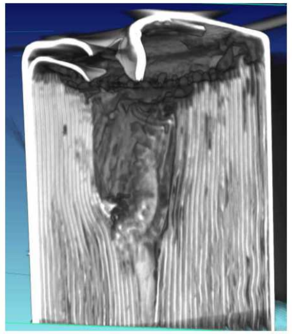
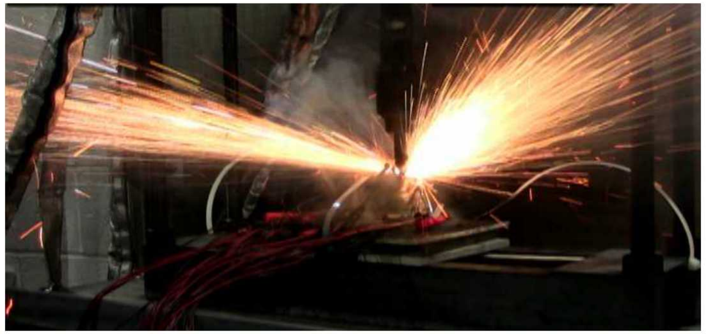
SAND2020-10026C

Material Science-Based Predictions of Single-Cell Thermal Failures





DOE Office of Electricity Peer Review: September 30, 2020

Randy Shurtz, John Hewson, Andrew Kurzawski, Loraine Torres-Castro

Sandia National Laboratories

Fire Science and Technology, Power Sources Research and Development

SAND

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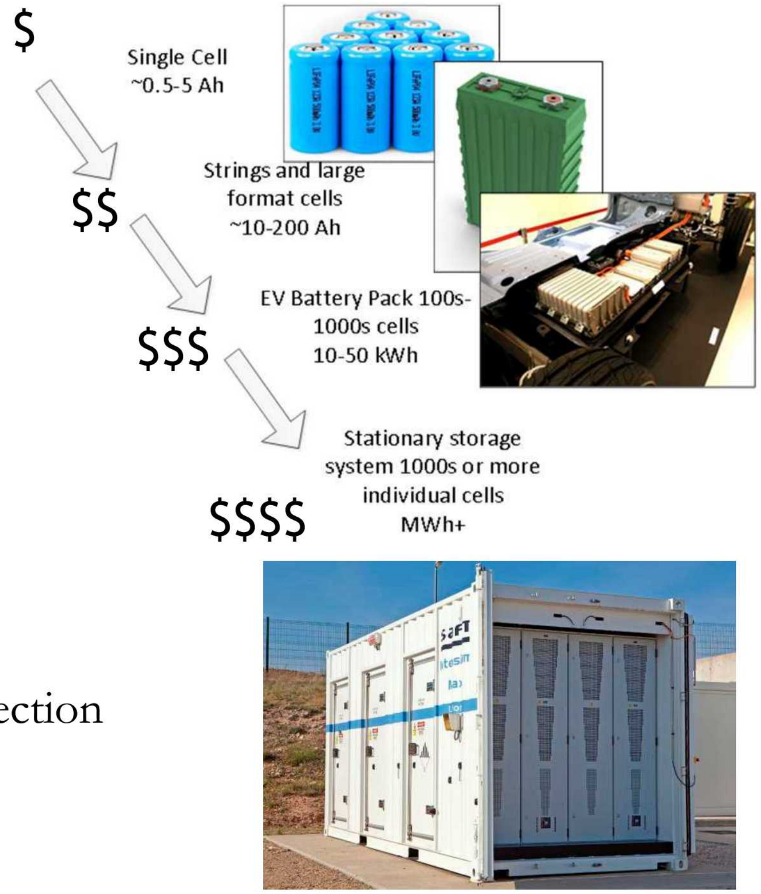
Overview of Thermal Runaway Modeling

SIGNIFICANCE:

- Heat source terms in legacy thermal runaway models have limitations
  - Outdated with respect to current battery materials
  - Designed for low-temperature onset rather than high-temperature propagation
- Models should be designed to keep pace with deployment of new materials
  - Transition from empirical approaches to materials-centric approaches
  - Gain ability to forecast safety characteristics in the early stages of materials selection

ALIGNMENT WITH CORE MISSION OF DOE OE:

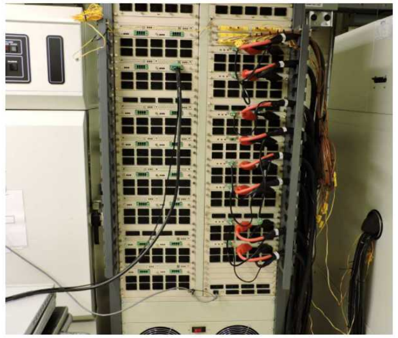
- Validated safety and reliability is one of the critical challenges identified in 2013 Grid Energy Storage Strategic Plan



www.cnn.com www.nissan.com
www.samsung.com www.saft.com
www.internationalbattery.com

