Large format Accelerating Rate Calorimetry testing

PRESENTED BY

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UL Battery Safety Science Symposium

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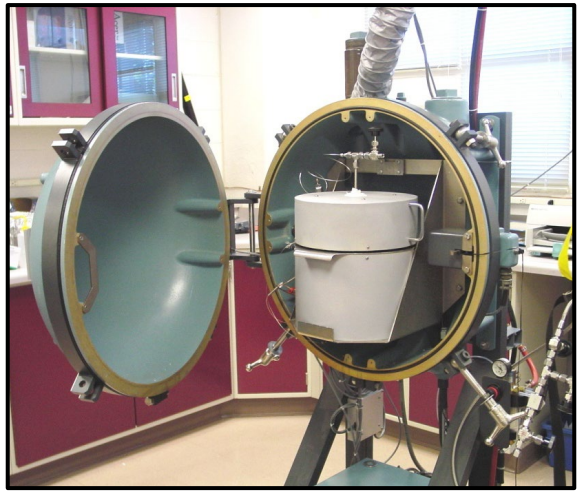
Battery Safety and Reliability R&D at Sandia National Laboratories

- Hundreds of independent channels for testing, from coin cells to kWh modules
- 150 uA to 2000 A current range capability
- R&D 100 Green Technology-awarded high-precision testers
- 70+ thermal chambers, ranging from 1.2 ft^3 to 25 ft^3
- –72°C to 95°C temperature capabilities
- Welding capabilities, including resistance, pinch, and spot
- Additional labs for materials characterization and 8000 ft^2 dry-room space for prototyping

Battery Abuse Laboratory

- Comprehensive abuse testing platforms for safety and reliability of cells, batteries and systems from mWh to kWh
- Mechanical abuse
  - Penetration
  - Crush
  - Impact
  - Immersion
- Thermal abuse
  - Over temperature
  - Flammability measurements
  - Thermal propagation
  - Calorimetry
- Electrical abuse
  - Overvoltage/overcharge
  - Short circuit
  - Overdischarge/voltage reversal
- Characterization/Analytical Tools
  - X-ray computed tomography
  - Gas analysis
  - Surface characterization
  - Optical/electron microscopy



Burn Site Test Site

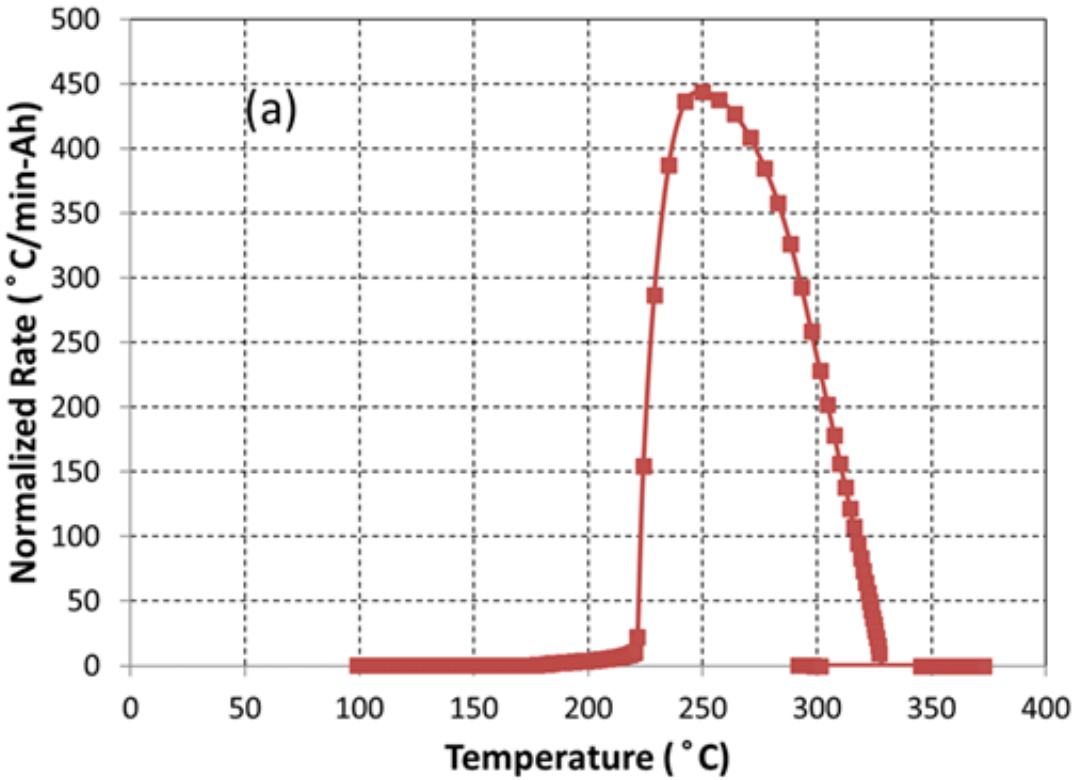
Owned by SNL Fire Sciences Dept.

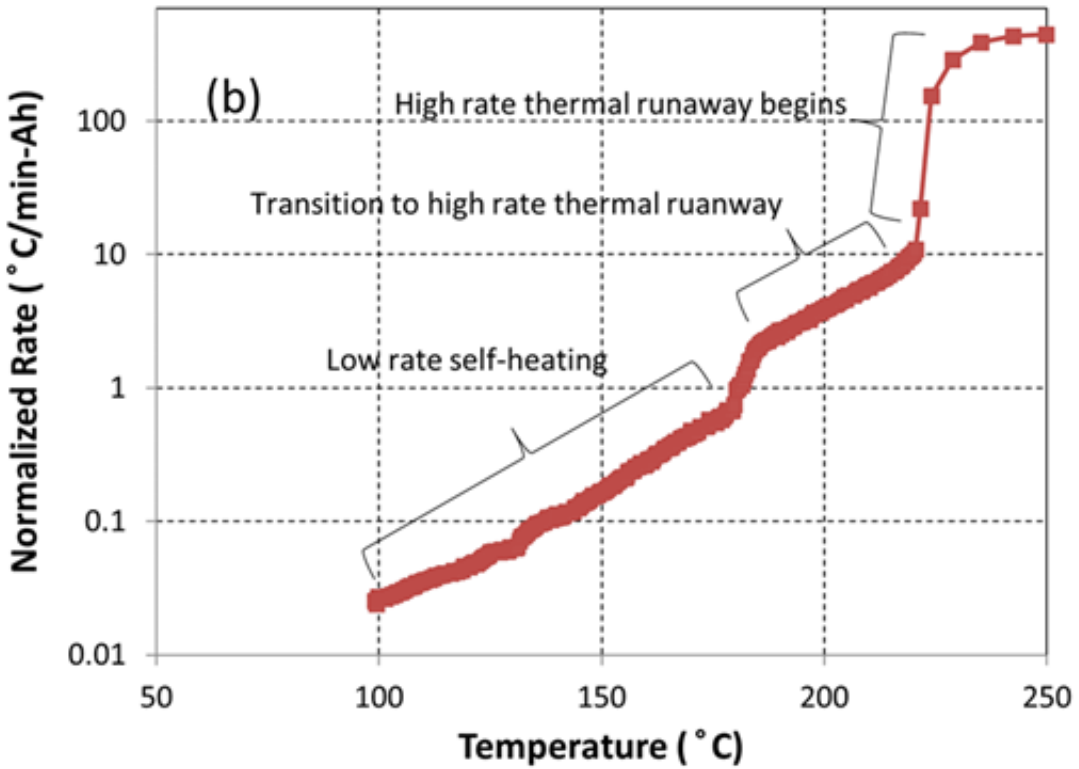
Design for large scale fire testing and high explosives (up to 100 kg)

