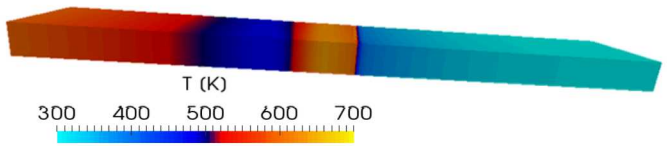
SAND2019-12402C

Modeling Thermal Decomposition of Metal Oxide Cathodes in Non-Aqueous Electrolytes for Prediction of Thermal Runaway in Lithium-Ion Batteries



PRESENTED BY

Randy Shurtz, John Hewson

236th ECS Meeting – Atlanta, Georgia

October 17, 2019

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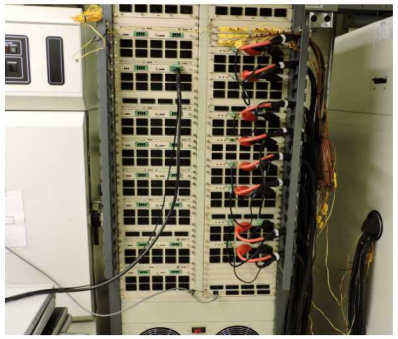
SANDIA BATTERY SAFETY TEAM

Sandia Battery Test Facilities



Yuliya Preger
Summer Ferreira
Armando Fresquez
Heather Barkholtz (former SNL)

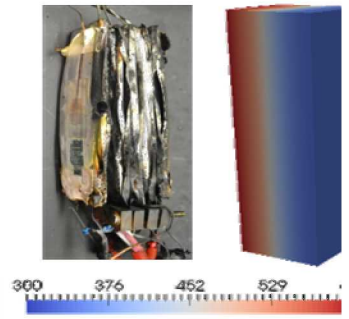
Sandia Battery Abuse Lab

- Loraine Torres-Castro

Joshua Lamb
June Stanley

- Chris Grosso
- Lucas Gray
- Jill Langendorf
- Eric Reichmann

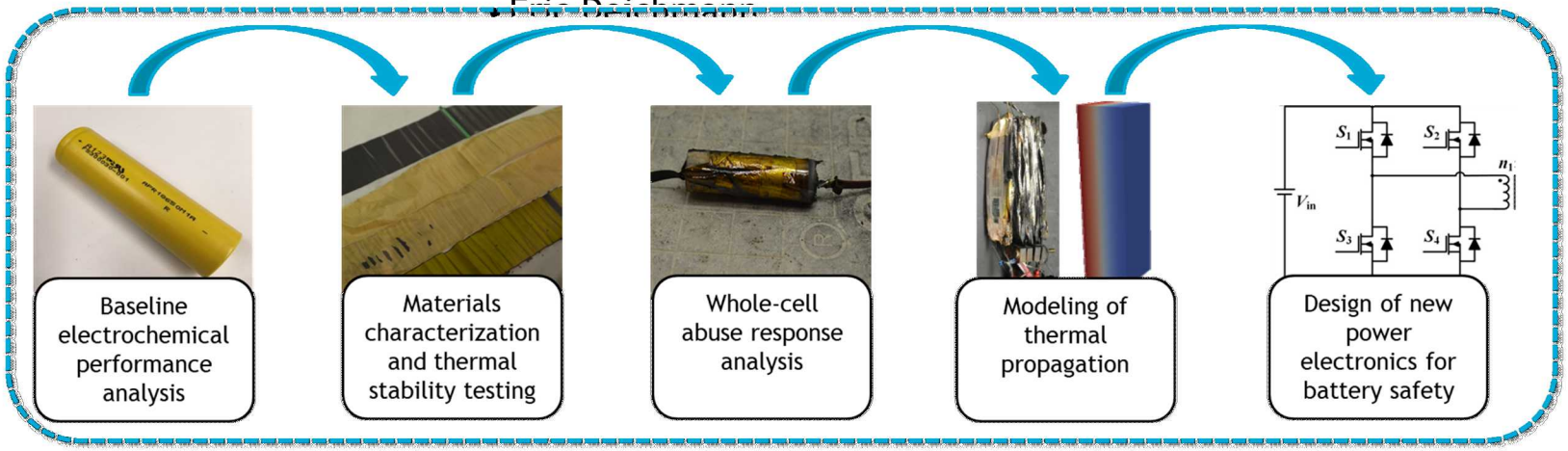
Sandia Fire Sciences



John Hewson
Randy Shurtz
Andrew Kurzawski

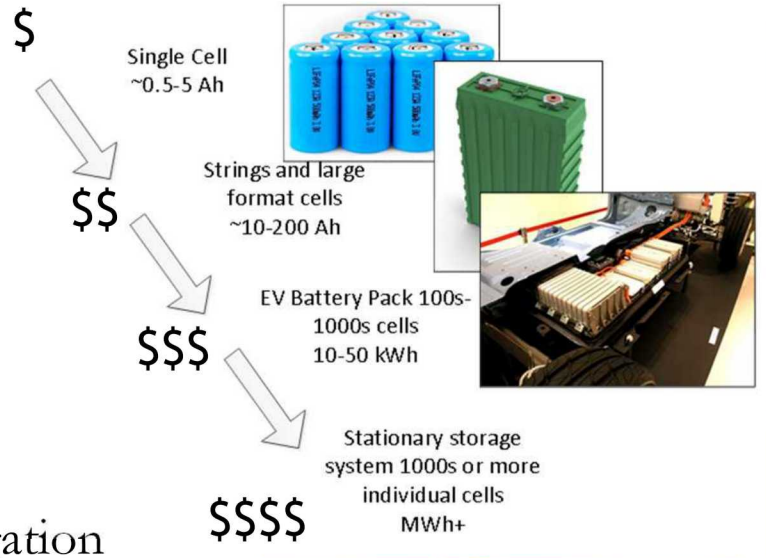
Center for Integrated Nanotechnologies

Sergei Ivanov



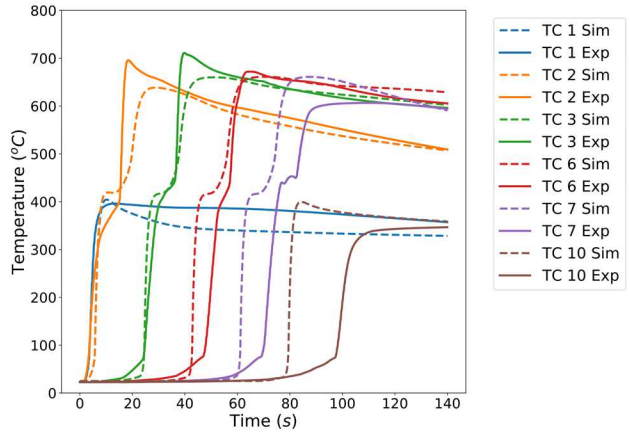
Motivation for Thermal Runaway Modeling

- Conventional approach is to test our way to safety
- Supplement testing with multi-physics models
- Heat sources in legacy thermal runaway models have limitations
  - Designed for low-temperature onset rather than high-temperature propagation
  - Outdated with respect to current battery materials
- Design models 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