Project Team

Sandia Battery Test Facilities



Yuliya Preger

Reed Wittman

Armando Fresquez

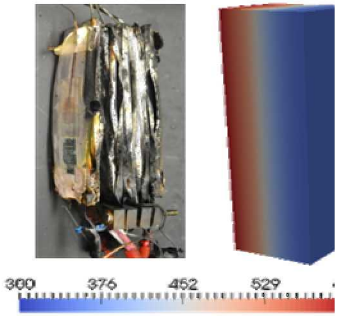
Sandia Battery Abuse Lab

- Loraine Torres-Castro

Joshua Lamb

- Chris Grosso
- Lucas Gray
- Jill Langendorf

Sandia Fire Sciences



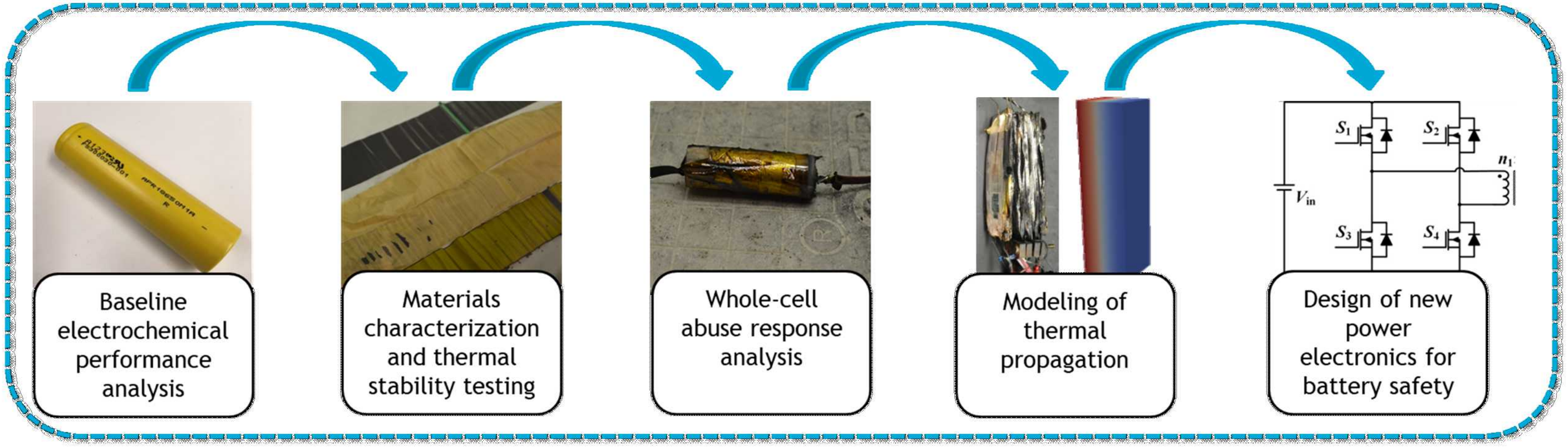
John Hewson

Randy Shurtz

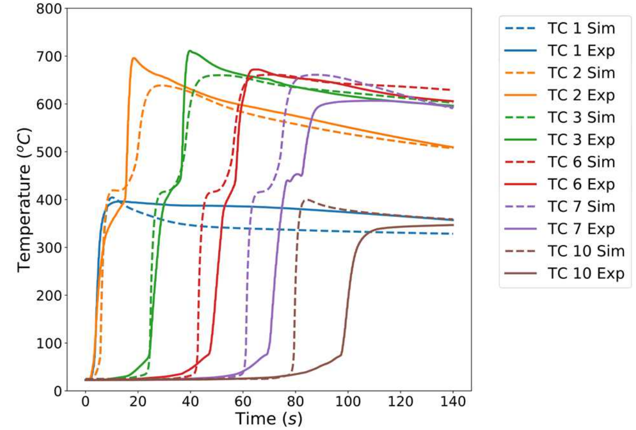
Andrew Kurzawski

Center for Integrated Nanotechnologies

Sergei Ivanov



Thermal Runaway Modeling Objectives

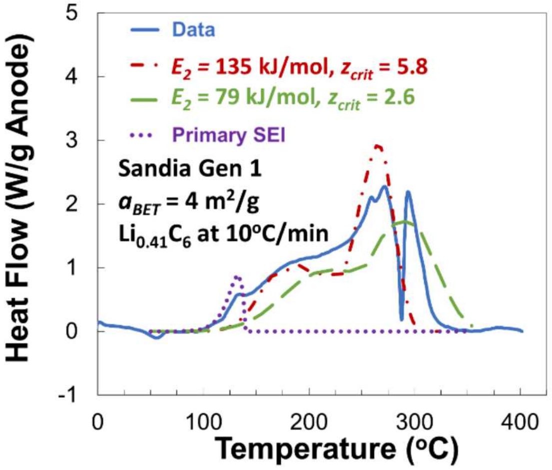


<u>Predict thermal runaway behavior in large systems (multi-cell)</u>

- 1 publication accepted in FY2020

<u>Develop improved heat-source models for thermal runaway</u>

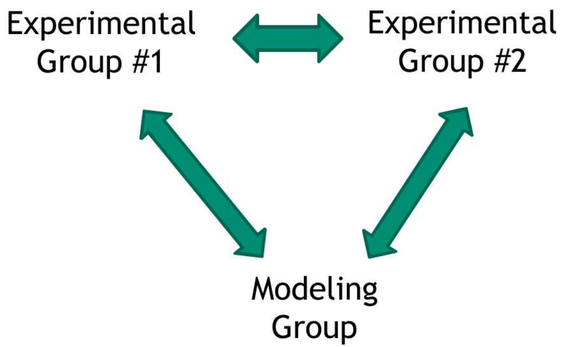
- Include proper dependence on material properties, temperature, state of charge
- Extend to additional electrode materials of commercial interest
- 1 publication accepted and 1 additional publication submitted in FY2020



<u>Promote effective methods and collaboration in thermal runaway studies</u>

- Publish perspectives, models, and tools
  - Thermodynamic reaction heat calculator for cathode decomposition posted online in FY2020
- Set up thermal runaway collaboration workshops (task for full project team)

<u>**Enhance Flow of Data and Insights**</u>



Motivation: Why Study Thermodynamics of Battery Materials?