Construction/design suitable for large scale battery abuse testing (10s of kWh Li-ion)

Fully instrumented data acquisition capabilities

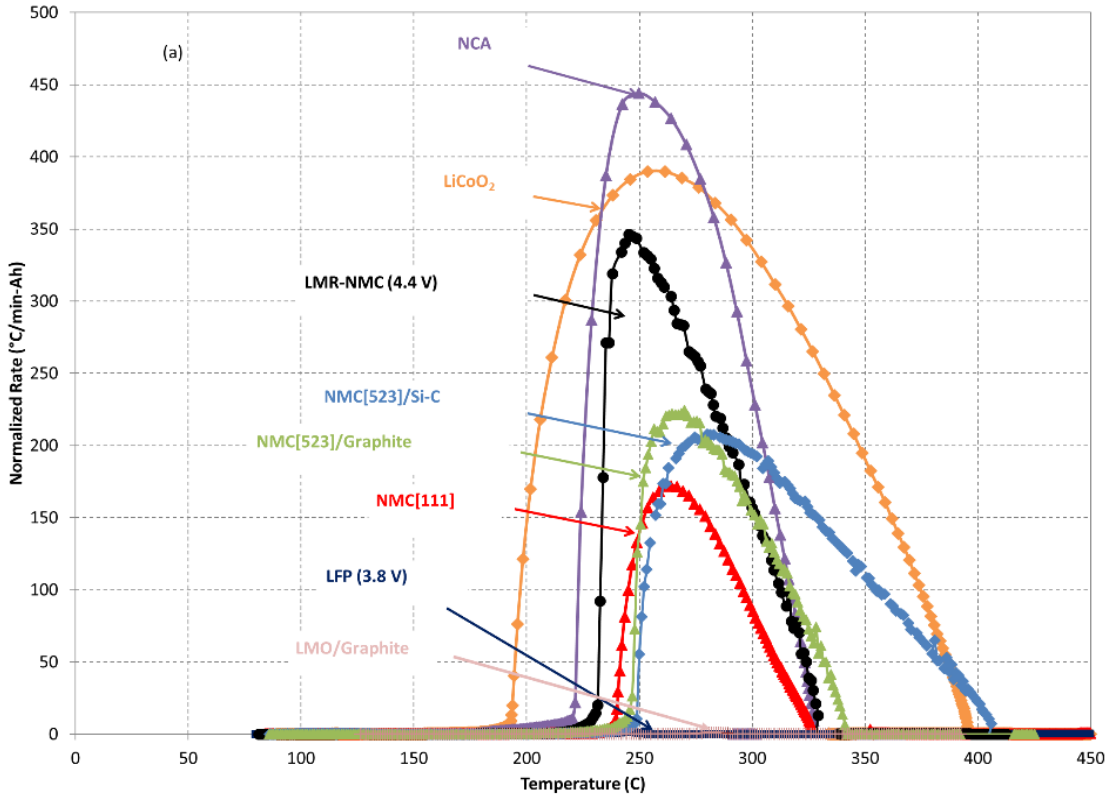
Characterizing Thermal Runaway



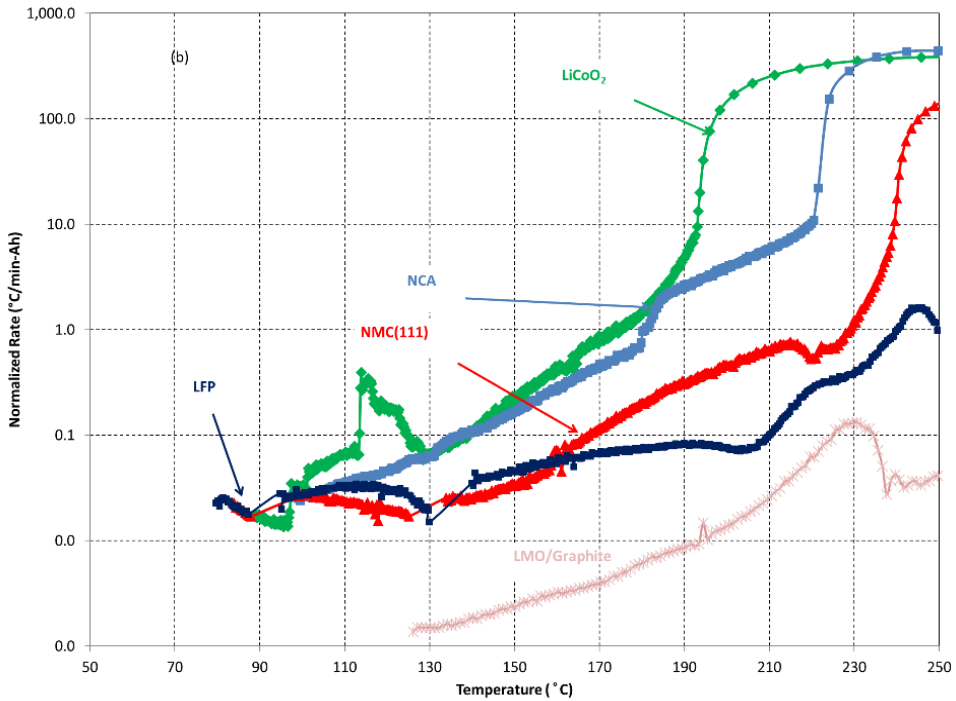


- Practical thermal runaway occurs when self-heating reactions exceed any cooling present
- Initial low-rate self-heating as electrolyte breakdown, SEI dissolution begin
- As SEI breaks down bulk reactions with the anode can occur
- These reactions accelerate as temperature increases
- At higher temperatures bulk decomposition of active materials leads to high-rate thermal runaway
- Materials with higher heating rates will more readily exceed natural heat loss and reach a catastrophic thermal runaway
- Even materials with lower rates may have significant energy avaialble

