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Fire Hazards of Lithium Ion Batteries

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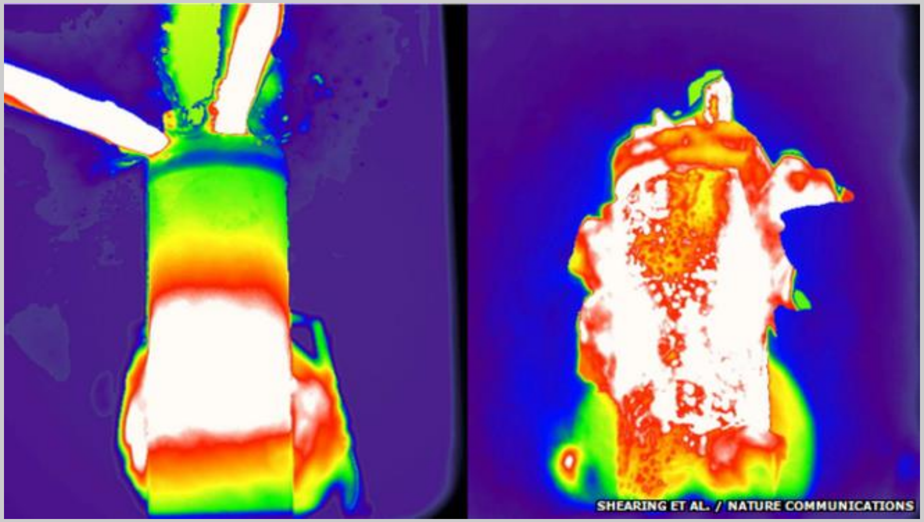
Objective: Measure Fire Hazards of LIBs

Passenger electronics

Typical packaging

Causes of Battery Failure

- **Thermal**
  - Separator melts due to high temperature causing internal short circuit that releases heat.
  - Contents mix, react and thermally decompose.
- **Electrical**
  - Overcharge
  - Rapid discharge
- **Mechanical**
  - Physical damage (puncture)
  - Manufacturing defect or contaminant



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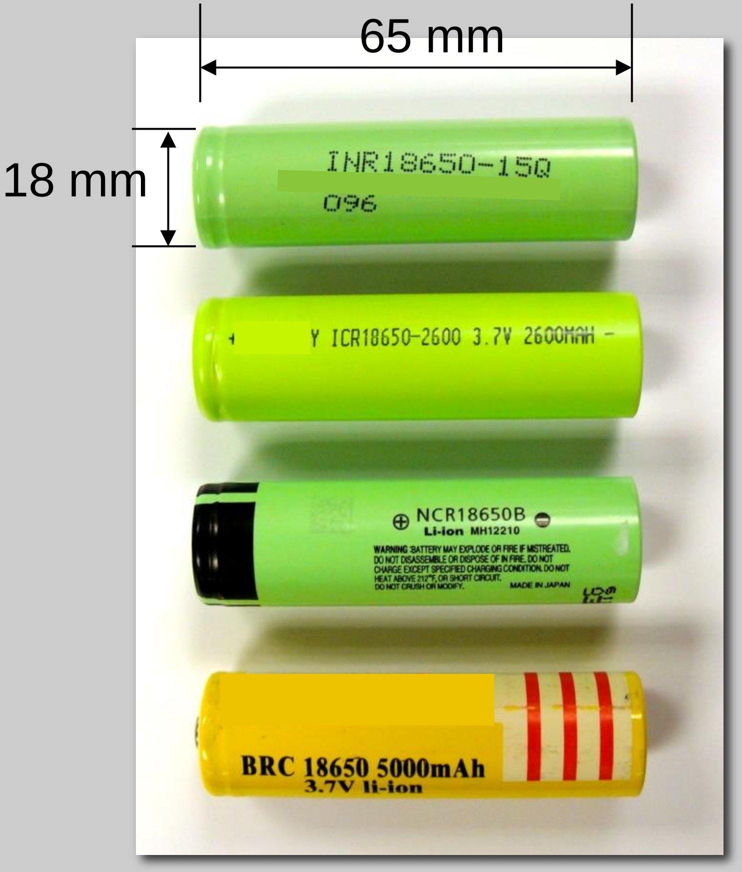
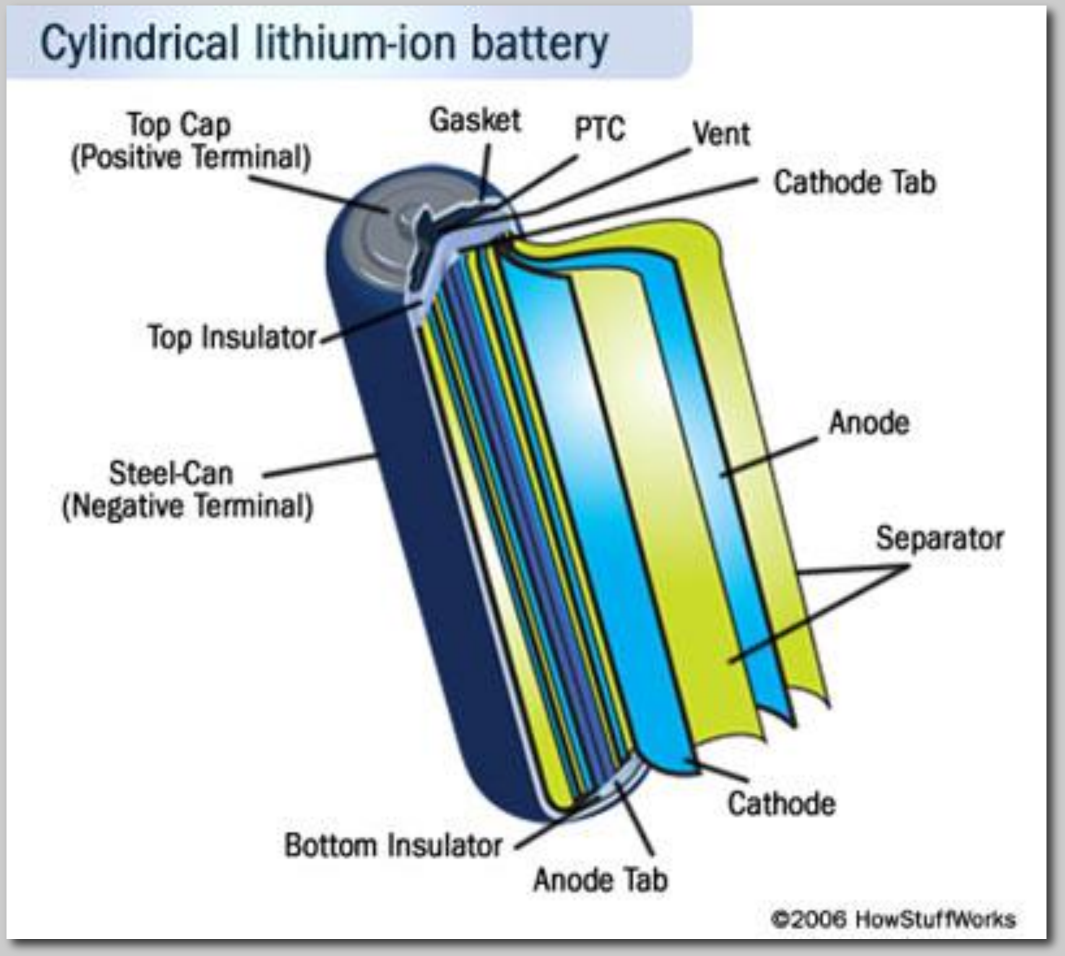
All lead to auto-accelerating heat generation and rapid temperature increase (Thermal Runaway) leading to fire and/or explosion