Variants of layered metal oxide cathodes too numerous for full experimental safety evaluation

Materials science/thermodynamic approach allows predictions of:

- Whether a decomposition reaction can occur
- How much heat release can be expected under different conditions

Heat sources from thermodynamics are readily adapted to new materials

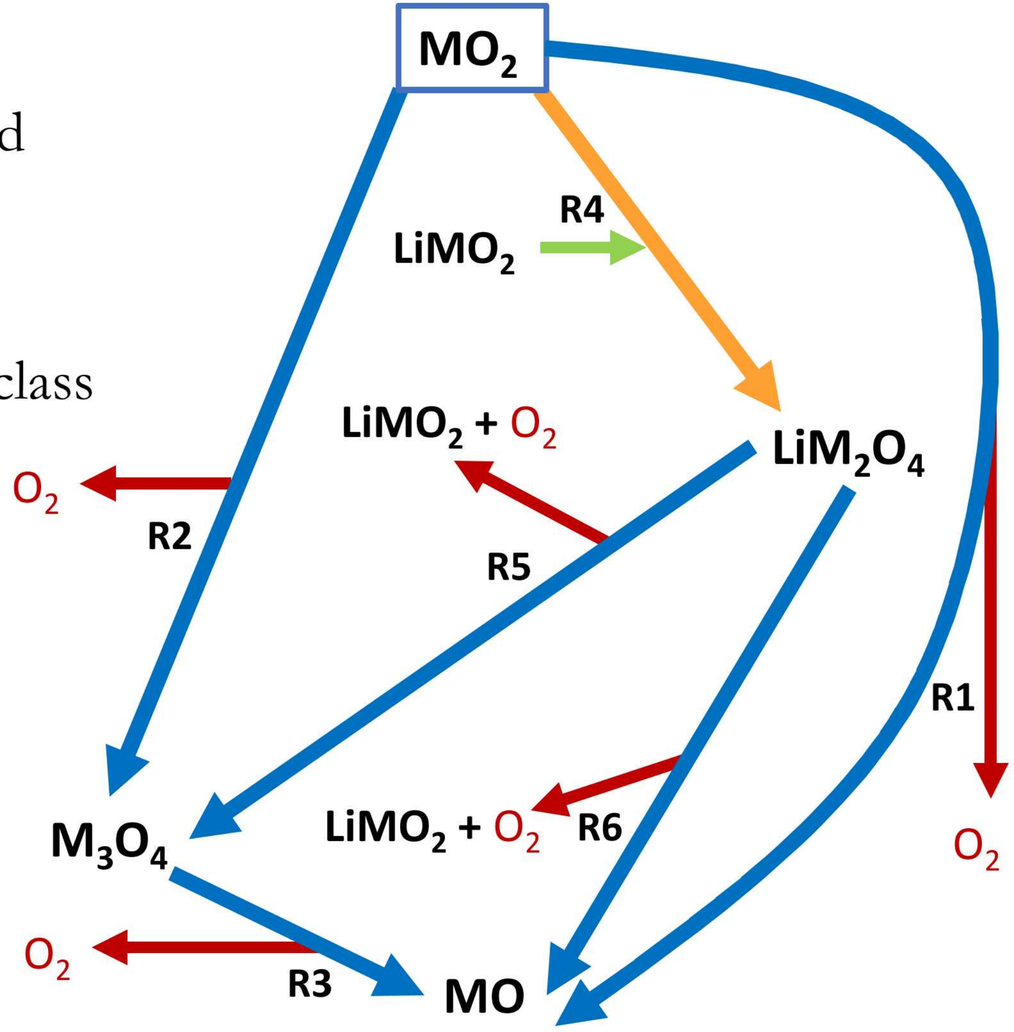
- Can account for multiple stages of heat release
- May also allow kinetic rates in thermal runaway models to be generalized for families of materials

Results: Thermodynamics of Cathode Thermal Runaway

Decomposition paths for de-lithiated Li_xMO_2

Layered metal oxide cathode decomposition

- Published database of 36 formation enthalpies compiled from over 42 literature sources for cathode materials
- Yields up-front predictions of heat release for a whole class of Li_xMO_2 cathode materials with electrolytes
  - Existing or proposed compositions
- Excel-based calculator released online
  - Simplified web calculator under development



M = Ni, Co, Mn, Al as well as mixtures (NMC, NCA, etc.)

R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9

R. C. Shurtz. "Thermodynamic Reaction Heat Calculator for Layered Metal Oxide Cathodes in Organic Electrolytes." https://www.sandia.gov/ess-ssl/thermodynamic-web-calculator/

