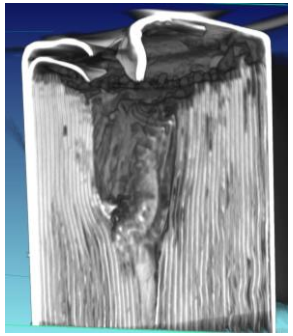
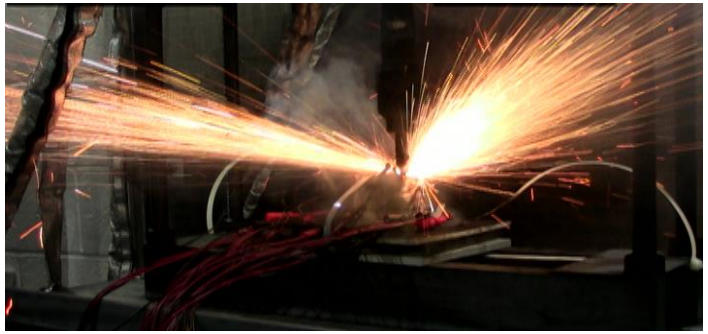
# Material Science-Based Predictions of Single-Cell Thermal Failures





*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*

SAND2020-10026 C

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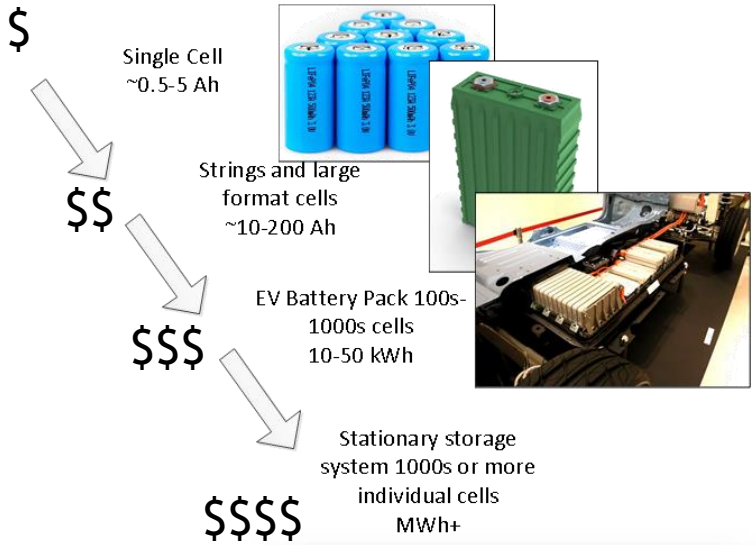
# Overview of Thermal Runaway Modeling

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  - Outdated with respect to current battery materials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:

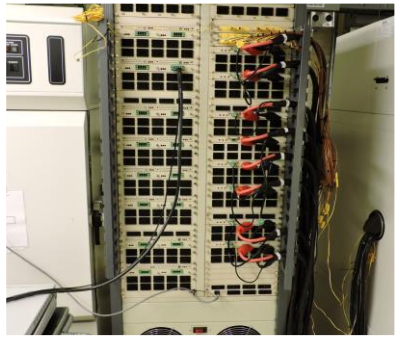
- Validated safety and reliability is one of the critical challenges identified in 2013 Grid Energy Storage Strategic Plan



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

# Project Team

## Sandia Battery Test Facilities

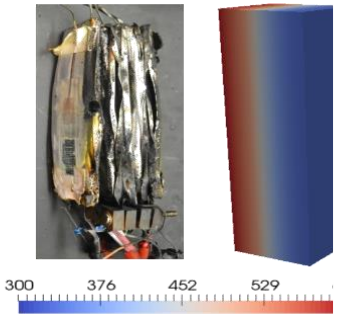


Yuliya Preger
Reed Wittman
Armando Fresquez

## Sandia Battery Abuse Lab

Loraine Torres-Castro
Joshua Lamb
Chris Grosso
Lucas Gray
Jill Langendorf

## Sandia Fire Sciences

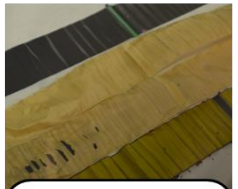



John Hewson
Randy Shurtz
Andrew Kurzawski

## Center for Integrated Nanotechnologies

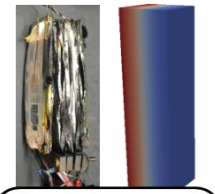
Sergei Ivanov

Baseline electrochemical performance analysis

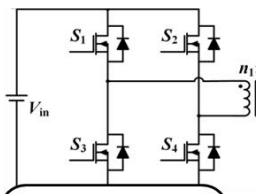


Materials characterization and thermal stability testing

Whole-cell abuse response analysis

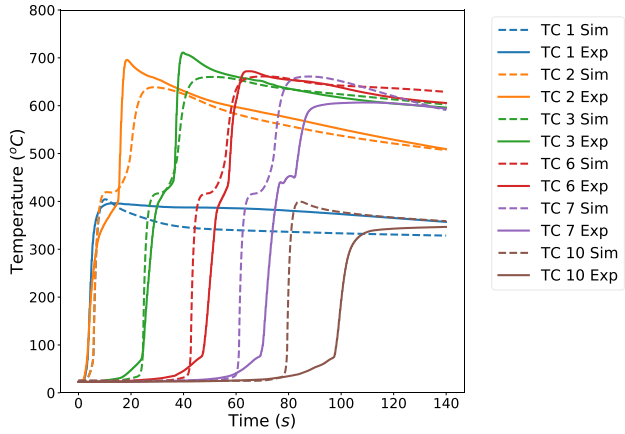


Modeling of thermal propagation




Design of new power electronics for battery safety

# Thermal Runaway Modeling Objectives

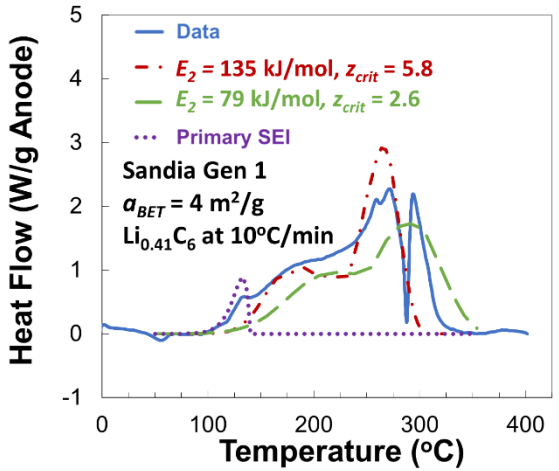



## Predict thermal runaway behavior in large systems (multi-cell)

- 1 publication accepted in FY2020

## Develop improved heat-source models for thermal runaway

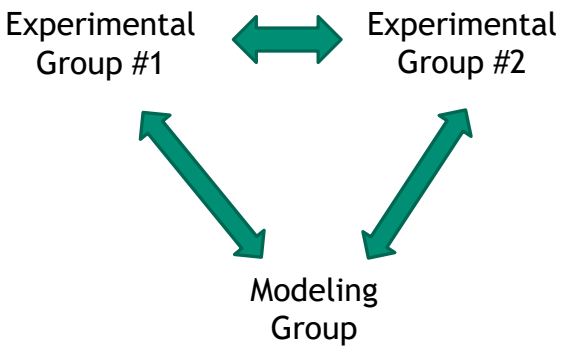
- Include proper dependence on material properties, temperature, state of charge
- Extend to additional electrode materials of commercial interest
- 1 publication accepted and 1 additional publication submitted in FY2020




