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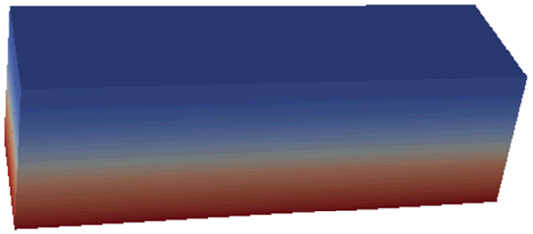

Modeling Thermochemical Sources for a Broader Range of Materials and Conditions

Randy Shurtz, John Hewson

231st ECS Meeting, New Orleans, LA

5/31/2017

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Models and Testing Mitigate Grid Storage Safety Risks

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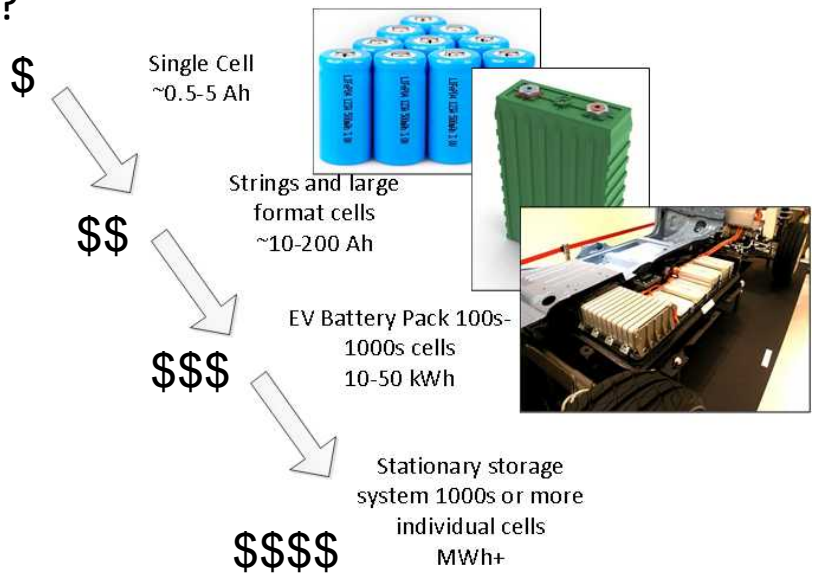
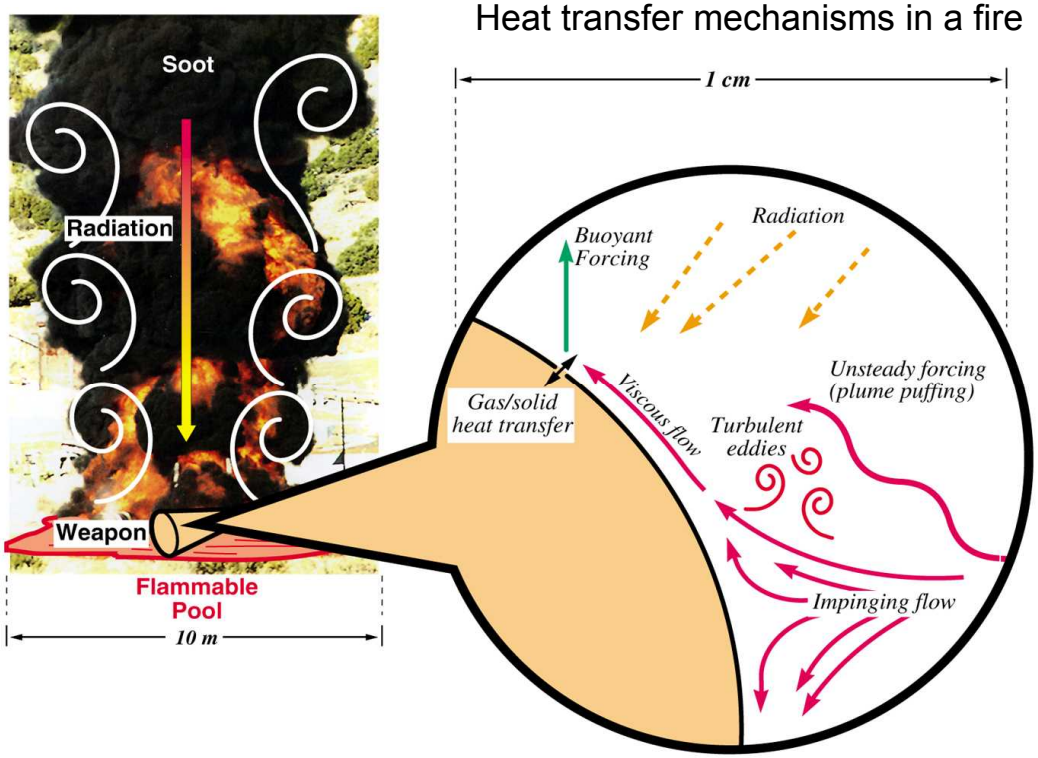
- How bad can a Li-Ion battery fire be at grid storage scale?
- Will a single cell in runaway cause cascading failure?
- Cost of safety testing increases with scale
- Models can complement test programs
  - Yield insight into causes of observed events
  - Extend experimental results to new scenarios
  - Evaluate standards and test configurations (existing and proposed)
  - Optimize product design



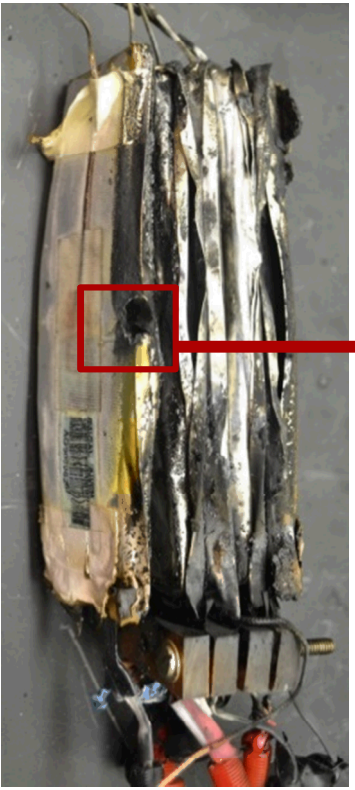
www.cnn.com
www.nissan.com
www.samsung.com
www.saft.com
www.internationalbattery.com

Sandia Tools Suitable for Battery Safety Analysis

- Sierra-Mechanics integrated simulation tools developed at Sandia
  - Original purposes included safety analysis of weapons in fire scenarios
  - Product of DOE-NNSA investments via Advanced Scientific Computing (ASC) program
- Charged batteries include both ‘fuel’ and ‘oxidizer’ internally
  - Similar to energetic materials such as rocket propellants



How Do We Model Thermal Runaway in Batteries?