Results: Thermodynamics of Solvent Oxidation

Spontaneous processes have negative ΔG

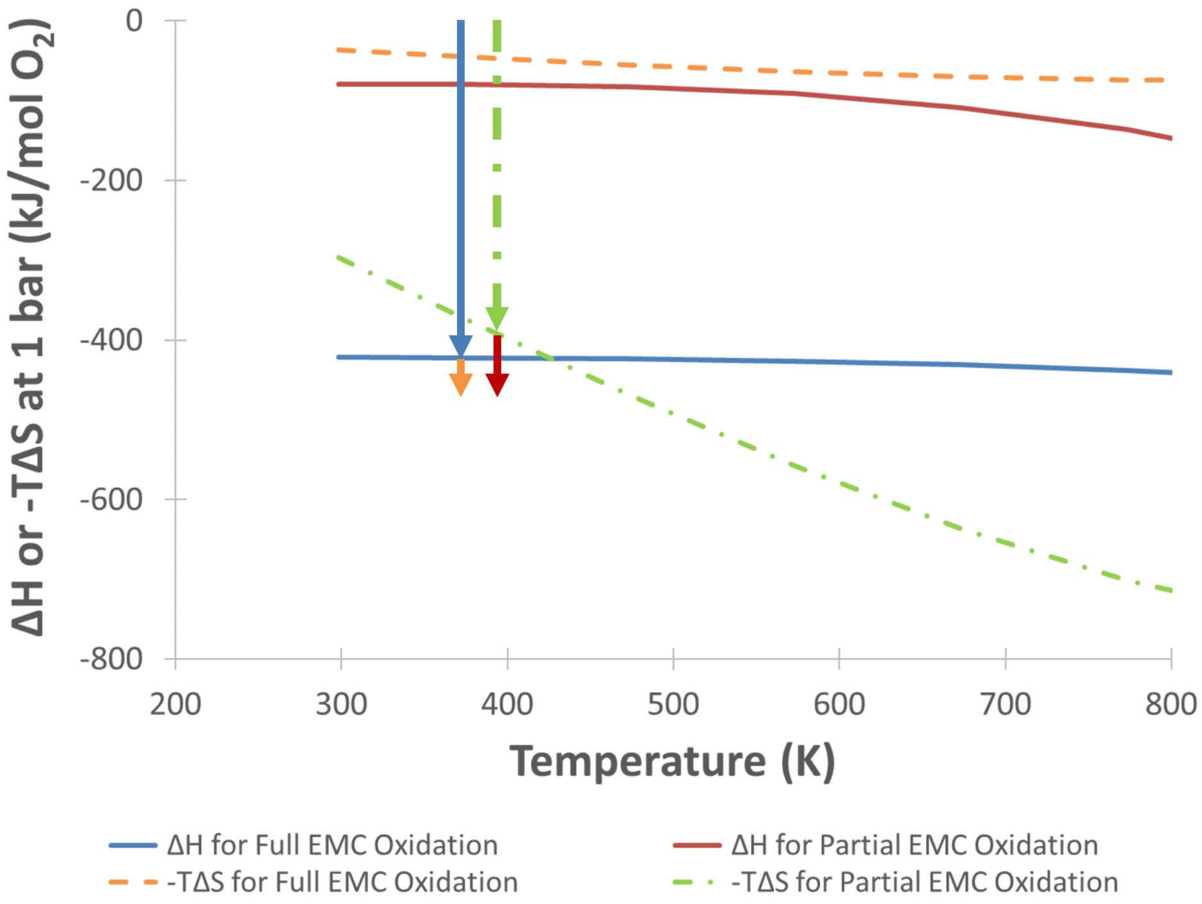
$$\Delta G = \Delta H - T\Delta S$$

Solvent oxidation has strong effects on

- Cathode heat release
- Gas emissions from decomposing batteries

Contributions to ΔG include

- Enthalpy (heat release, solid lines)
  - Favors full oxidation
- Entropy term (dashed lines)
  - Favors more gas generation through partial oxidation
  - Bigger impact at high temperature



Full EMC Oxidation:

$$2\ C_4H_8O_3 + 9\ O_2 \rightarrow 8\ CO_2 + 8\ H_2O$$

Partial EMC Oxidation:

$$2\ C_4H_8O_3 + 2\ O_2 \rightarrow 2\ CO_2 + 6\ CO + 8H_2$$

R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9

Results: Effect of Pressure on Solvent Decomposition

Full EMC Oxidation: $2\ C_4H_8O_3 + 9\ O_2 \rightarrow 8\ CO_2 + 8\ H_2O$

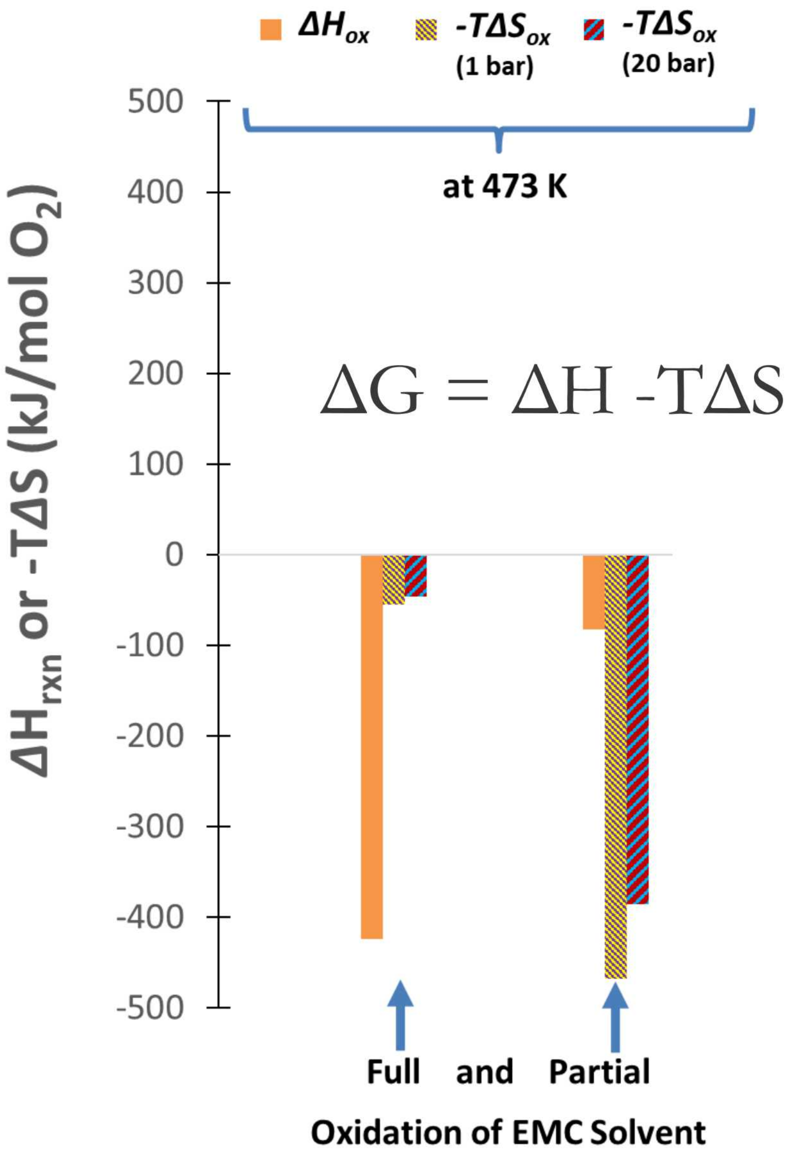
Partial EMC Oxidation: $2\ C_4H_8O_3 + 2\ O_2 \rightarrow 2\ CO_2 + 6\ CO + 8H_2$

Entropy contribution is stronger at low pressures

- Cell venting pressure expected to affect gaseous product distribution and heat release

