International Aircraft Systems Fire Protection Working Group Meeting
Atlantic City, New Jersey, October 21-22, 2015

Fire Hazards of Lithium Ion Batteries

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Outline of Talk

- Motivation: Safe Shipment of Batteries
- Background: Lithium Ion Cells/Batteries
- Methodologies
- Findings

William J. Hughes Technical Center, Atlantic City, NJ

Aircraft Fire Incidents Involving Li Batteries

- Fire erupted in a cargo plane that landed in Philadelphia on Feb. 7, 2006.
- A cargo plane with 81,000 lithium batteries caught fire and crashed after it left Dubai on Sept. 3, 2010.
- A cargo jet crashed into the East China Sea on July 28, 2011, after the crew reported a fire on board.

Objective: Measure Fire Hazards of LIBs

Passenger electronics

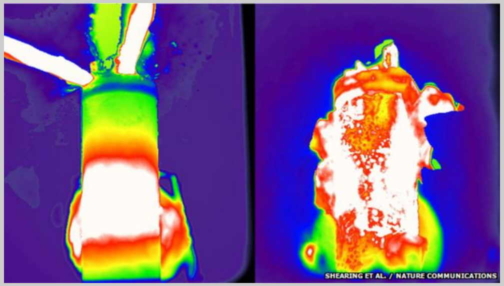
Typical packaging

Bulk shipment as cargo

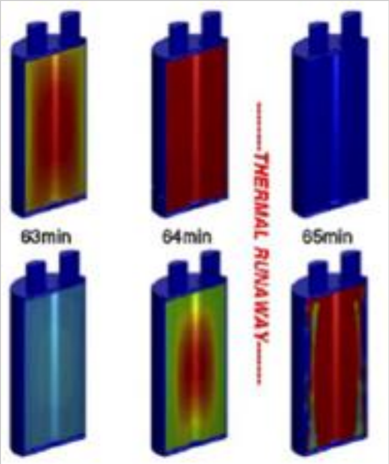
Applications and Industry Research

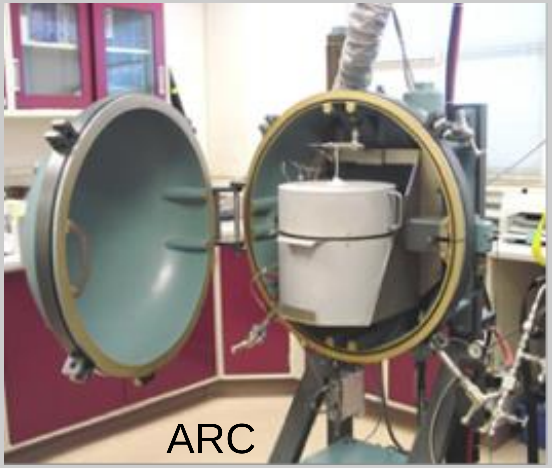
- Increasing applications
  - More widely used
  - Higher energy densities

- Modeling of Failure (Thermal Runaway)
  - Up to 6 decomposition reactions
  - CFD thermal-chemical-electrical analyses