Characterizing new materials

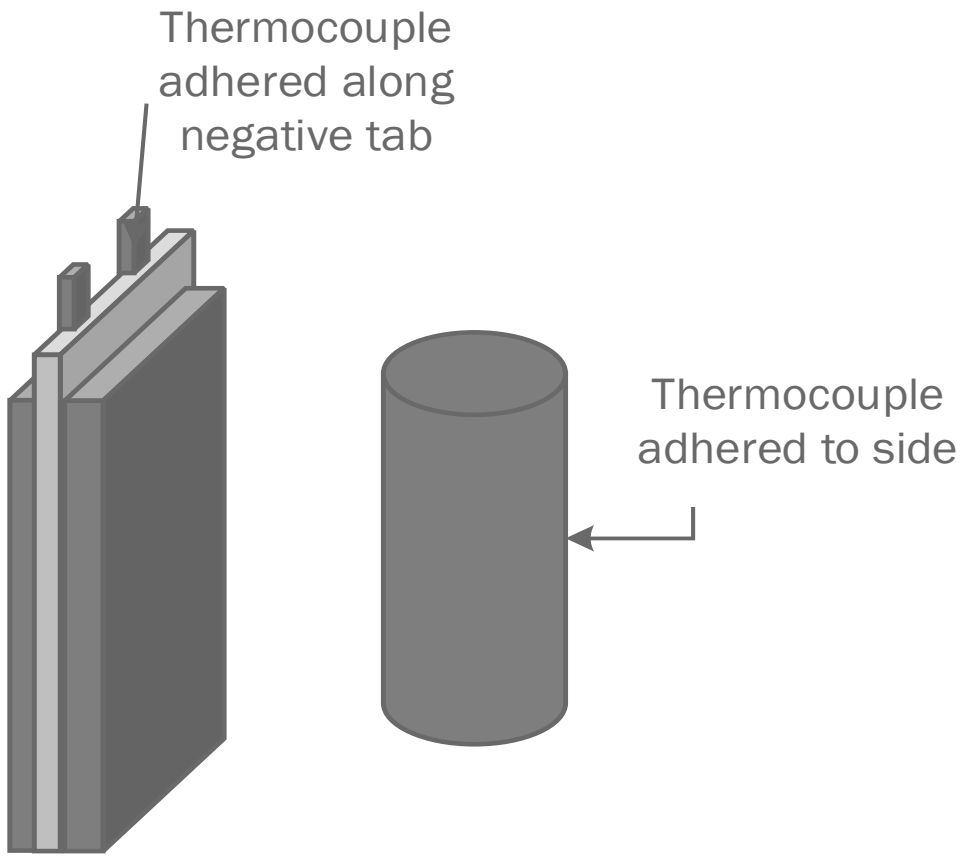


- Accelerating rate calorimetry shows the behavior of various chemistries.
- This gives information about peak heating rates and total energy of the thermal runaway.
- Newer materials such as LFP provide significantly reduced thermal runaway intensities but have limited energy density.



- ARC has been a powerful tool in performing these evaluations of new materials
- However, all work is generally performed on 18650 cells, how results change as we scale cell size?

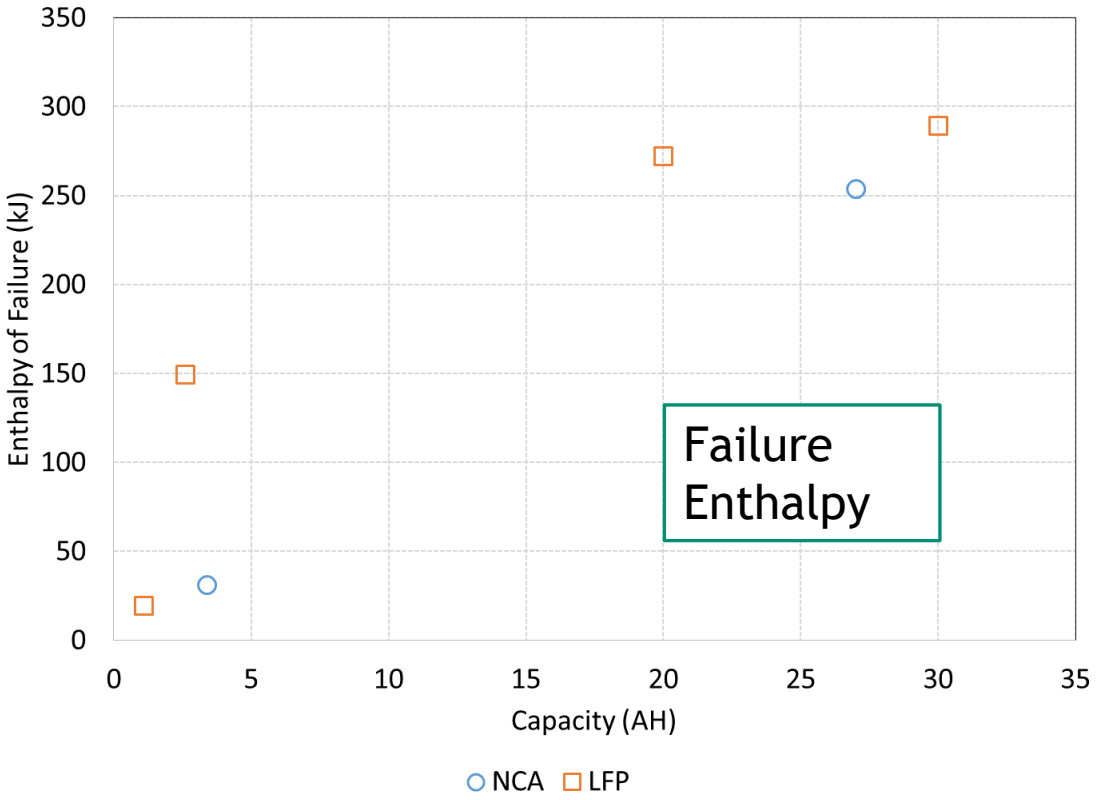
Experimental setup for large format cells