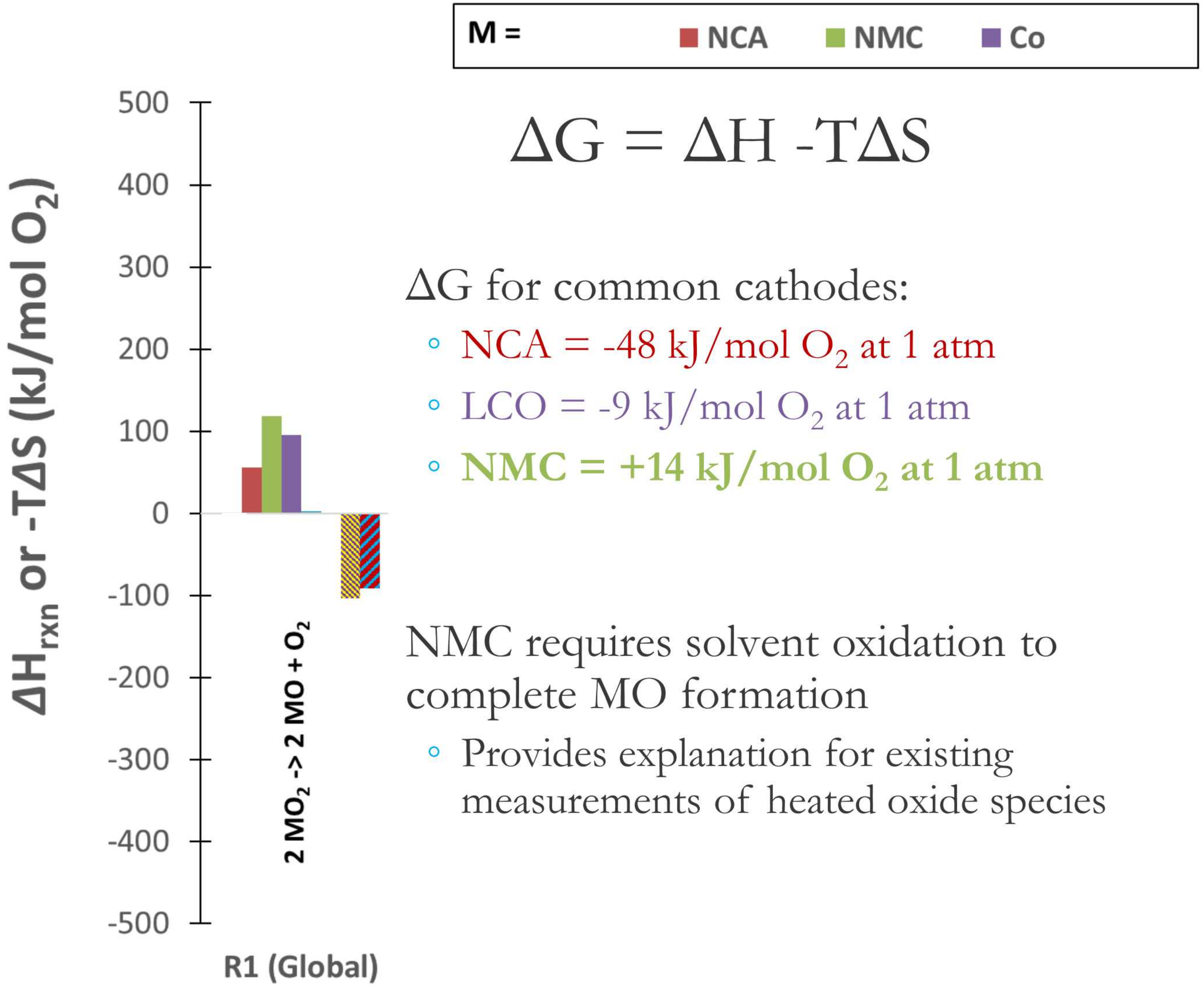
Weaker confinement in pouch cells compared to cylindrical cells may lead to more partial oxidation

- Partial oxidation leads to explosive mixtures
  - ➢ Higher production rates of CO and H_2



R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9

Results: Combined Effects of Metal Oxide Decomposition



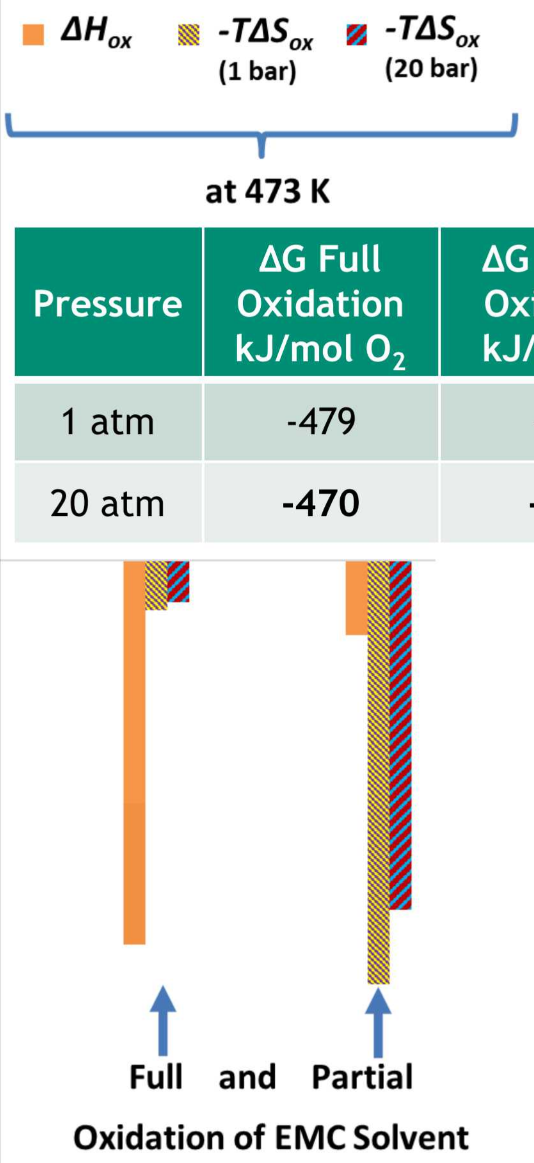
$$\Delta G = \Delta H - T\Delta S$$

ΔG for common cathodes:

- NCA = -48 kJ/mol O_2 at 1 atm
- LCO = -9 kJ/mol O_2 at 1 atm
- **NMC = +14 kJ/mol O_2 at 1 atm**

NMC requires solvent oxidation to complete MO formation

- Provides explanation for existing measurements of heated oxide species



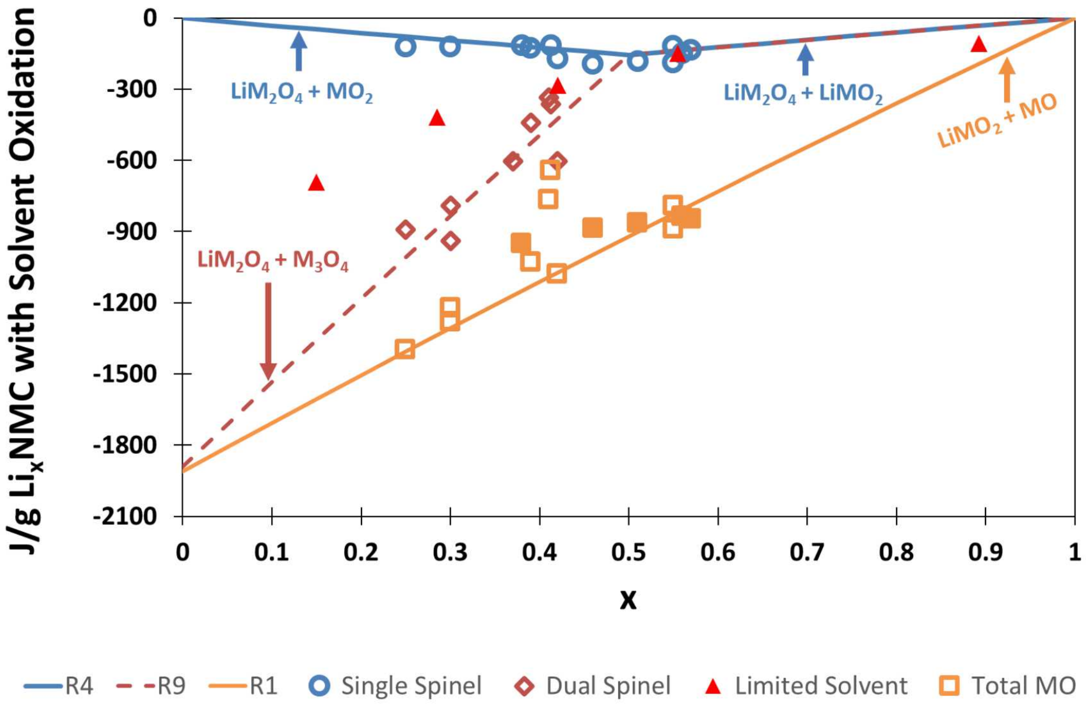
Pressure	ΔG Full Oxidation kJ/mol O_2	ΔG Partial Oxidation kJ/mol O_2
1 atm	-479	-551
20 atm	**-470**	**-468**

R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9

Results: Full-Oxidation Predictions Consistent with Calorimetry

136 total calorimetry measurements compiled from 28 articles for LCO, NMC, and NCA

- Explains variability observed with state of charge
  - ➢SOC proportional to 1-x
- High pressure in calorimetry containers favors full oxidation of solvent



Example: $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 1:1:1)

R1 (orange line) is production of MO rock salt

- Most common final product
  - ➢ Lower maximum temperature or minimal solvent will limit reactions and reduce measured heat (red triangles)

R. C. Shurtz, "A Thermodynamic Reassessment of Lithium-Ion Battery Cathode Calorimetry " *J. Electrochem. Soc.*, (submitted September 2020).

Results: Effects of Metal Oxide Composition and SOC

Similarities and differences in cathode decomposition mechanisms identified from thermodynamic analysis

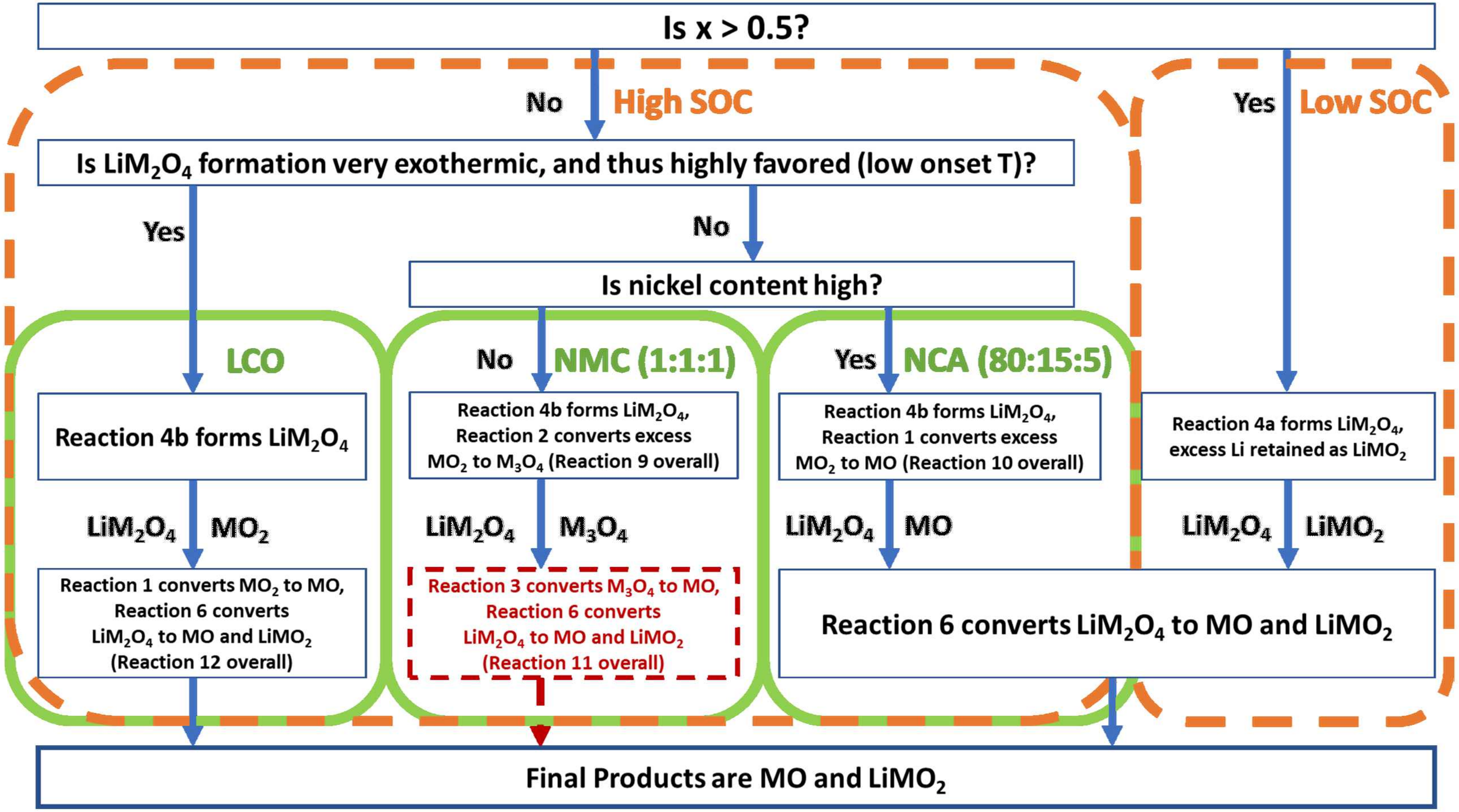
- Verified through calorimetry and species measurements from literature