1) Simplify & Discretize Geometry

2) Define initial composition, thermal properties, reactions (species & energy source terms)

3) Define convection and radiation boundary conditions

4) Define initial energy source

5) Calculate internal conduction and reaction rates

Models Need Parameters

- Preliminary chemistry model from literature
  - Derived from calorimetry data (ARC and DSC)
  - Yields reasonable predictions of thermal runaway onset (time and temperature)

- Empirical chemical reactions

- SEI decomposition $2\ ROCO_2Li \rightarrow Li_2CO_3 + prod$
- Cathode-electrolyte $CoO_2 + C_3H_4O_3 \rightarrow \frac{1}{3}Co_3O_4 + prod$
- Electrolyte-salt $C_3H_4O_3 + LiPF_6 \rightarrow prod$
- Anode-electrolyte $C_6Li + C_3H_4O_3 \rightarrow Li_2CO_3 + prod$

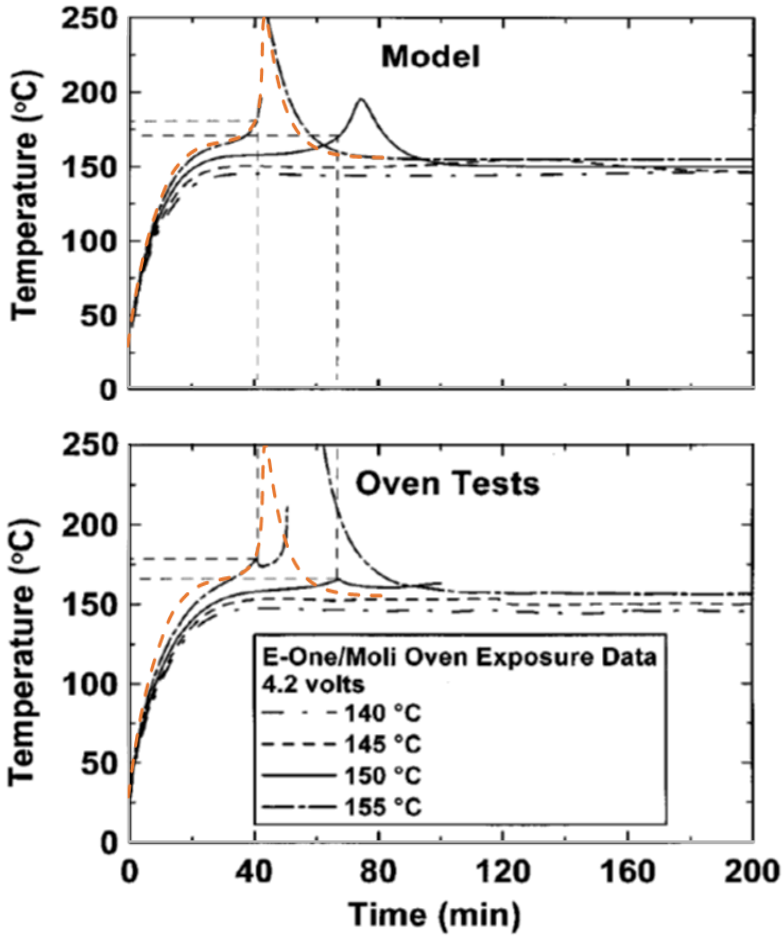


Figure 2. A comparison of oven exposure test results to model predictions: (top) model predictions and (bottom) oven test results for 18650 E-One/Moli Energy cells charged to 4.2 V.

ARC measurement from MacNeil, D. D. and J. R. Dahn (2001). Journal of Physical Chemistry A **105**(18): 4430-4439.

Cathode Chemistry Drives Cell Failure

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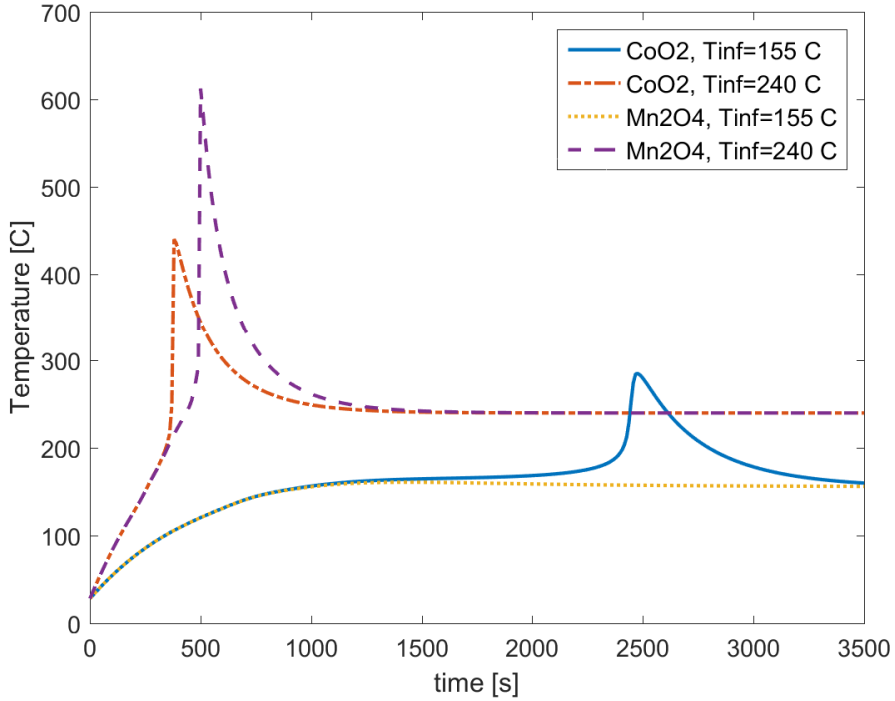
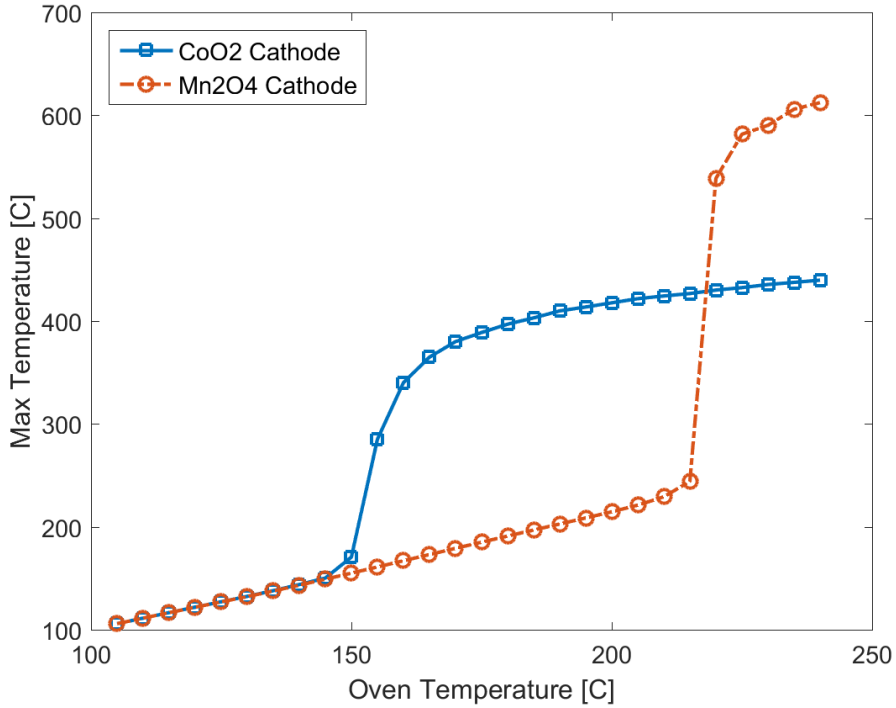
Simulated oven tests for 18650 cells
2 cathode materials, 2 temperatures





