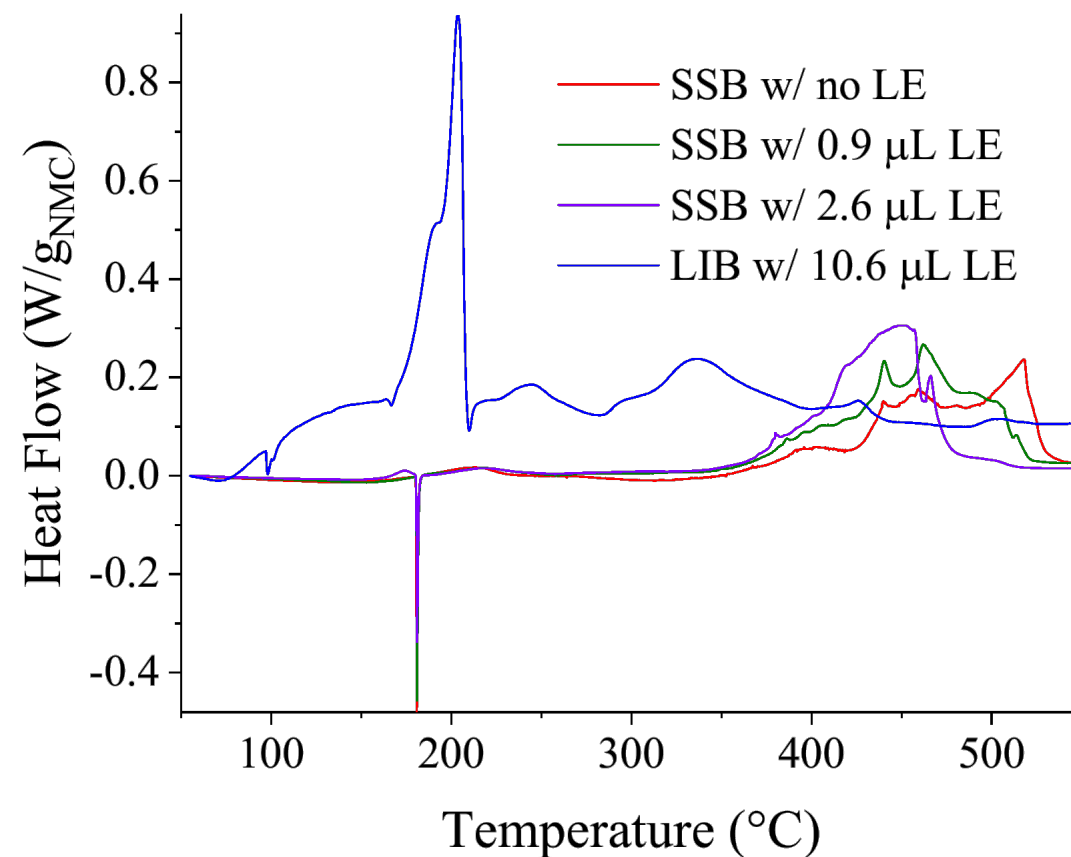
DSC Results of Microcells

Point where in the theoretical graph that
Corresponds to experimental results

Theoretical Model



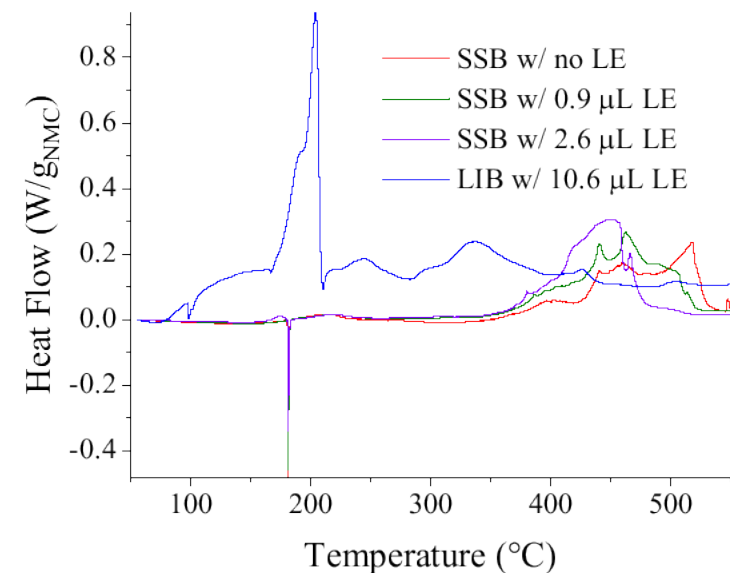
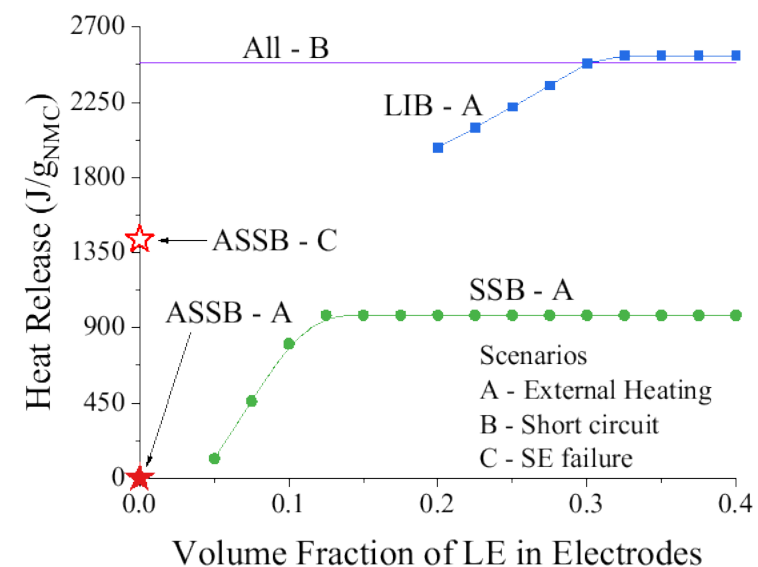
Experimental Results