Common M atoms in Li_xMO_2

- Ni (high energy)
- Co (crystallographic stability)
- Mn or Al (strong O-atom binding)

Some steps change with composition

Simpler mechanism at low SOC



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R. C. Shurtz, "A Thermodynamic Reassessment of Lithium-Ion Battery Cathode Calorimetry " *J. Electrochem. Soc.*, (submitted September 2020).

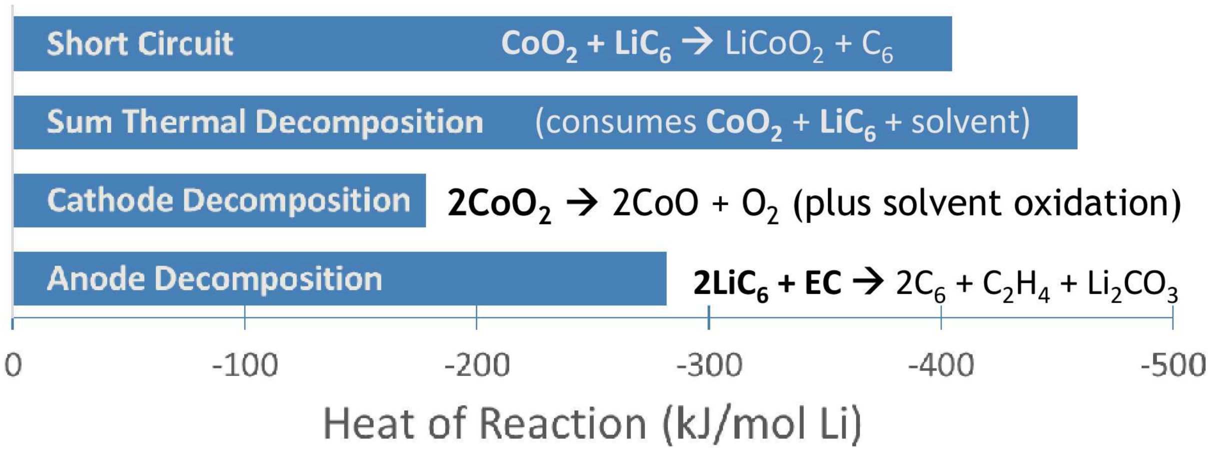
Results: Modeling Short Circuits in Tandem with Thermal Runaway

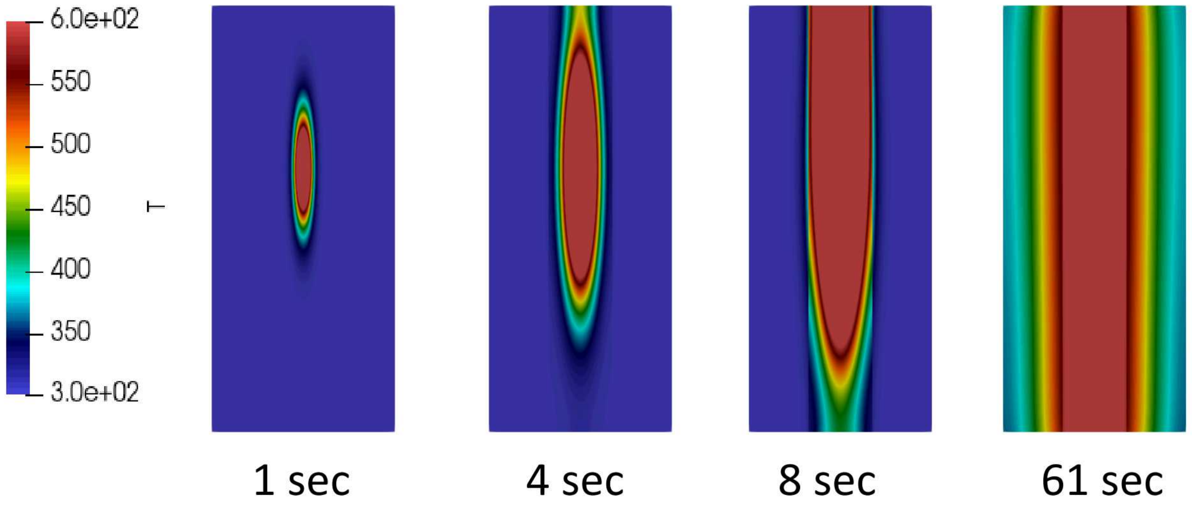
Materials science perspective applied to short-circuit ignition of thermal runaway yields predictive insights