Materials: Commercial 18650 LIB Cells

18650 Rechargeable Cells (≈ 44 grams each)





Electrical Properties of Tested Cells

Cathode	Maximum Capacity, Q_{max} (A-s) Rated	Maximum Capacity, Q_{max} (A-s) Actual	Cell Potential, ε (V) Nominal	Cell Potential, ε (V) Max.	$-\Delta G$, εQ_{max} (kJ/cell)
$LiMn_2O_4$-$LiNiCoO_2$	11,700	11,200	3.6	4.1	**41**
$LiCoO_2$	9,400	8,300	3.7	4.1	**31**
$LiNiCoAlO_2$	5,400	5,000	3.7	4.1	**19**
Unknown	18,000	3,600	3.7	4.0	**13**

Chemical Energy Available to Do Useful Work (Free Energy), $\Delta G = -\varepsilon Q$

State-of-Charge, $SOC = Q/Q_{max}$

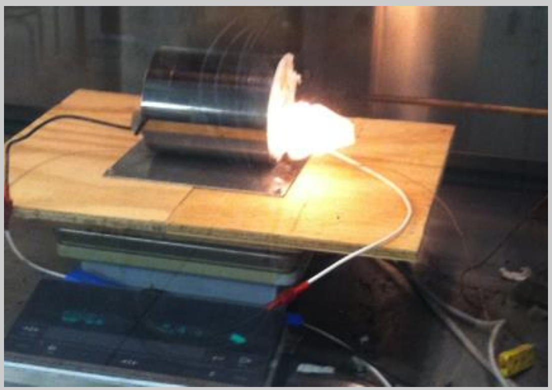
Experimental Methods: Cell Charging

- Charge / Discharge 4 cells simultaneously
- Record: charge / discharge capacity
- Programmable for different states of charge

Methods: Hazard Measurements

Energetics of Cell Failure

ASTM D 5865-14, Standard Test Method for Gross Calorific Value of Coal and Coke



Thermal Effects of Cell Failure

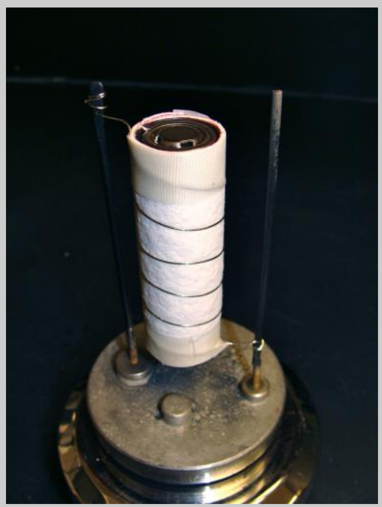
Purpose-Built Thermal Capacitance (Slug) Calorimeter

Fire Behavior of Lithium Cells

(ASTM E 1354, Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter)

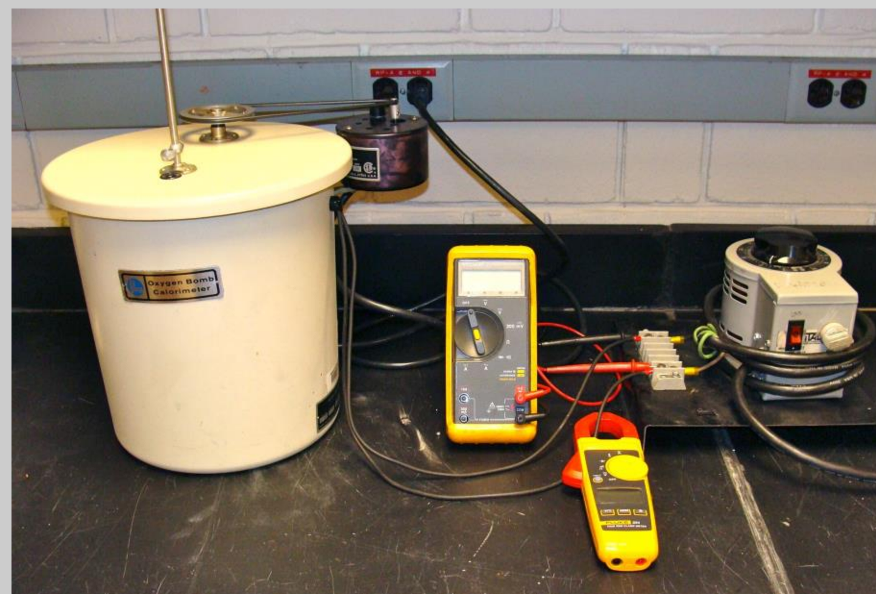
Bomb Calorimeter (ASTM D 5865)

- Parr Instruments Model 1341 Plain Jacket Oxygen Bomb Calorimeter
- Resistance heating to force thermal runaway of LIBs
- Nitrogen blanket (1 Atm) to prevent oxidation of contents after failure
- Temperature, voltage and current logged for all tests



Bomb and other components for 18650 battery tests

Experimental Setup



Thermodynamics of Cell Failure

Depends on
cell chemistry

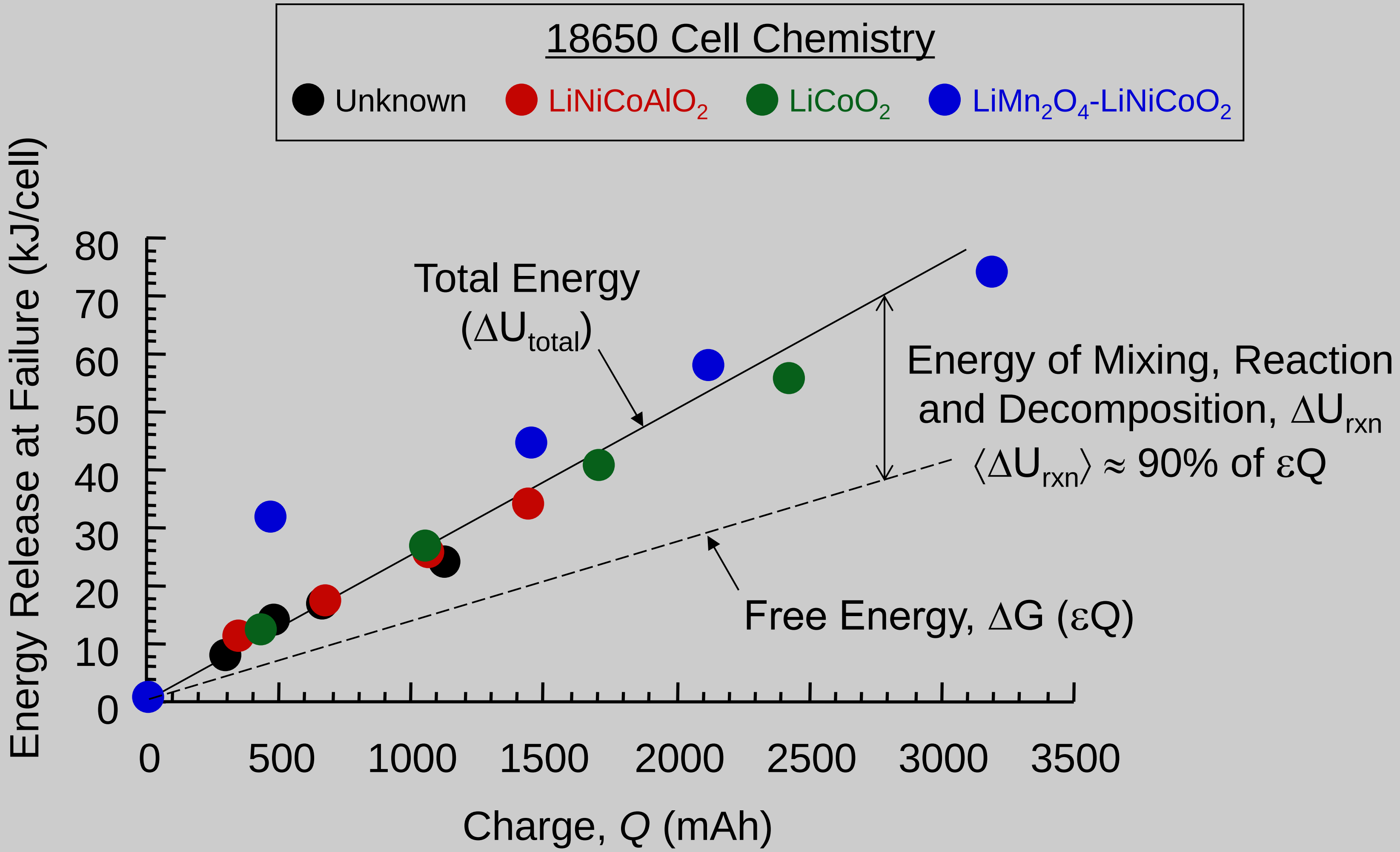
$$\Delta U_{Total} \approx \Delta U_{rxn} + \varepsilon Q$$

