SAND2017-10683C

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

Materials Science-Based Thermochemical Decomposition Model for Lithium-Ion Battery Thermal Runaway

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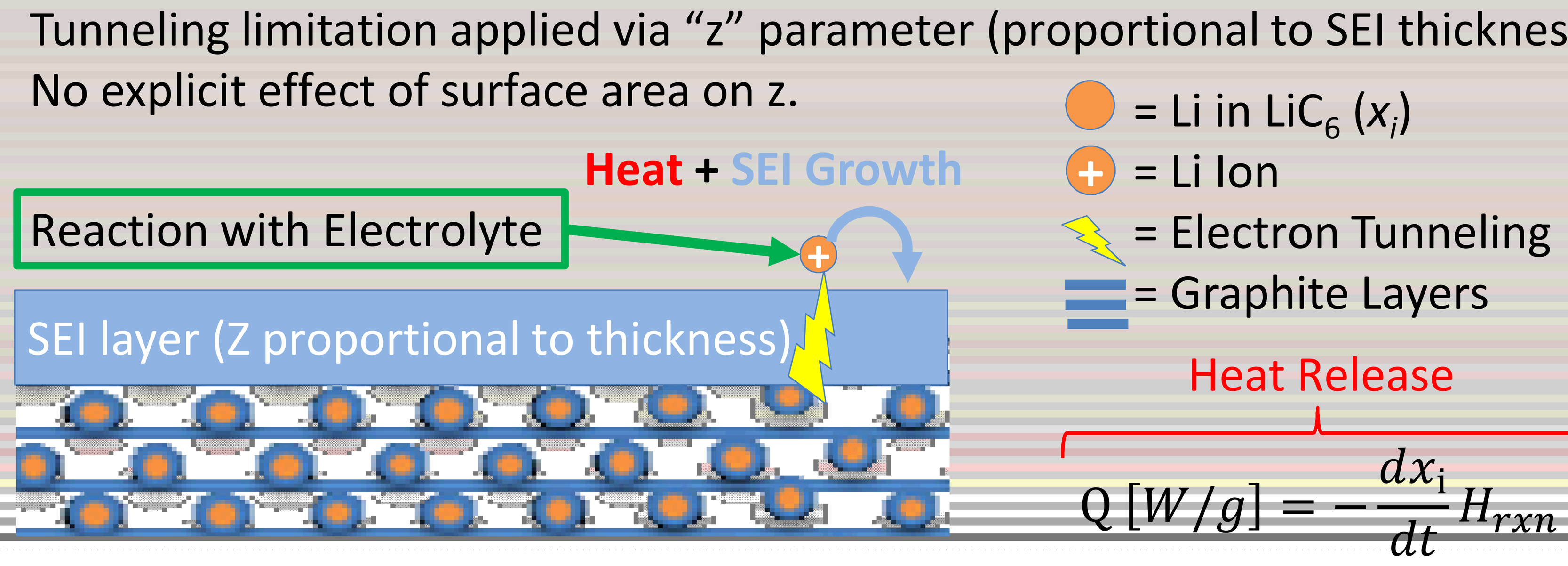
Introduction

- 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.
  - Dahn 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.

Anode Decomposition Model Development

Dahn Anode Model (Richard & Dahn 1999, Hatchard et al. 2001)

- SEI formation from electrolyte + intercalated Li limited by electron tunneling.
- Tunneling limitation applied via "z" parameter (proportional to SEI thickness).
- No explicit effect of surface area on z.



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

Layer Growth; Li_xC_6 Depletion; Li in Li_xC_6; Temperature Dependence; Electron-Tunneling Limiter

$$\frac{dz}{dt} \propto -\frac{dx_i}{dt} = x_i \; A_0 \exp\left(-\frac{E_a}{R_g T}\right) \exp\left(-\frac{z}{z_0}\right)$$

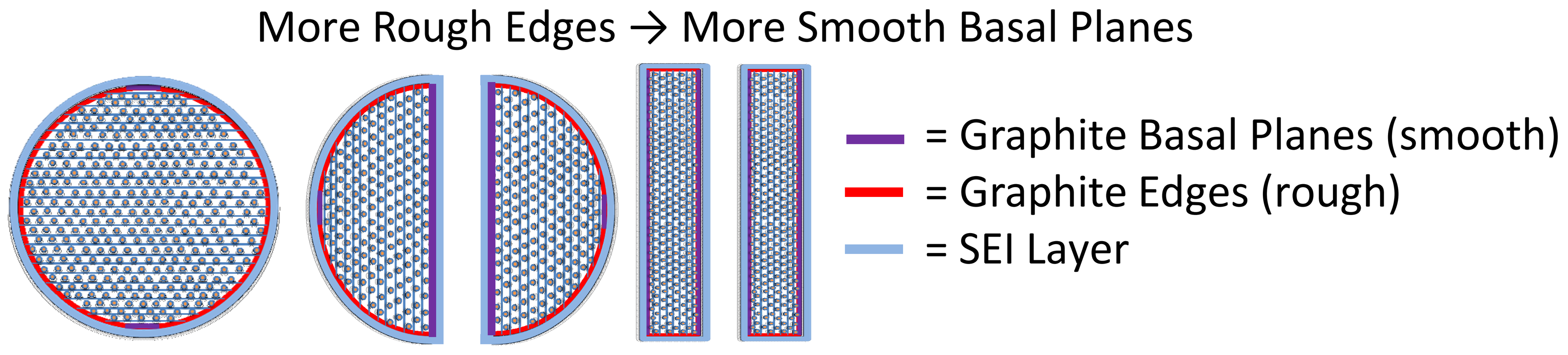
Area-Scaled Model (First Attempt to Upgrade Dahn Model)