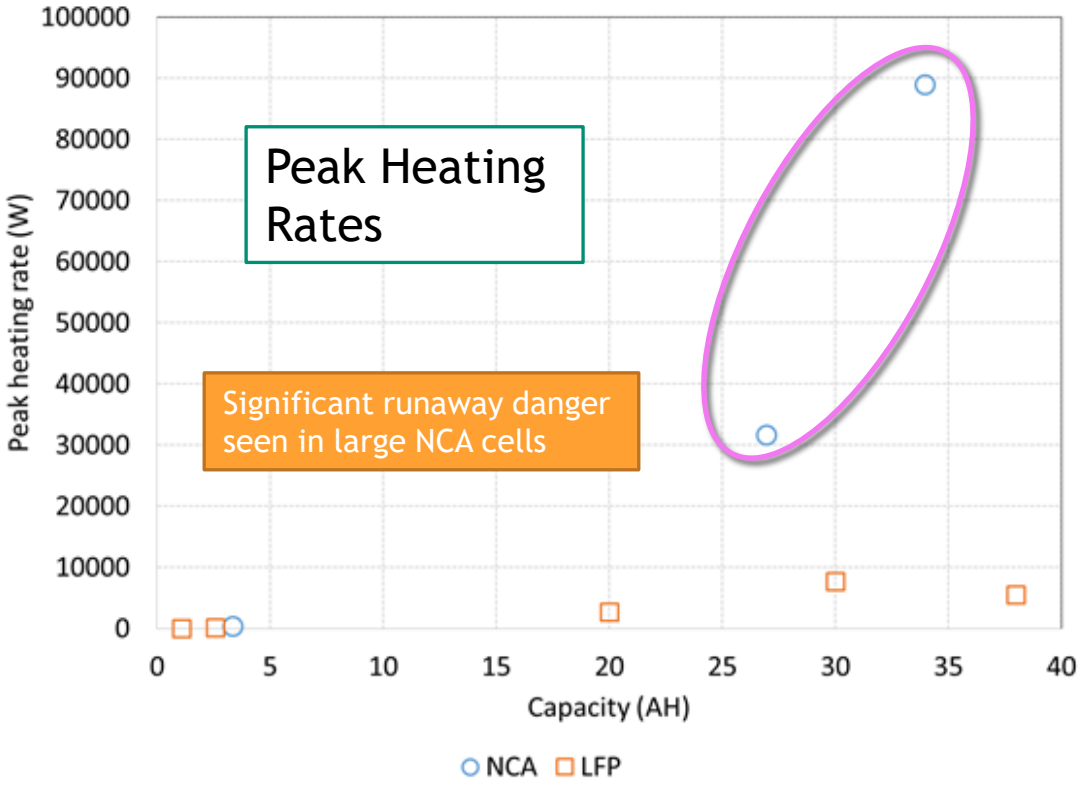


- Large format/high energy density ARC testing performed in Thermal Hazard Technologies EV ARC
- Large format cells tested in open air
- Cylindrical cells unconstrained
- Pouch cells constrained with ¼” aluminum plates
  - Heat capacity of constraint considered in total heat capacity of cells
- Thermocouples placed per diagram

- Overtemperature testing started at 50 °C
- Forced heating in 5 °C steps
- Self-heating threshold of 0.02 °C/minute
- Maximum forced heating temperature of 400 °C