Total energy released at cell failure (*measured in bomb*)

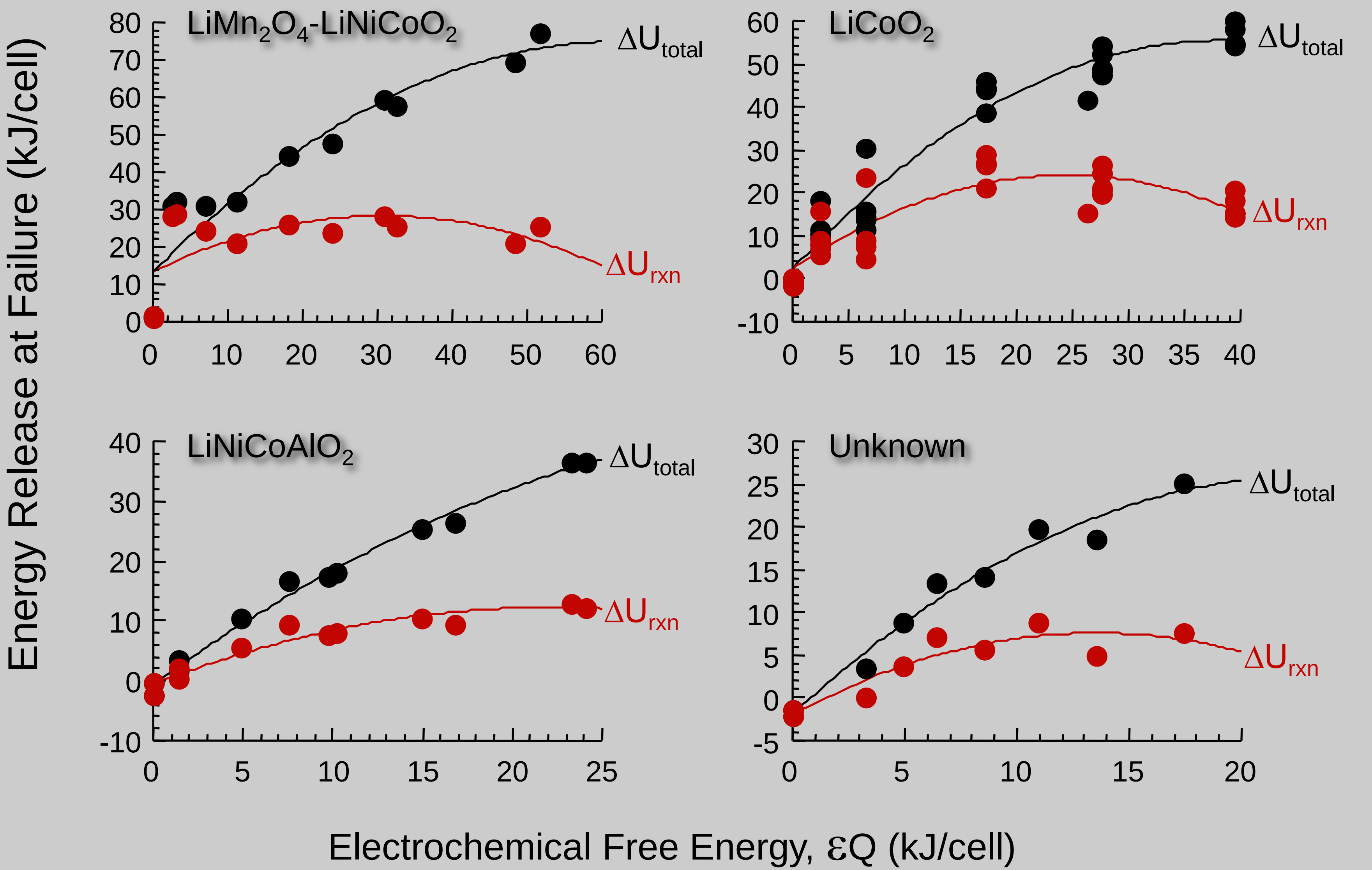
Electrochemical (Free) energy release (*Calculable from cell potential ε(V) and charge Q (A-s)*)

Energy released by mixing, chemical reaction and thermal decomposition of cell components.

