Sandia National Laboratories
SNL Energy Storage Technology and Systems – Energy Storage Safety
Funded by Dr. Imre Gyuk
U.S. Department of Energy; Office of Electricity; Energy Storage Systems Program
SAND2018-10527C

Physics-Based Models for Thermal Runaway Heating Rates: Advanced Anode Models

Randy C. Shurtz, John C. Hewson
Fire Science and Technology, Sandia National Laboratories, Albuquerque, NM

Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Models allow projection of knowledge to different scenarios and larger scales.
- Existing thermal runaway models successful for initial single-cell thermal runaway.
  - HMBD01 model for graphite anode + $LiCoO_2$ cathode (Hatchard et al. 2001).
- Needed model features to evaluate safety for large Li-Ion systems include:
  - Applicability to batteries with different form factors, chemistries, SOC.
  - Prediction dependent on material properties.
  - High-temperature chemistry to predict propagation.

Comprehensive Model of Lithiated Graphite Decomposition

$$2LiC_6 + EC(liq) \rightarrow 2C_6 + C_2H_4(g) + Li_2CO_3(cr)$$

$$\Delta H_{rxn} = 281.4\,\frac{kJ}{mol\ Li}$$

→ Yields ~650°C temperature rise in a typical cell

Li_xC_6 Depletion | Edge Area Effect | Limiting Electrolyte | Temperature Dependence | Rate Limiter (Electron-Tunneling Barrier)

$$-\frac{dx_i}{dt} = x_i\,\frac{a_e}{a_0}\,\frac{m_E}{(m_{50}+m_E)}\,A_2\exp\left(-\frac{E_2}{RT}\right)\exp(-z_t)$$

Barrier Growth | Variable Area Effect | Critical Barrier | Allows Acceleration

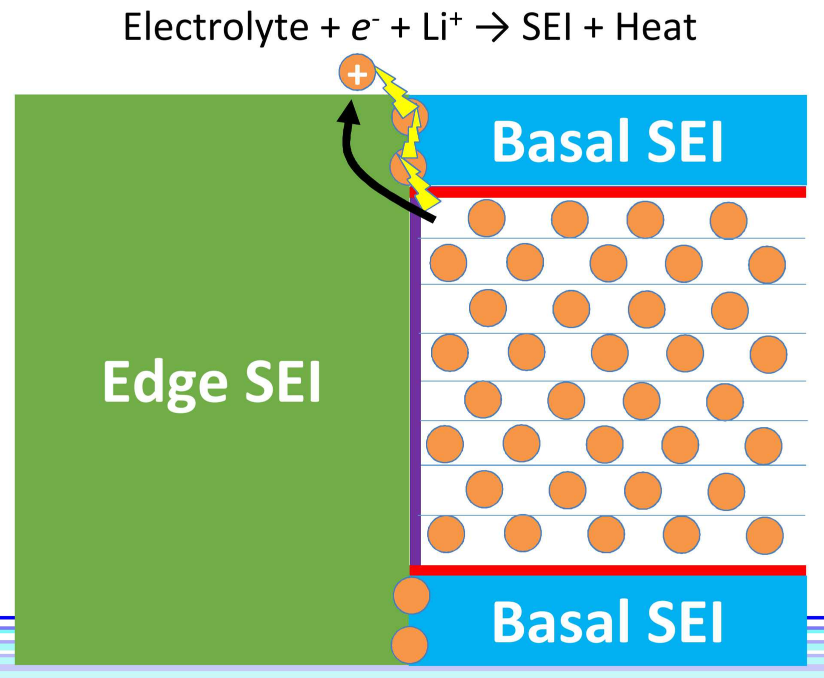
$$\frac{dz_t}{dt} = -\frac{dx_i}{dt}\,\frac{C_t}{\left(\frac{a_{BET}}{a_0}\right)^{n_t}}\ \text{for}\ z_t < z_{crit}\text{, and}\ \frac{dz_t}{dt} = 0\ \text{otherwise}$$

Heat Release with new ΔH_{rxn}

$$Q\,[W/g] = -\frac{dx_i}{dt}\,\frac{\Delta H_{rxn}}{W_a}$$

$n_t \approx 0.5$ suggests a length scale

Electrolyte + e^- + Li^+ → SEI + Heat



- = Graphite Layers
- = Prismatic Surfaces
- = Basal Surfaces
- = SEI Layer on Edges
- = SEI Layer on Basal Planes
- = Lithium atom
- = Lithium Ion
- = Electron Tunneling
- = Lithium-Ion Diffusion