- Updated H_{rxn} thermodynamically consistent with complete reaction of all LiC_6

$$2LiC_6 + EC \rightarrow 2C_6 + C_2H_4 + Li_2CO_3$$

- Growth of z scales with reactive surface area (SEI area × defect concentration).
- Defects in SEI more likely when underlying graphite surface is rough (edges).

Round Particles → Flat Particles
Low Surface Area → High Surface Area
More Rough Edges → More Smooth Basal Planes



$$\frac{dz}{dt} \propto \frac{A_{rxn,ref}}{A_{rxn}} = \frac{A_{BET,ref} X_{edges,ref}}{A_{BET} X_{edges}} \approx \left(\frac{A_{BET,ref}}{A_{BET}}\right)^{n_1}, n_1 < 1$$

Critical Thickness Model (Area-Scaled Model + Anode Runaway)

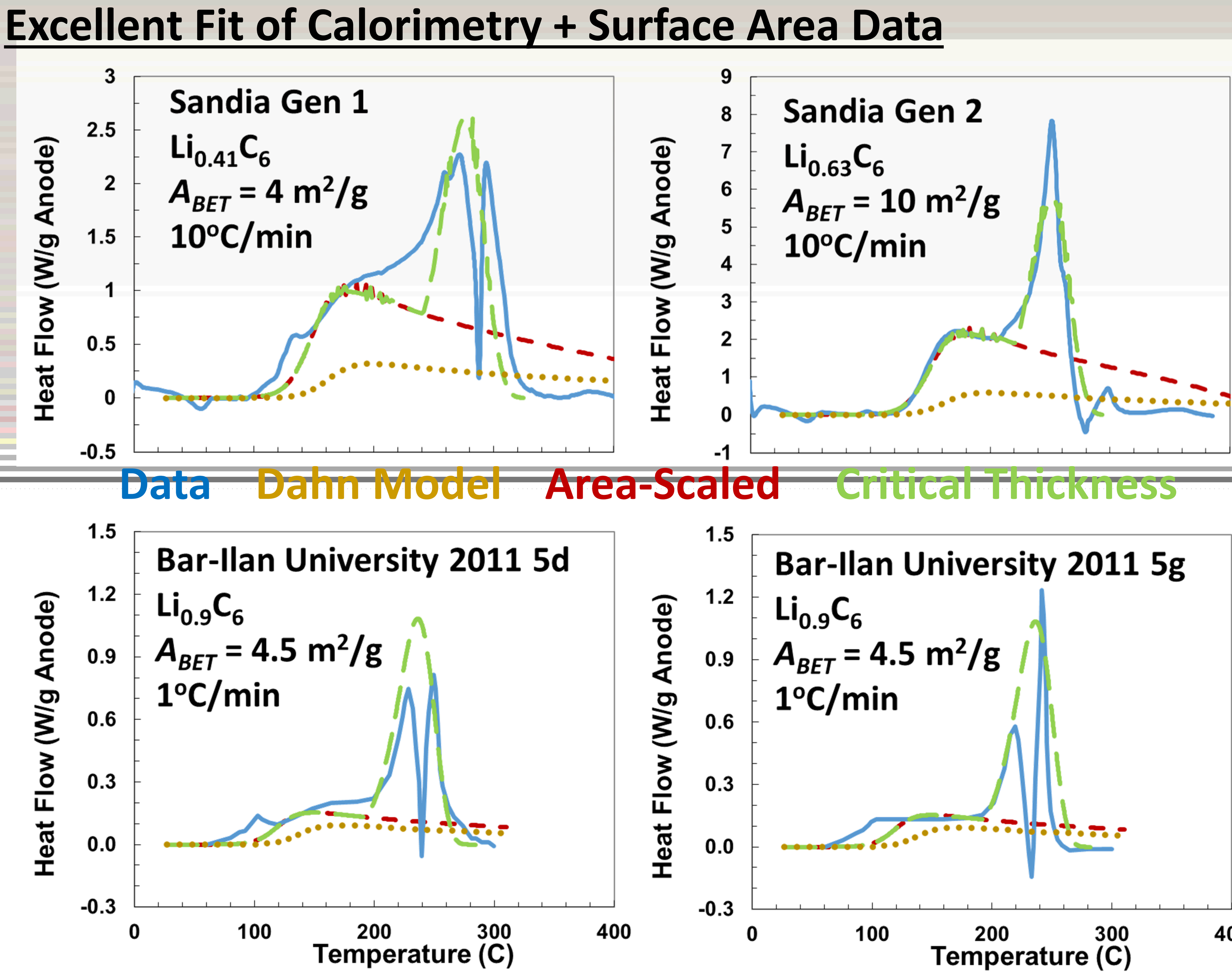
- Effective passivation layer thickness does not increase indefinitely.
- Model limits maximum layer thickness, presumably mechanically limited.