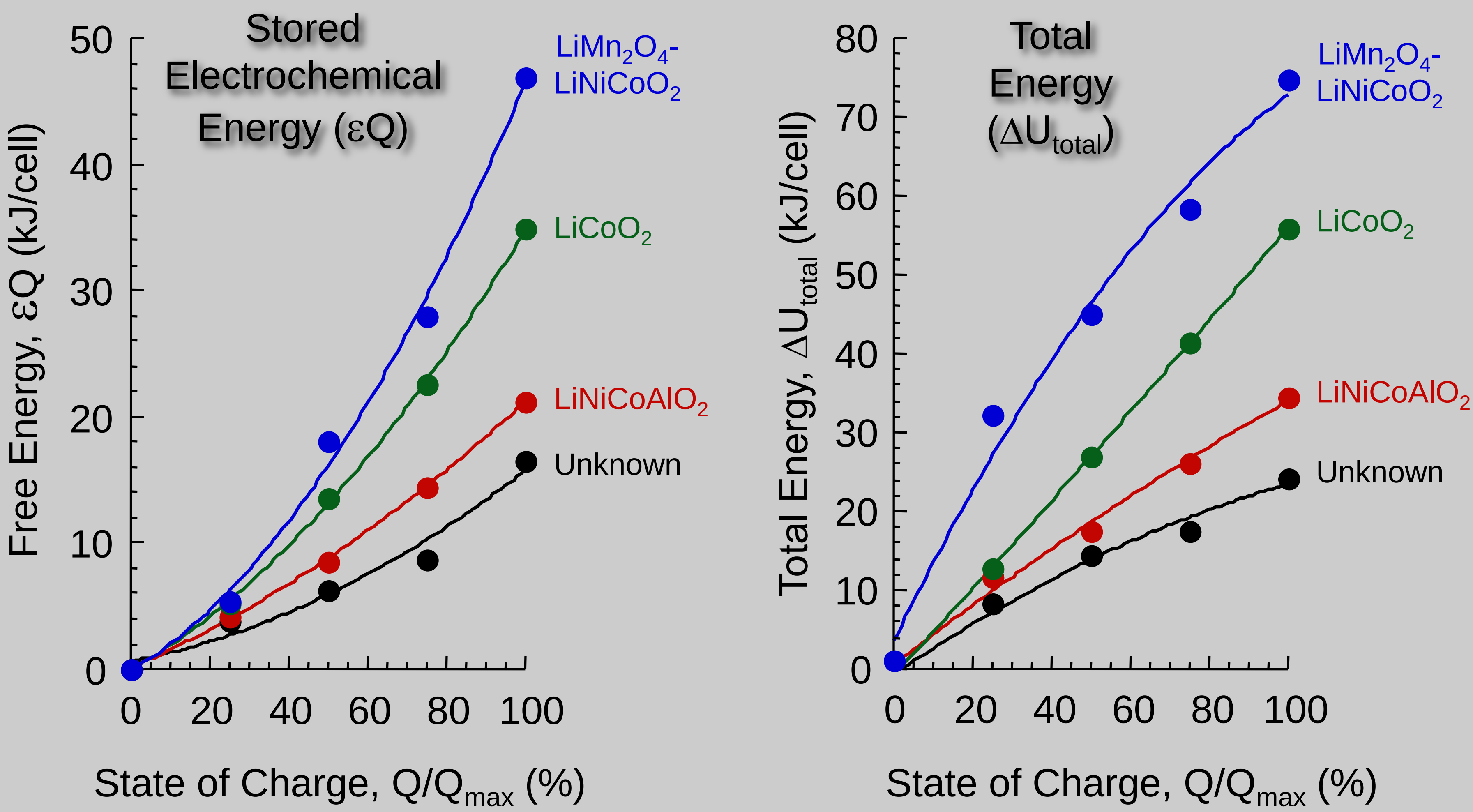
Analysis of Bomb Calorimeter Data



Energetics of Individual Cell Failure



State-of-Charge is Not a Good Predictor of Energetics for Different Chemistries and Cell Potentials