## Promote effective methods and collaboration in thermal runaway studies

- 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)

**Enhance Flow of Data and Insights**



# **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

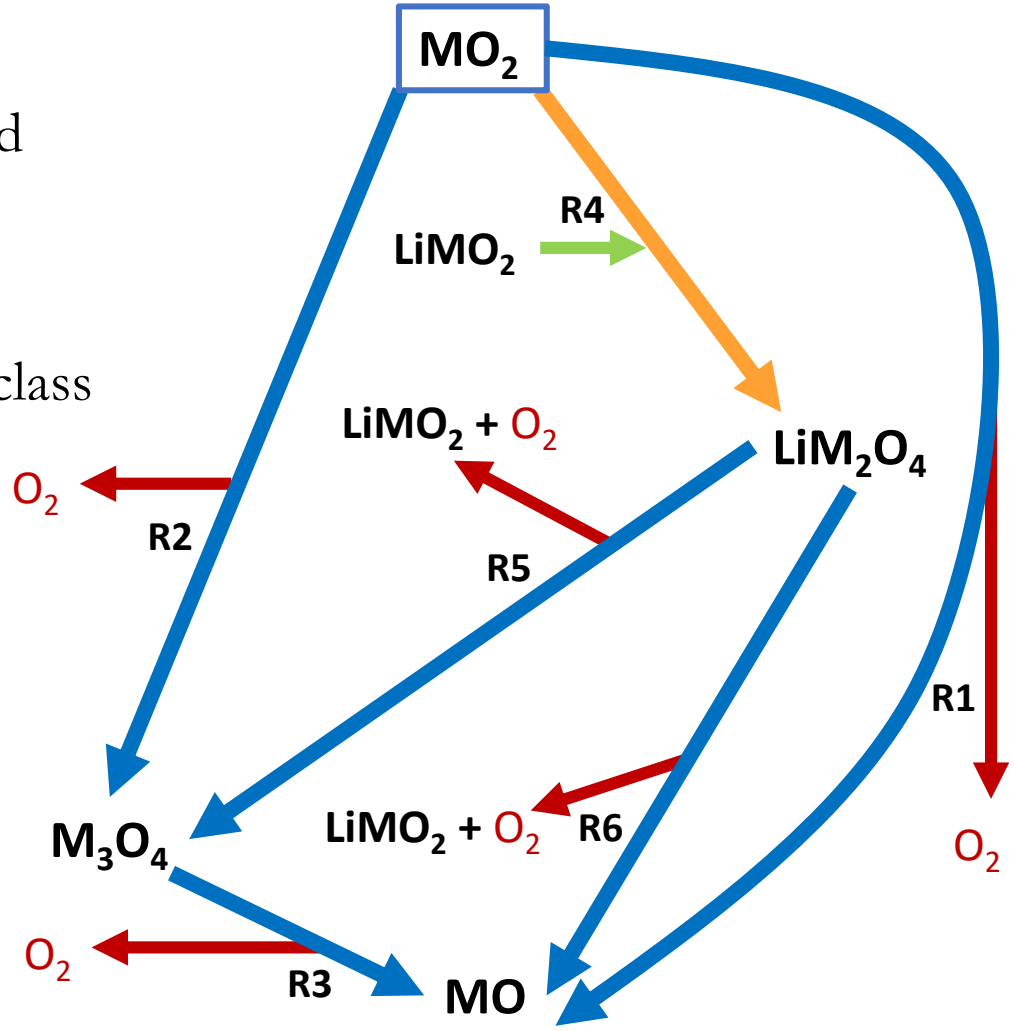
- Can account for multiple stages of heat release
- May also allow kinetic rates in thermal runaway models to be generalized for families of materials

# **Results:** Thermodynamics of Cathode Thermal Runaway

## 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

Decomposition paths for de-lithiated $Li_xMO_2$




**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

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:

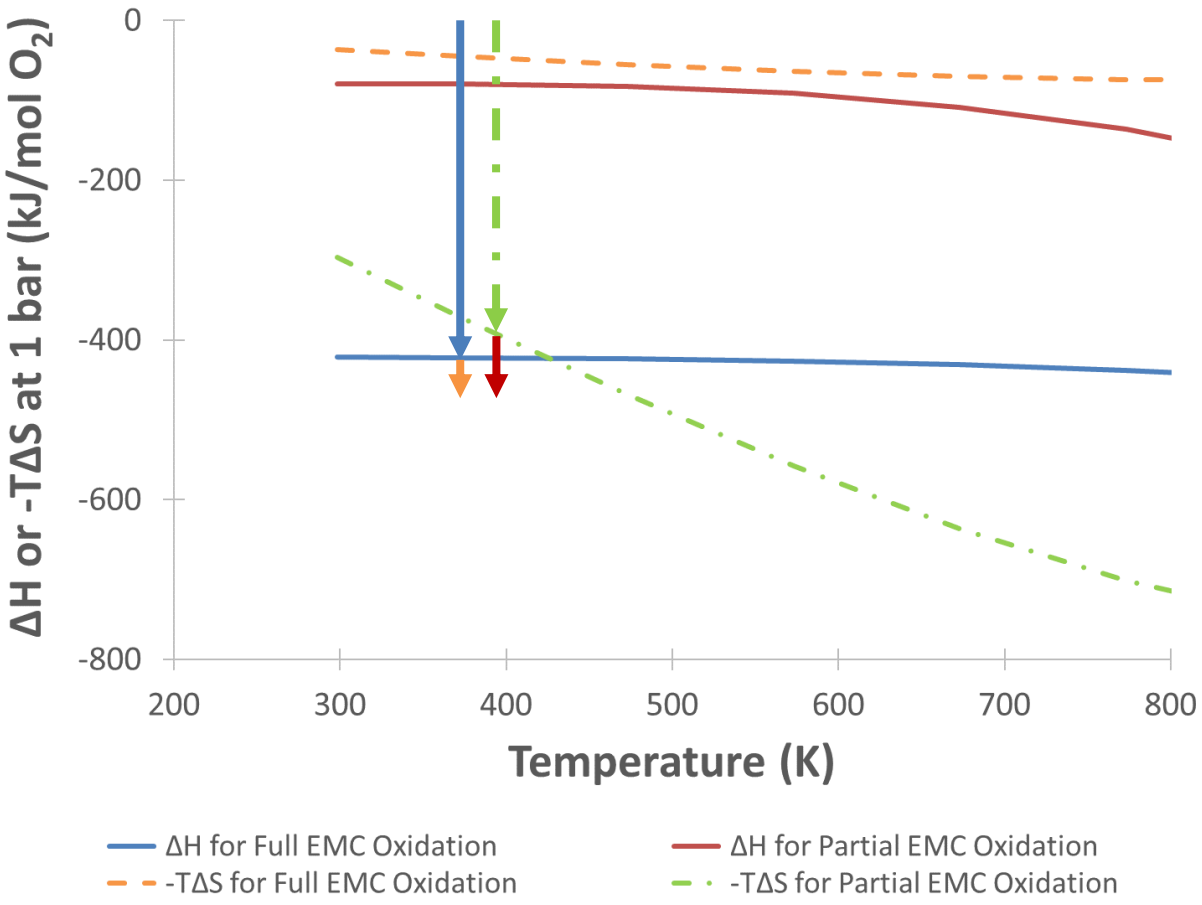
$$2\ C_4H_8O_3 + 9\ O_2 \rightarrow 8\ CO_2 + 8\ H_2O$$