Cell Size and Thermal Runaway

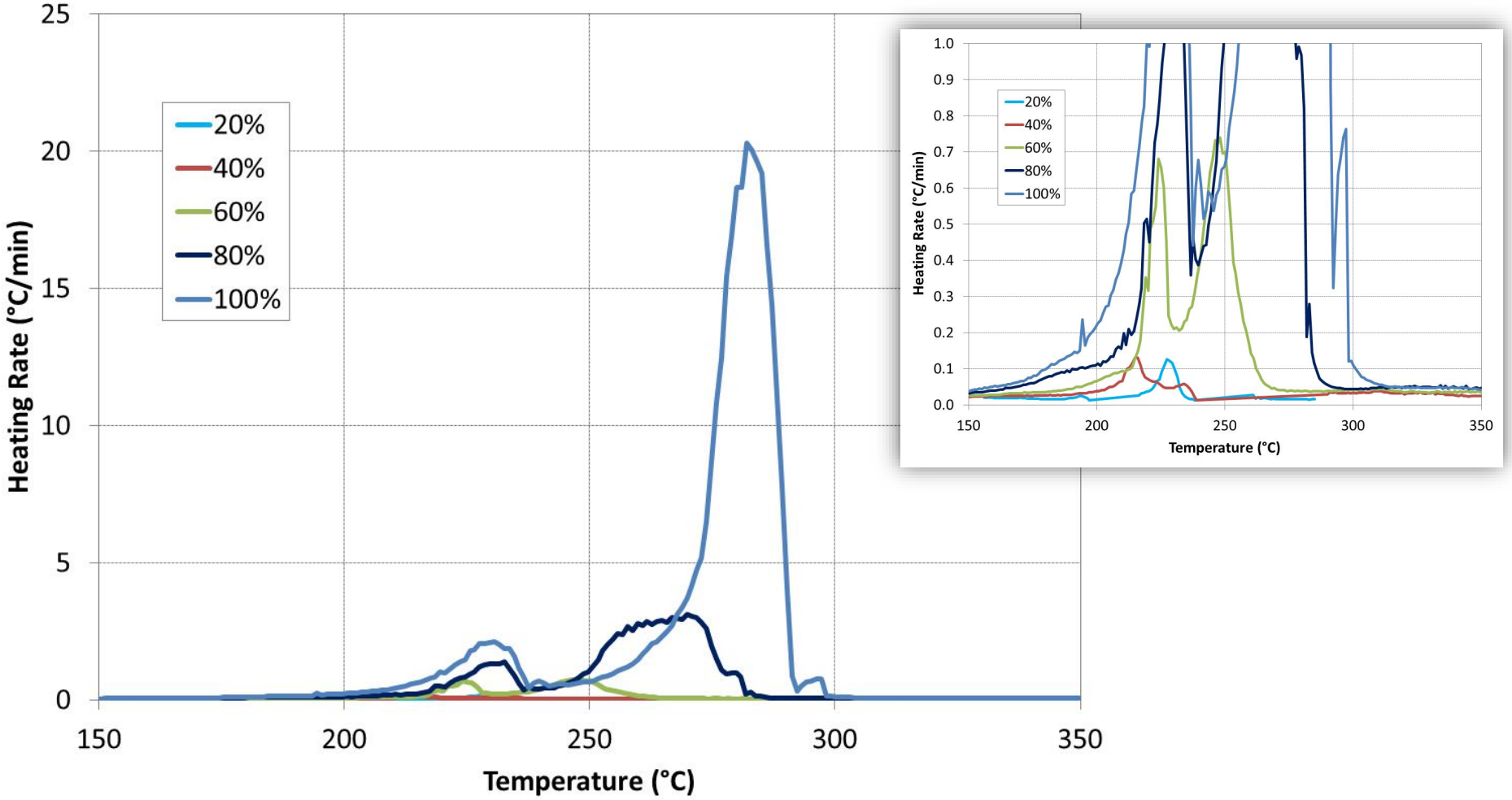




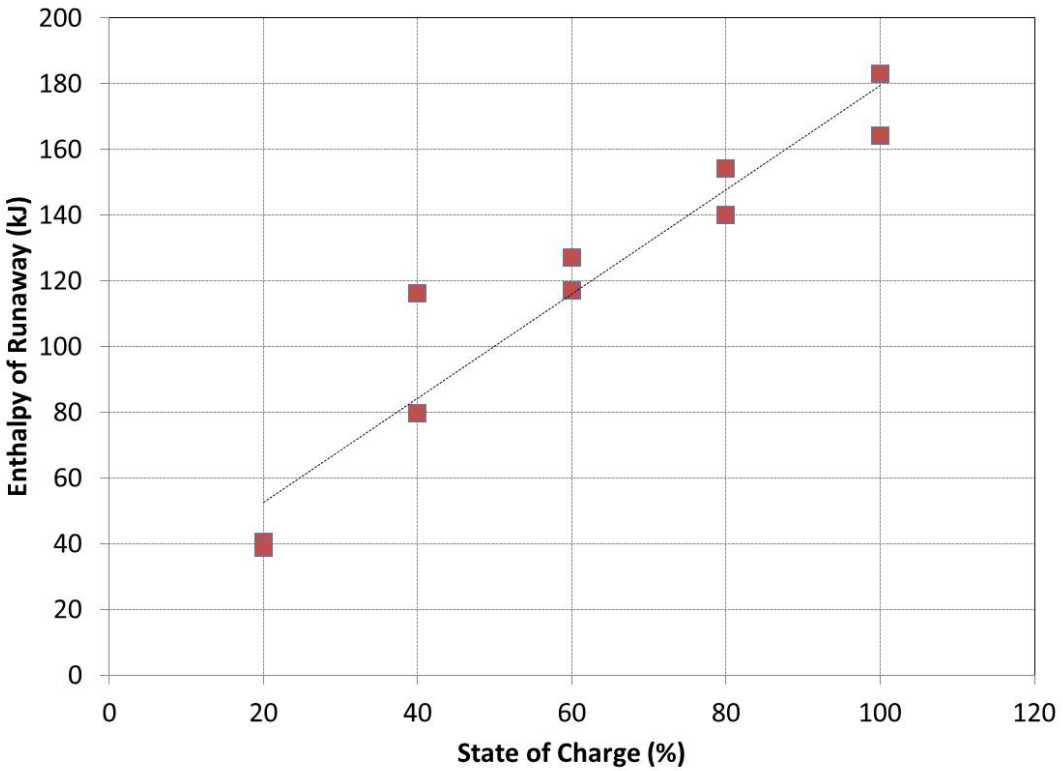
- Enthalpy scales generally linearly with size, and is similar for both chemistries – This early data suggests that failure enthalpy is largely tied to the available stored energy
- Peak heating rates significantly higher for large NCA cells
- High peak heating rates are generally thought to carry a higher thermal runaway risk, but what is the impact when significant energy is available in numerous smaller cells?

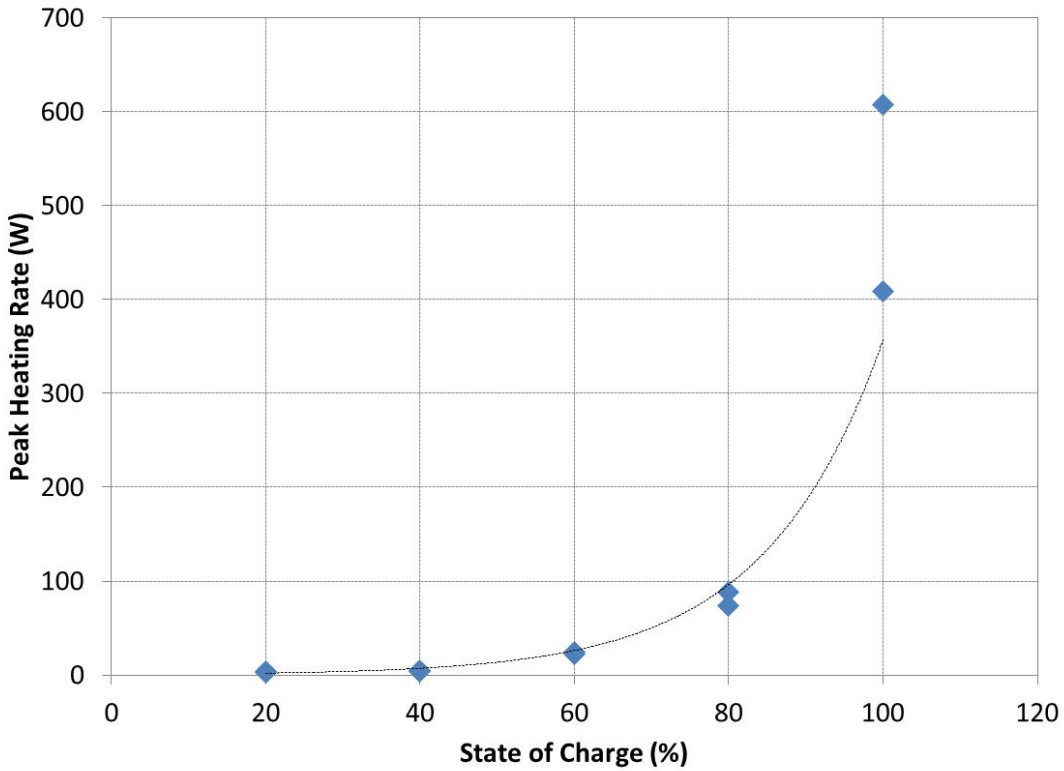
SOC and Thermal Runaway

- 16 Ah automotive (PHEV) pouch cells (mixed $LiMn_2O_4$ spinel)
- Significant impact can be easily observed above 60% SOC, very low rate self heating below that