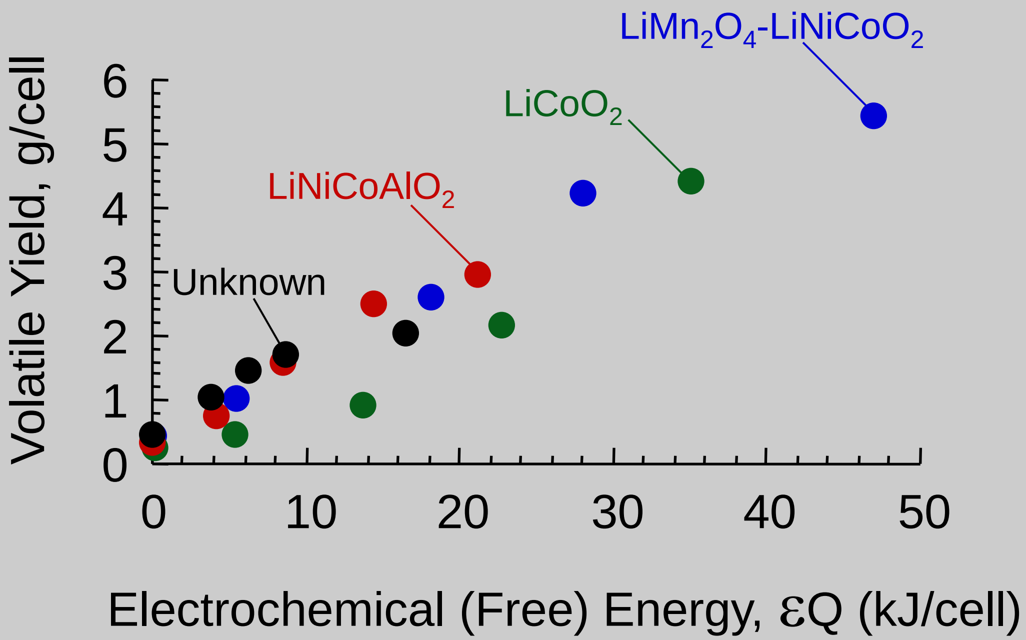


Li-Ion 18650 Batteries - Post Test

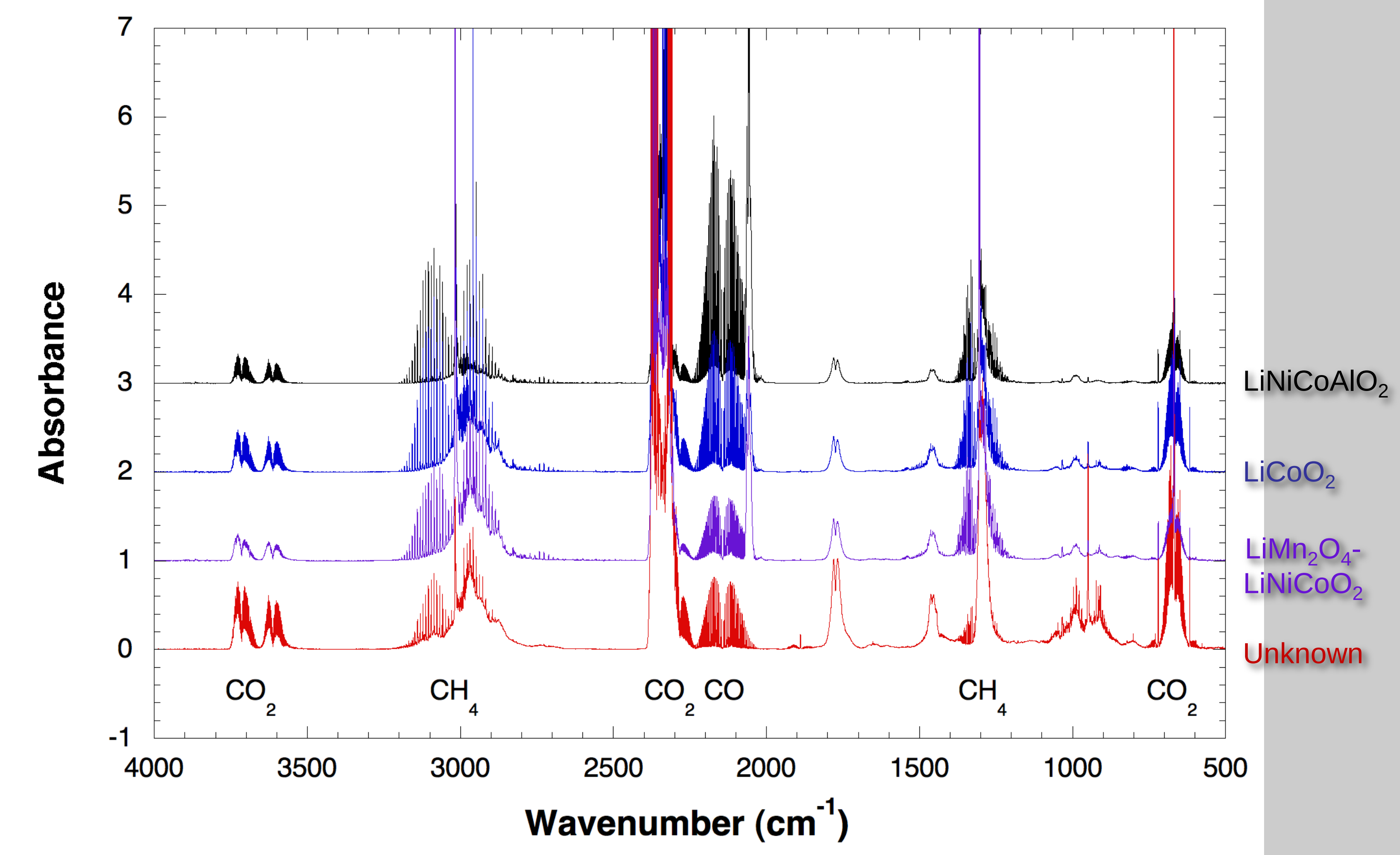
Zero Charge	50% Charged	100% Charged

Gravimetric Analysis for Volatile Yield

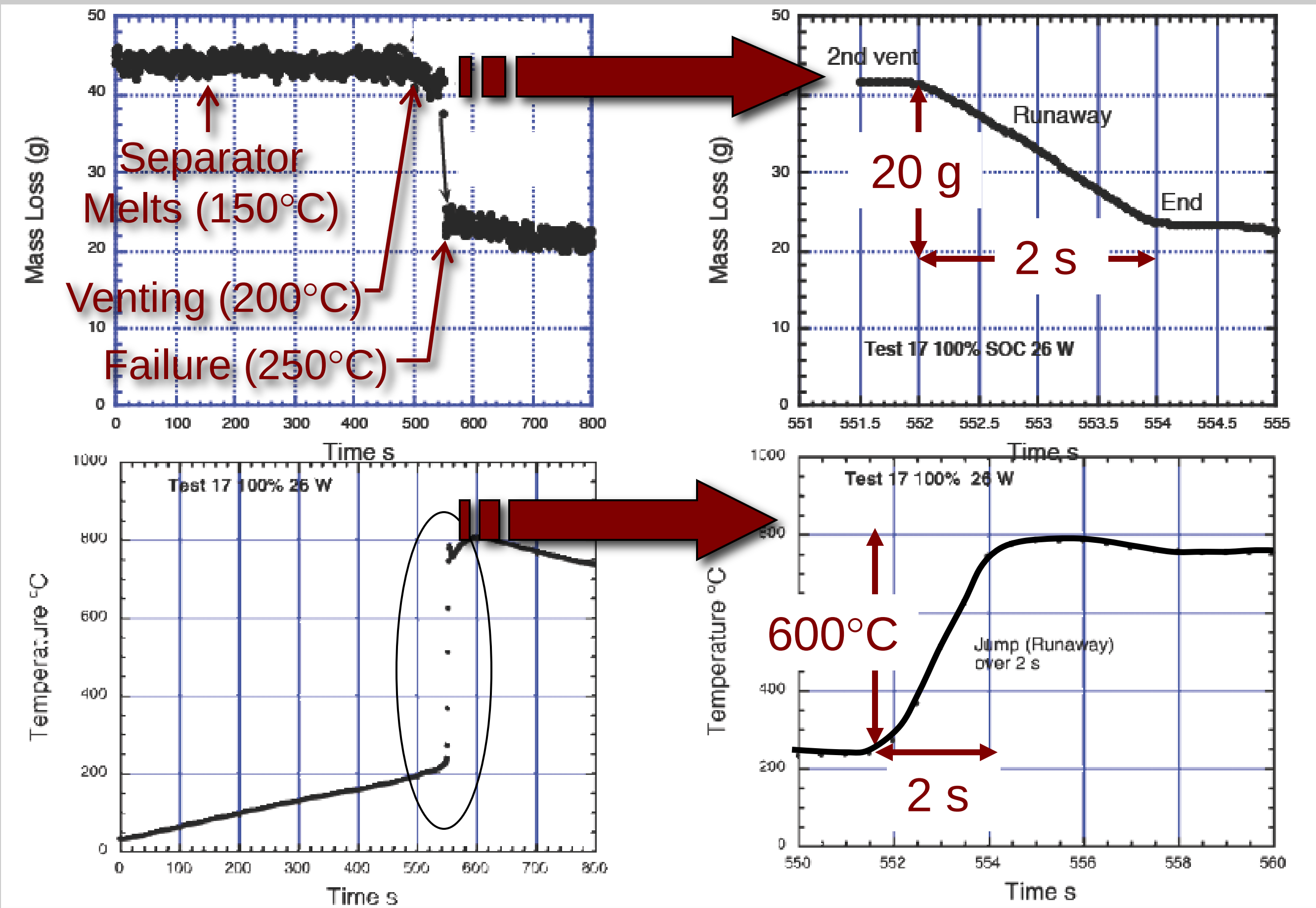
- Bomb weighed before and after venting to atmosphere to determine volatile yield
- Volatiles are combustible
- Yield $\propto \varepsilon Q$

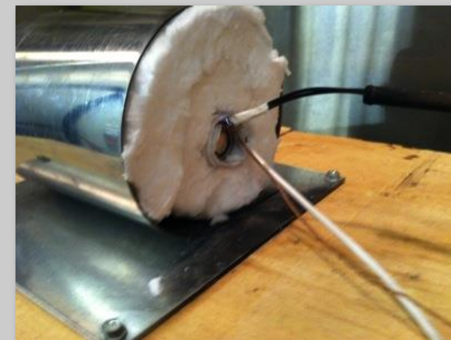


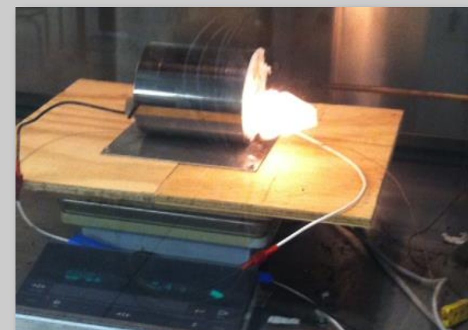
Infrared Spectra of Gaseous Decomposition Products



