MEASURING STORED CHEMICAL ENERGY IN LITHIUM ION BATTERIES USING A BOMB CALORIMETER

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Objective

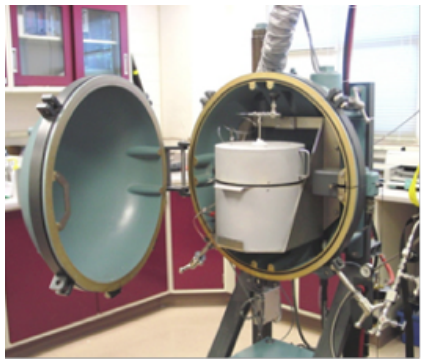
- **Characterize chemical energy released from batteries at different states of charge (SOC)**

Background

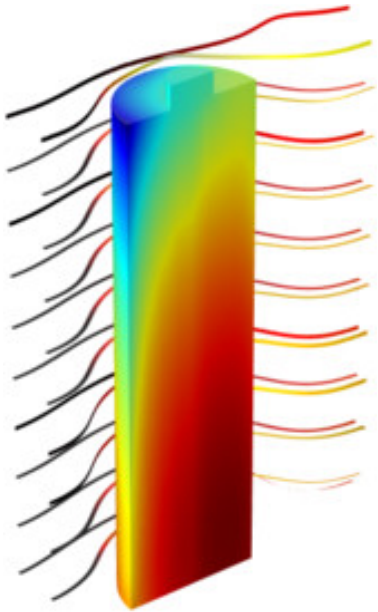
- 0ver 30 years of R&D on Li-ion batteries
- Increasing applications
  - More widely used
  - Higher energy densities

Car

- Experimental
  - Component studies
  - DSC, ARC devices



- Modeling of Runaway
  - Up to 6 decomposition reactions
  - CFD thermo-chem-electrical analyses



Background

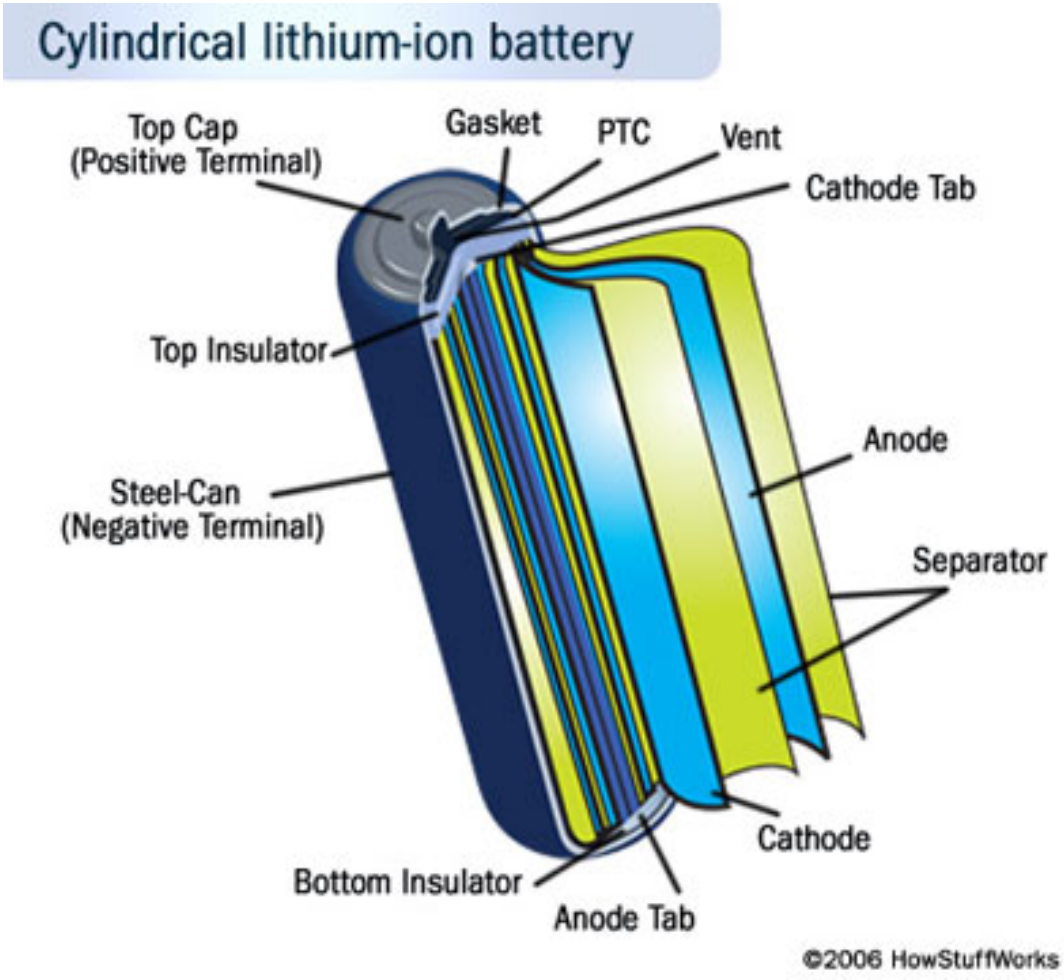
- A fire erupted in a cargo plane that landed in Philadelphia on Feb. 7, 2006.