Partial EMC Oxidation:

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

Spontaneous processes have negative ΔG

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




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

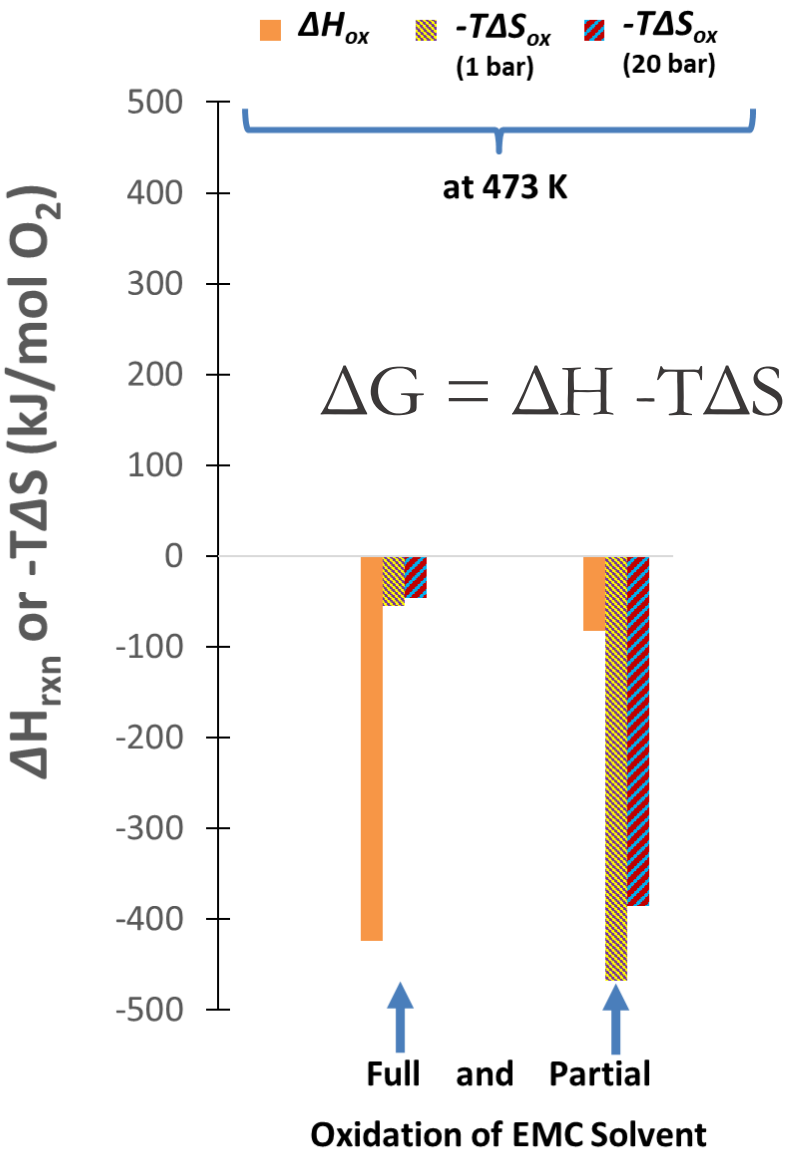
Partial EMC Oxidation: $2\ C_4H_8O_3 + 2\ O_2 \rightarrow 2\ CO_2 + 6\ CO + 8H_2$

Entropy contribution is stronger at low pressures

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

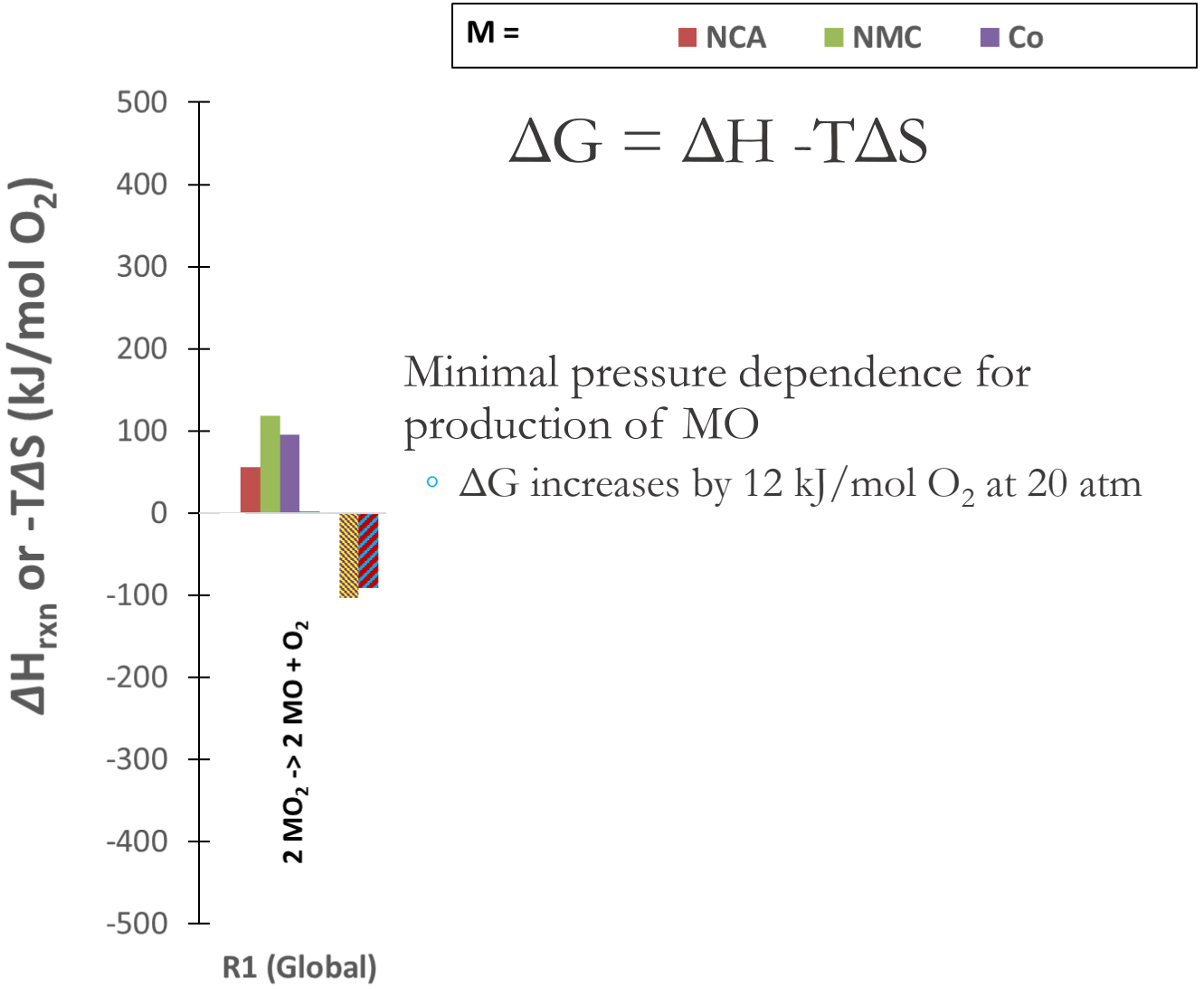
Weaker confinement in pouch cells compared to cylindrical cells may lead to more partial oxidation