Critical Effective Layer Thickness

$$z = min(z, z_{crit}) \quad \text{where} \quad z_{crit} \propto x_{sei,crit} \left[\frac{A_{BET}}{A_{BET,ref}}\right]^{n_2}$$

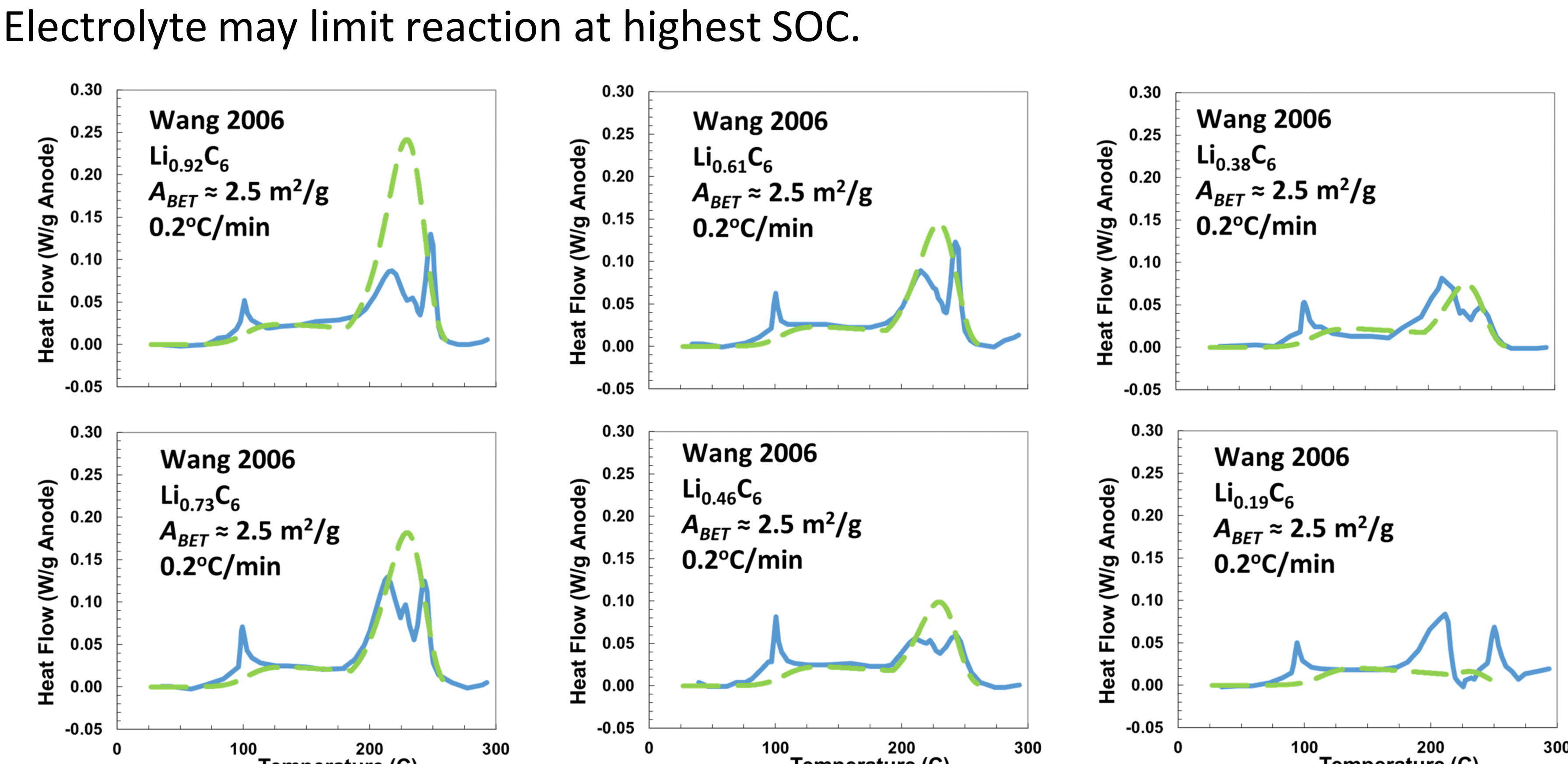
Upgraded Anode Model Performance

Excellent Fit of Calorimetry + Surface Area Data



Final Model Exhibits Proper Trends with State of Charge (SOC)

- A_{BET} estimated (not originally reported).
- Electrolyte may limit reaction at highest SOC.



Summary of Benefits for New Anode Decomposition Model

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

Sandia National Laboratories is a multimission 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-NA0003525.

Acknowledgements:
- Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity
- A special thanks to the following people for providing experimental data, thoughtful discussions, and advice
- Heather Barkholtz • Summer Ferreira • Loraine Torres-Castro • Joshua Lamb • Leigh Anna Steele • Jeff Engerer

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