Tabulated Heat Release Data

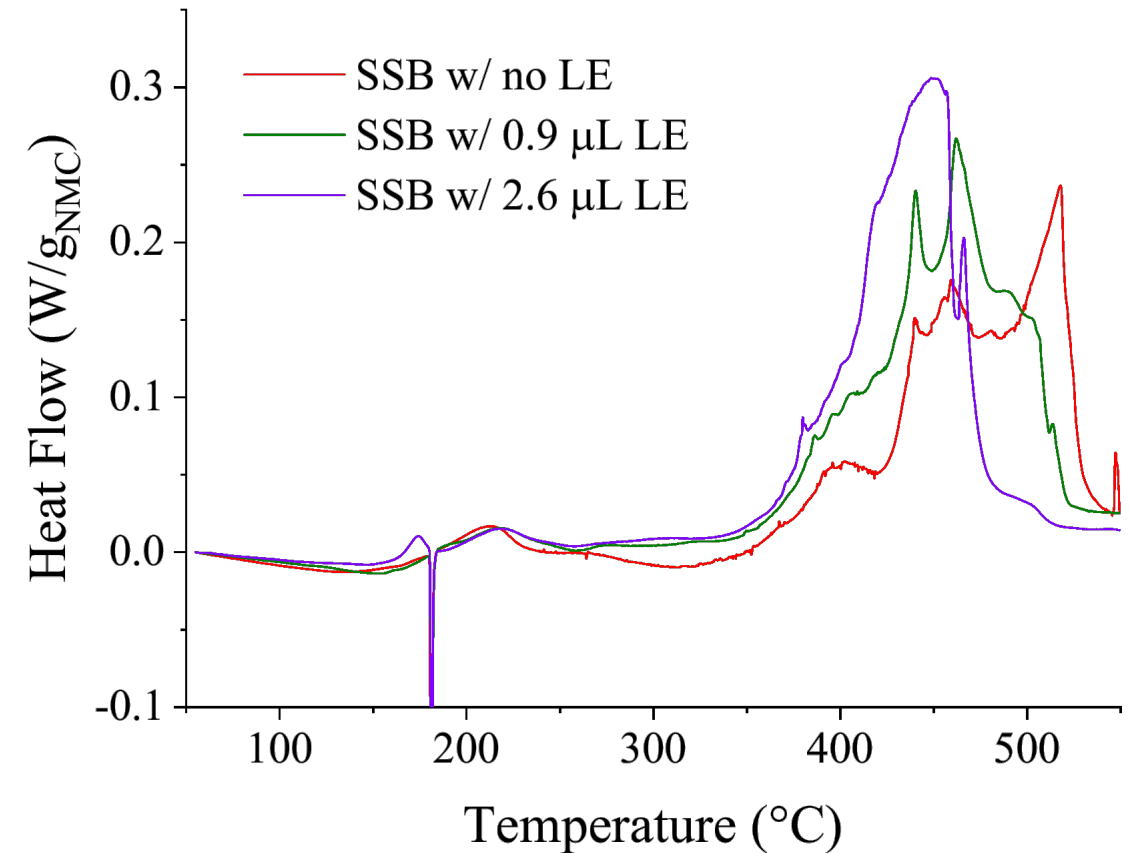
Configuration	Theoretical (J/g _{NMC})	% Change	Experimental (J/g _{NMC})	% Change
ASSB*	0 or 1429		1082	
SSB 10% (0 μ L LE)	804		1199	
SSB 30% (2.6 μ L LE)	975	21.3	1250	4.25
LIB 30% (10.6 μ L LE)	2481	154.5	3218	157.4