- 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

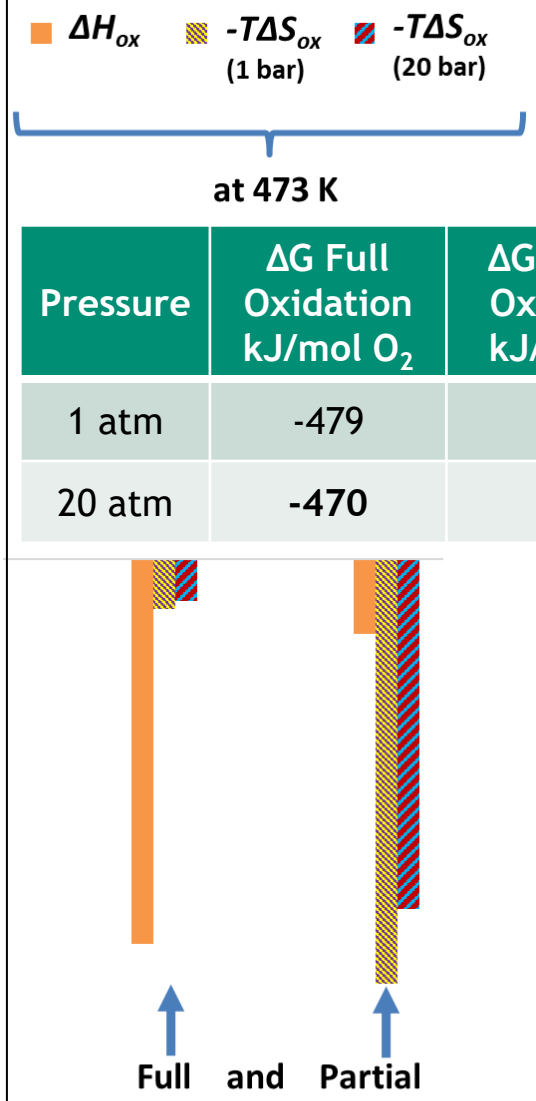
# Results: Combined Effects of Metal Oxide Decomposition




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

Minimal pressure dependence for production of MO

- $\Delta G$ increases by 12 kJ/mol $O_2$ at 20 atm




| 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

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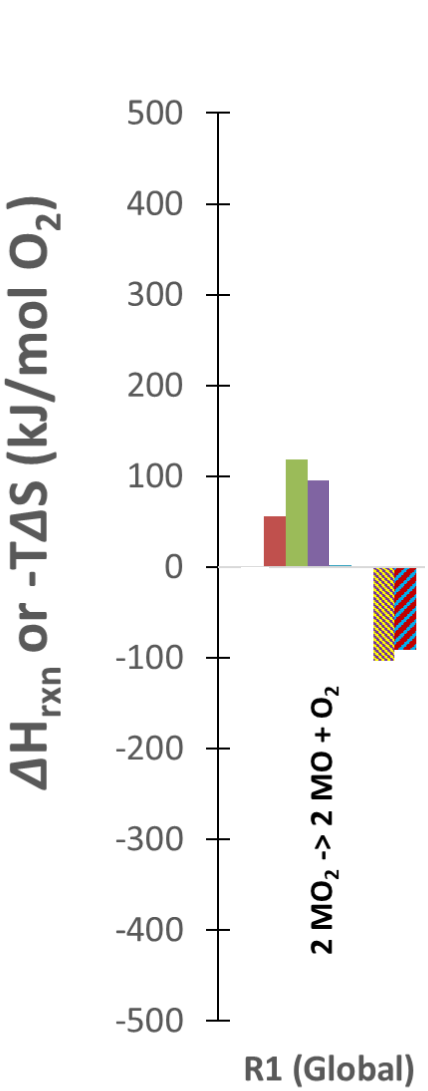