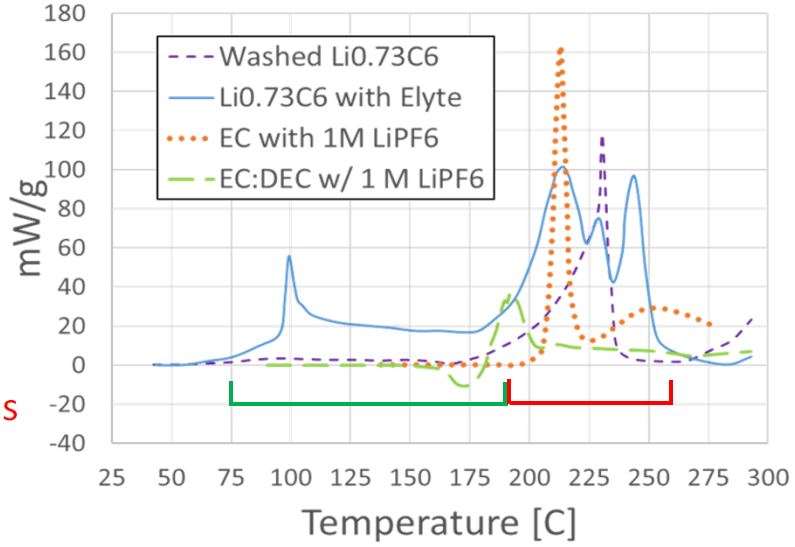
- Differences in cathode chemistry must be understood and quantified to predict thermal runaway of single cells

$LiCoO_2$ model from Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society 148(7): A755-A761.
$LiMn_2O_4$ model from Spotnitz, R. and J. Franklin (2003). Journal of Power Sources **113**(1): 81-100.

Limitations of Literature Chemistry Models

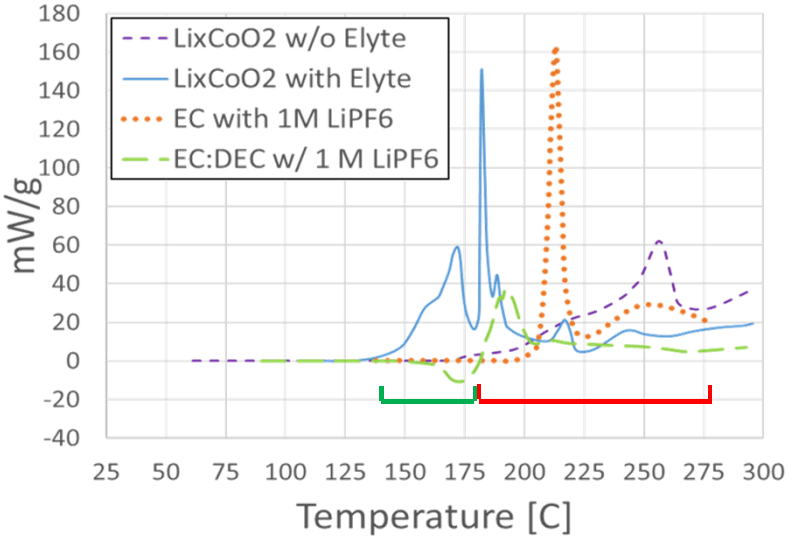
- Limited to low-temperature reactions
  - Sufficient to predict initiation of thermal runaway
    - Driven by 1st stage of cathode decomposition
    - Original intent of published models
  - Under-predicts maximum cell temperatures
    - Missing heat release from high-temperature reactions
  - Cannot accurately predict cascading failure

Anode & Electrolyte DSC data at 0.2°C/min



- Limited in terms of applicable materials
  - Few cathode materials
  - Optimized for a single build and state of charge
    - Does not account for real property variations

Cathode & Electrolyte DSC data at 0.2°C/min



Data from Wang, Q., J. Sun, X. Yao and C. Chen (2005). Thermochimica Acta **437**(1–2): 12-16.