New Physics Understanding from Plateau Model Development

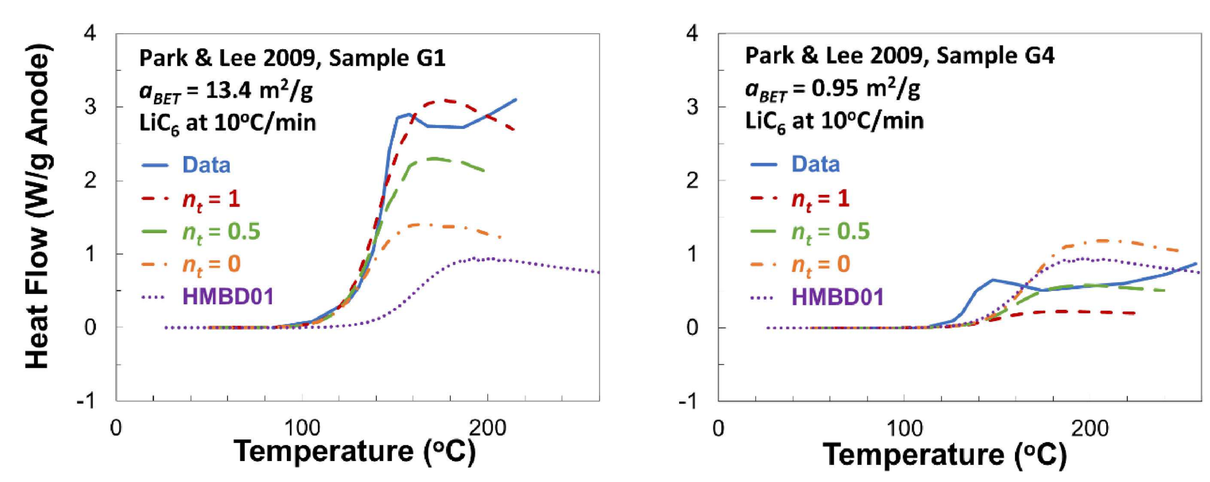
- Prismatic and basal SEI differ in composition and thickness.
- Defect formation favored at grain boundaries and/or the basal-prismatic interface.
- Defects include neutral Li atoms and other features that promote tunneling.
- Tunneling barrier inversely proportional to the length of the defect-rich interfaces.

New Physics Understanding from Anode Runaway Model

- Contraction of graphite during rapid delithiation may strain and damage SEI.
- Onset of exfoliation may deform and rupture SEI.
- Any significant damage to SEI allows the reaction to accelerate.