$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$ 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 $O_2$ |
|---|---|---|
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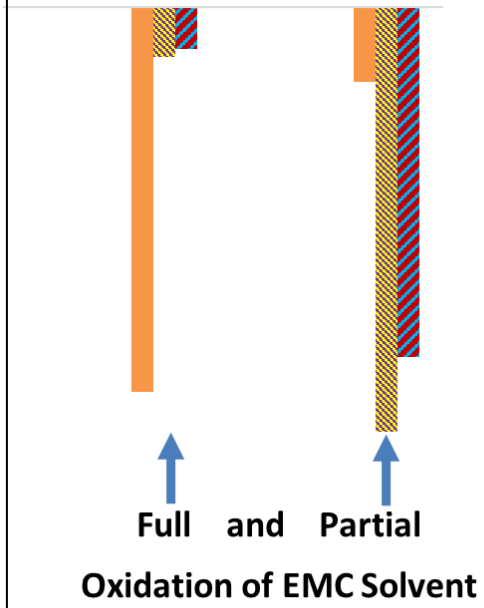
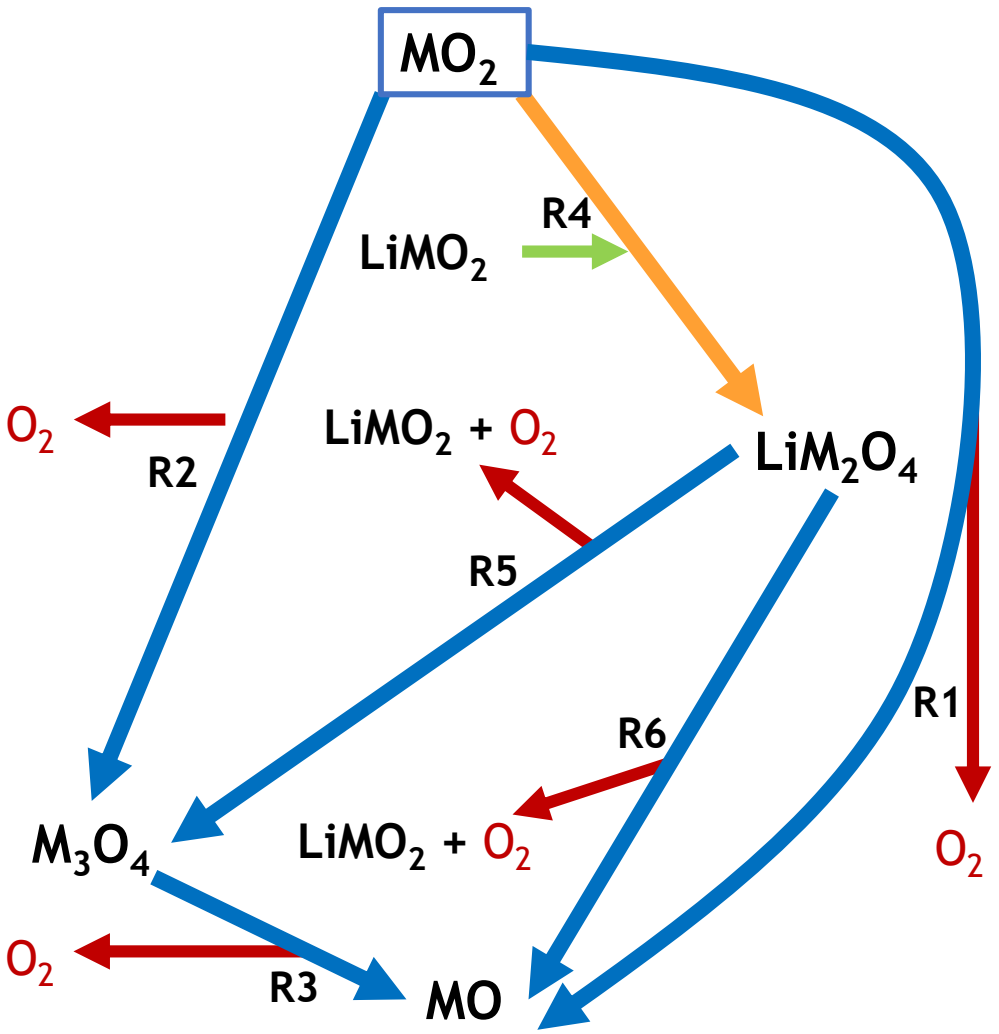
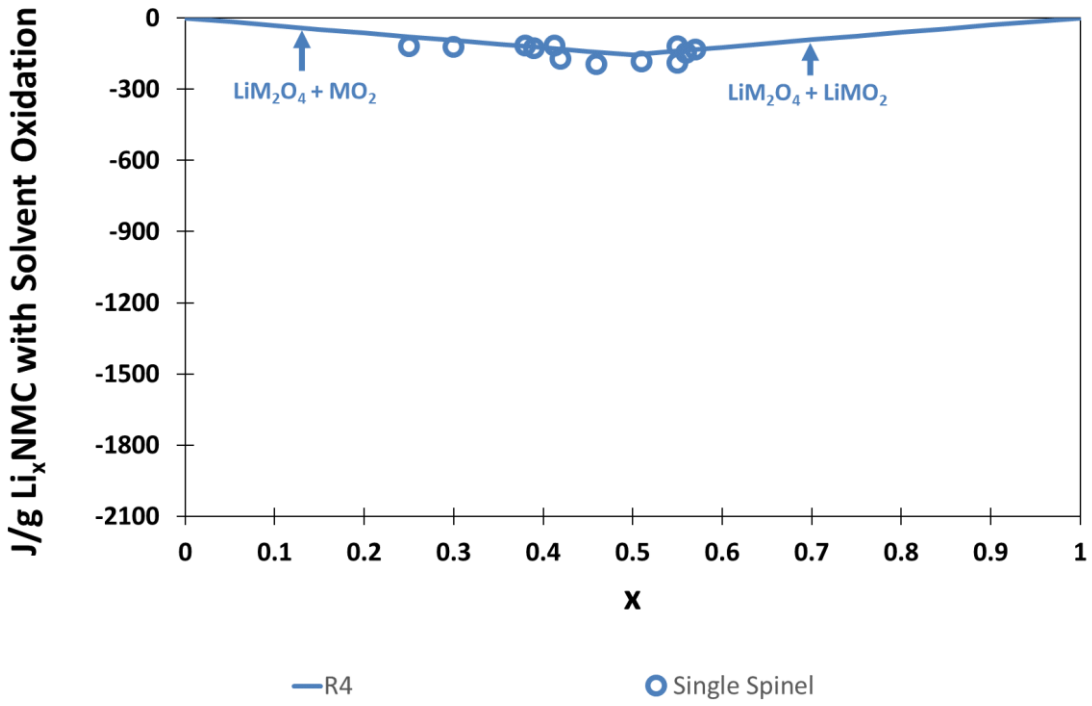



R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, 167, 090543 (2020) https://dx.doi.org/10.1149/1945-7111/ab8fd9

# **Results:** Full-Oxidation Predictions Consistent with Calorimetry



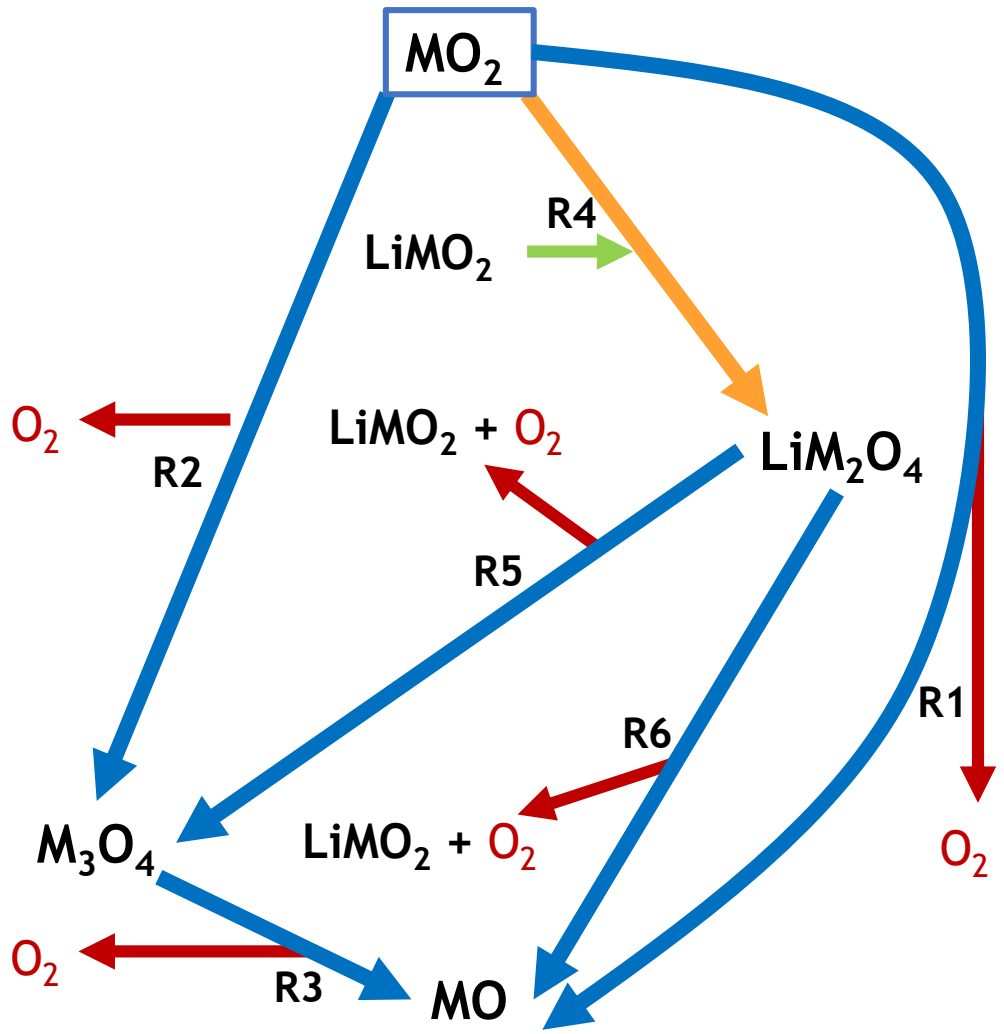

Example: $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 1:1:1)