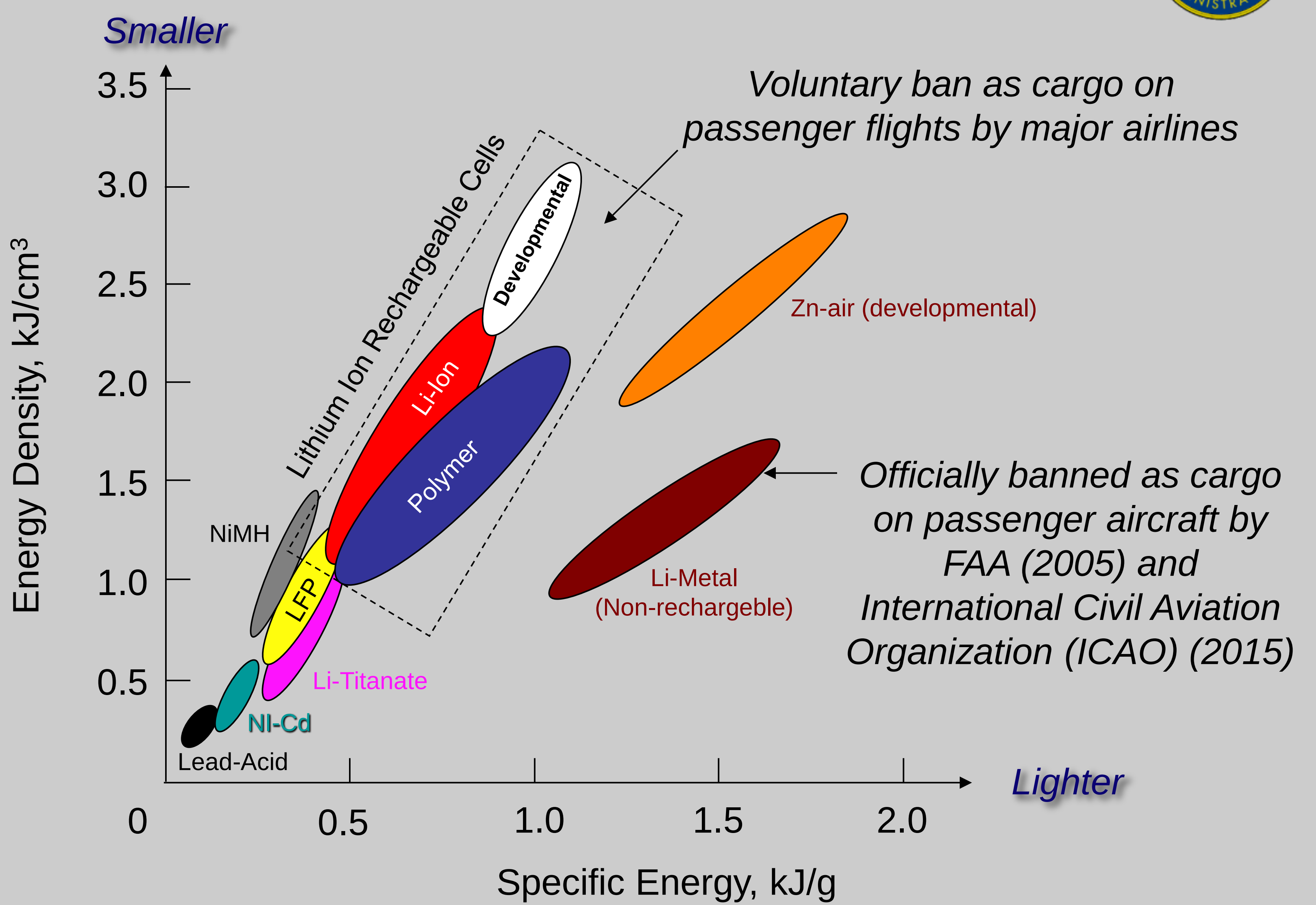


- Experimental Studies
  - Component studies
  - DSC, ARC studies

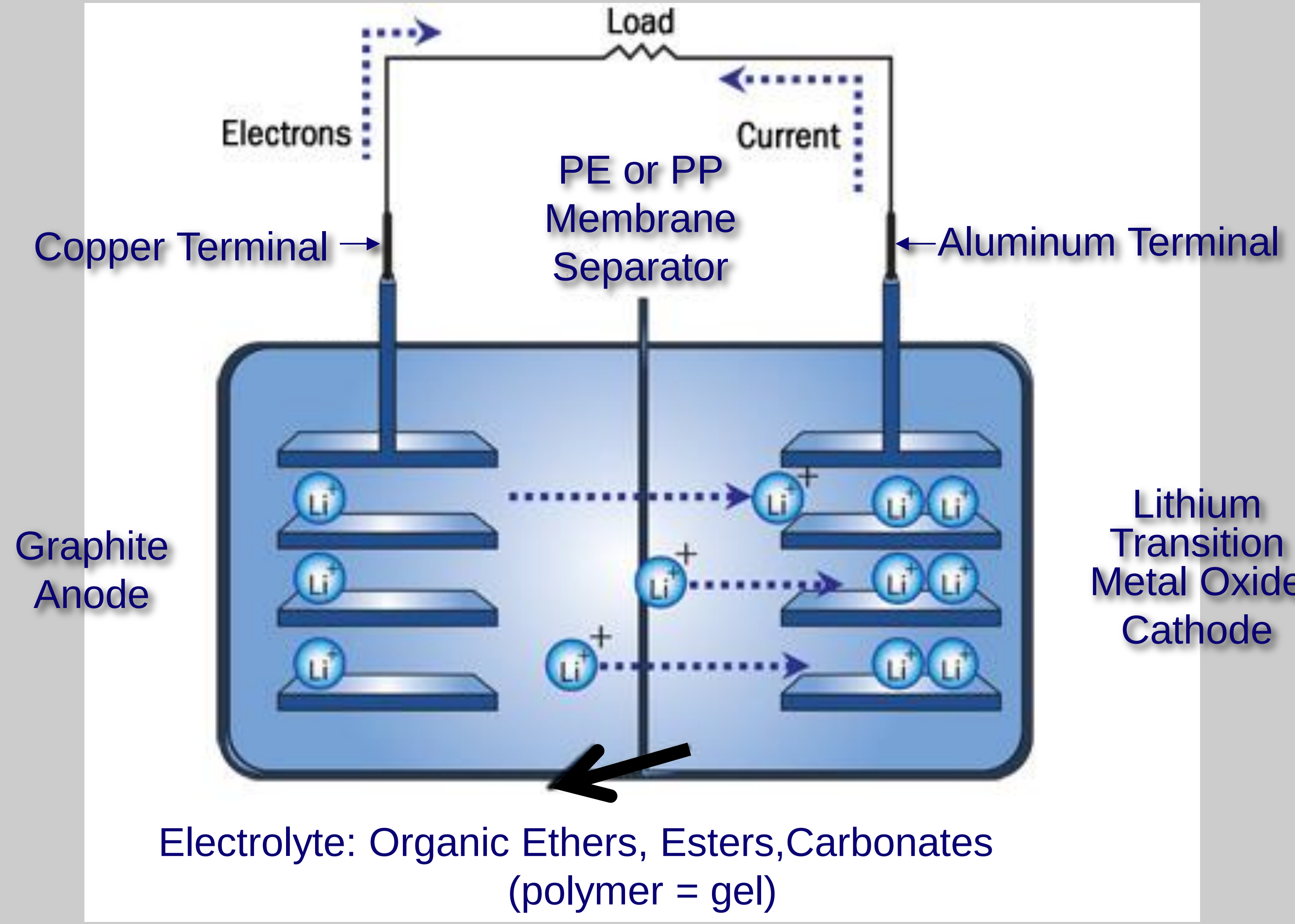




Energy Density and Cell Chemistry

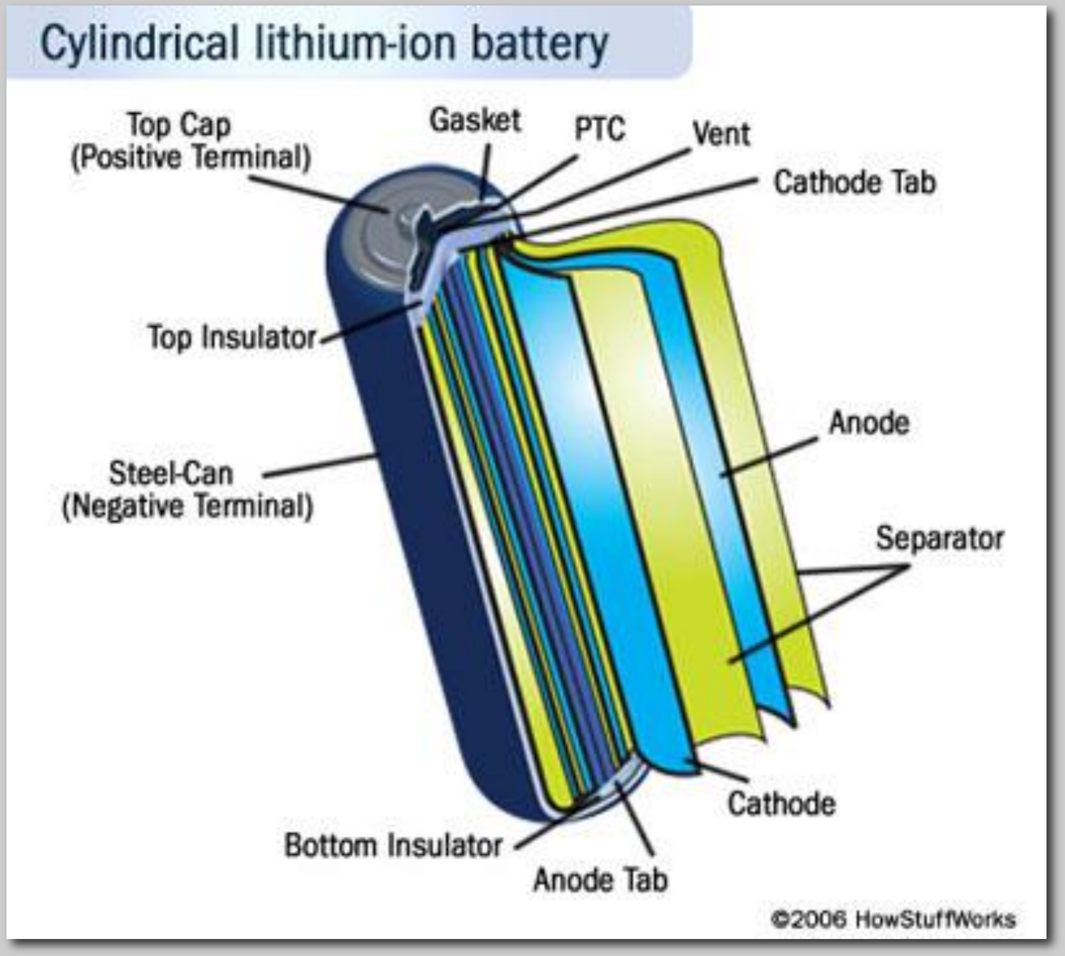


Normal Discharge of Lithium Ion Cell



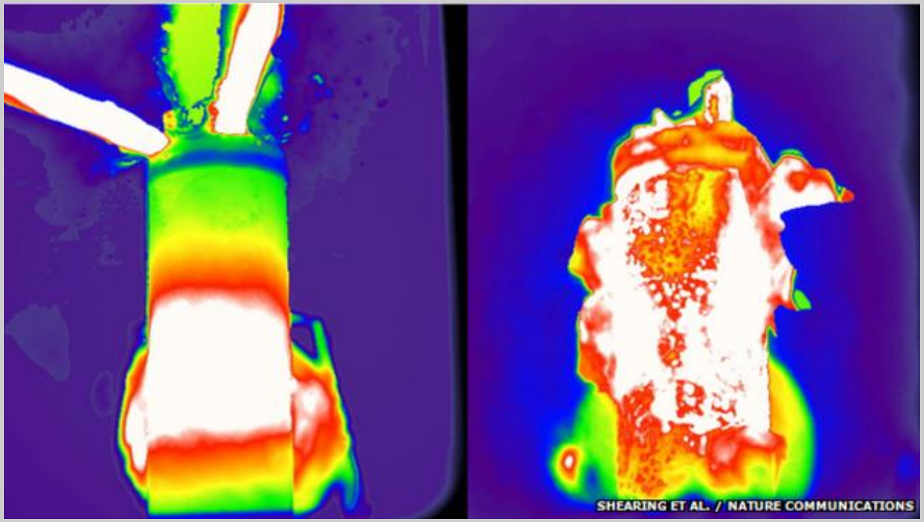
Materials: Commercial 18650 LIB Cells

18650 Rechargeable Cells (≈ 44 grams each)



Causes of Battery Failure

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



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Thermal Runaway

- *Auto-accelerating heat generation*
- *Rapid temperature increase*
- *Expulsion of flammable gases and liquids*

Experimental Methods: Cell Charging

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

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**

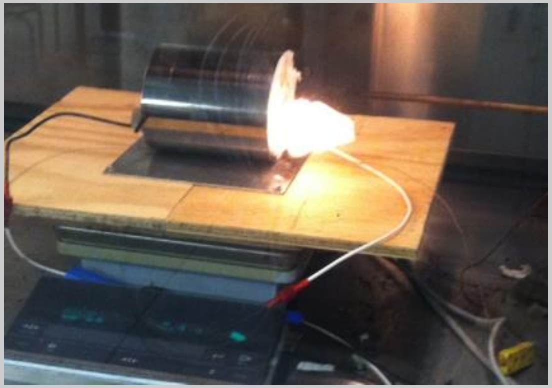
Chemical Energy Available to Do Useful Work (Free Energy), $\Delta G = -\varepsilon Q$