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

RESEARCH OBJECTIVES

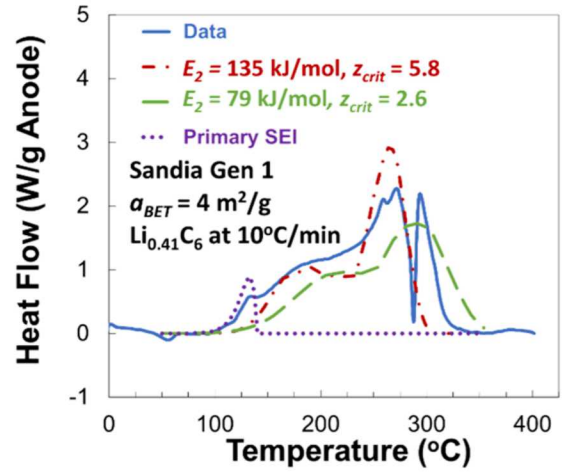


Predict thermal runaway behavior in large systems (multi-cell)

- Ongoing, requires improved heat sources for cascading failure

Develop improved heat-source models for thermal runaway

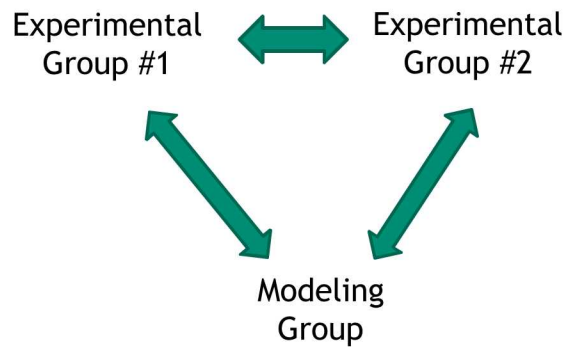
- **Primary topic of this presentation**
- Include proper dependence on material properties, temperature, state of charge
- Extend to additional electrode materials of commercial interest



Promote effective methods and collaboration in thermal runaway studies

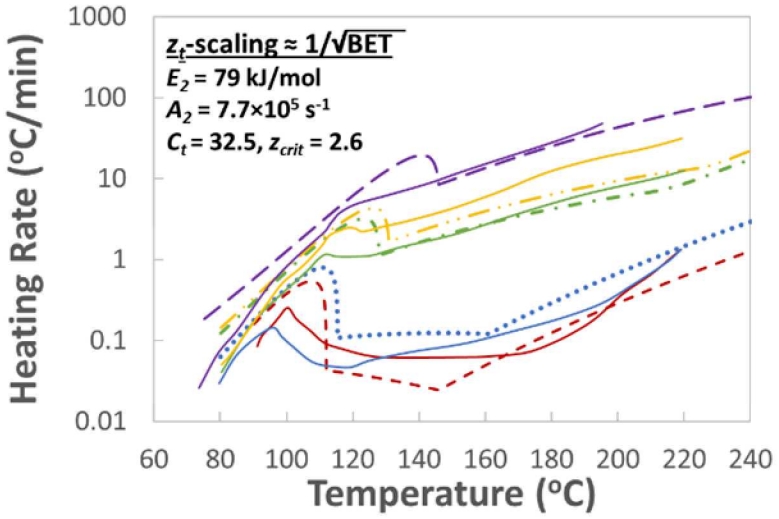
- Publish new models and perspectives
  - R. C. Shurtz, Y. Preger, L. Torres-Castro, J. Lamb, J. C. Hewson and S. Ferreira, "From Calorimetry Measurements to Furthering Mechanistic Understanding and Control of Thermal Abuse in Lithium-Ion Cells" *J. Electrochem. Soc.*, **166**, A2498 (2019). DOI 10.1149/2.0341912jes
- Establish calorimetry collaborative to bridge experiments and modeling

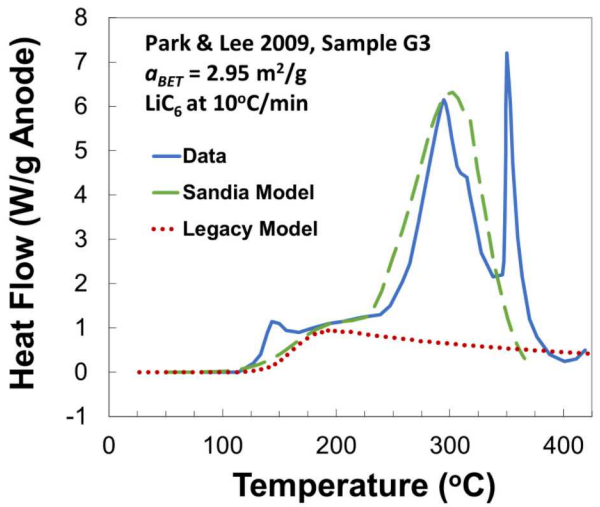
Enhance Flow of Data and Insights

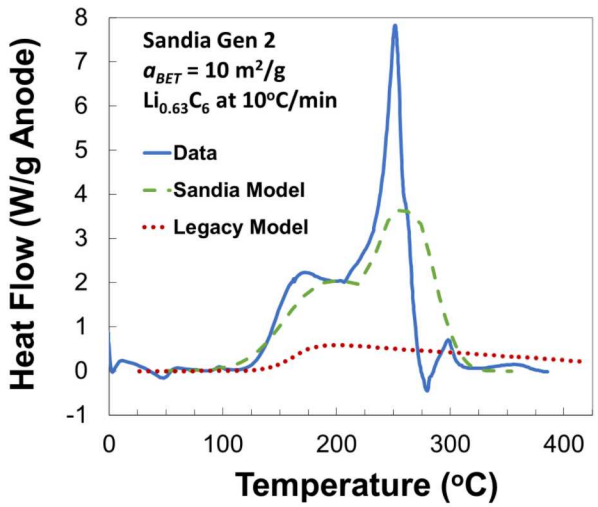


MODELING DECOMPOSITION OF LITHIATED GRAPHITE

- Improves predictions of maximum cell temperatures and cascading failure rates
  - Total heat release from reaction thermodynamics rather than empirical
  - Includes large exotherm occurring after onset of thermal runaway in full cells
  - Accounts for effects of graphite surface area and limited electrolyte on heat generation rates
  - Successfully predicts a wide variety of published calorimetry measurements
- Published in the Journal of the Electrochemical Society as two open-access papers
  - R. C. Shurtz, J. D. Engerer and J. C. Hewson, *J. Electrochem. Soc.*, **165**, A3878 (2018). DOI 10.1149/2.0171814jes
  - R. C. Shurtz, J. D. Engerer and J. C. Hewson, *J. Electrochem. Soc.*, **165**, A3891 (2018). DOI 10.1149/2.0541816jes