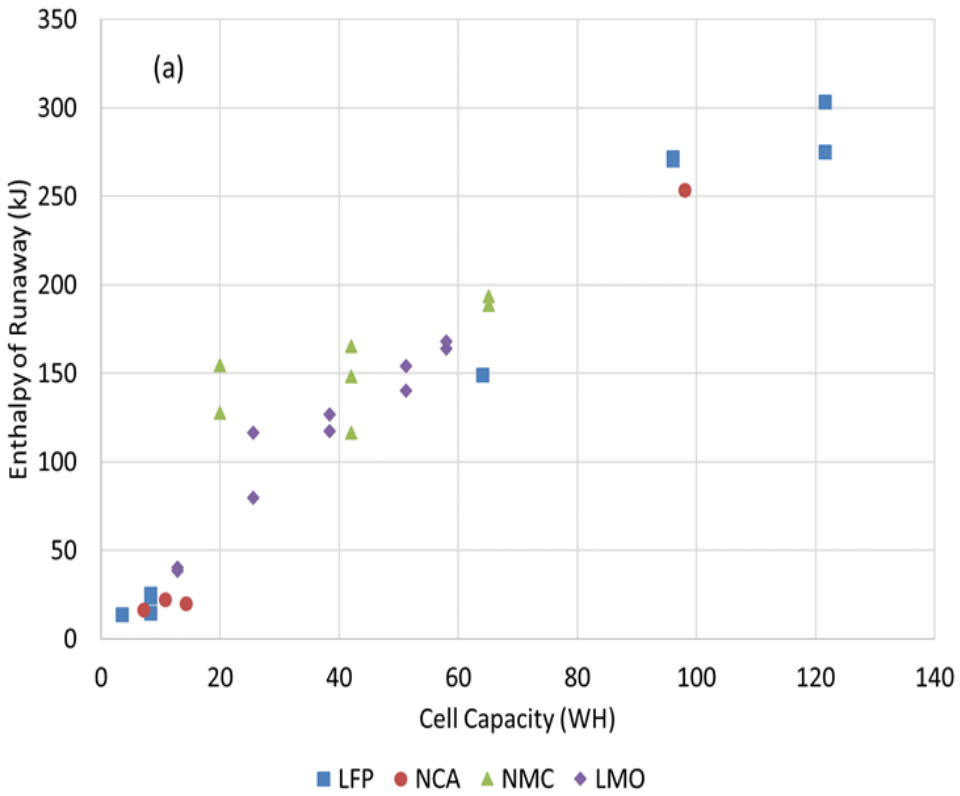
Impact of SOC on Runaway

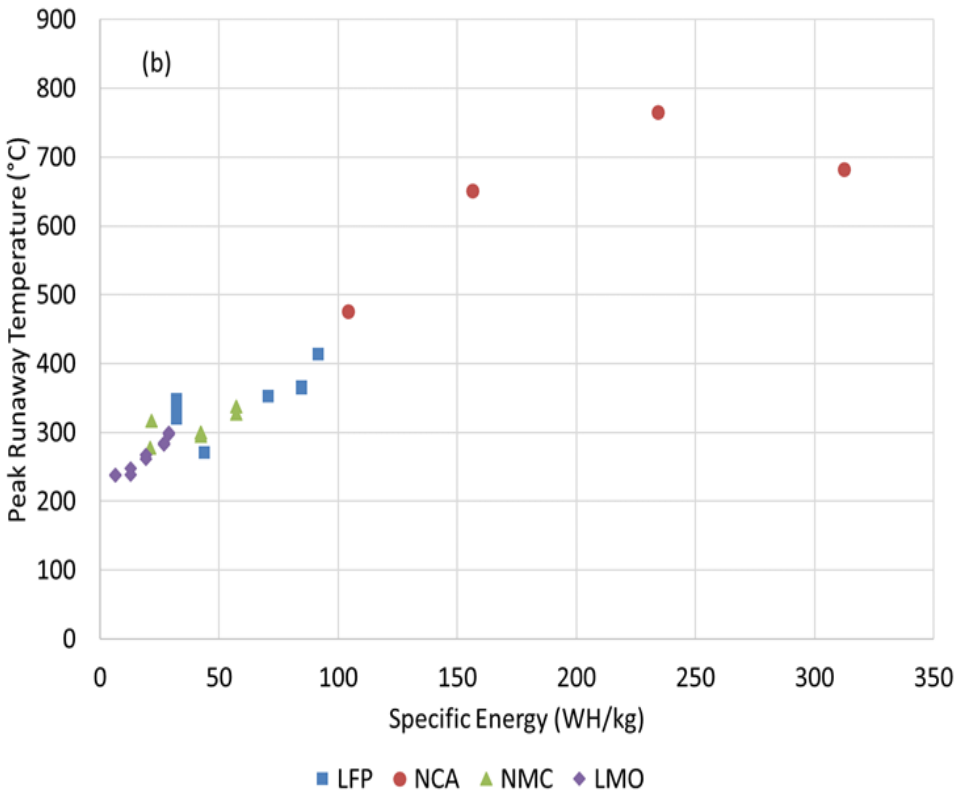




- Results show a nearly linear relationship between total heat release (kJ) and cell SOC – similar to data for cell size this suggests that failure enthalpy is based largely on the stored energy available
- Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC – again this is traditionally thought to cause a greater risk of thermal runaway
- Could a runaway still occur with large numbers of low SOC cells or cells in well insulated conditions?