Thermal Effects of Cell Failure

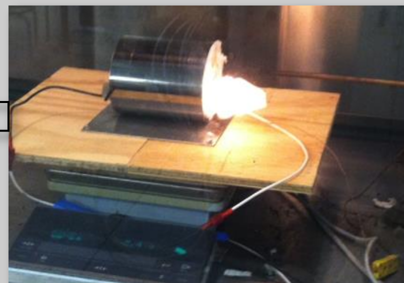




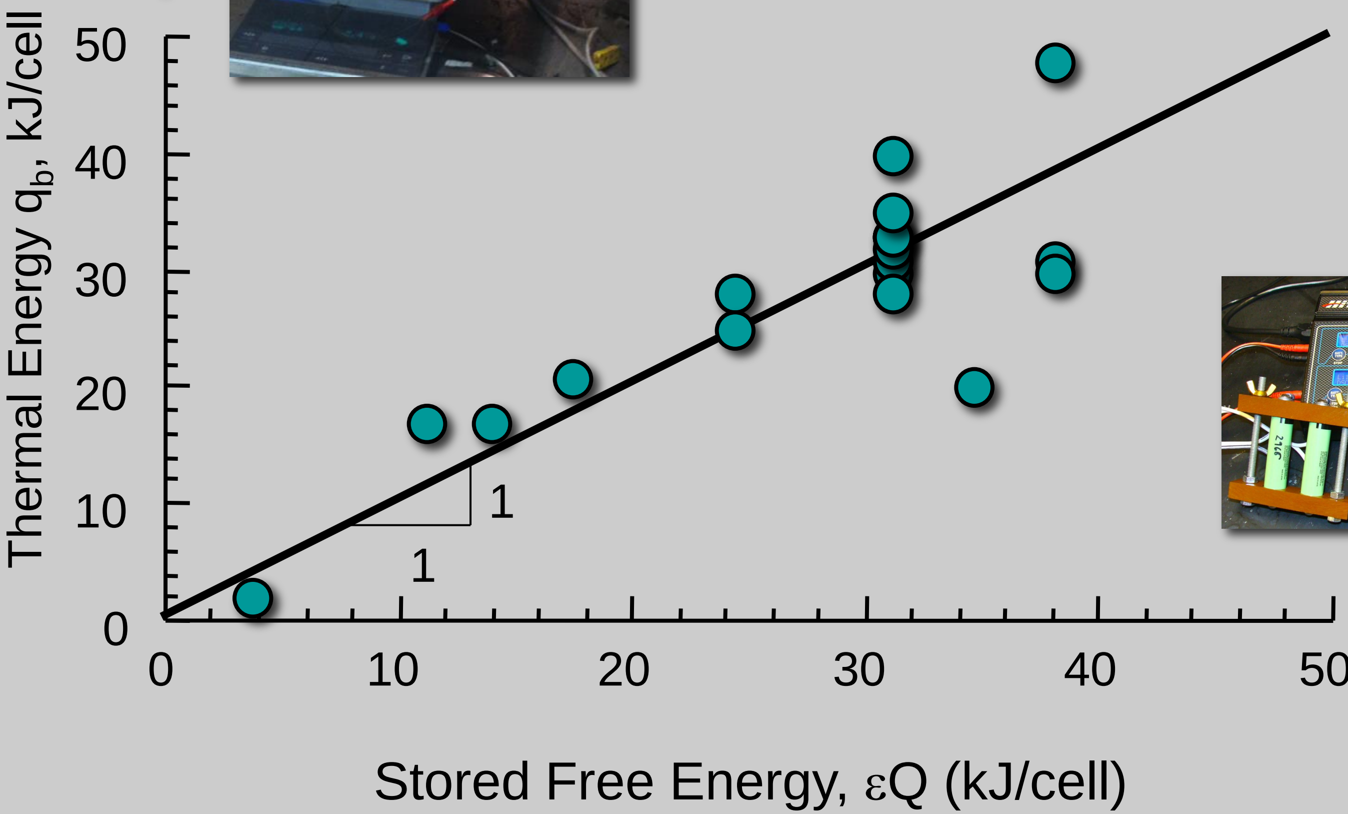


J.G. Quintiere & S.B. Crowley, Thermal Dynamics of 18650 Li-ion Batteries, The Seventh Triennial International Fire & Cabin Safety Research Conference, Philadelphia, PA, 2013.

Thermal Energy Release (q_b) ≈ Free Energy (εQ)



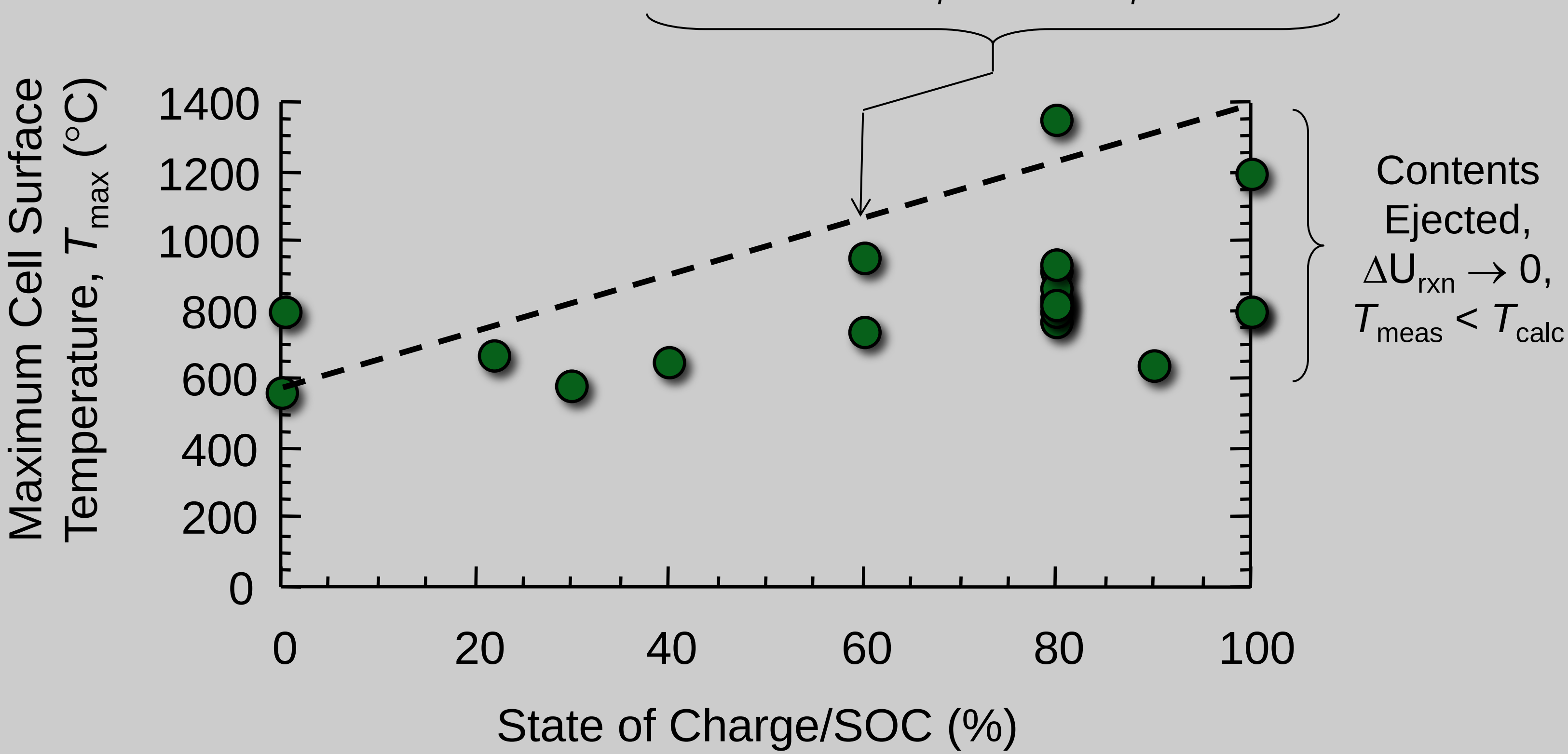
Implies chemical reactions of electrolytes (ΔU_{rxn}) take place outside of cell when contents are ejected