Short circuits and thermal decomposition compete for same reactants
- Thermal decomposition more energetic
- Thermal decomposition faster once ignited
- Depletion of solvent can limit either process

Series resistances specify rate and distribution of heat release from short circuit
- Fraction of total resistance specifies heat release in nail versus cell
  - ➢ Concentrating heat release in nail yields faster ignition

Voltage and hence short circuit rate calculated from limiting reactive electrode material





Results: Modeling Ignition from Nail Penetration in Pouch Cells

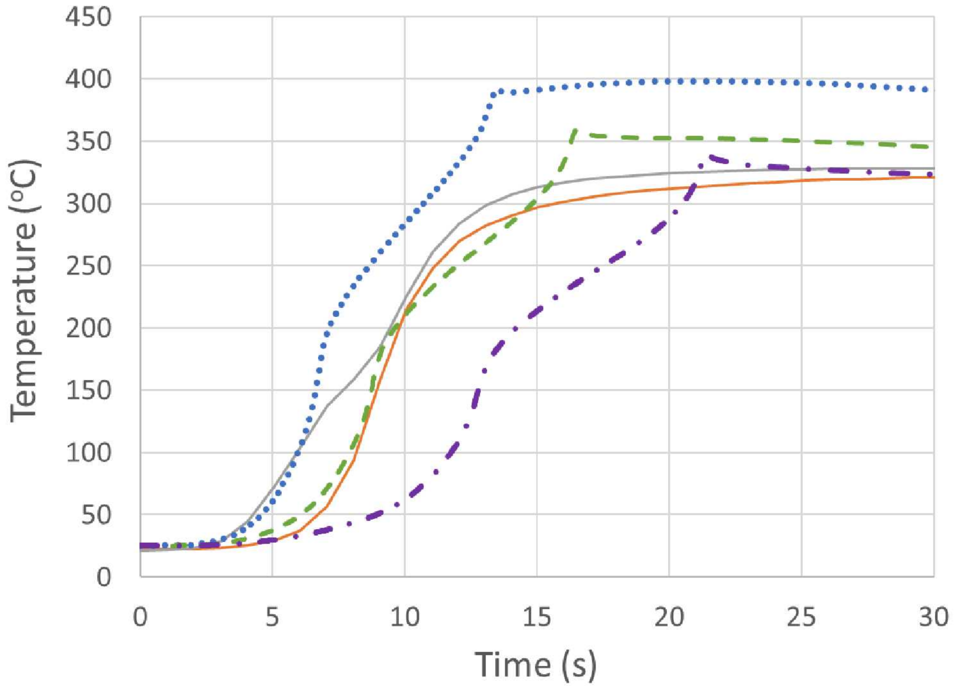
Identified effects of short circuit geometry and location

- Central heat release yields sharp peak in cell surface temperature
- Off-center heat release slows rise to final temperature
  - ➢Makes internal propagation limiting (see previous slide)

Total temperature rise can be limited by

- Quantity of electrolyte
- High short-circuit resistance
  - ➢Slower short circuit competes poorly with thermal runaway

Resistance variation



__Legend for plot:__

---- , ---- = measured cell surface temperature

- - - - - = baseline simulation

• • • • = ½ resistance

--• --• = 2x resistance

Looking Forward

Cathode Decomposition Modeling

- Develop and publish new kinetic models for thermal runaway in Li_xMO_2 cathodes
  - Build on heat release from recent thermodynamic analysis
- Integrate improved heat source models into cascading failure simulations
  - Demonstrate and publish practical methods to assess safety risks in larger systems

Lithium-Ion Battery Calorimetry Workshops (with full safety team)

- Set up website for sharing and modeling thermal runaway data
  - Example data set from Sandia Battery Abuse Laboratory has now been prepared for this purpose
- Schedule first workshop, continue recruiting participants

FY2020 Publication Summary

Peer-reviewed Publications

- A Kurzawski, L. Torres-Castro, R. Shurtz, J. Lamb, and John Hewson, "Predicting cell-to-cell failure propagation and limits of propagation in lithium-ion stacks," *Proceedings of the Combustion Institute* (2020) https://doi.org/10.1016/j.proci.2020.06.270
- R. C. Shurtz and J. C. Hewson, "Materials Science Predictions of Thermal Runaway in Layered Metal-Oxide Cathodes: A Review of Thermodynamics," *J. Electrochem. Soc.,* 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9.
- R. C. Shurtz, "A Thermodynamic Reassessment of Lithium-Ion Battery Cathode Calorimetry " *J. Electrochem. Soc.*, (submitted September 2020).

Presentations

- R.C. Shurtz and J.C. Hewson "Modeling Thermal Decomposition of Metal Oxide Cathodes in Non-Aqueous Electrolytes for Prediction of Thermal Runaway in Lithium-Ion Batteries" 236th ECS Meeting, Atlanta, GA, October 17, 2019

Online Tool:

- R. C. Shurtz. "Thermodynamic Reaction Heat Calculator for Layered Metal Oxide Cathodes in Organic Electrolytes" (2020) https://www.sandia.gov/ess-ssl/thermodynamic-web-calculator/

Project Contacts

THANK YOU

- 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, contact Randy Shurtz: rshurtz@sandia.gov

For further details pertaining to thermal runaway modeling, see the following presentations and posters:

- Thermal Analysis to Mitigate Cascading Propagation of Lithium-Ion Cell Stacks (presentation by John Hewson)
- Mitigation of Failure Propagation Through Active Cooling: A Model Based Experimental Design (presentation by Loraine Torres-Castro)
- Predicting Thermal Responses for Actively Cooled Designs Following Thermal Runaway (poster by Randy Shurtz)
- High-Temperature Kinetics of Thermal Runaway Reactions (poster by Andrew Kurzawski)