- A cargo plane with 81,000 lithium batteries caught fire and crashed after it left Dubai on Sept. 3, 2010.

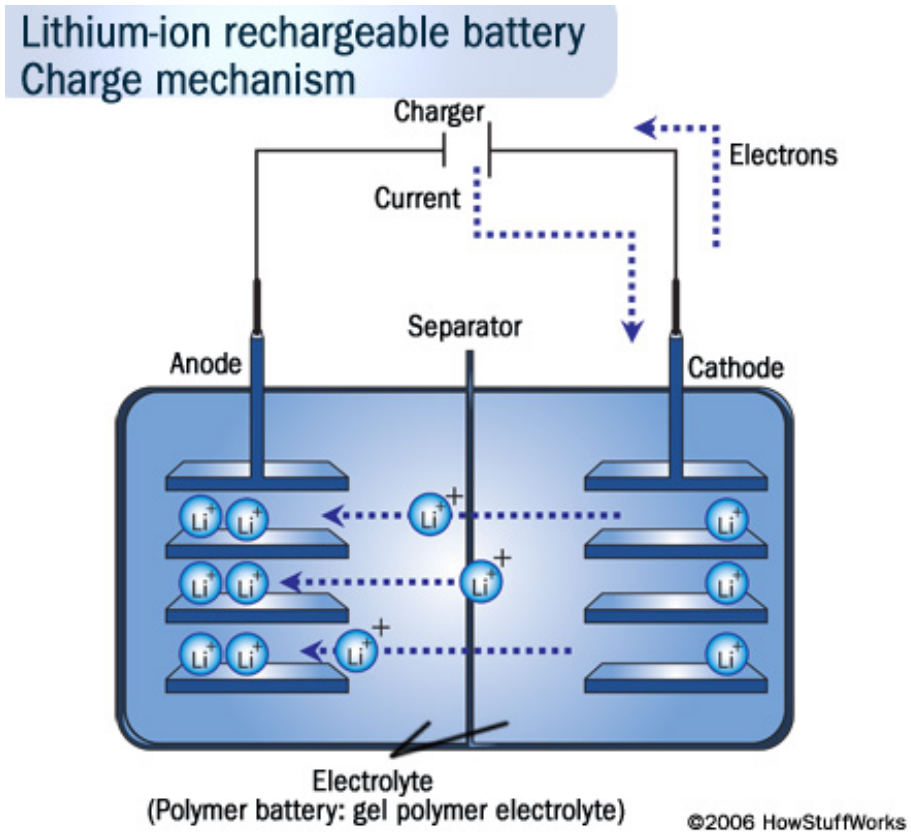
- A cargo jet crashed into the East China Sea on July 28, 2011, after the crew reported a fire on board.