High-Fidelity Models Required for Cascading Failure

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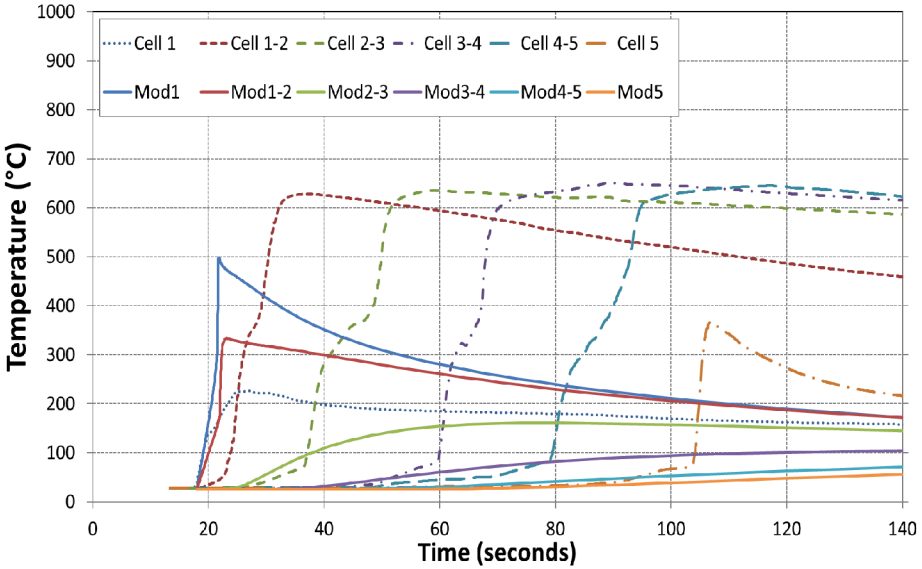
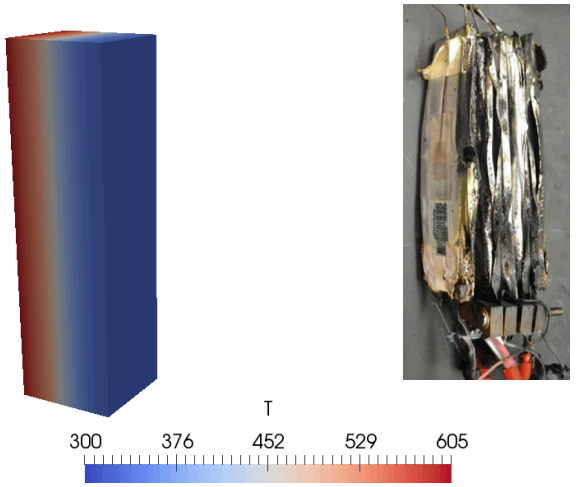
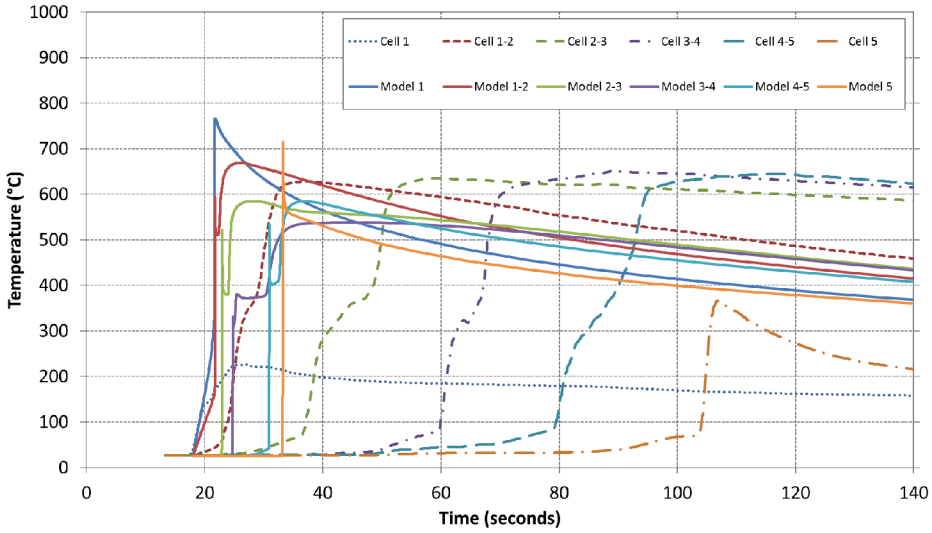
Baseline Chemistry Model