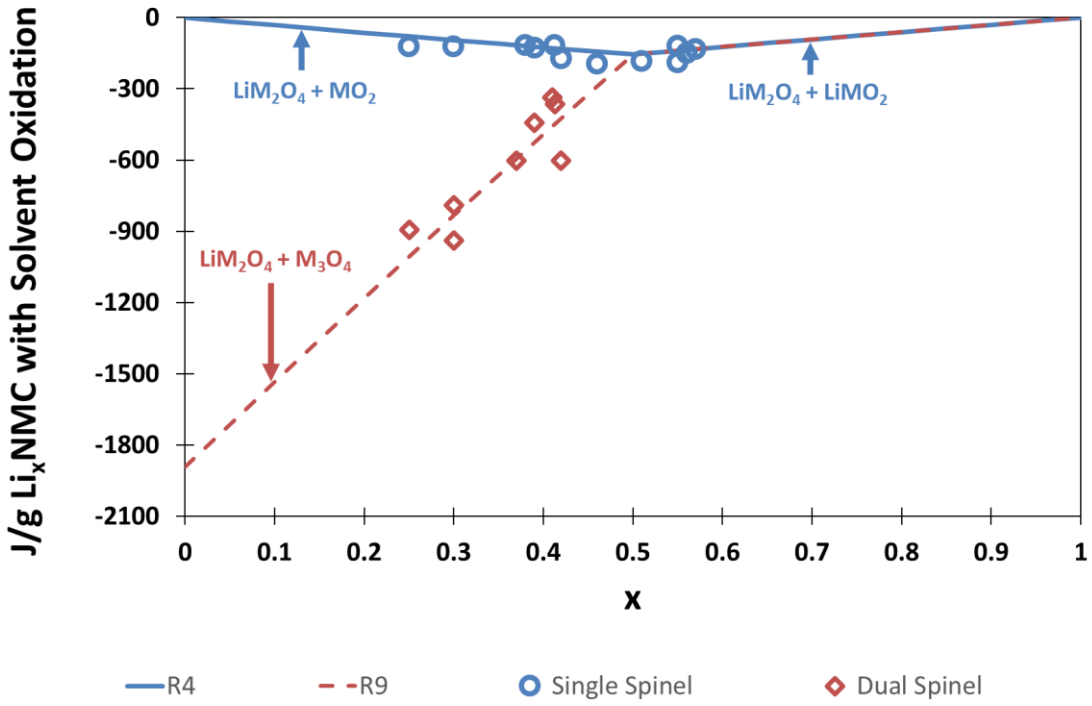
**R4 (blue line) is initial production of $LiM_2O_4$**

- Lithiated spinel created w/o oxygen production

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

# **Results:** Full-Oxidation Predictions Consistent with Calorimetry



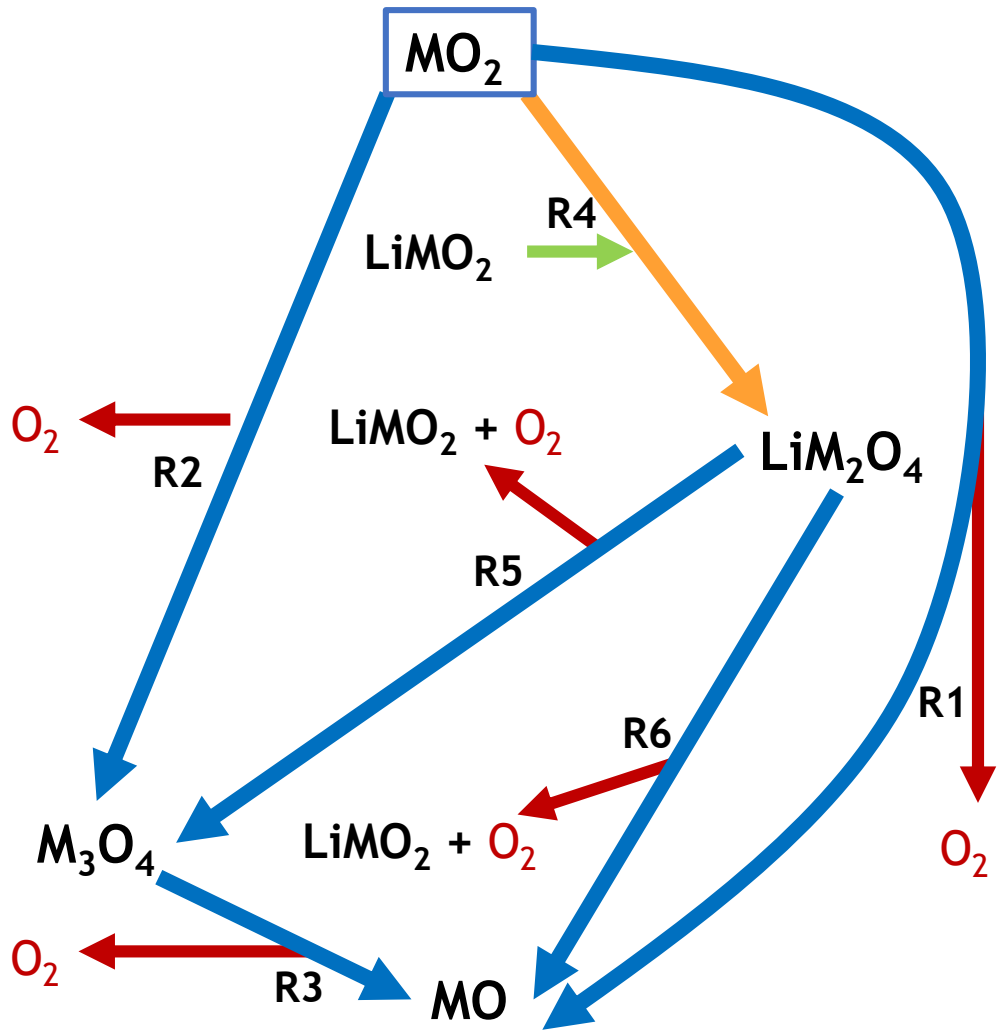

Example: $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 1:1:1)