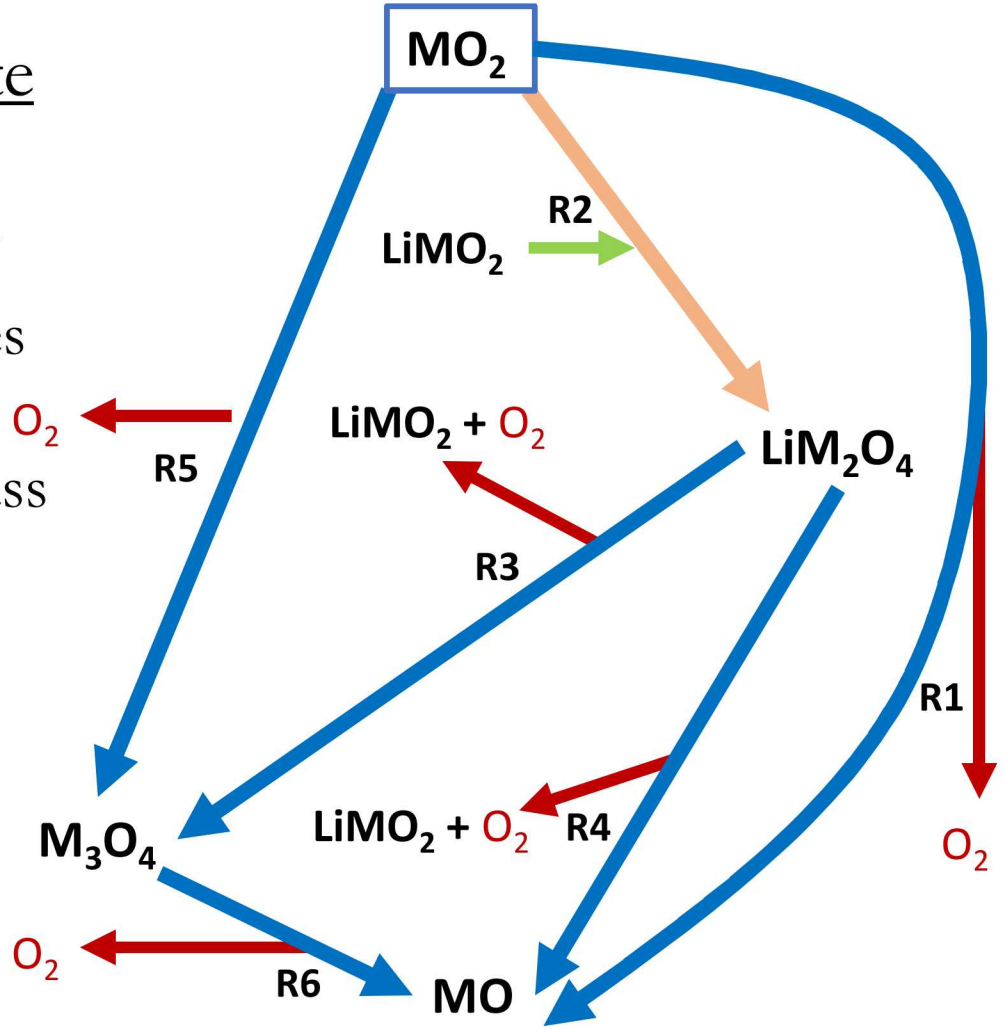


THERMODYNAMICS OF CATHODE RUNAWAY

Decomposition paths for de-lithiated Li_xMO_2

Layered Metal Oxide Decomposition in Electrolyte

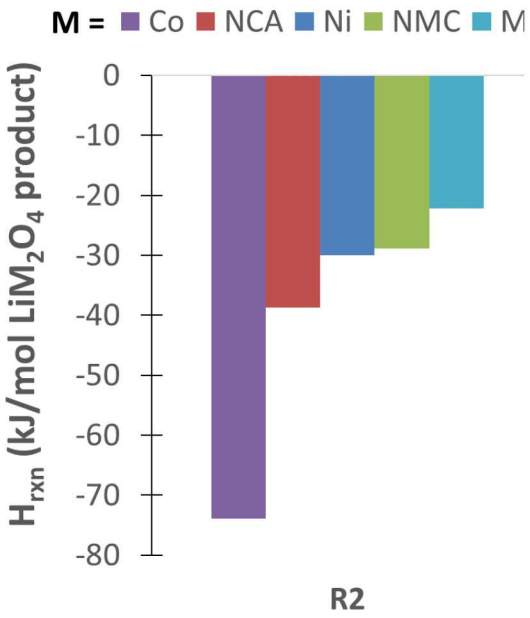
- Compiled a database of 36 enthalpies of formation for cathode materials from over 42 literature sources
- Up-front predictions of heat release for a whole class of Li_xMO_2 cathode materials with electrolytes
  - Existing or proposed compositions
- Web-based calculator to be developed