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

Methods: Hazard Measurements

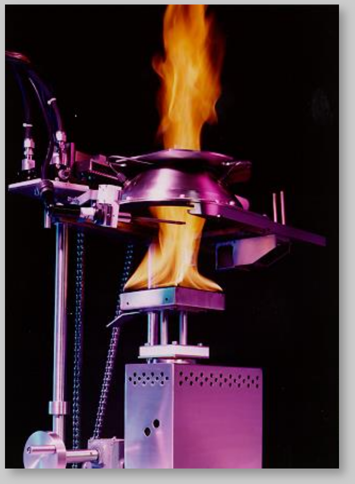
Energetics of Cell Failure

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

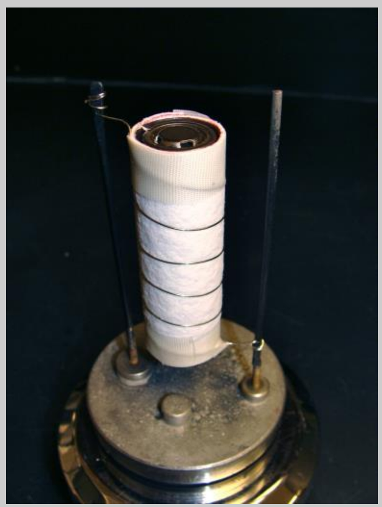


Fire Behavior of Lithium Cells

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

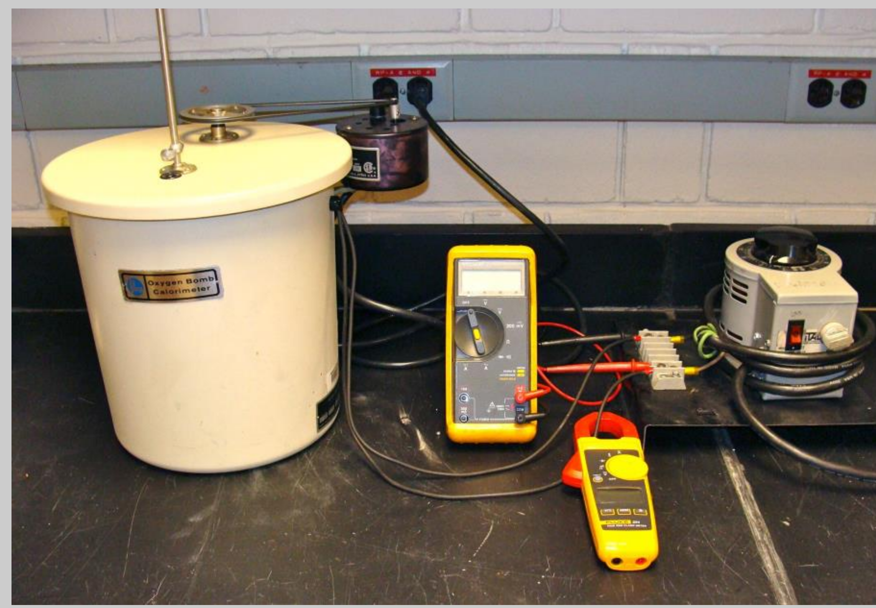
Bomb Calorimeter (ASTM D 5865)

- Standard Test Method for Gross Calorific Value of Coal and Coke
- 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



Cell Thermodynamics (see Paper)

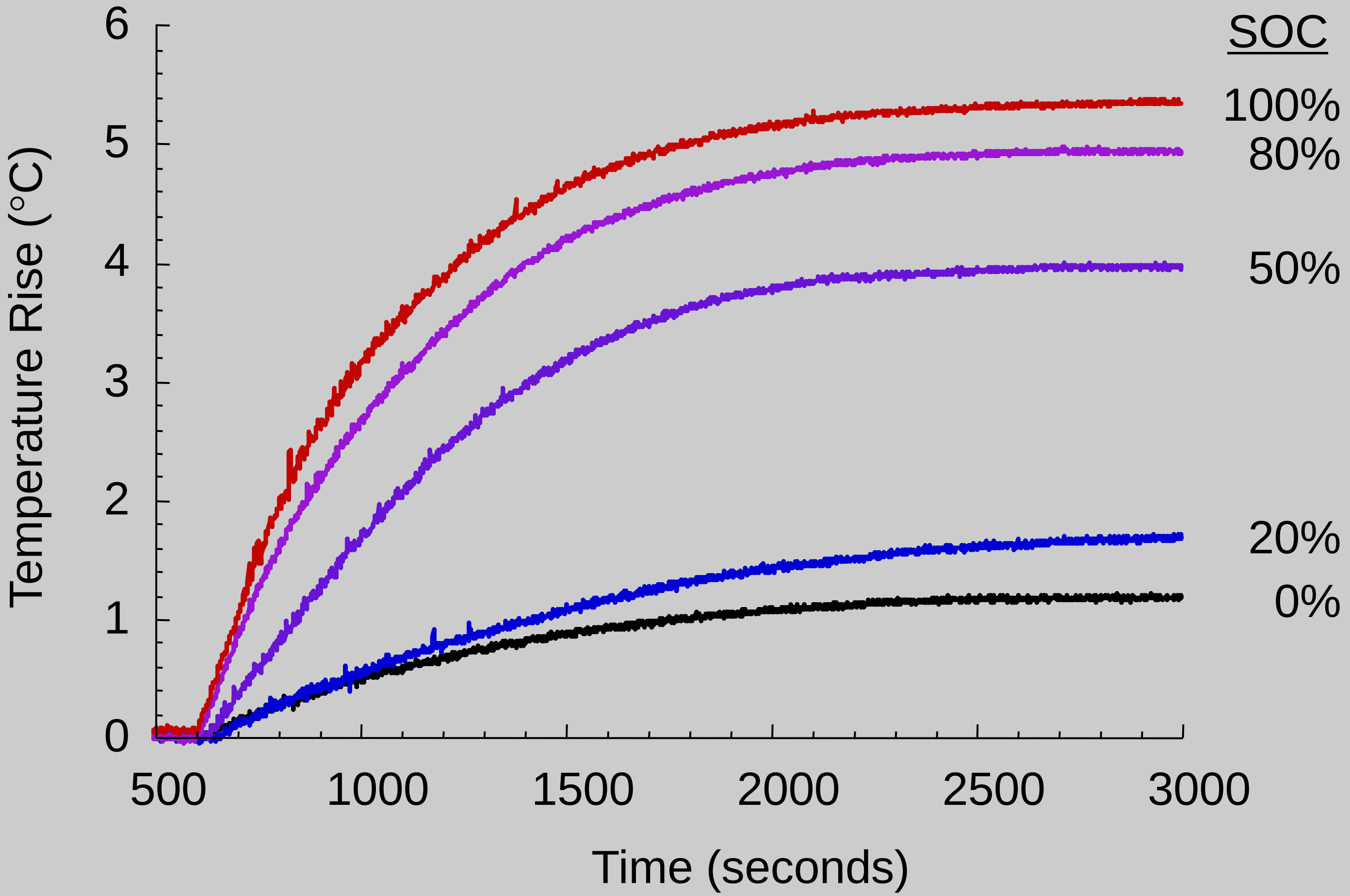
$$\Delta U_{Total} \approx \underbrace{\Delta U_{rxn} + \varepsilon Q}_{\text{Depends on cell chemistry}}$$

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

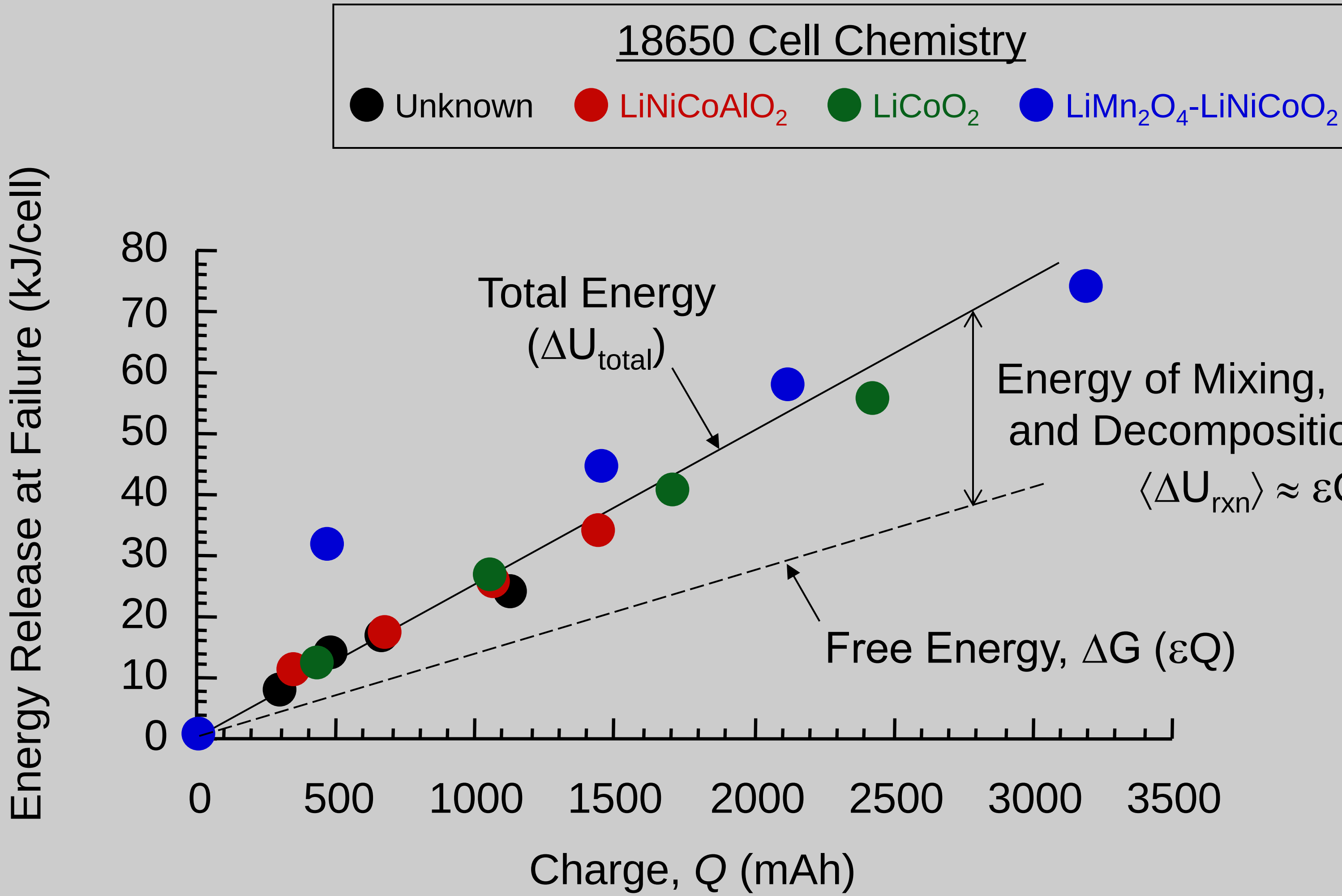
Electrochemical (Free) energy, ΔG (*Equal to cell potential* ε*(V) times charge Q (A-s)*)