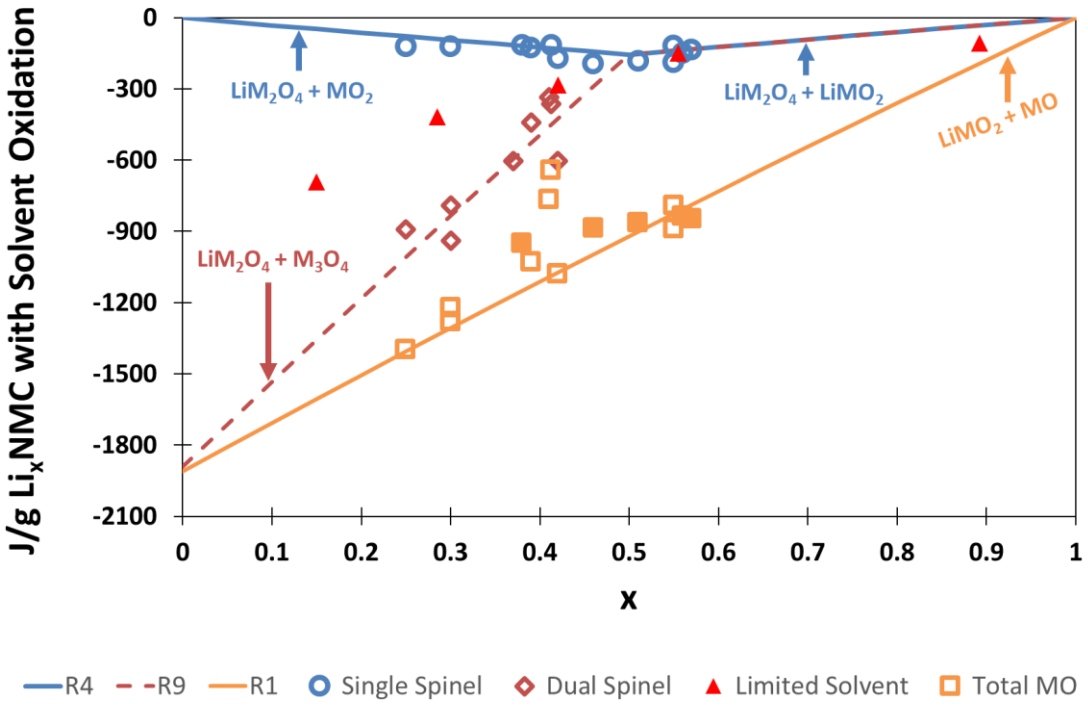
**R9 (red line) produces dual-spinel mixture**

- Residual $MO_2$ → $M_3O_4$ (R2 follows R4)

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

# Results: Full-Oxidation Predictions Consistent with Calorimetry




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**

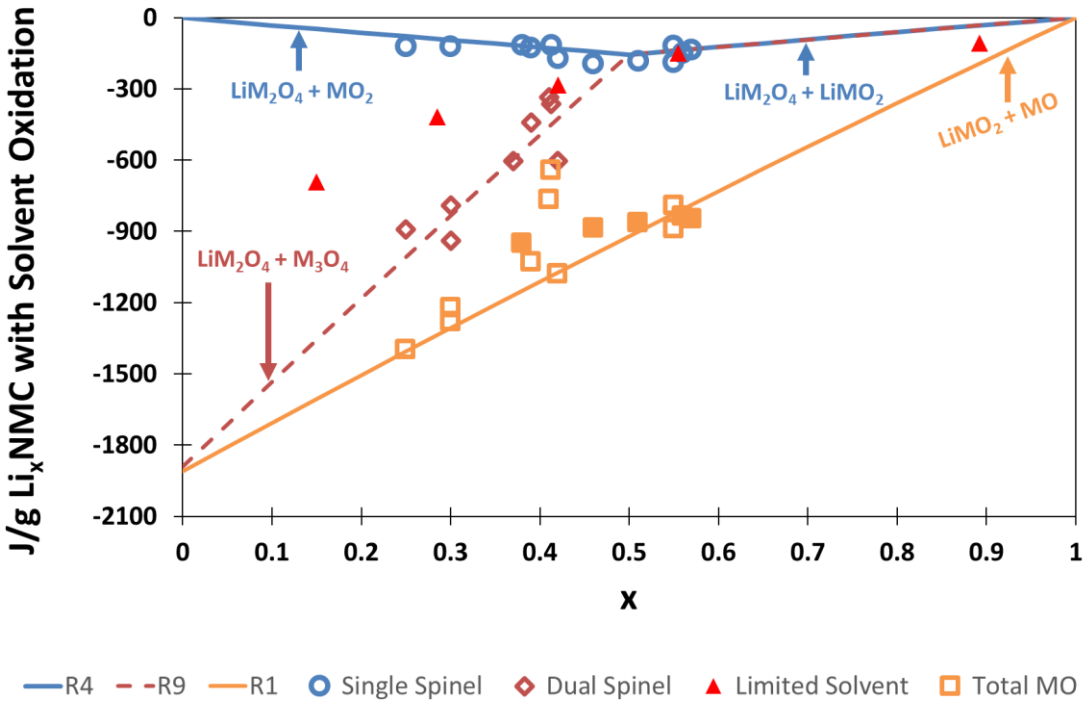
- Most common final product
  - Lower maximum temperature or minimal solvent will limit reactions and reduce measured heat (red triangles)

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

# **Results:** 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

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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

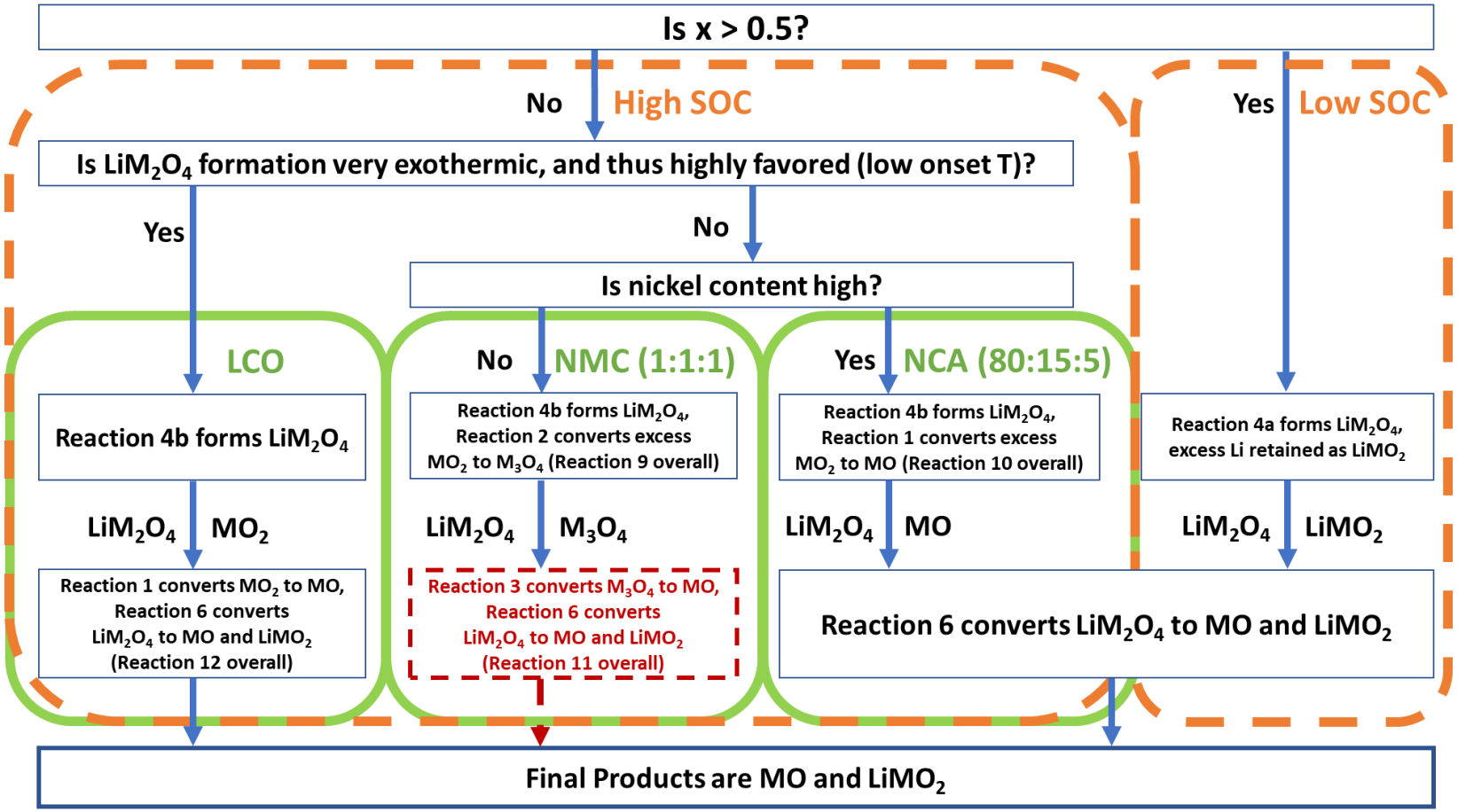
- Verified through calorimetry and species measurements from literature