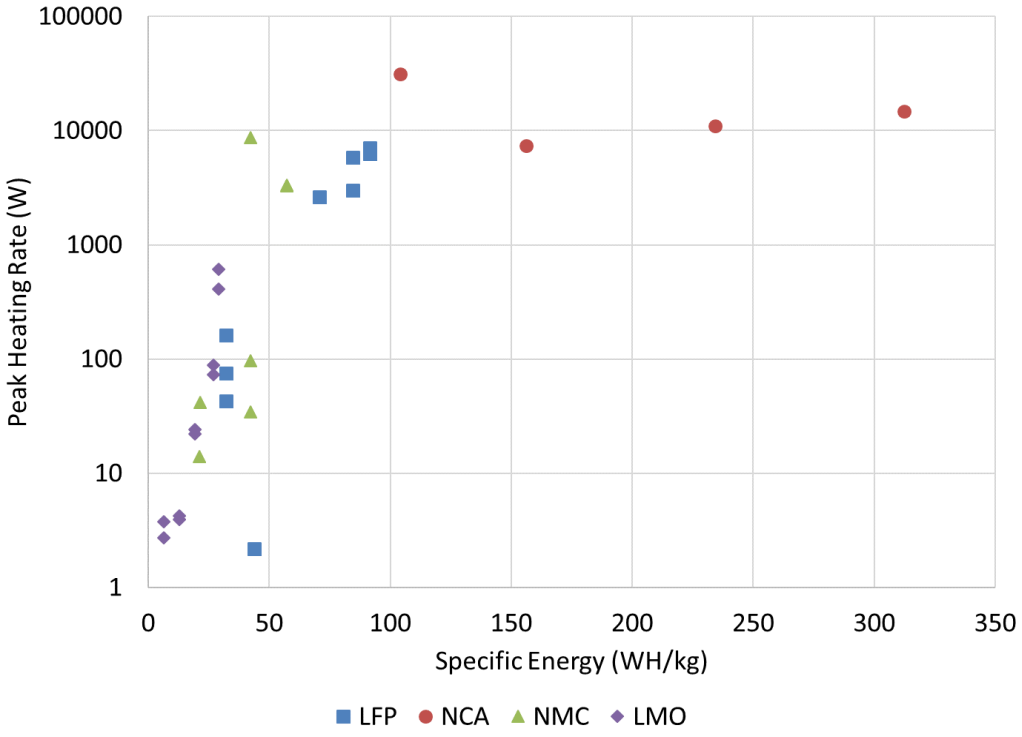
Evaluation of historic data

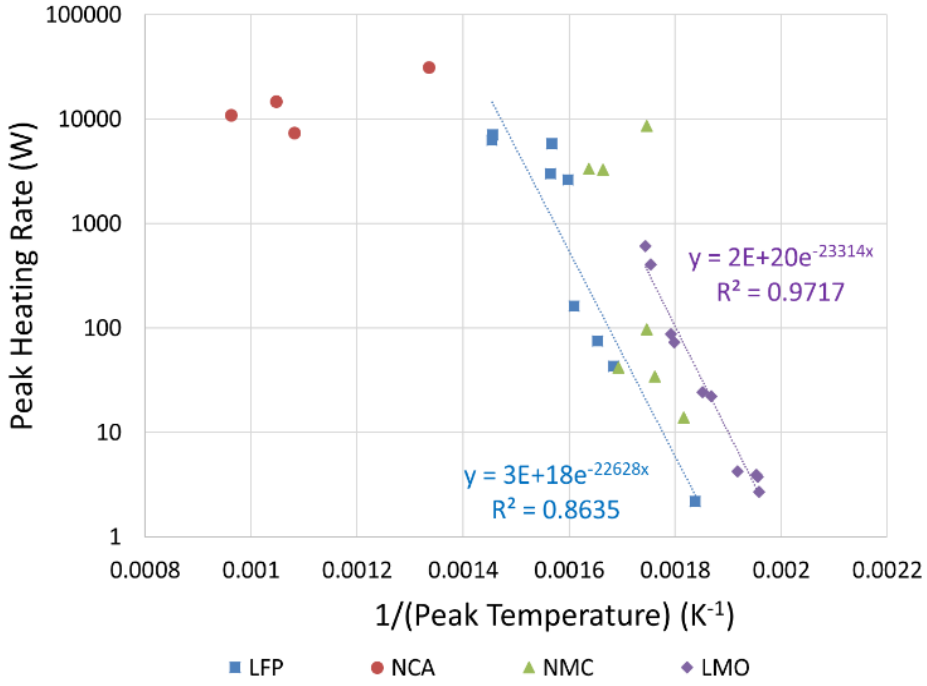




- Data includes cells from 1.08-38 AH (3.5-122 WH)
  - Chemistries include LFP, NMC and NCA
  - Formats include 18650, 26650, pouch cell, and large format cylindrical (steel cylindrical cells with machined stamped vents)
- Total energy of runaway maintains a linear relationship to cell capacity
- Peak runaway temperatures also appear highly tied to specific energy

Peak heating rates

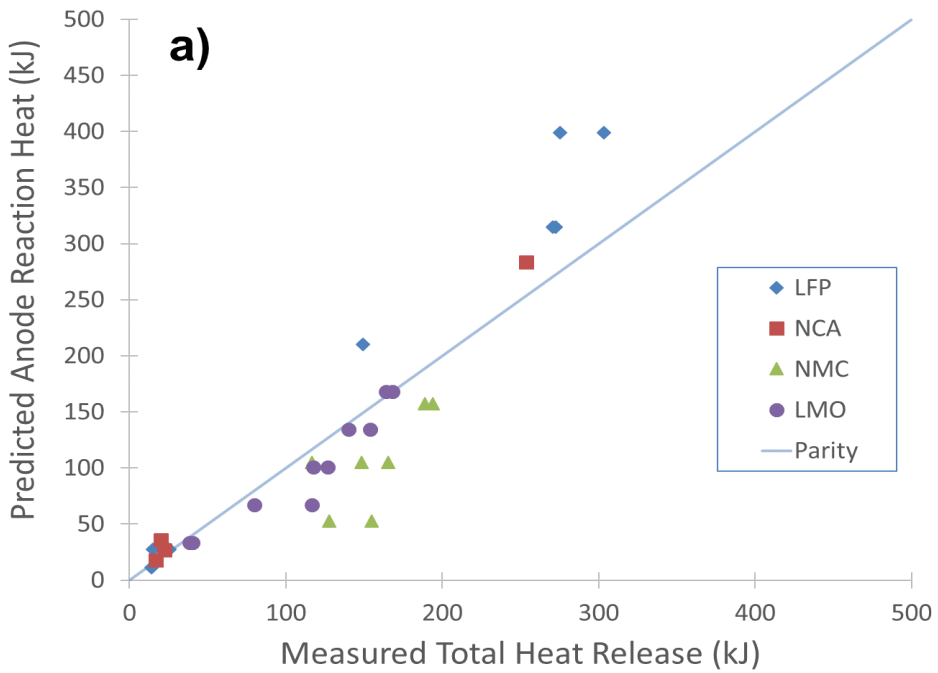


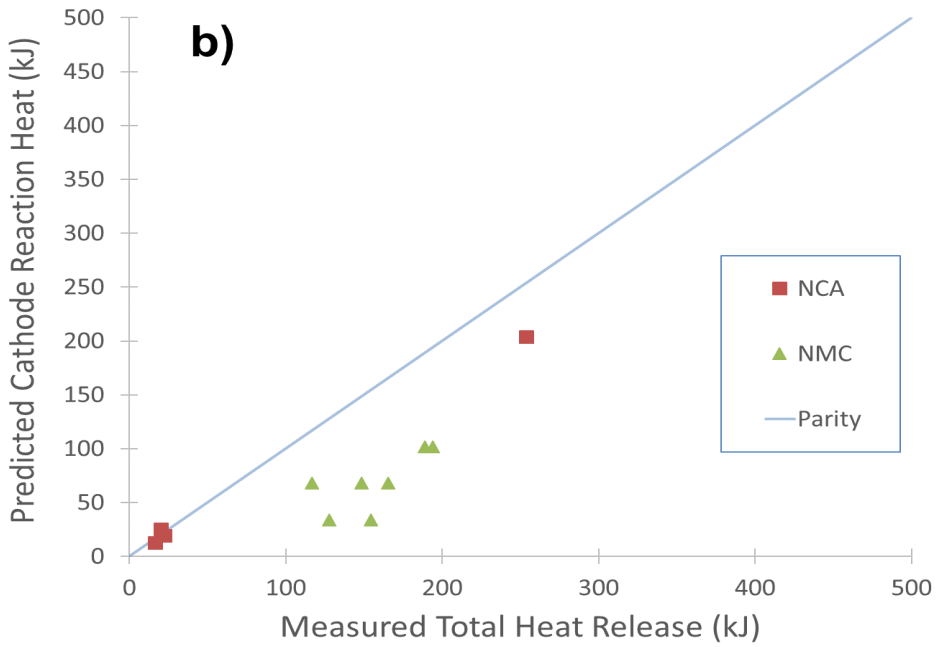


- Evaluation of peak heating rates shown as a function of specific energy and 1/Peak temperature
- Show a logarithmic behavior up to very high specific energies
  - Ability of equipment to evaluate very high peak heating rates is limited- the flat line behavior at this point may be because of this
- Evaluation vs 1/peak temperature shows activation energies of ~190 kJ/mole for LFP, LMO, and NMC, with the most variability in NMC
  - NCA precludes meaningful evaluation
  - Literature reports show a range of 108-682 kJ/mol with most values below 225 kJ/mol*

*C.-Y. Jhu, Y.-W. Wang, C.-M. Shu, J.-C. Chang, and H.-C. Wu, *Journal of Hazardous Materials*, **192** (1), 99-107 (2011).
*C.-Y. Jhu, Y.-W. Wang, C.-Y. Wen, and C.-M. Shu, *Appl. Energy*, **100** 127-131 (2012).
*W. C. Chen, Y. W. Wang, and C. M. Shu, *J. Power Sources*, **318** 200-209 (2016).