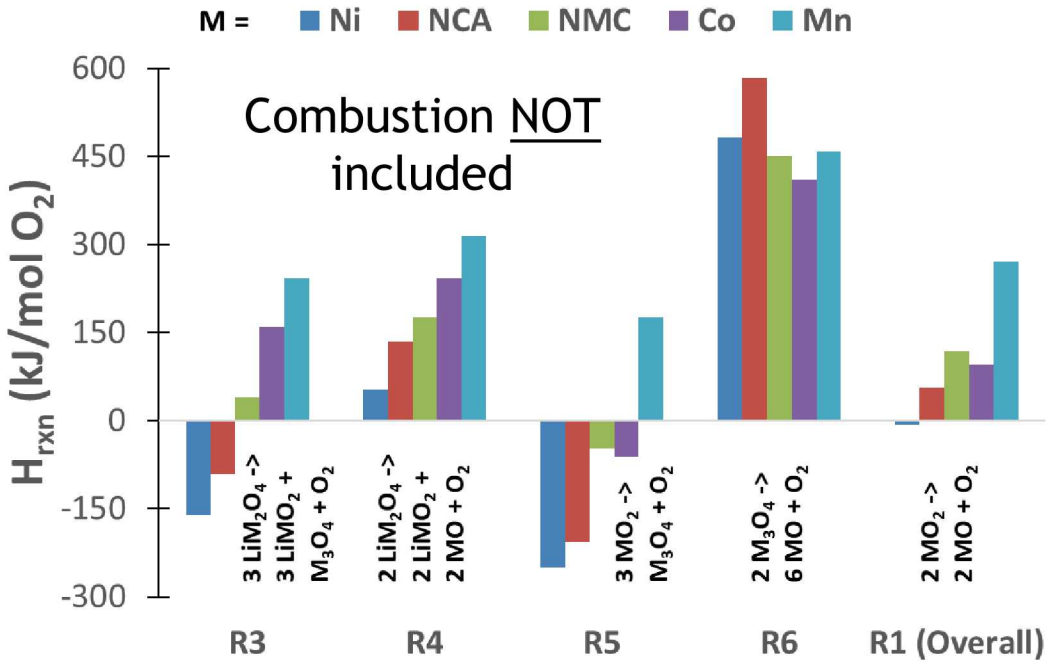
M = Ni, Co, Mn, Al as well as mixtures (NMC, NCA, etc.)

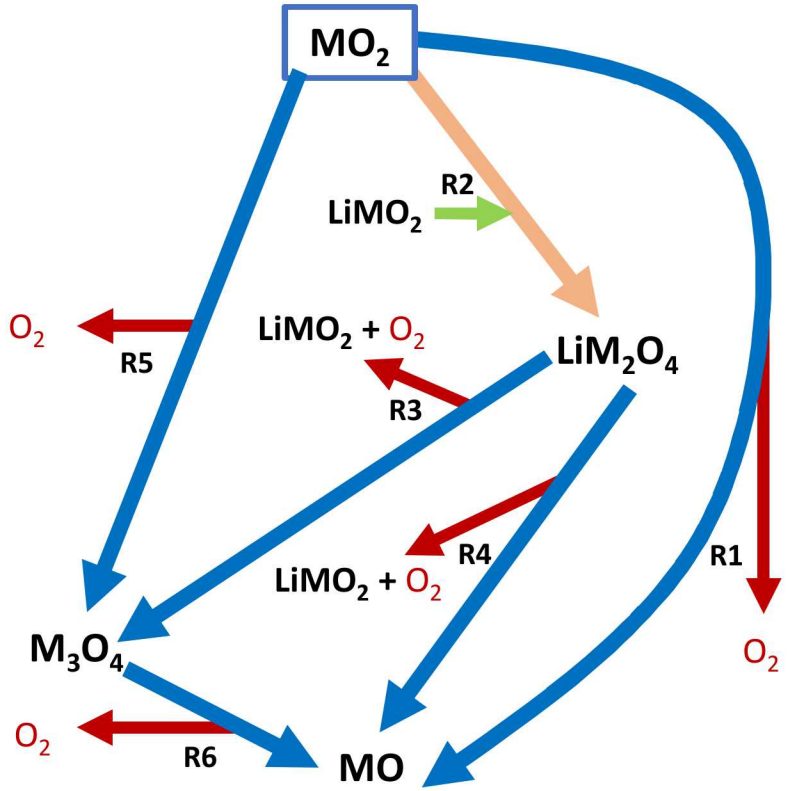
Both Combustion and Phase-Change Enthalpy are Important

Initial phase change produces no oxygen



Subsequent phase changes produce oxygen that promotes solvent combustion





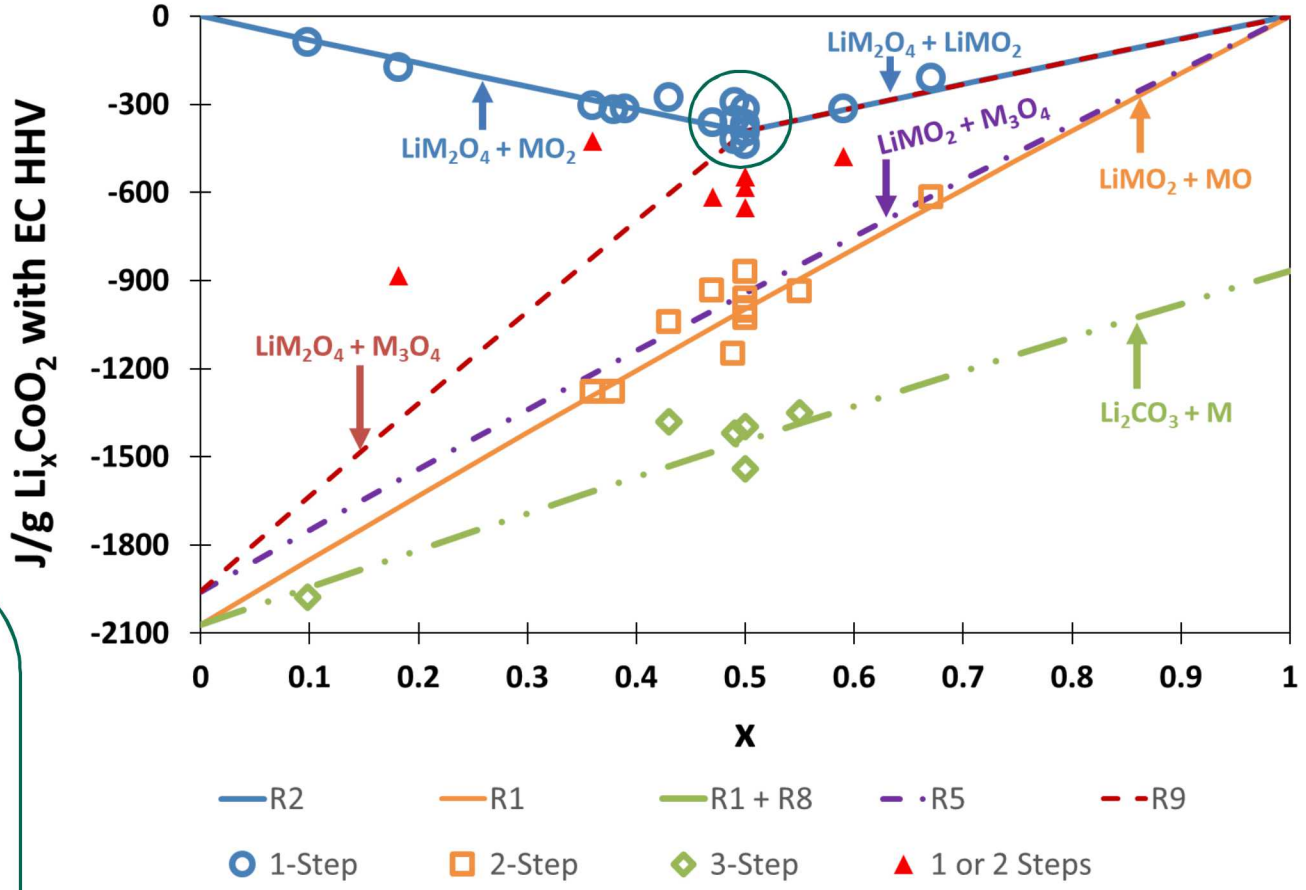
- M_3O_4 formation (R5 or R3) is most exothermic phase change producing O_2
- MO formation (R6 or R4) is most endothermic per O_2 produced
  - R6 plus **EC combustion enthalpy of -472 kJ/mol O_2** consumed is approximately thermal neutral