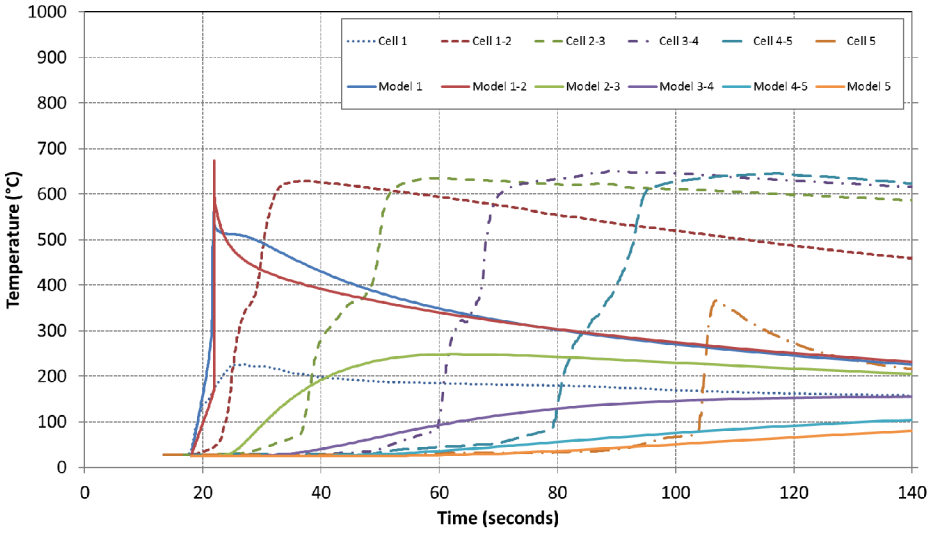




Add extra high-temperature reaction

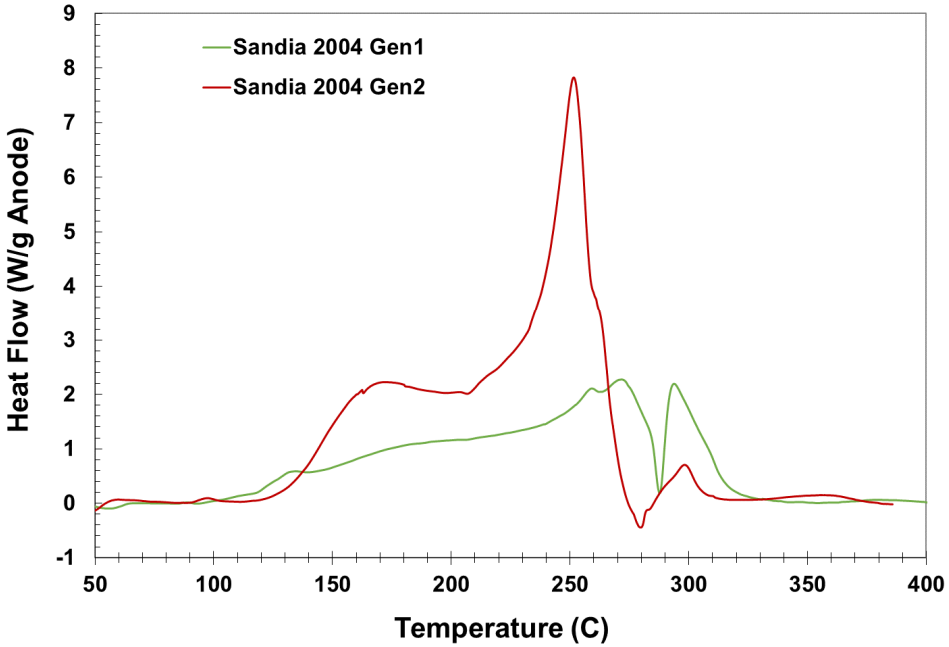


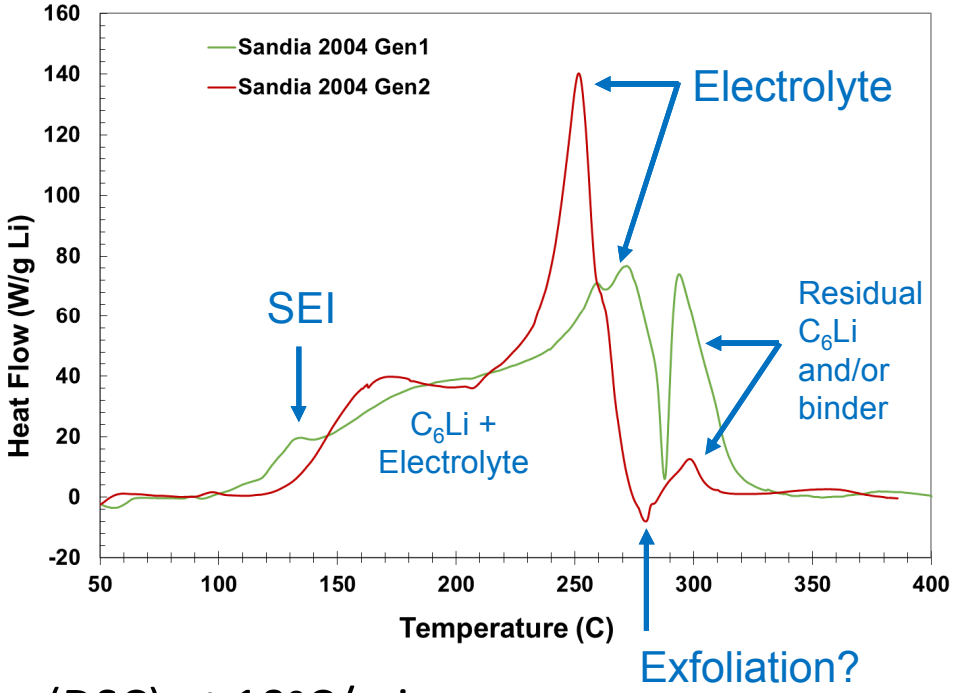
Decrease high-temperature reaction rate by 4x



Data from Lamb, J., et al. (2015). Journal of Power Sources **283**: 517-523.

Correct Thermodynamic Basis Critical for Modeling

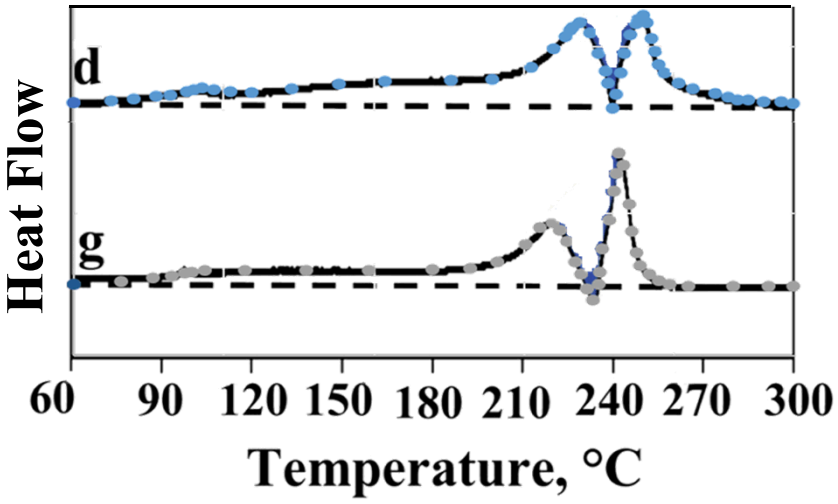


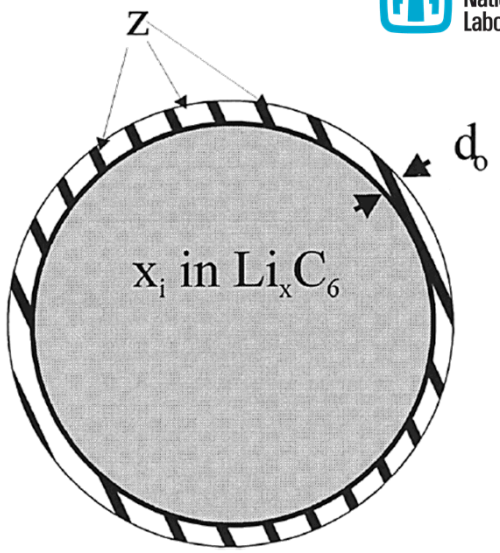


- Anode Differential Scanning Calorimetry (DSC) at 10°C/min
  - H_{rxn} = (DSC Area)/(DSC Rate)
    - Different reaction regimes should be compared on appropriate stoichiometric basis
  - $C_6Li + EC \rightarrow C_6 + C_2H_4 + Li_2CO_3$ yields H_{rxn} = **42.5** kJ/g Li
  - Integration of 2 experimental DSC curves yields 48.9 kJ/g Li and 41.3 kJ/g Li
    - Good agreement considering differences in electrolyte, etc.