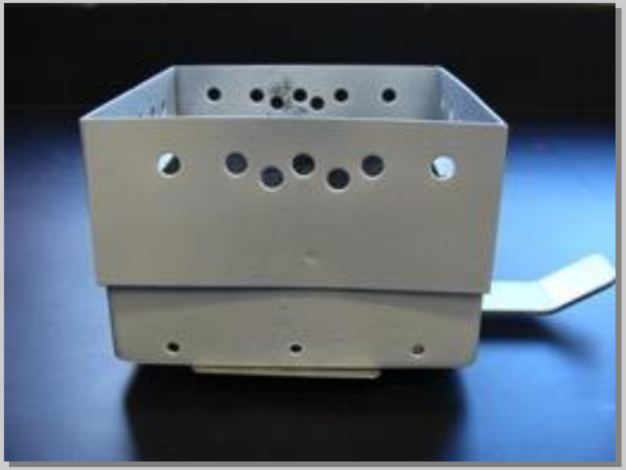
Adiabatic (Surface) Temperature Rise

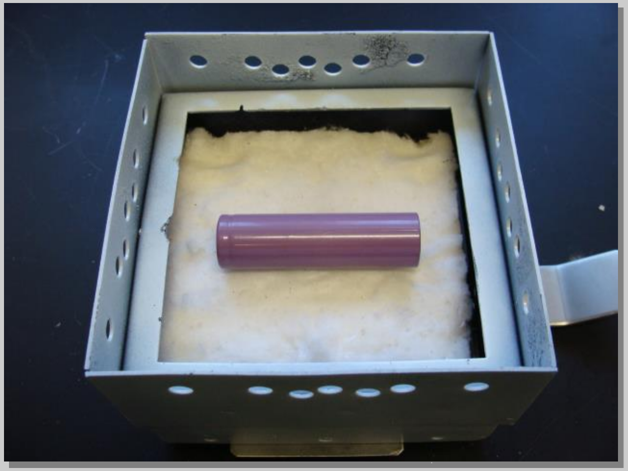
$$T_{\max} = T_f + \frac{\Delta U_{total}}{mc_p} = T_f + \frac{\Delta U_{rxn}}{mc_p} + \frac{\varepsilon Q}{mc_p}$$

$$\approx 250^\circ\mathrm{C} + \frac{\langle \Delta U_{rxn} \rangle}{mc_p} + \frac{\varepsilon Q_{\max}}{mc_p} * \frac{SOC}{100}$$