Comparison to predicted heat release from cathode and anode

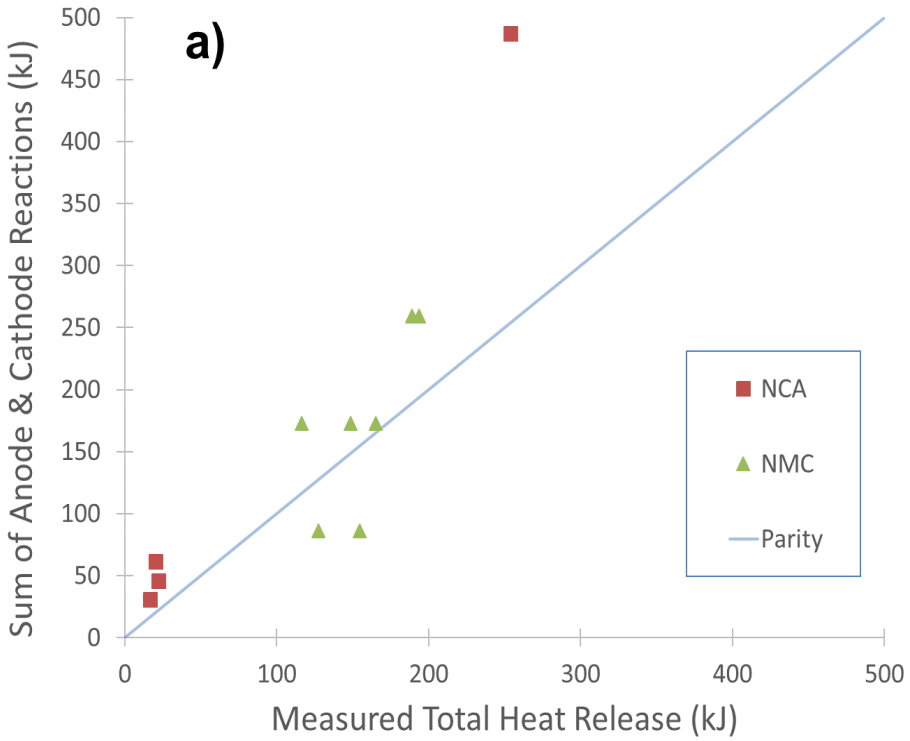


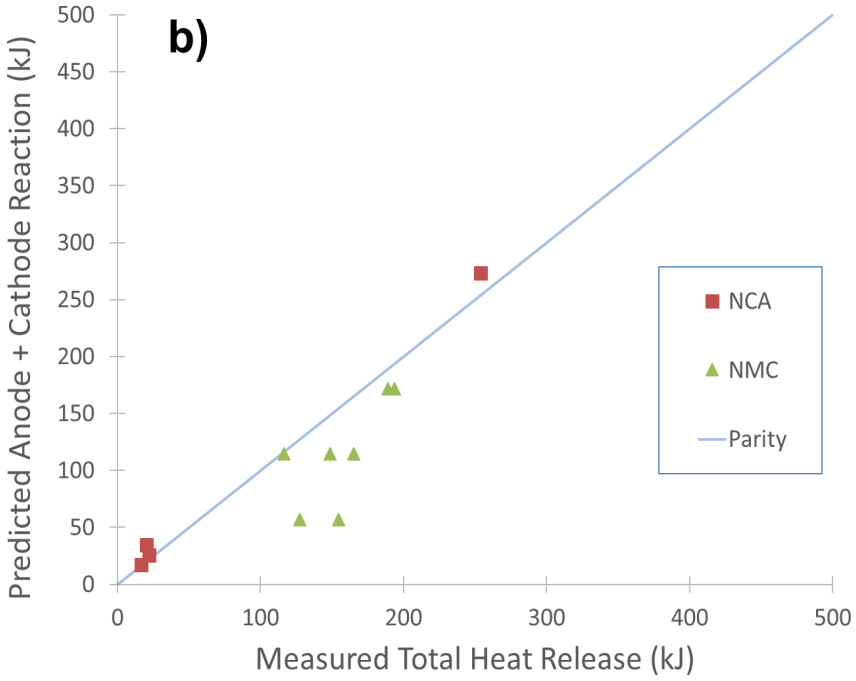


- Comparison to predicted heat release rates based on previous heat release models from our group**; currently only NCA and NMC cathodes have been considered with work considering LFP cathodes in progress
- Behavior tracks well with predicted anode heat reaction; this goes somewhat against the conventional wisdom of thermal runaway being predominantly influenced by the cathode
- The cathode reactions here do not account for reaction of released oxygen with electrolyte or available lithium, which may explain under-prediction of cathode contribution in this case
    - This is discussed in the next slide

R. C. Shurtz, J. D. Engerer, and J. C. Hewson, *J. Electrochem. Soc.*, **165 (16), A3891-A3902 (2018).
R. C. Shurtz, J. D. Engerer, and J. C. Hewson, *J. Electrochem. Soc.*, **165 (16), A3878-A3890 (2018).
R. C. Shurtz and J. C. Hewson, *J. Electrochem. Soc.*, **167 (9), 090543 (2020).
R. C. Shurtz, *J. Electrochem. Soc.*, **167 (14), 140544 (2020).

Influence of anode-cathode interaction





- Comparison of the sum of predicted reactions to measured heat release with no interactions (a) and with the inclusion of proposed reactions of oxygen from the cathode reacting with lithium at the anode*** (b).
- This shows that an interaction between the two electrodes via oxygen release is consistent with full cell runaway data
  - Also underscored here is the importance of full cells in thermal runaway evaluations

***X. N. Feng, S. Q. Zheng, D. S. Ren, X. M. He, L. Wang, H. Cui, X. Liu, C. Y. Jin, F. S. Zhang, C. S. Xu, H. J. Hsu, S. Gao, T. Y. Chen, Y. L. Li, T. Z. Wang, H. Wang, M. G. Li, and M. G. Ouyang, *Appl. Energy*, **246** 53-64 (2019).
***Y. Shigematsu, S. Kinoshita, and M. Ue, *J. Electrochem. Soc.*, **153** (11), A2166-A2170 (2006).
***T. Inoue and K. Mukai, *ACS Appl. Mater. Interfaces*, **9** (2), 1507-1515 (2017).
***D. S. Ren, X. Liu, X. N. Feng, L. G. Lu, M. G. Ouyang, J. Q. Li, and X. M. He, *Appl. Energy*, **228** 633-644 (2018).
***X. Liu, D. Ren, H. Hsu, X. Feng, G.-L. Xu, M. Zhuang, H. Gao, L. Lu, X. Han, Z. Chu, J. Li, X. He, K. Amine, and M. Ouyang, *Joule*, **2** (10), 2047-2064 (2018).

Summary

- Data collected so far suggests that while the intensity of a single cell failure is highly dependent on cell size, chemistry and state of charge, the total energy of a failure is largely only dependent on the stored energy
  - A further refinement of the data, looking at the specific energy of the cell (and material in intimate thermal contact with the cell) show that peak heating rates may be scaling well with specific energy, independent of chemistry and cell construction.
- This distinction is of greater consequence as more energy is made available, demonstrated here by adding multiple cells to a single system
- Evaluation of activation energies shows values similar to those reported elsewhere in literature, and suggests a fairly constant activation energy for layered metal oxide families
- Data supports proposed reactions of lithium with released oxygen during thermal runaway as a contributor to energy release
- Future questions include how large amounts of stored energy might impact a system even at low states of charge

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