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

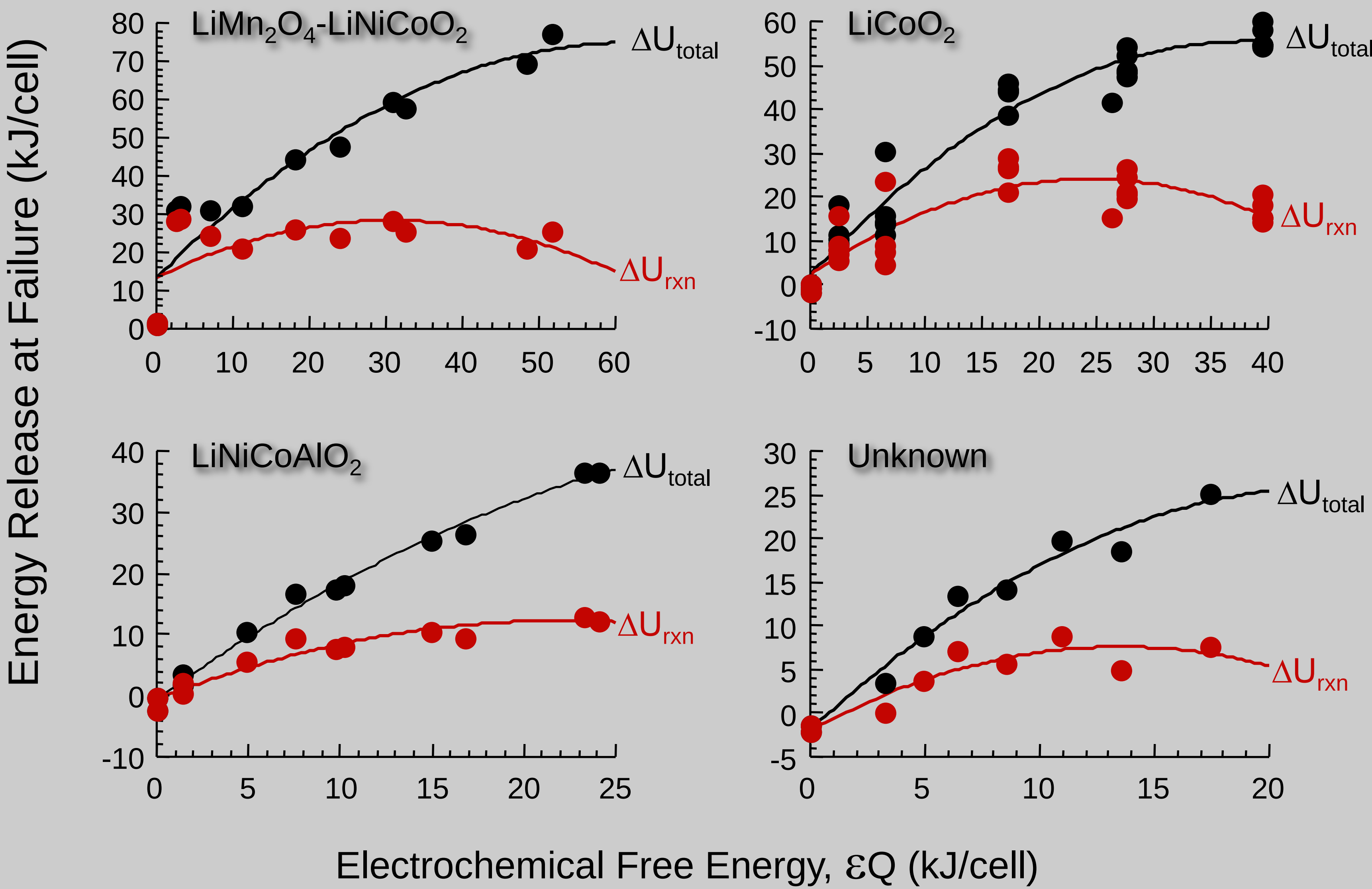
Baseline-Corrected Temperature History In Bomb



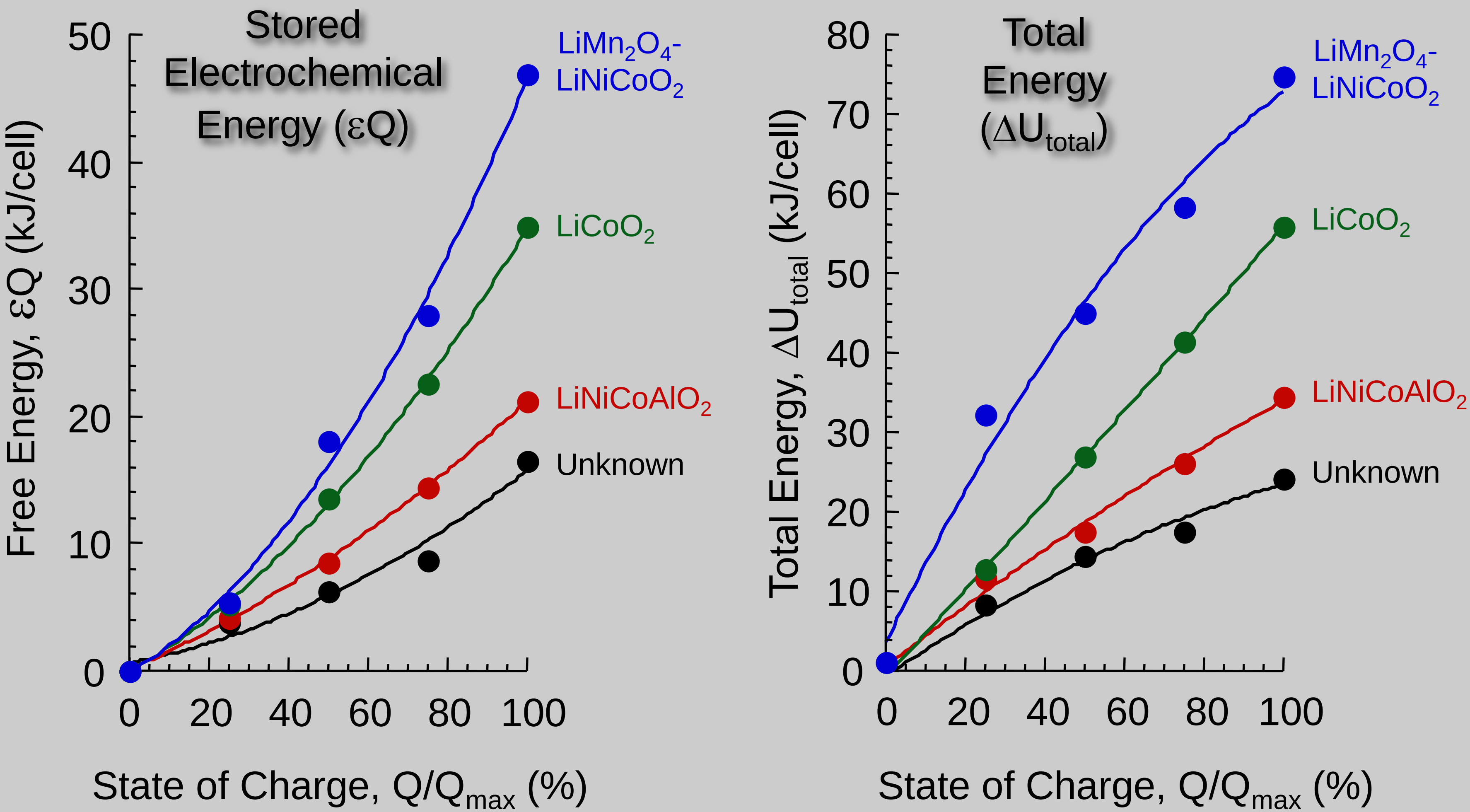
Generalized Energetics of Cell Failure



Energetics of Individual Cell Failure



SOC is a Poor Predictor of Energy Release for Different Chemistries (and Cell Potentials)