Roth, E. P. and D. H. Doughty (2004). "Thermal abuse performance of high-power 18650 Li-ion cells." Journal of Power Sources **128**(2): 308-318.

Staged C_6Li Consumption in Anode





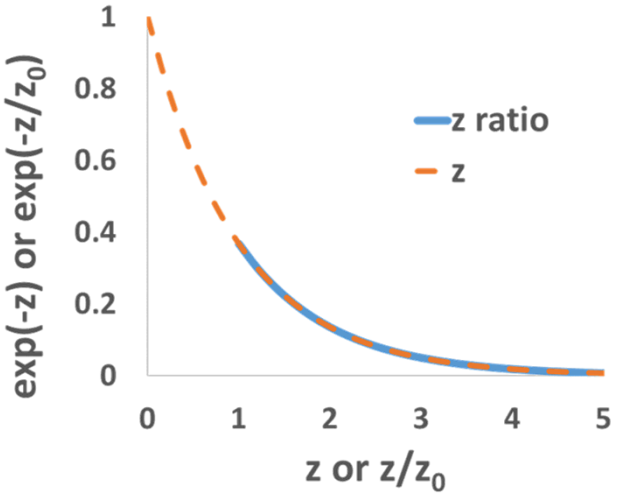
- C_6Li + Electrolyte reaction shows up as "plateau" in DSC
  - Literature model couples $\exp(-z/z_0)$ limiter with Arrhenius chemical rate function
  - Results in considerable unconverted lithium in model
  - z treated as a normalized SEI thickness
    - No dimensions or scaling rules provided
    - $z_0 = 0.033$ in 2001 paper, $z_0 = 0.15$ in 1999
- Exposure of new surface area should trigger consumption of residual intercalated lithium
  - Graphite exfoliation and/or breakdown of SEI layer
  - Corresponds to one or more of the large DSC peaks
  - Should be included to model reasonable high-temperature heat release from anode

Haik, O., S. Ganin, G. Gershinsky, E. Zinigrad, B. Markovsky, D. Aurbach and I. Halalay (2011). Journal of the Electrochemical Society **158**(8): A913-A923.

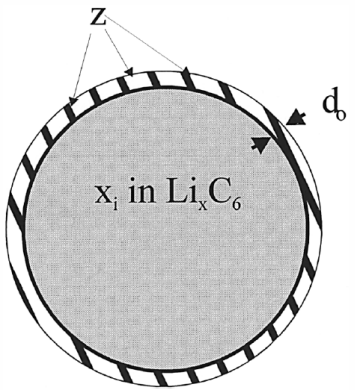
Richard, M. N. and J. R. Dahn (1999). Journal of the Electrochemical Society **146**(6): 2068-2077.
Richard, M. N. and J. R. Dahn (1999). Journal of the Electrochemical Society **146**(6): 2078-2084.
Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society **148**(7): A755-A761.

Modified Approach for C_6Li Plateau

- Use exp(-z) instead of exp(-z/z_0) to limit rate
  - Allows initial reaction rate to be specified independent of layer growth rate
  - Layer growth rate should be inversely proportional to surface area (use BET)
- New rules for scaling growth in z
  - Initially set z_0 = 0, calibrate when data available
    - Likely scales with mass of SEI per unit surface area
  - Set reference condition to BET_{ref} = 10 m^2/g
  - ρ_{S2} = mass concentration of salt deposited on particle surface from C_6Li + Electrolyte reaction
  - C_z = scaling factor that specifies layer growth rate
    - Calibrate simultaneously with Arrhenius parameters



$$z = z_0 + \frac{C_z \rho_{S2} BET_{ref}}{BET}$$



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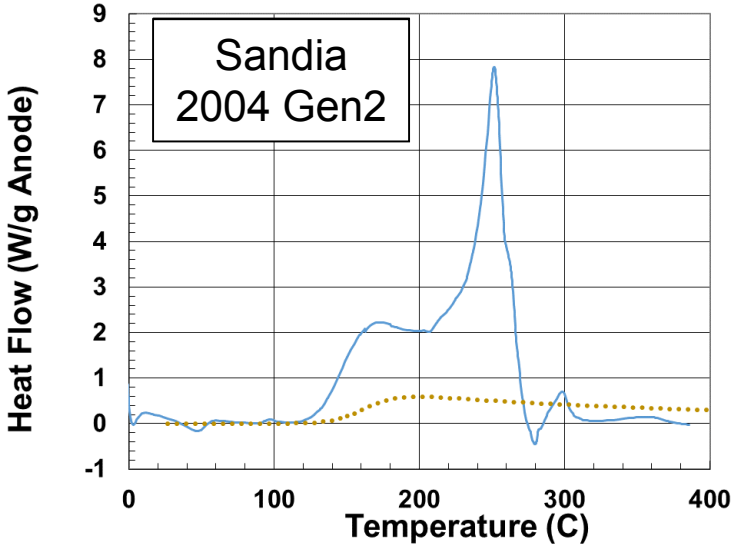
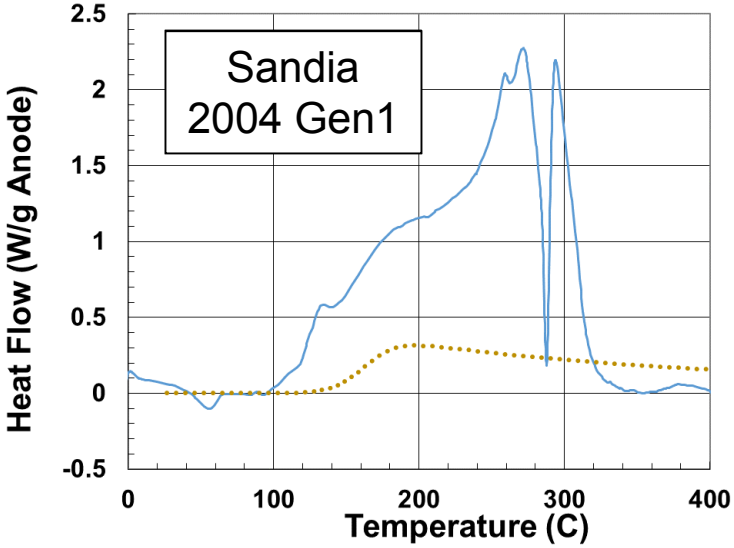
Richard, M. N. and J. R. Dahn (1999). Journal of the Electrochemical Society **146**(6): 2078-2084.
Hatchard, T. D., D. D. MacNeil, A. Basu and J. R. Dahn (2001). Journal of the Electrochemical Society **148**(7): A755-A761.