LCO Cathode Calorimetry with Electrolyte Consistent with Predictions

Predictions provide means to compare diverse measurements

- Li_xCoO_2 (LCO, **shown here**)
- $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 1:1:1)
- $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA 80:15:5)

- Most detailed comparison for Li_xMO_2 materials
- 136 total calorimetry measurements compiled from 28 articles for LCO, NMC, and NCA
  - Each point on plots required careful evaluation and conversion to common basis
- Comparisons clearly demonstrate and explain variability observed with state of charge (SOC)
  - SOC proportional to 1-x



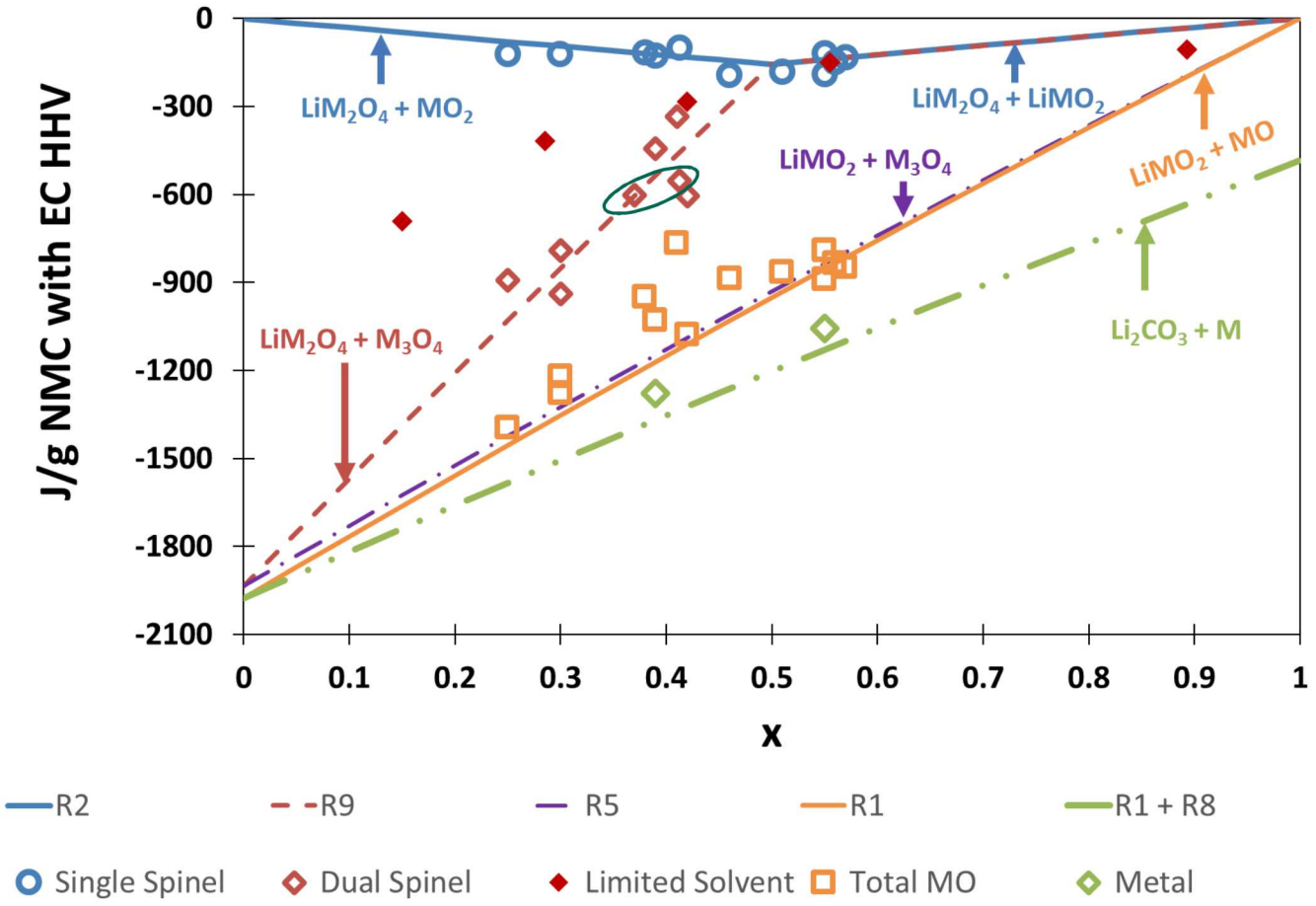
R8 (green line) is reduction to metal

- $4\ LiMO_2 + 2\ CO_2 \rightarrow 2\ Li_2CO_3 + 4\ M + 3\ O_2$
- May occur in calorimetry, less likely in vented batteries

NMC (1:1:1) Calorimetry with Electrolyte Consistent with Predictions

- Filled red diamonds had limited electrolyte, additive concentrations not reported
- 2 open red diamonds were total measurements rather than partial measurements
  - Suggests **R9** rather than expected **R1**
  - These measurements removed excess electrolyte or used vented pans
  - XRD studies show that transition from M_3O_4 to MO does not happen for NMC without solvent

Challenge: How to design experiments and models to represent batteries that are initially pressure-tight and subsequently vent?