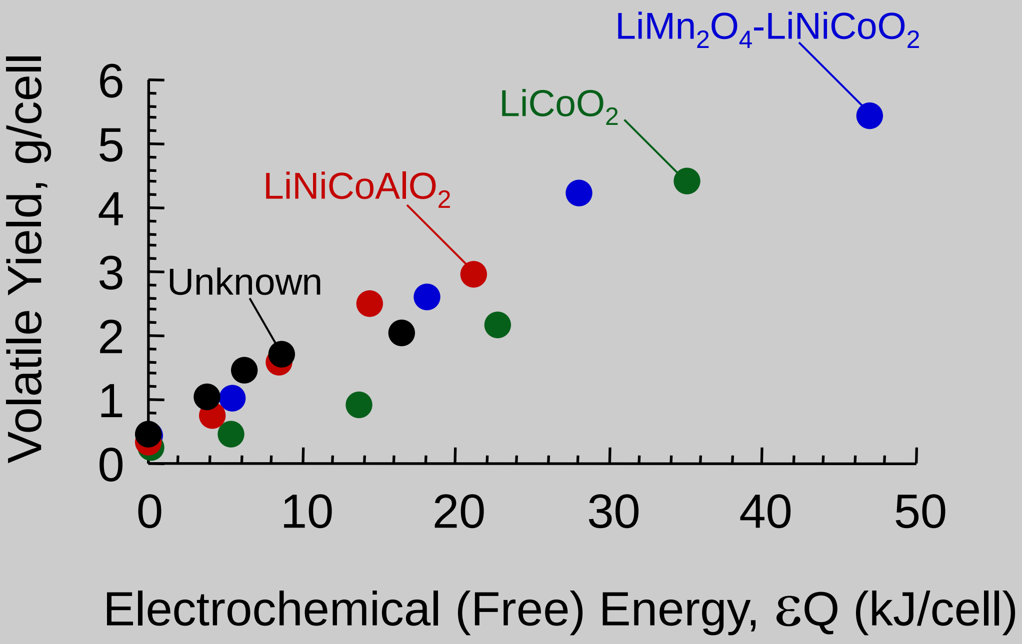


Li-Ion 18650 Batteries - Post Test

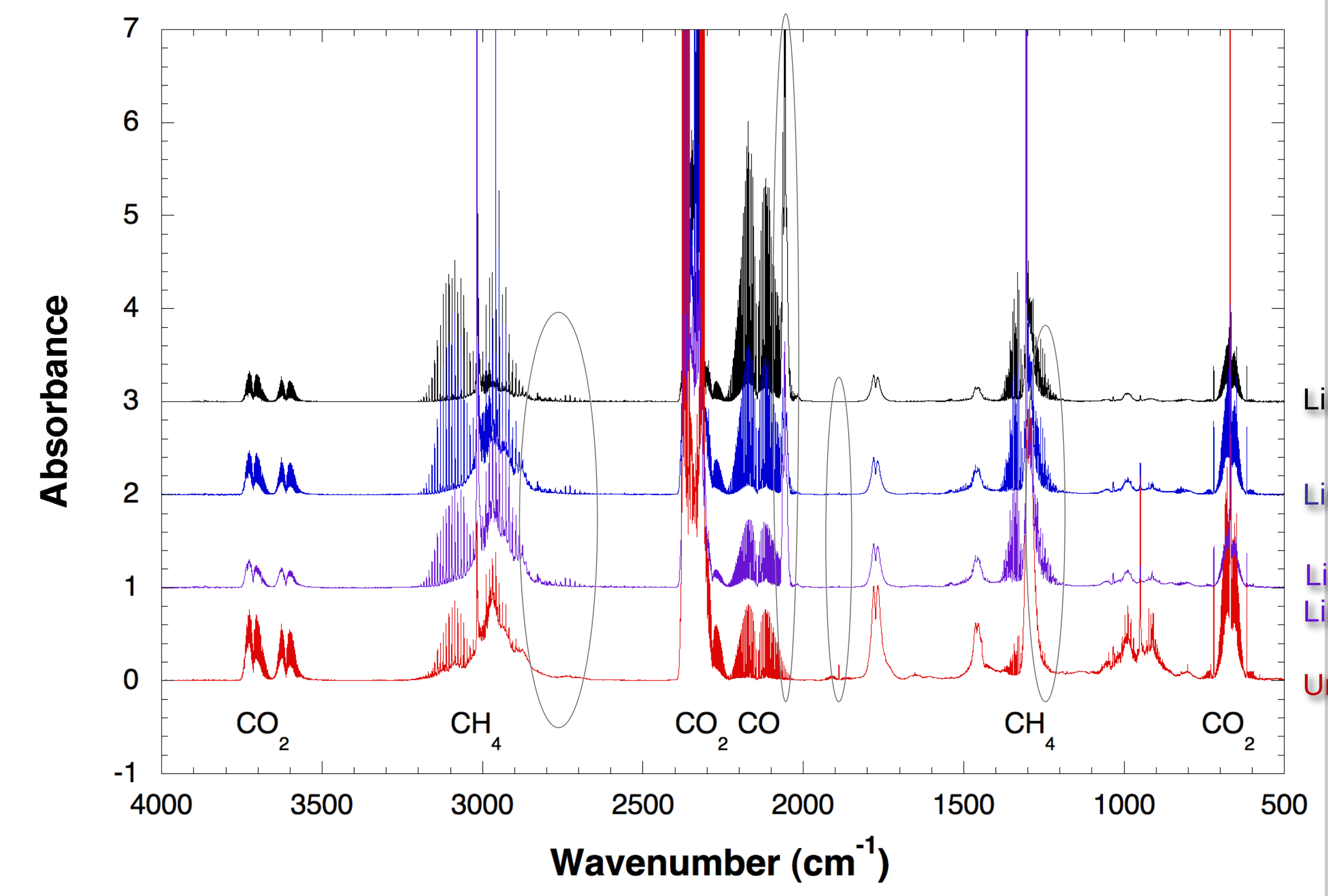
Zero Charge | **50% Charged** | **100% Charged**

Gravimetric Analysis for Volatile Yield

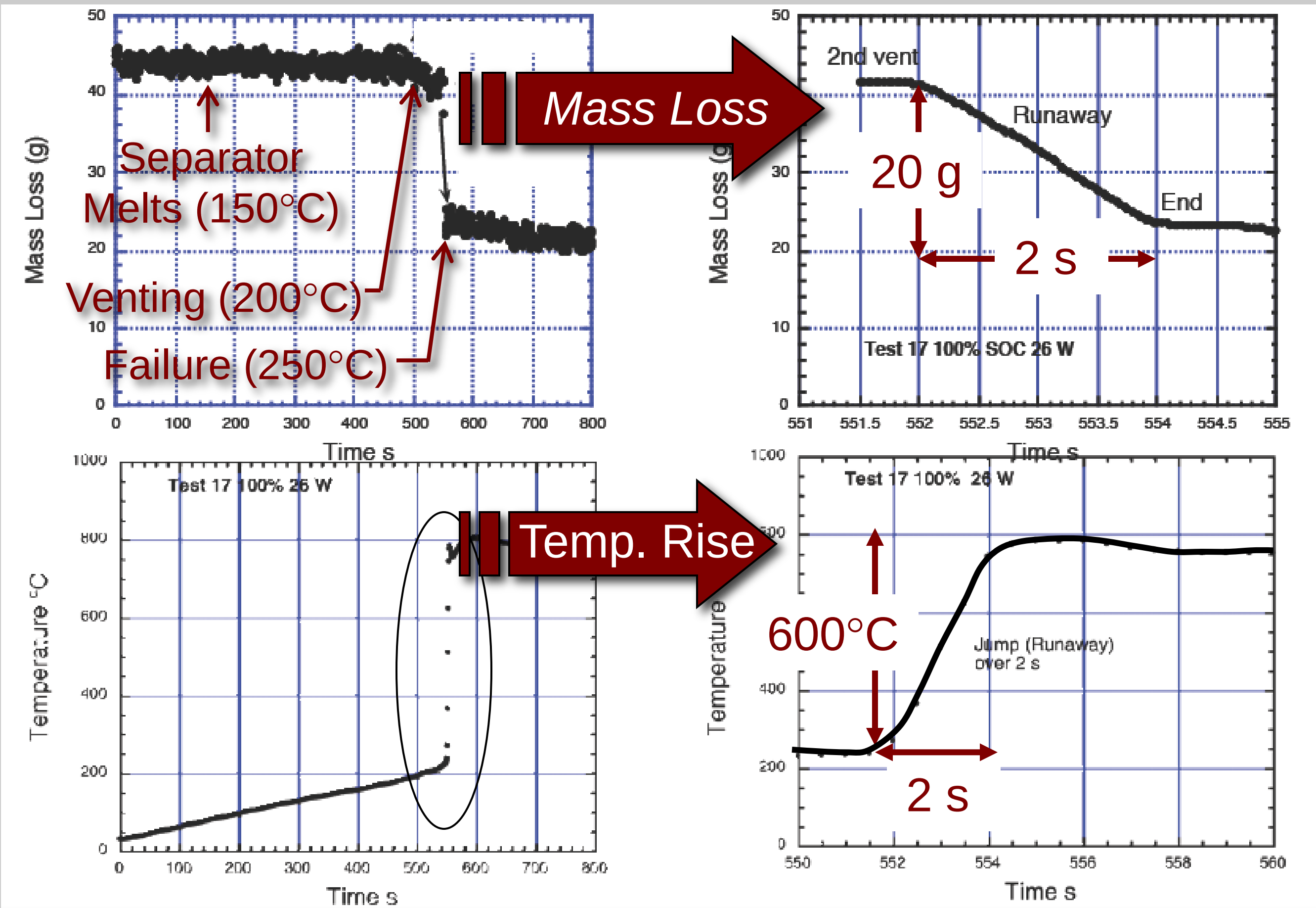
- Bomb weighed before and after venting
- Volatiles are combustible
- Yield $\propto \varepsilon Q$