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

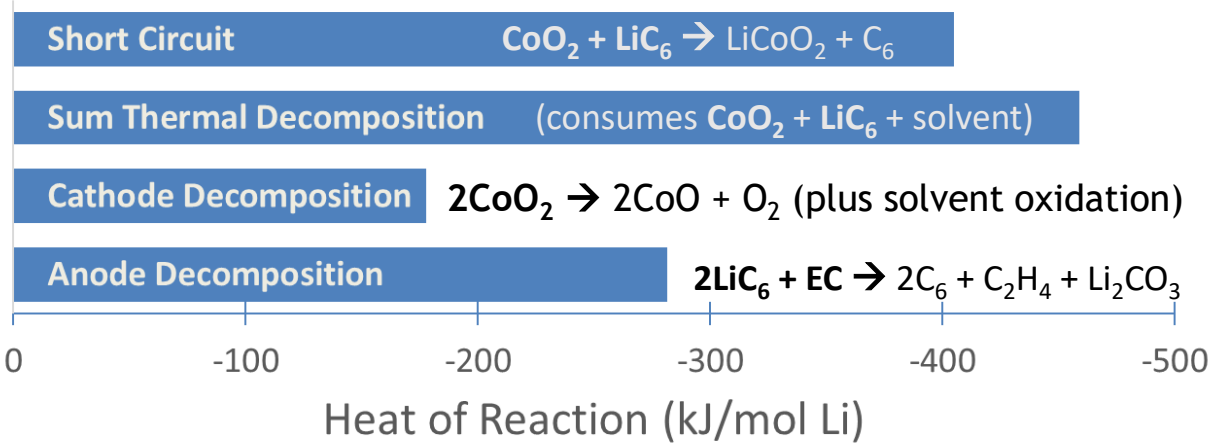
Short circuits and thermal decomposition compete for same reactants

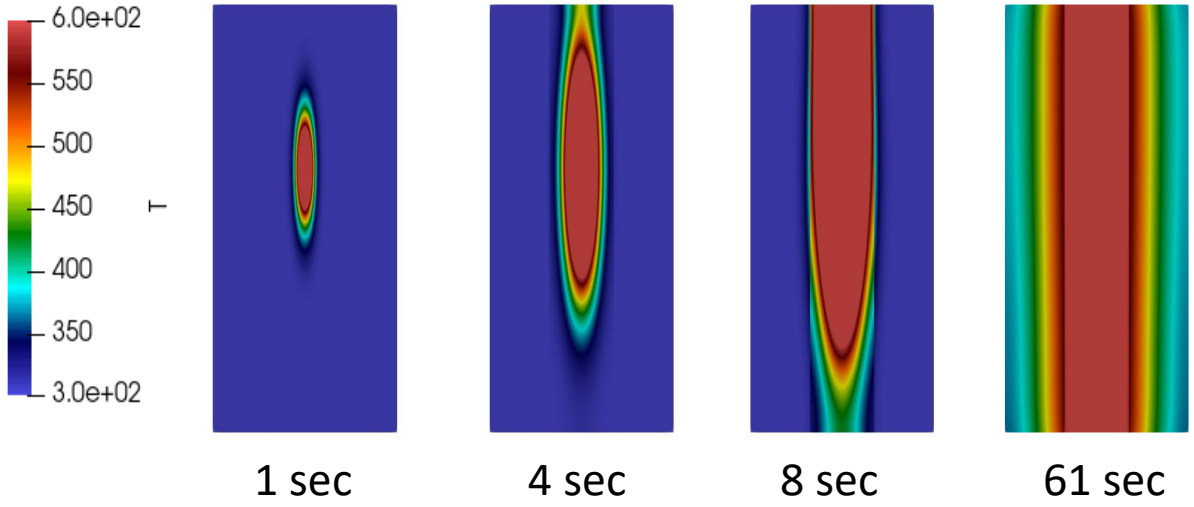
- Thermal decomposition more energetic
- Thermal decomposition faster once ignited
- Depletion of solvent can limit either process

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



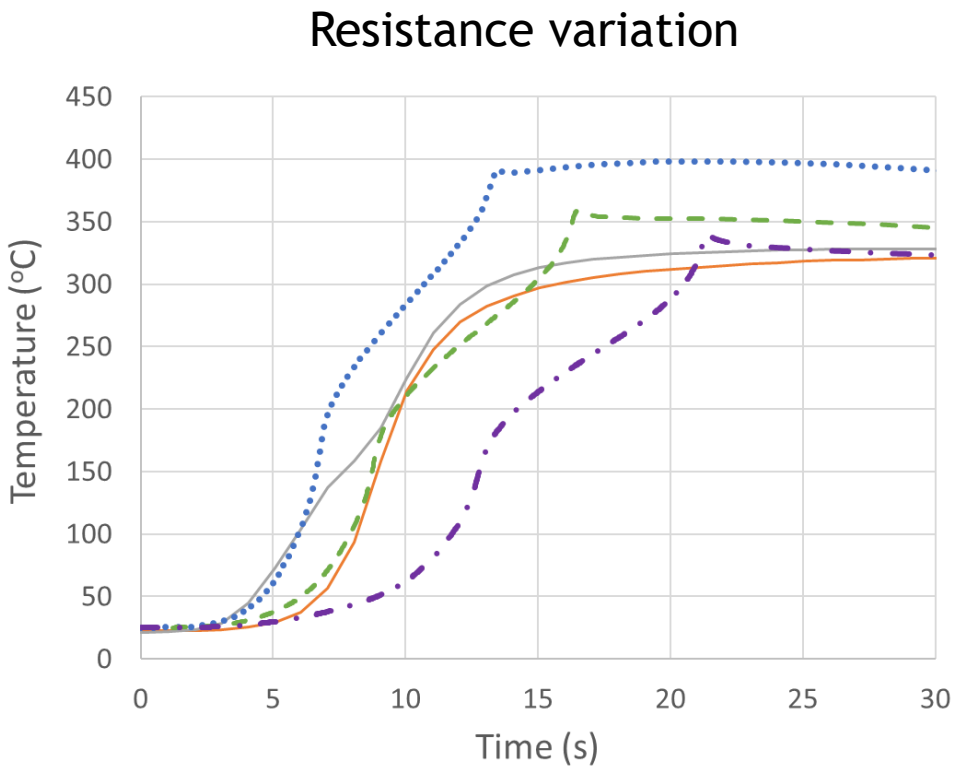
# **Results:** Modeling Ignition from Nail Penetration in Pouch Cells

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




***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.
- 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.


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)