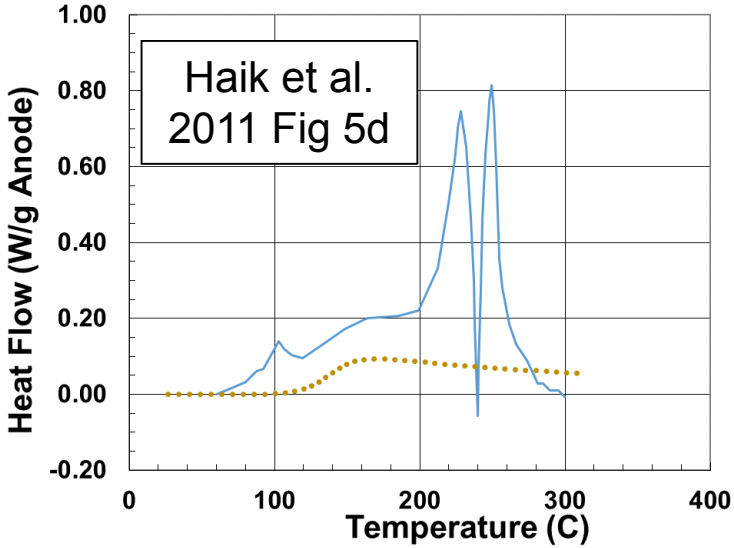
DSC Compared to Literature C_6Li Model

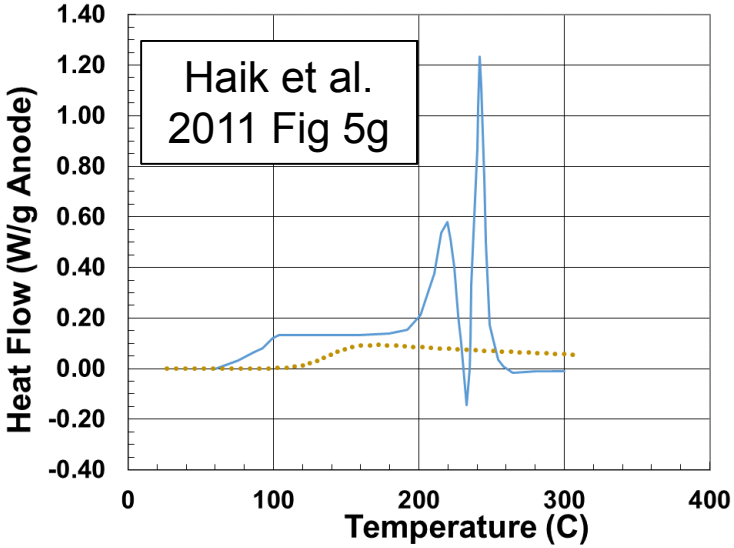


Data

Old Model







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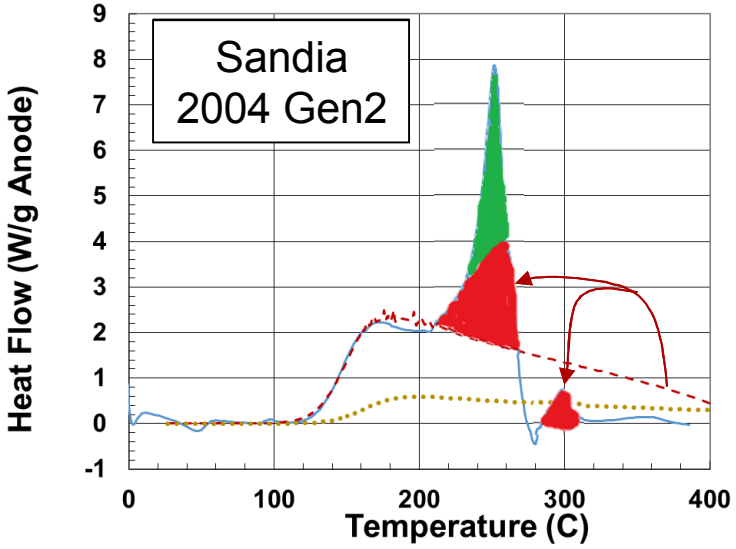
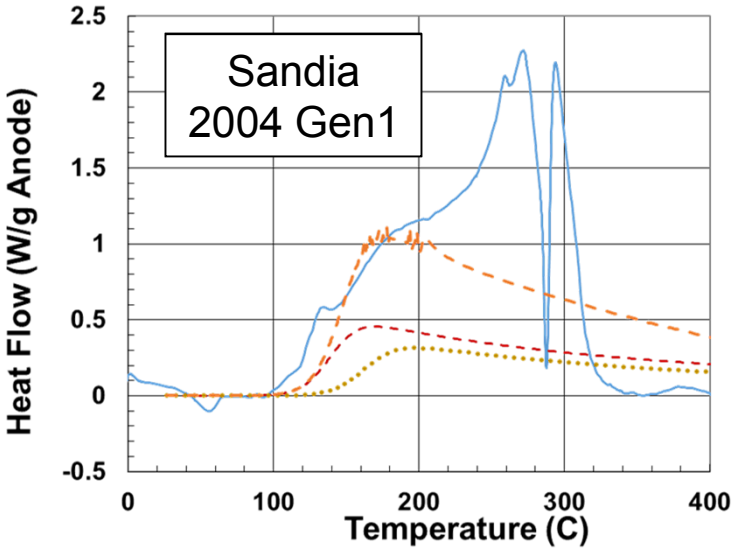
DSC Compared to Improved C_6Li Model