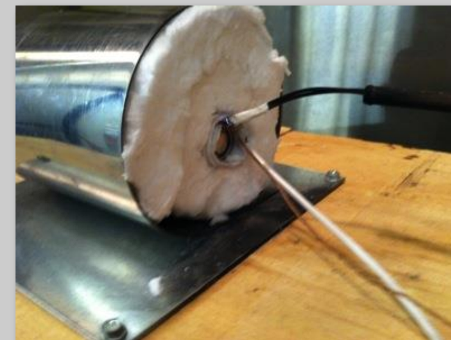


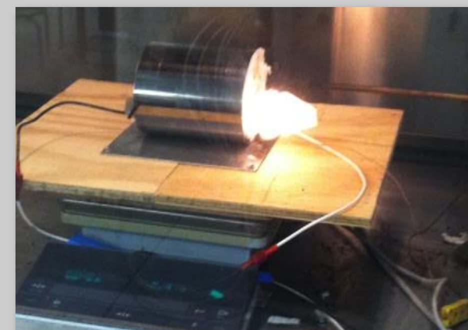
Infrared Spectra of Gaseous Decomposition Products



Thermal Effects of Cell Failure



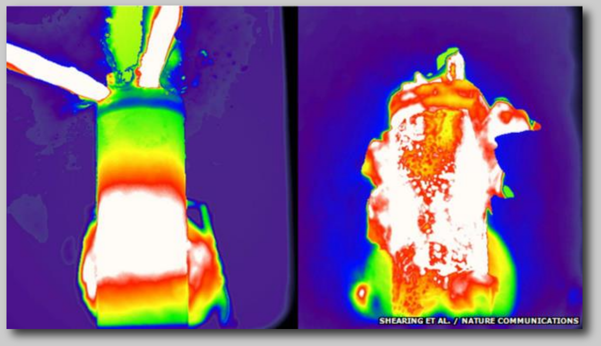


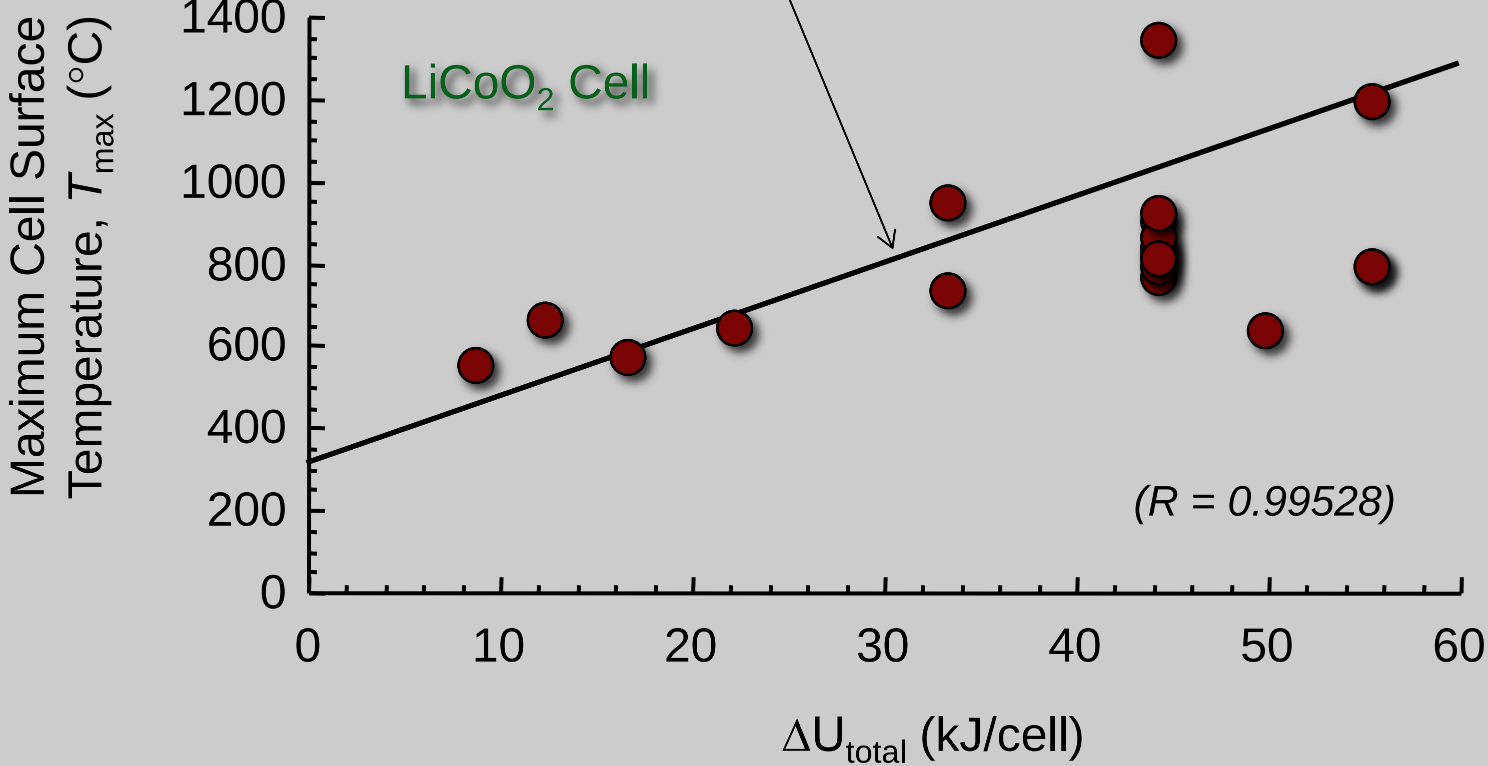


J.G. Quintiere & S.B. Crowley, Thermal Dynamics of 18650 Li-ion Batteries, The Seventh Triennial International Fire & Cabin Safety Research Conference, Philadelphia, PA, 2013.

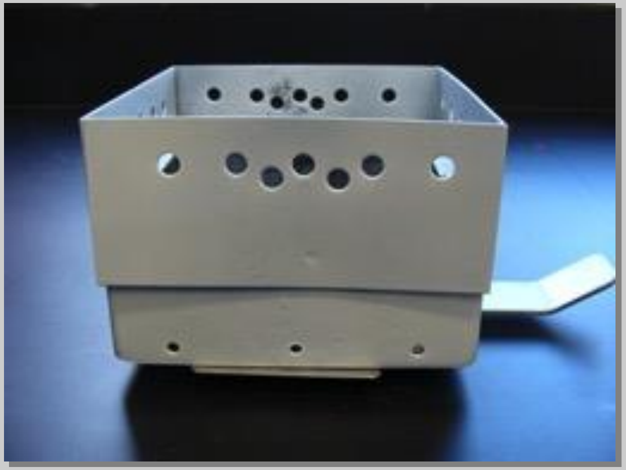
Adiabatic (Surface) Temperature Rise

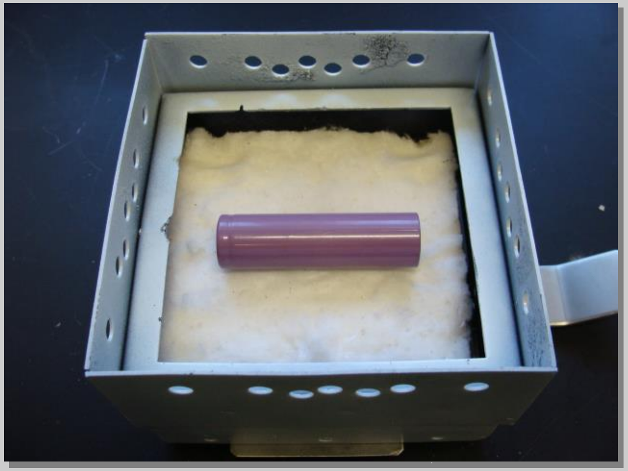
$$T_{max} = T_f + \frac{\Delta U_{total}}{mc_p}$$