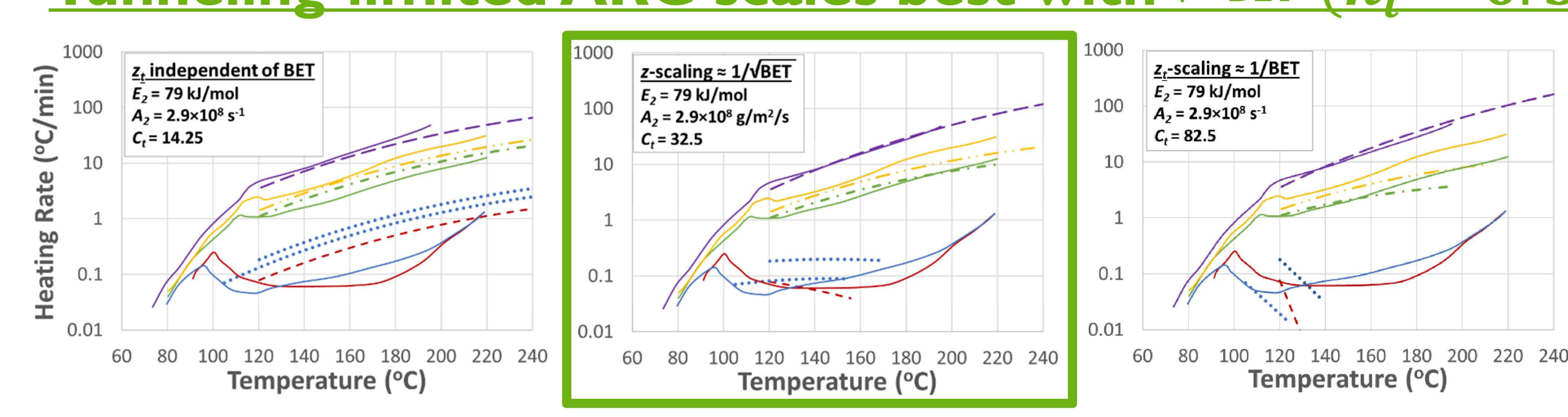
Enhanced Model Predictive Capability

DSC Plateau heat release trends best for $n_t = 0.5$

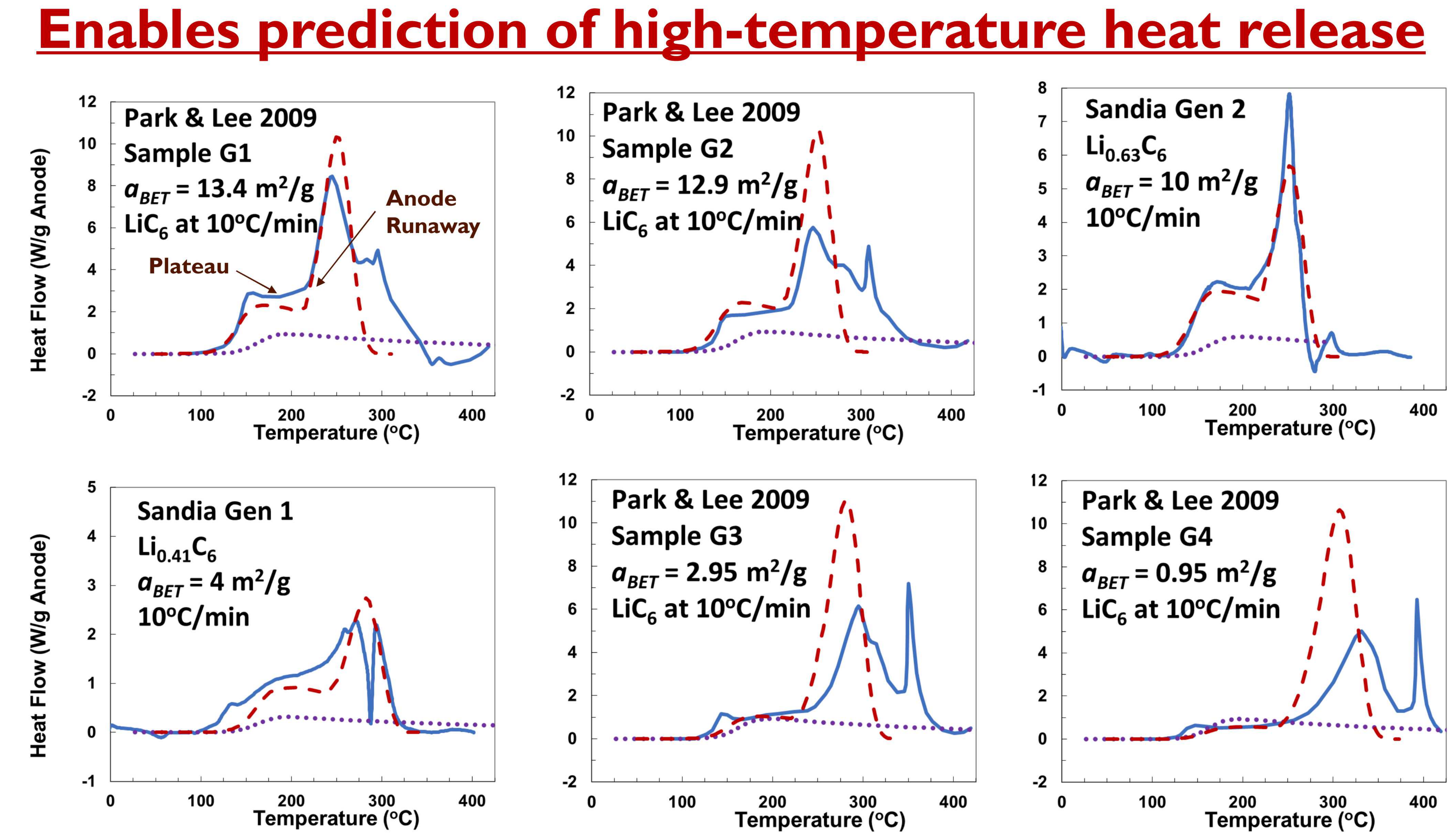


The HMBD01 model shown uses a different ΔH_{rxn} and lacks area scaling, limiting electrolyte, and anode runaway capabilities.