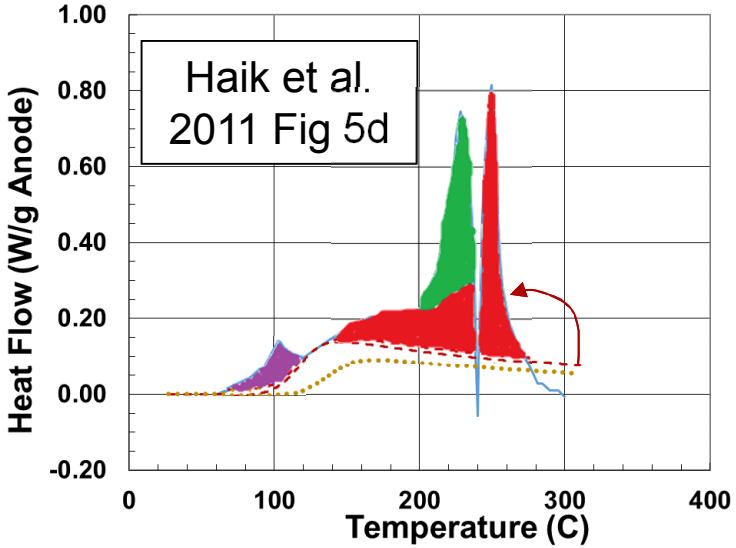


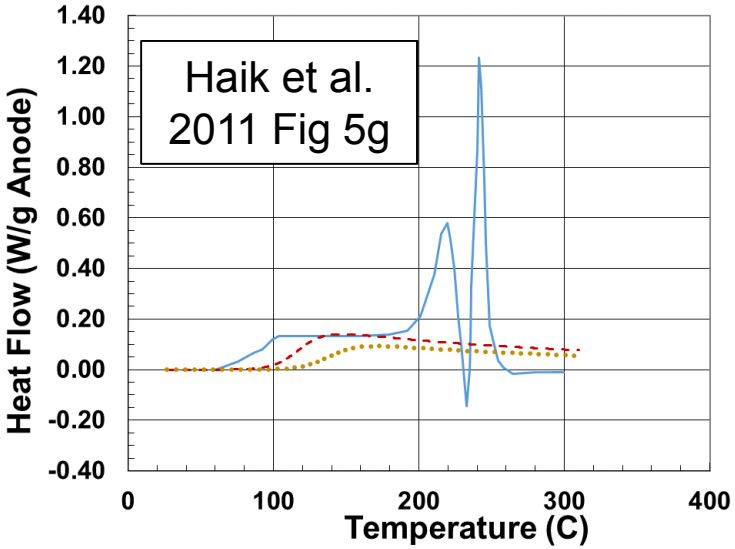


Data

Old Model

Updated Model (Gen1 BET Uncertainty)





Next Steps:

- Calibrate SEI reaction
- Allow C_6Li reaction(s) to accelerate
- Improve Electrolyte Model

Roth, E. P. and D. H. Doughty (2004). "Thermal abuse performance of high-power 18650 Li-ion cells." Journal of Power Sources **128**(2): 308-318.
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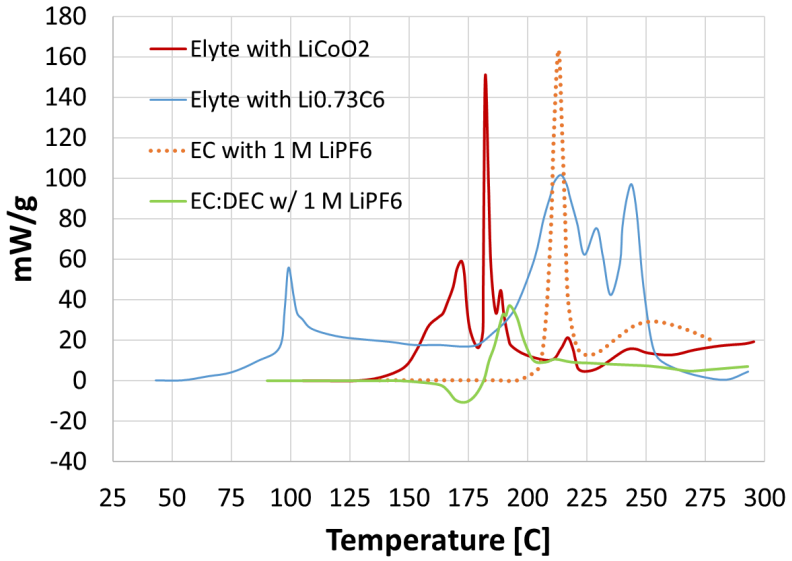
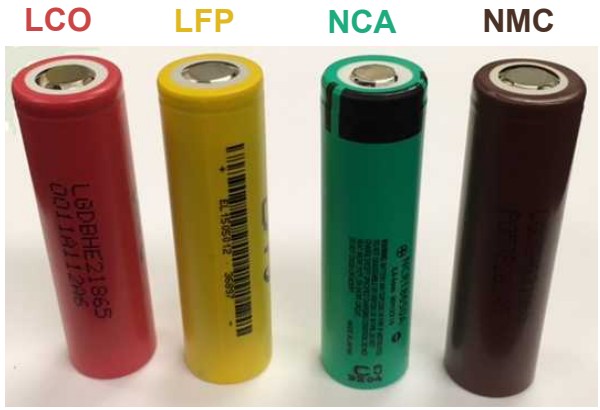
Path Forward for Thermal Runaway Models at Sandia

- Use Sandia and literature data to add high-temperature reactions to model
  - Identify reactions for cathode, anode, and electrolytes
  - Fit corresponding rate parameters
  - Extend model to additional cathode materials
  - Apply in cascading failure scenarios, validate with data
- Include better physics in upgraded models
  - Rigorous thermodynamics
  - Detailed material property dependence
  - Mass transport limitations
- Include additional phenomena
  - External discharge
    - Quantify impact and practicality during runaway
  - Pressurization and venting
    - Quantify and evaluate toxic gas release and fire risks





Data from Wang, Q., J. Sun, X. Yao and C. Chen (2005). Thermochimica Acta **437**(1–2): 12-16.
Pictured cells from ongoing Sandia investigations (Barkholtz)

Acknowledgements

- Dr. Imre Gyuk for supporting energy storage safety work
- DOE OE Funding