Fire Calorimeter Testing of Lithium Cells



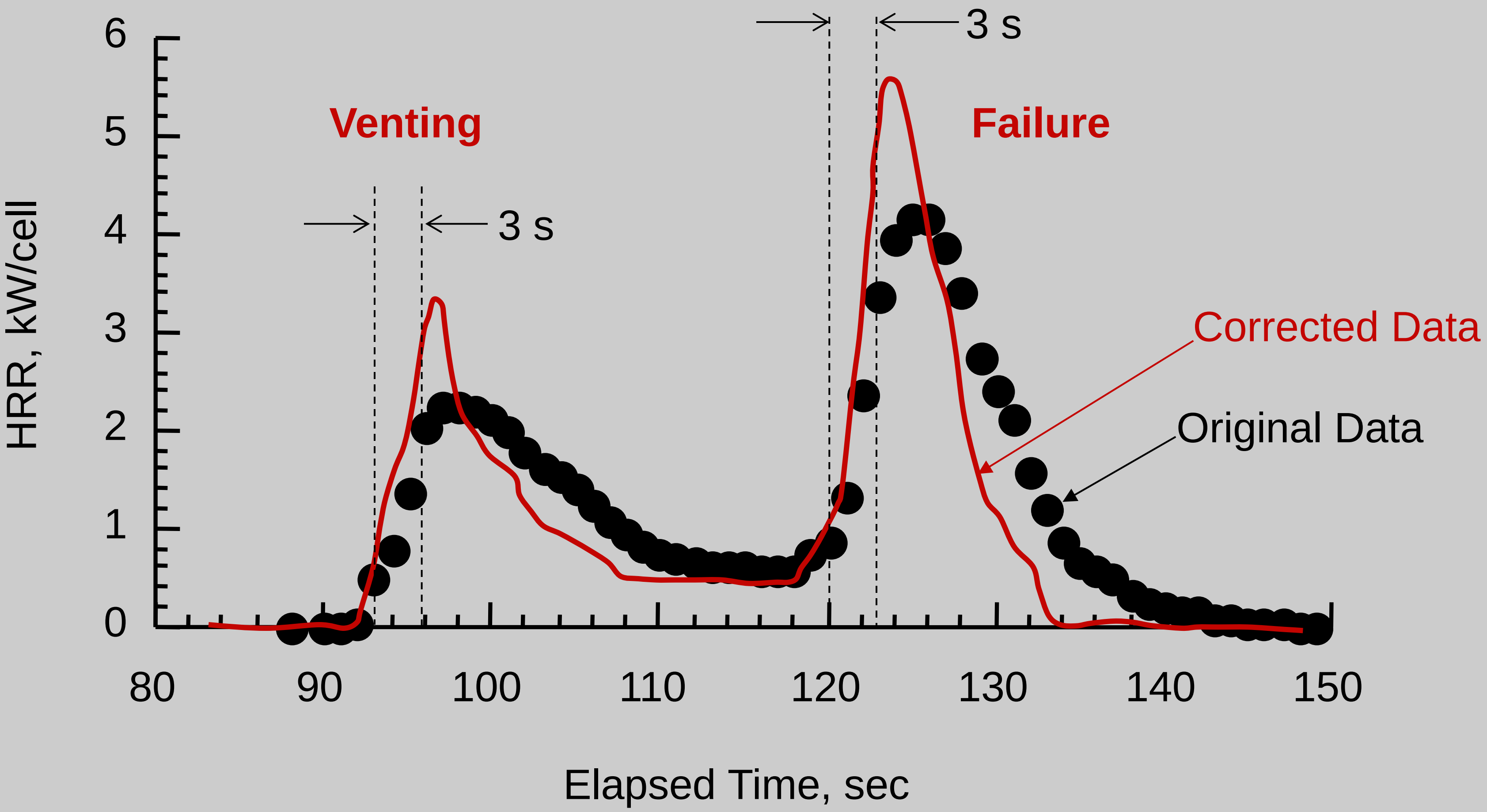


Special holder designed to
prevent rocketing of cell at failure

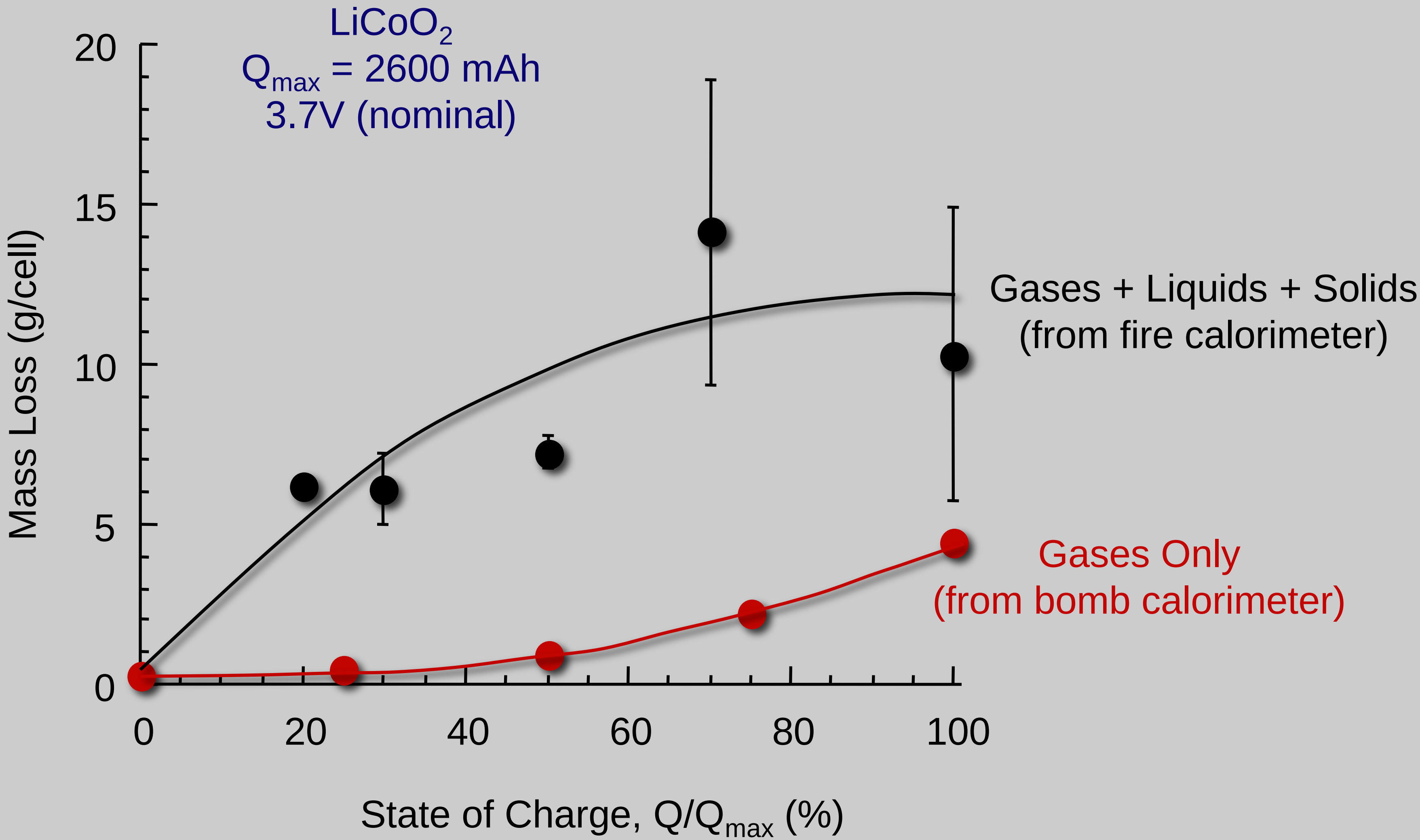
Standard ASTM E 1354 Operation

HRR of 18650 $LiCoO_2$ Cell in Cone

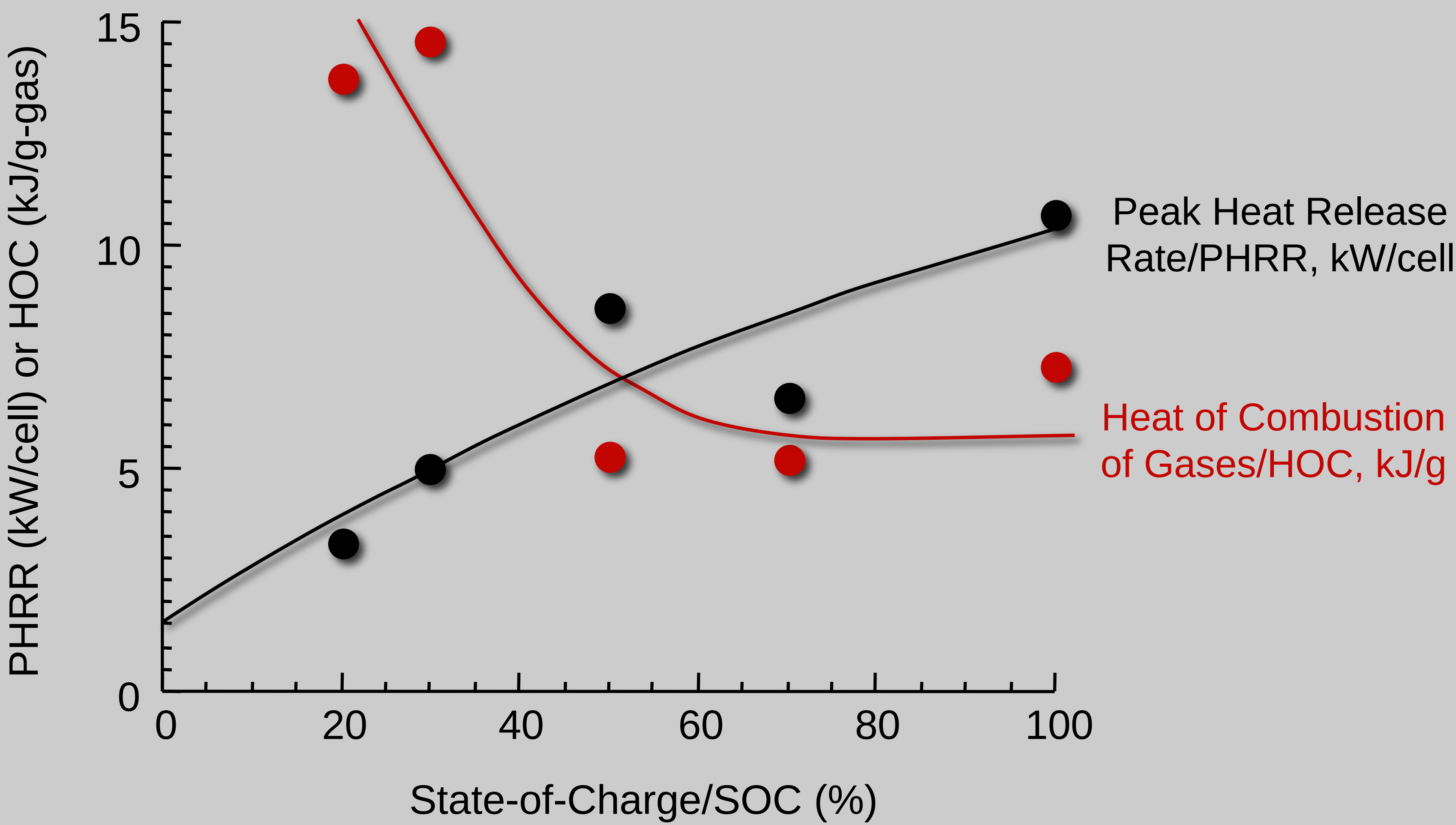
HRR corrected for response time of cone calorimeter