Impact of Liquid Electrolyte on SSB Heat Release

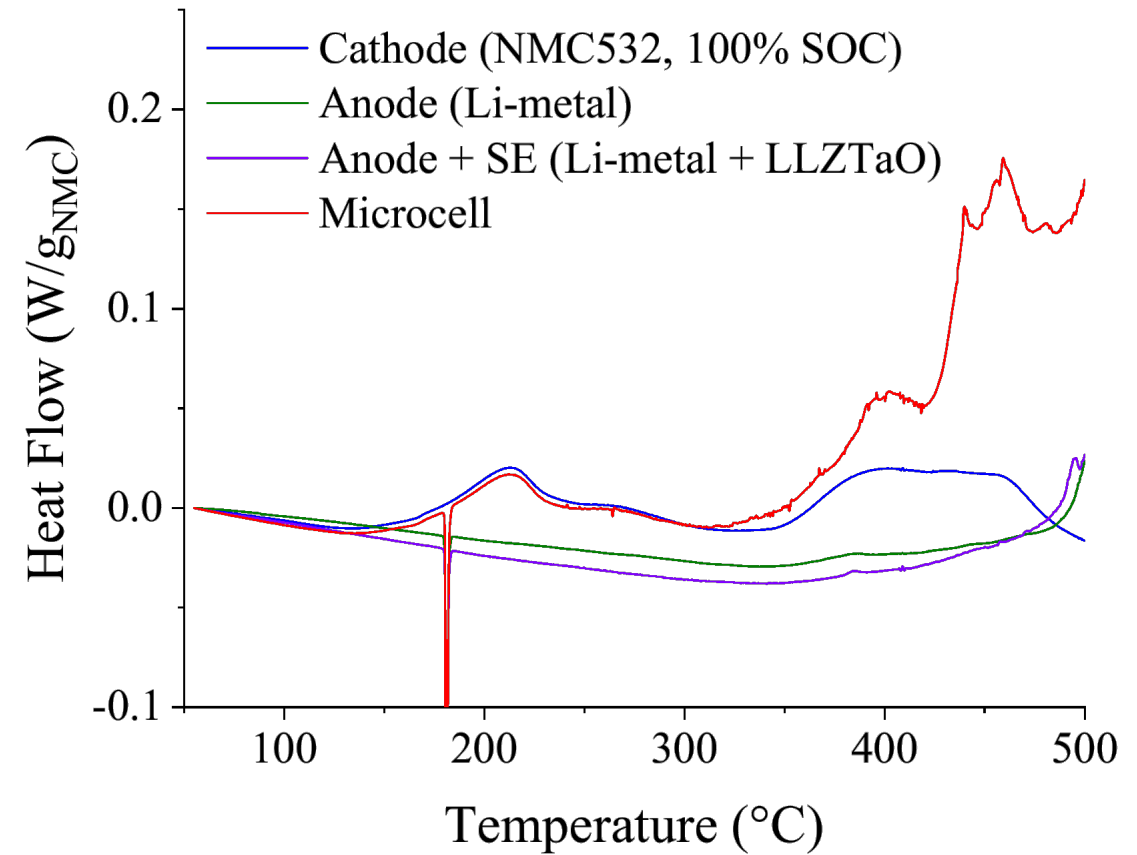
- Large exotherms occur at high temperatures relative to the LIB
- Onset temperature to large exotherms remains around 350 °C, regardless of LE volume
- LE volume has an impact on the peak exotherm position (lower temperature)





Effect of Li-metal on SSB Heat Release

- Without Li-metal (or with only Li-metal), the high temperature exotherms remain relatively small
- With the cathode in proximity of Li-metal (separated by SE), the exothermic heat release increases dramatically





Conclusions

- Experimental DSC results corroborate theoretical values well
 - The jump in heat release moving from SSB with LE to LIB is spot on
- Liquid electrolyte does have an impact on heat release in a SSB
 - Heat release remains relatively small with a potentially higher onset temperature
- Adding and increasing the volume of LE in an SSB has an impact on heat release
 - Heat release, and potentially onset temperature, remains small relative to the LIB, even with LE
- Li-metal has a significant impact on the heat release of an NMC532 cathode at 100% SOC
 - The ability of the SE to separate cathode generated species from reacting with the Li-metal anode can significantly impact this heat release

Can I abuse your batteries?



Co-authors for Joule Publication on Thermodynamic Modeling of SSBs



Yuliya Preger



Loraine Torres-Castro



Katharine L. Harrison



Stephen J. Harris



John Hewson



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.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.



Questions?

Alex Bates

ambates@sandia.gov

[https://www.linkedin.com/in/
alex-bates/](https://www.linkedin.com/in/alex-bates/)