Fire Calorimeter Testing of Lithium Cells



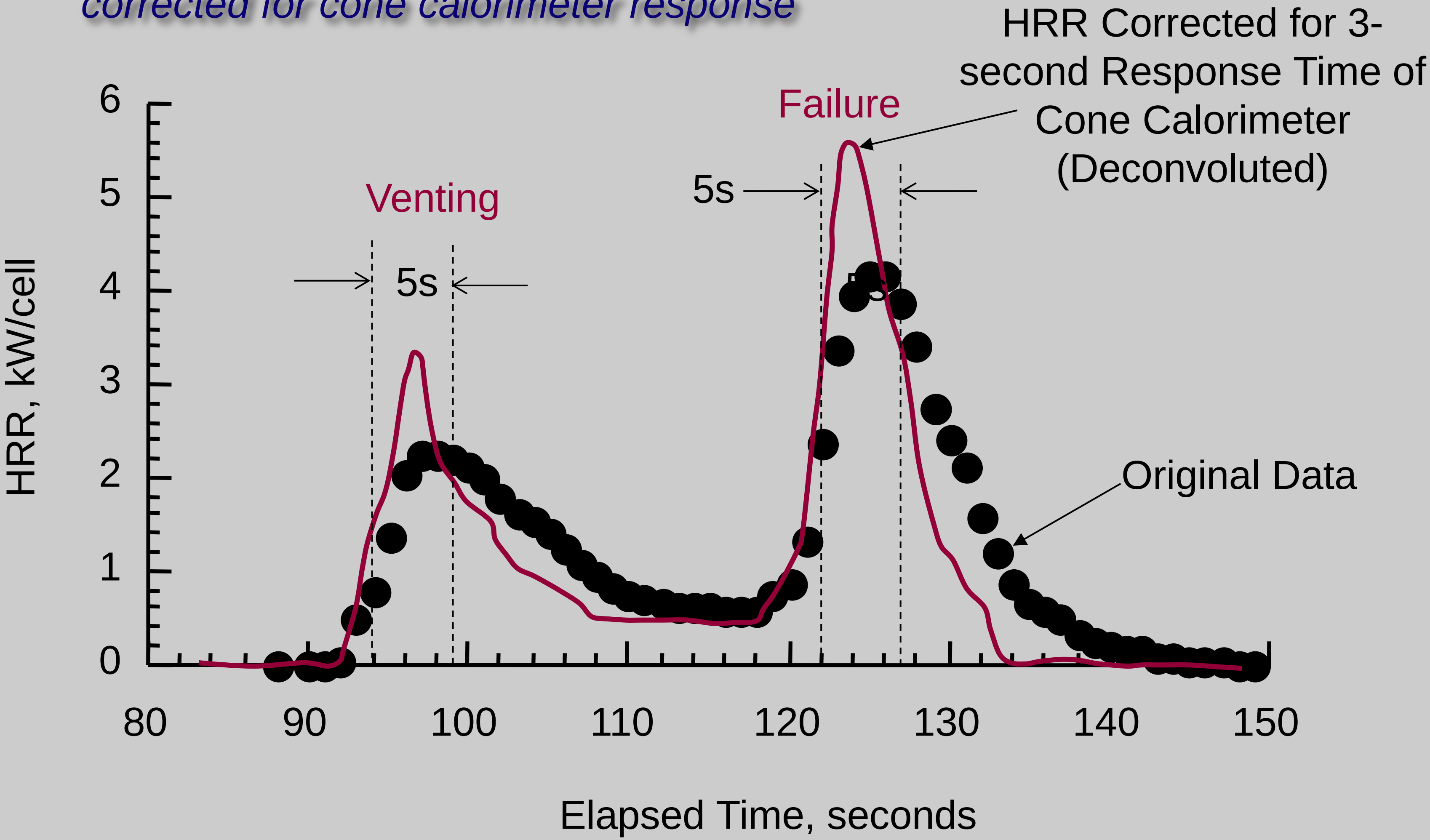


Special holder designed to
prevent rocketing of cell at failure

Standard ASTM E 1354 Operation

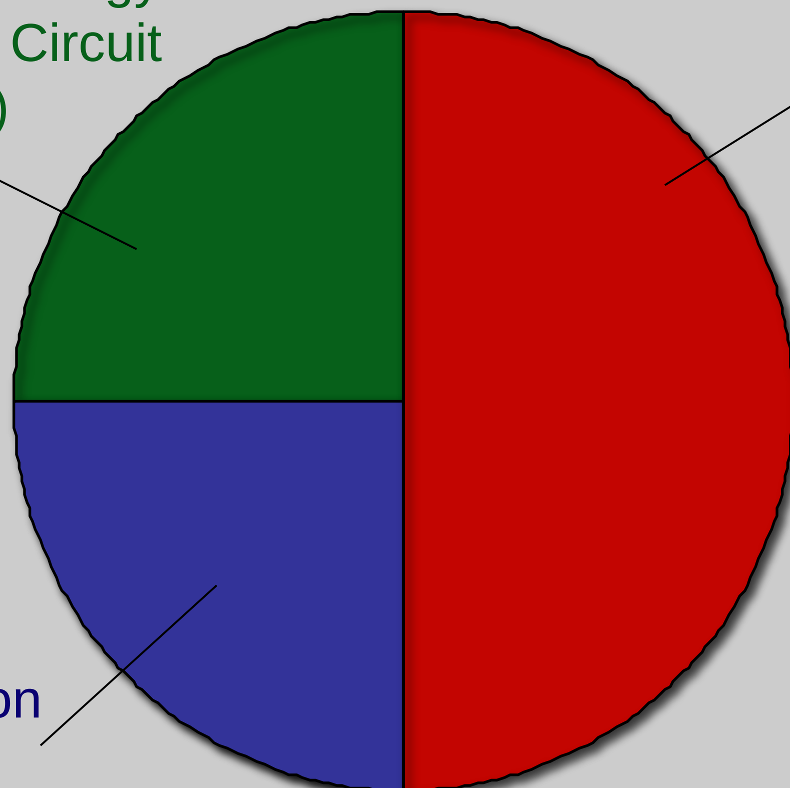
Heat Release Rate in Cone Calorimeter

Failure is so rapid that HRR must be corrected for cone calorimeter response



Fire and Thermal Hazards of 18650 Cell

Total ≈ 103 kJ/cell = 2.3 kJ/g ≈ 1/20 jet fuel

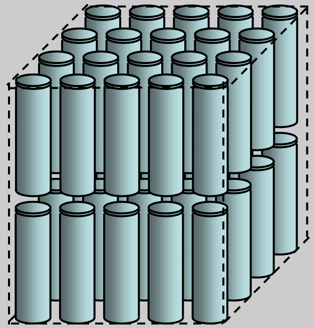


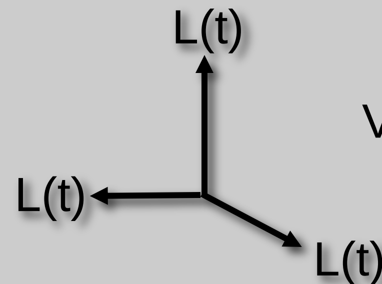
$$q_v = \frac{75 \text{ kJ/cell}}{6.62 \times 10^{-5} \text{ m}^3\text{/ cell}}$$

$$= 10^9 \text{ J/m}^3$$

$LiCoO_2$ Cell at 50% SOC

Analytic Model of 18650 Cargo Fire Growth





Combustion Volume at time *t*, $V(t) = L(t)^3$

- *Effective Length of 18650,* $\bar{L} = \sqrt{(18mm)(65mm)} = 34mm$
- *Constant linear fire growth rate,* $L_0' = \frac{\bar{L}}{\tau} = \frac{\bar{L}^2}{mc/\kappa} = 3x10^{-4}\, m/s$
- *Heat Release in Flaming Combustion,* $q_v = 10^9$ J/m^3

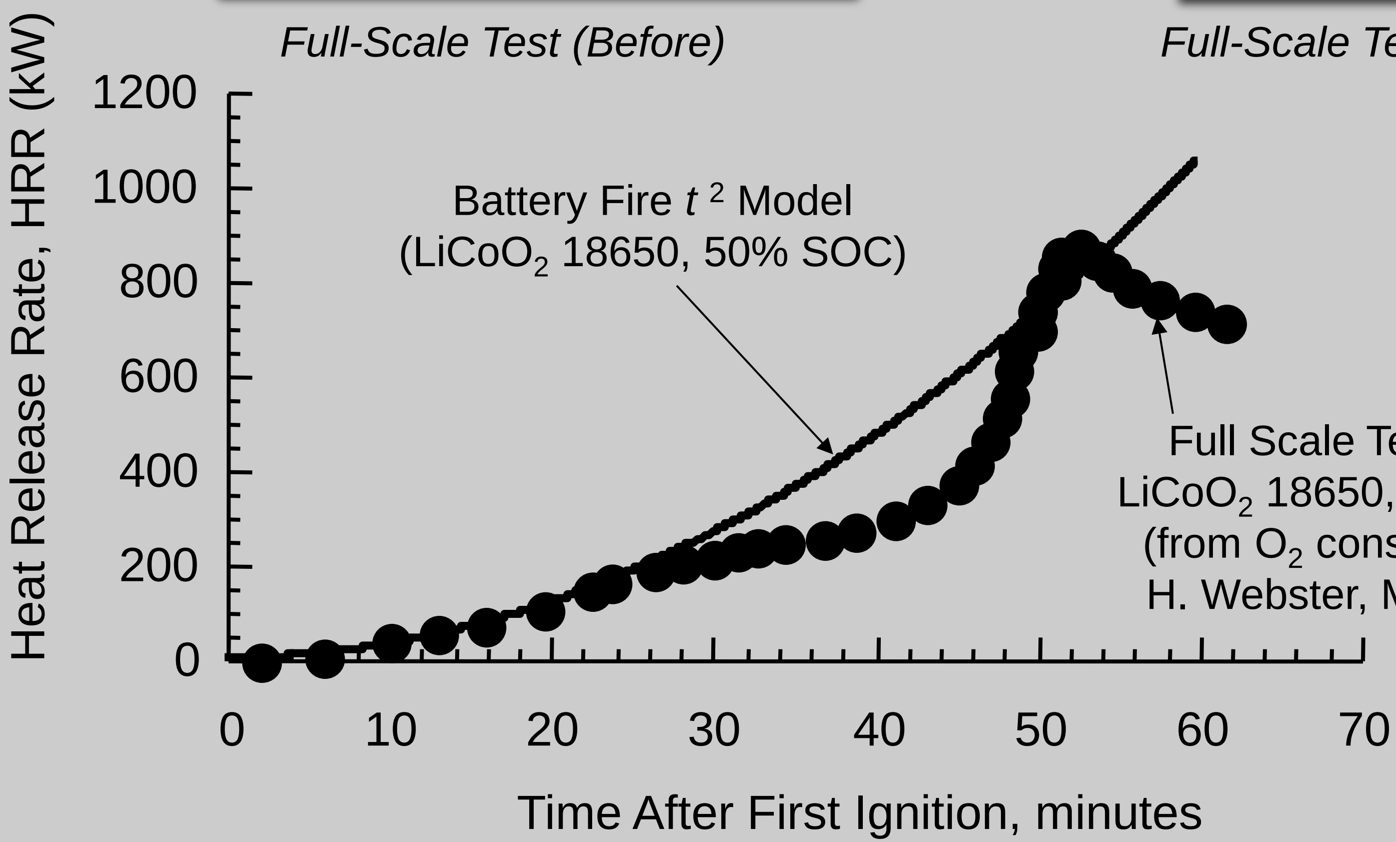
$$HRR(t) = q_v \frac{dV}{dt} = q_v \frac{dL(t)^3}{dt} = 3q_v (L_0')^3 t^2$$

Model Versus Full Scale Test Data

Full-Scale Test (Before)

Class E
Main Deck
Cargo

Full-Scale Test (After)



Summary

State-of-charge is a poor predictor of fire hazard for different batteries and cell chemistries.

Total energy at failure of Li Ion cells/batteries (LIB), ΔU_{total} is almost twice the stored electrochemical energy εQ for the 18650 cell chemistries of this study.