Mass Loss of 18650 Cell in Fire Calorimeter Test

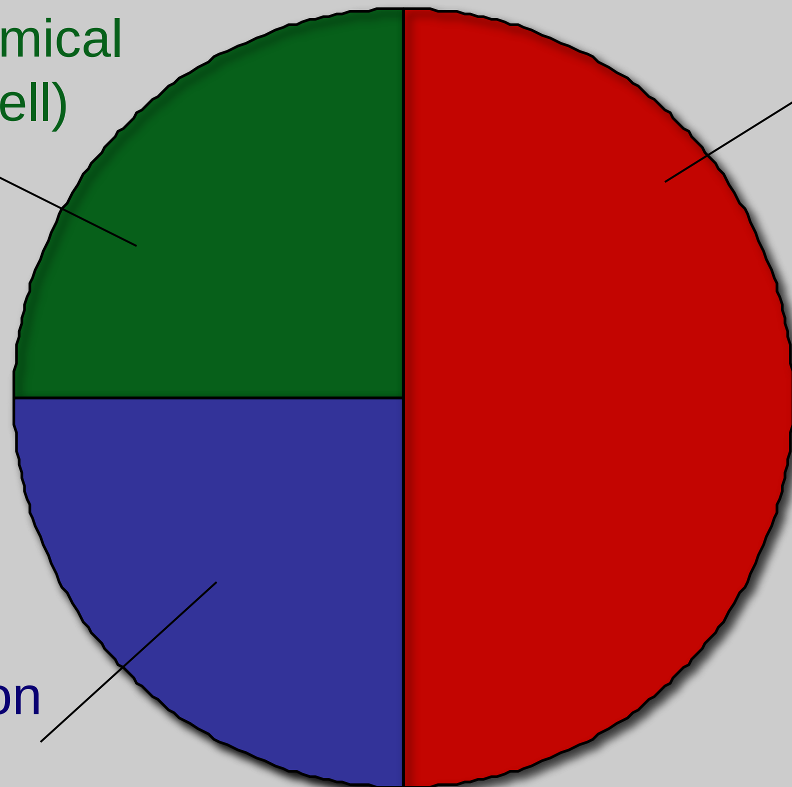


PHRR and HOC for $LiCoO_2$ 18650 Cell



Fire and Thermal Hazards of 18650 Cell

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

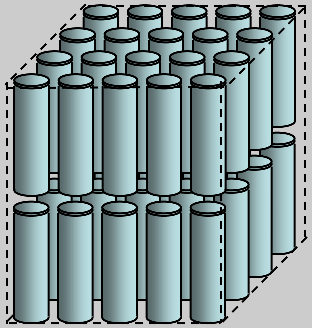


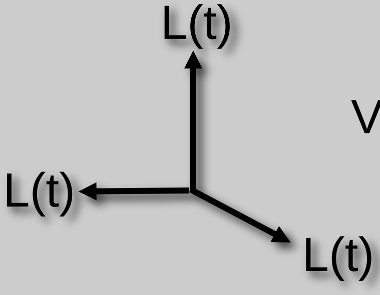
$$q_v = \frac{75 \text{ kJ/cell}}{6.62 \times 10^{-5} \text{ m}^3\text{/ cell}}$$

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

$LiCoO_2$ Cell at 50% SOC

Analytic Model of LIB 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

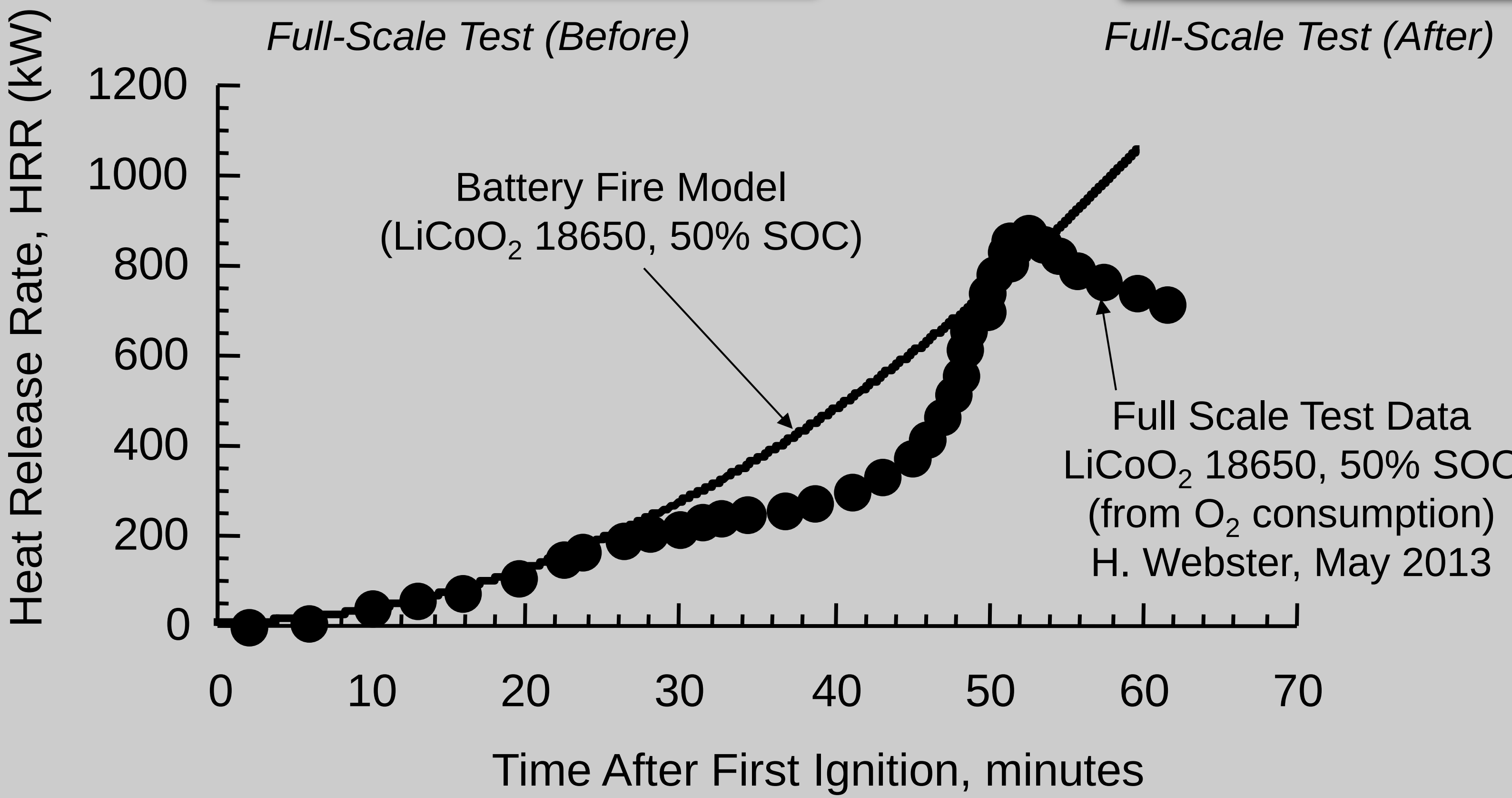
$$HRR(t) = q_v \frac{dV}{dt} = q_v \frac{dL(t)^3}{dt} = 3q_v (L_0')^3 t^2$$

Model Versus Full Scale Test Data

Full-Scale Test (Before)

Class E
Main Deck
Cargo

Full-Scale Test (After)



Summary

Thermal Energy Released at Cell Failure of 18650 LIBs (ΔU_{total}) is:

- Dependent on cell chemistry (voltage and capacity)
- Equal parts electrical (εQ) and chemical (ΔU_{rxn})
- Responsible for fire propagation
- Half of total fire hazard when combustion of contents is included combustion.