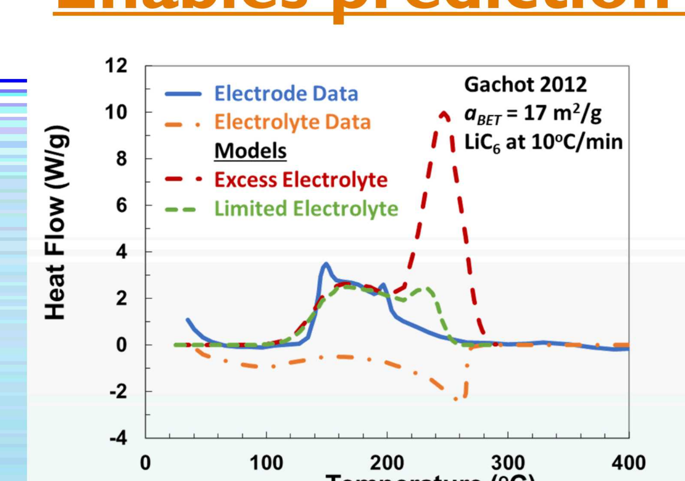
Tunneling-limited ARC scales best with $\sqrt{a_{BET}}$ ($n_t = 0.5$)



Enables prediction of high-temperature heat release

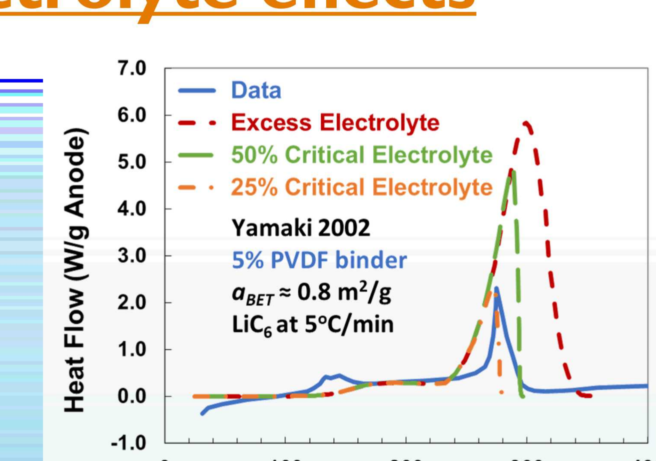


Enables prediction of limiting-electrolyte effects



Gachot et al. 2012 (left): Open DSC pans allowed electrolyte evaporation

Yamaki et al. 2002 (right): Electrode/electrolyte ratio not reported, but no electrolyte was added



Anode Decomposition Model Benefits

- More fundamental in terms of thermodynamics and materials science.
- Heat release rates scale properly with material properties, cell build, and SOC.
- Effect of limiting reactants included.
- High-temperature heat release included; more suitable for propagation studies.

U.S. Department of Energy · NNSA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & 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.
SAND No. ____________

Acknowledgements:
- Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity
- Special thanks to the following people for providing experimental data, thoughtful discussions, and advice
- Summer Ferreira • Loraine Torres-Castro • Joshua Lamb • Jeff Engerer • Andrew Kurzawski • Yuliya Preger

Sandia National Laboratories

T. D. Hatchard, D. D. MacNeil, A. Basu and J. R. Dahn, *J. Electrochem. Soc.*, **148**, A755 (2001).
M. N. Richard and J. R. Dahn, *J. Electrochem. Soc.*, **146**, 2078 (1999).
E. P. Roth and D. H. Doughty, *J. Power Sources*, **128**, 308 (2004). (Sandia Gen1 and Gen 2)
Y. S. Park and S. M. Lee, Electrochim. Acta, 54, 3339 (2009).
D. D. MacNeil, D. Larcher and J. R. Dahn, J. Electrochem. Soc., 146, 3596 (1999).
G. Gachot, S. Grugeon, G. G. Eshetu, D. Mathiron, P. Ribiere, M. Armand and S. Laruelle, Electrochim. Acta, 83, 402 (2012).
J. Yamaki, H. Takatsuji, T. Kawamura and M. Egashira, Solid State Ion., 148, 241 (2002).
R. C. Shurtz, J. D. Engerer and J. C. Hewson, J. Electrochem. Soc., submitted (2018). Parts I and II