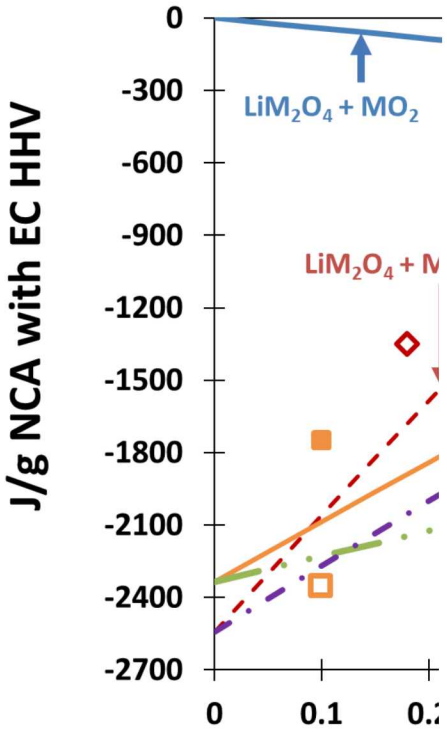


NCA (80:15:5) Calorimetry with Electrolyte Consistent with Predictions

- Filled symbols are solvent-free measurements
  - Why is agreement with calculations still good?
  - Binders and conductive fillers have O_2-basis combustion enthalpies within 11% to 18% of EC

- Derived equivalence ratio ϕ_a for cathode additives with respect to R1 (MO production)
  - $\phi_a > 1$ for cases without solvent indicates excess fuel with respect to oxygen production
  - Cathode additives less reactive than solvents (combustion at higher temperatures)

- Measurements at x = 0.1 are the same cathode with/without electrolyte
  - DSC measurement w/o electrolyte has long tail
    - Decomposition may not be complete (less reactive)?
    - Possibly skewed baseline for integration?
  - Mass basis conversion relied on average cathode mass
    - Reported as 3 mg to 5 mg (plot based on 4 mg)



Original Mass Basis was Electrode + Current Collector

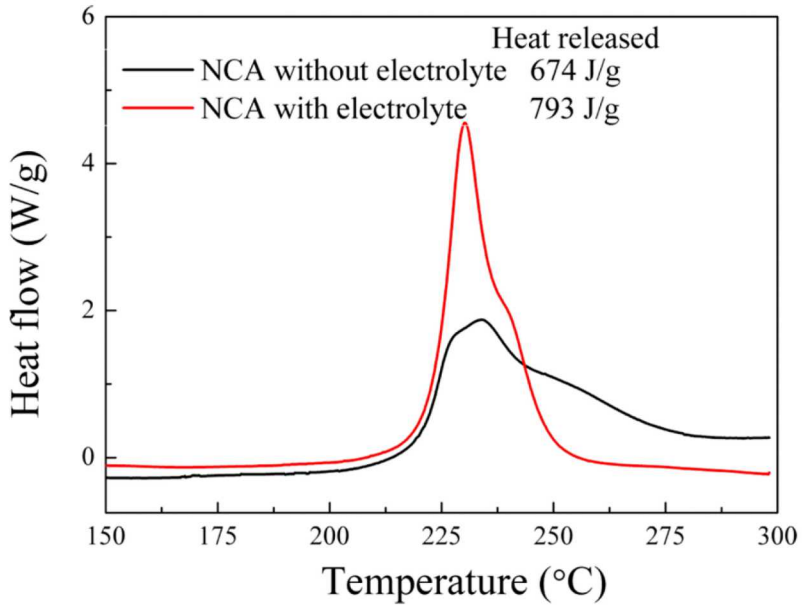


Figure 3. DSC of $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ charged electrode.

Y. Huang, Y. C. Lin, D. M. Jenkins, N. A. Chernova, Y. Chung, B. Radhakrishnan, I. H. Chu, J. Fang, Q. Wang, F. Omenya, S. P. Ong and M. S. Whittingham, *ACS Appl. Mater. Interfaces*, **8**, 7013 (2016).

$$\phi_a = \frac{n_{ox,bc}}{n_{ox,p}} = \frac{6y_b + 16y_c}{y_a(1-x)}$$

NEXT STEPS FOR CATHODE MODELING

Quantify Cathode Decomposition Rates

- Normalize rates by predicted heat for each process to identify trends
- Correlate normalized rates within families of cathodes such as NMC
  - Gain predictive/interpolative capabilities
- Consider model forms with proper surface area and SOC dependence that can be generalized within material families
- Consider effects of lower rates observed in the presence of limited electrolyte

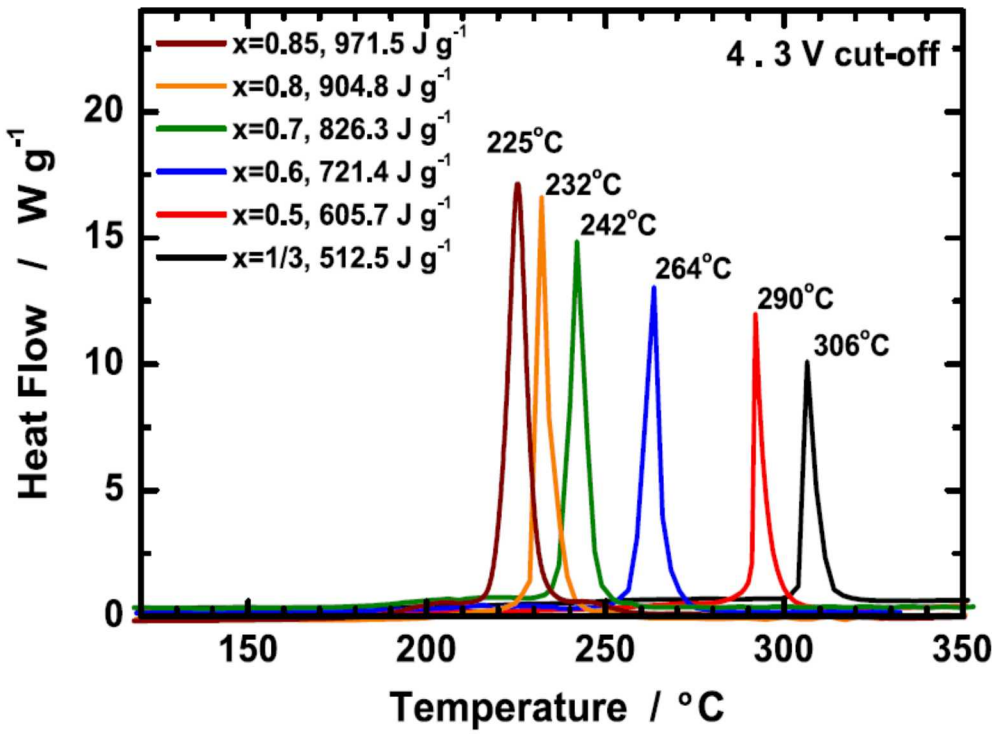


Fig. 10. DSC results of the $Li_{1-\delta}[Ni_xCo_yMn_z]O_2$ materials ($x = 1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85).

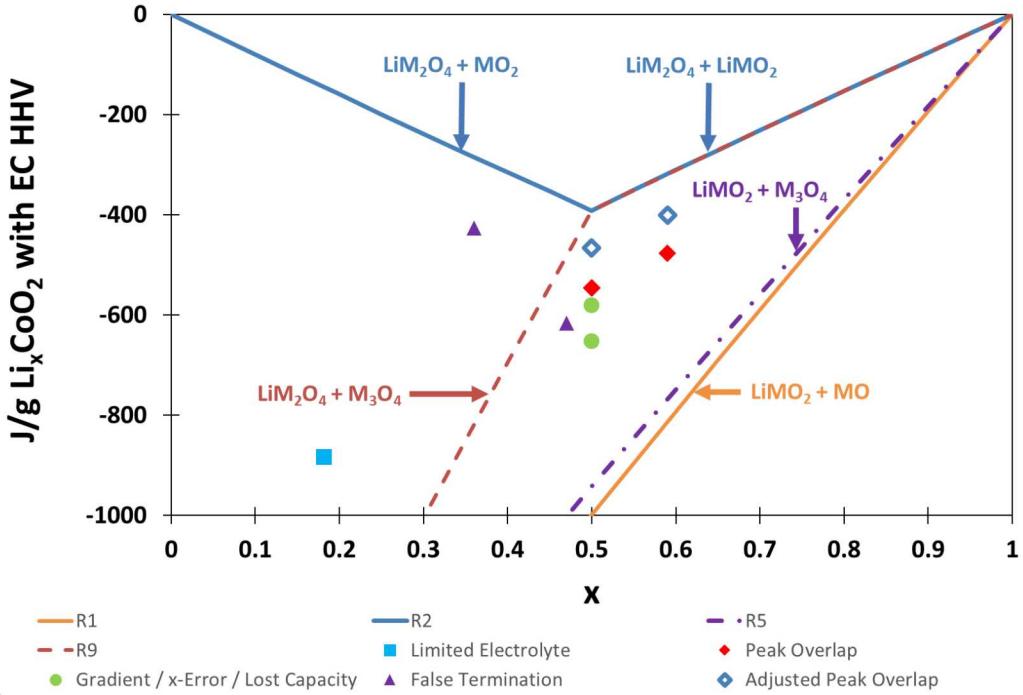
H.-J. Noh, S. Youn, C. S. Yoon and Y.-K. Sun, *J. Power Sources*, **233**, 121 (2013).

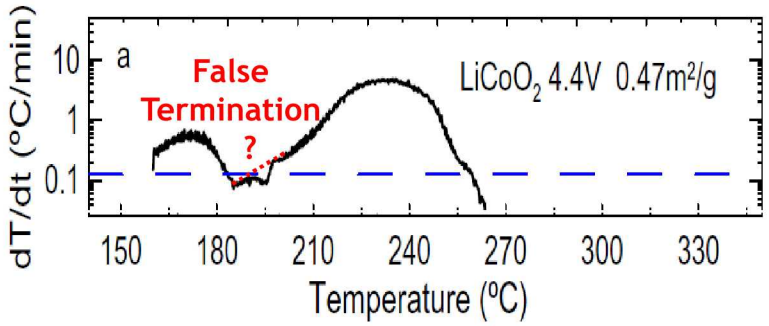
Discrepancies Provide Opportunities for Questions and Learning

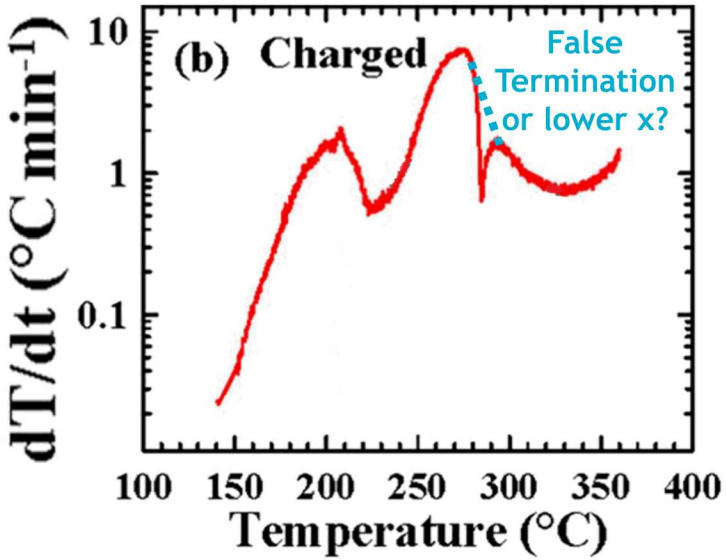
Thermodynamic comparisons provide perspective/basis to ask whether a measurement is unusual and why

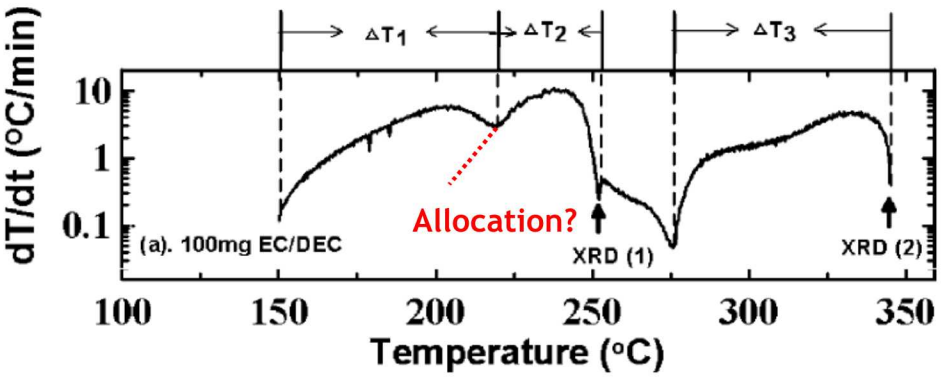
Largest observed LCO discrepancies can be explained by

- Limited electrolyte (incomplete combustion)
- False/apparent termination of exotherm
- Uncertainty/nonuniformity in assigned x (often from voltage)
- Uncertainty in heat allocation between overlapping exotherms









Y. D. Wang, J. W. Jiang and J. R. Dahn, *Electrochem. Commun.*, **9**, 2534 (2007).
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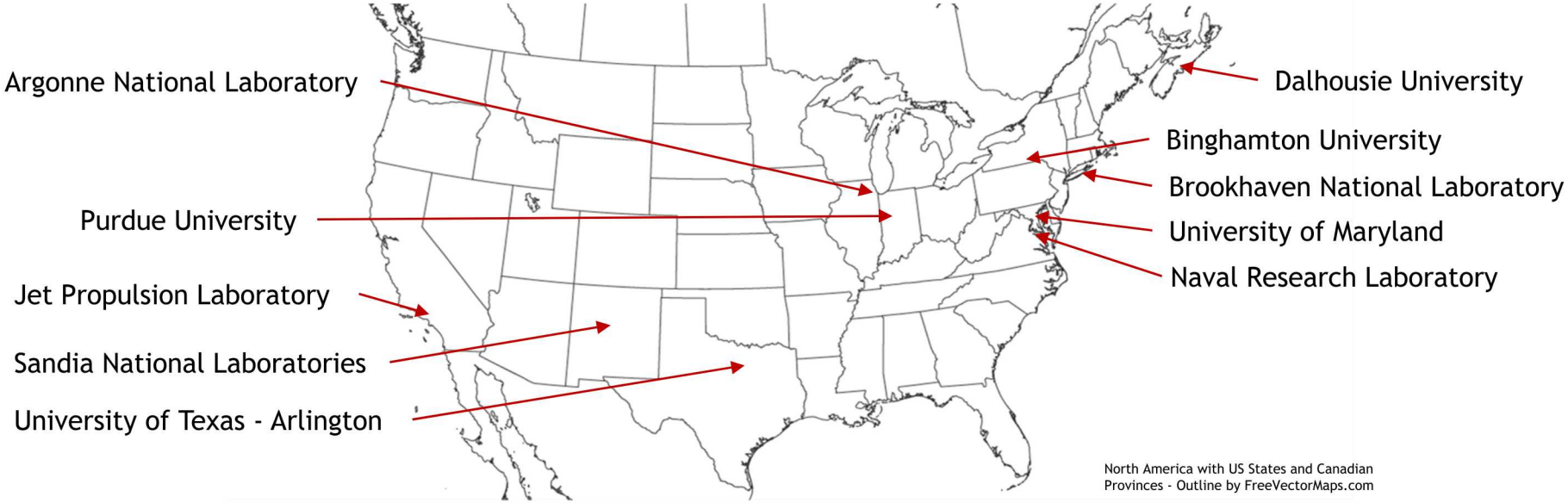
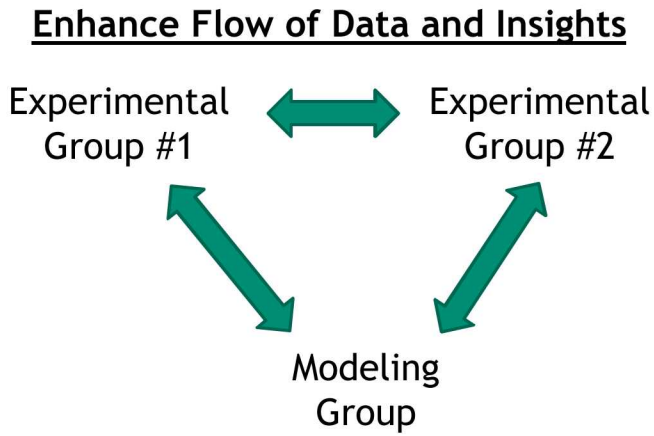
LITHIUM-ION BATTERY CALORIMETRY COLLABORATIVE

Collaborative workshops: Thermal Runaway Investigation, Prediction, and Prevention

- Follow models of
  - *Turbulent Nonpremixed Flames Workshop* (https://www.sandia.gov/TNF/abstract.html)
  - *Measurements and Computation of Fire Phenomena Workshop* (https://iafss.org/macfp/)
- Initial organizational meeting held in May 2019 (ECS @ Dallas)
  - 8 groups shared feedback about directions to take the workshop series and how to collaborate
- Online forum to be established to share validation-quality measurements and validated predictive models
- Collaboratively address inconsistencies across literature
- Planning meeting in May 2020 (ECS @ Montreal), first full-scale workshop in June 2021 (ECS @ Chicago)

Let us know if you're interested!





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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Calorimetry Collaborative Bridging Experiment and Modeling

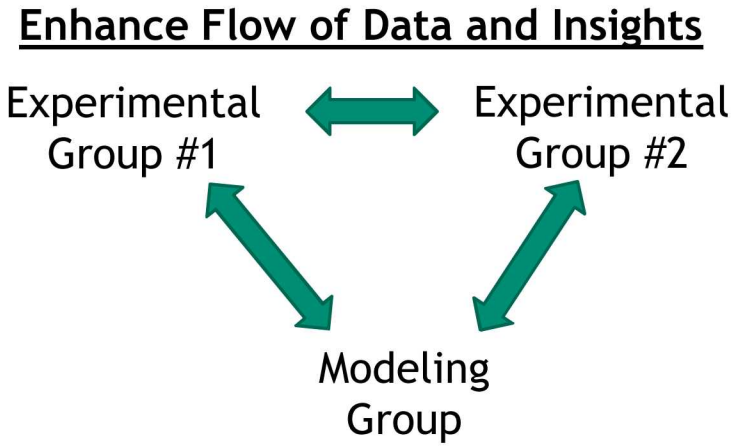
Based on initial feedback:

Dominant concerns for research into thermal response of lithium-ion batteries are:

- Incomplete details reported for both experimental testing and modeling
- Variation from group to group in results (due to stochastic nature of battery failures or inadvertent differences in experiment/materials) can have consequences for the models developed
- Not all appropriate component-level interactions considered to model full-cell thermal evolution

Next steps:

- Develop an open database of well-documented experimental measurements/procedures and computational approaches



Let us know if you're interested!

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136 Calorimetry Measurements Evaluated from 28 Articles

Literature for LCO Comparisons (37 points)

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