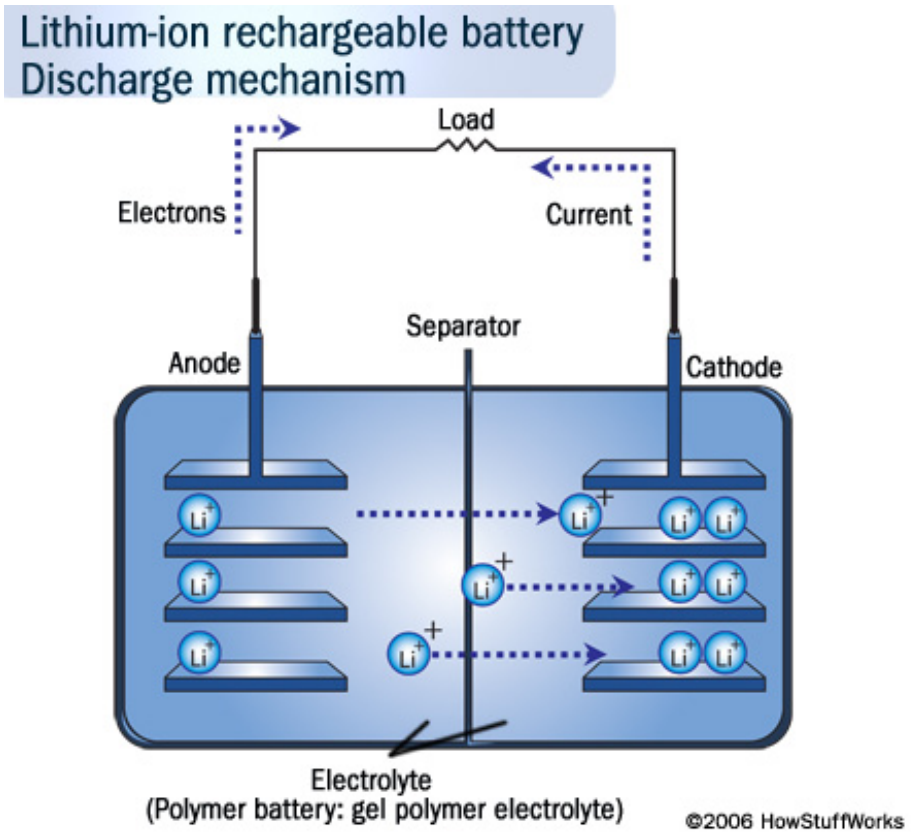
Typical Li Ion Battery

- 18650: 18 mm diameter, 65 mm length
- ~ 44 g
- Anode
  - Carbon, Copper
- Cathode
  - $LiCoO_2$, aluminum
- Separator
  - PE or PP membrane
  - Regulates ion flow
- Electrolyte
  - Organic, combustible



Li Ion Battery Mechanisms





Process can be cycled hundreds of times with little to no cell deterioration

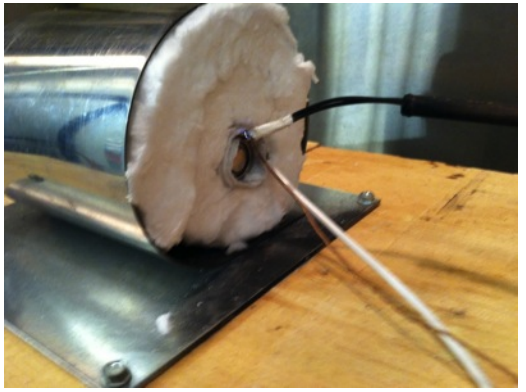
Causes of Thermal Runaway

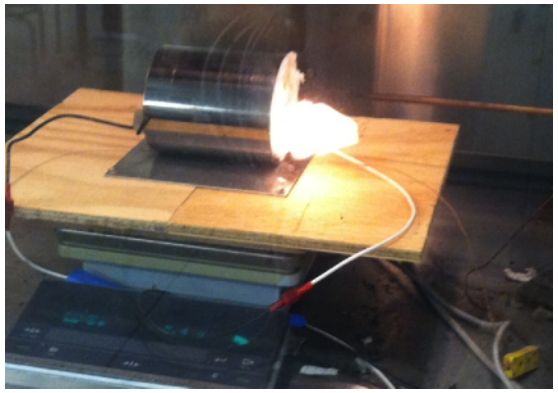
- **Thermal**
  - **Critical temperature triggers**
    - **Due to heat source**
      - **Separator melts**
- **Mechanical**
  - **Physical damage**
    - **Li dendrite grows to cause short**
- **Electrical**
  - **Overcharge**
  - **Rapid discharge**

All lead to temperature increase and acceleration of chemical decomposition

Previous Thermal Runaway Energy Experiments at FAA on 18650 Li-Ion Battery

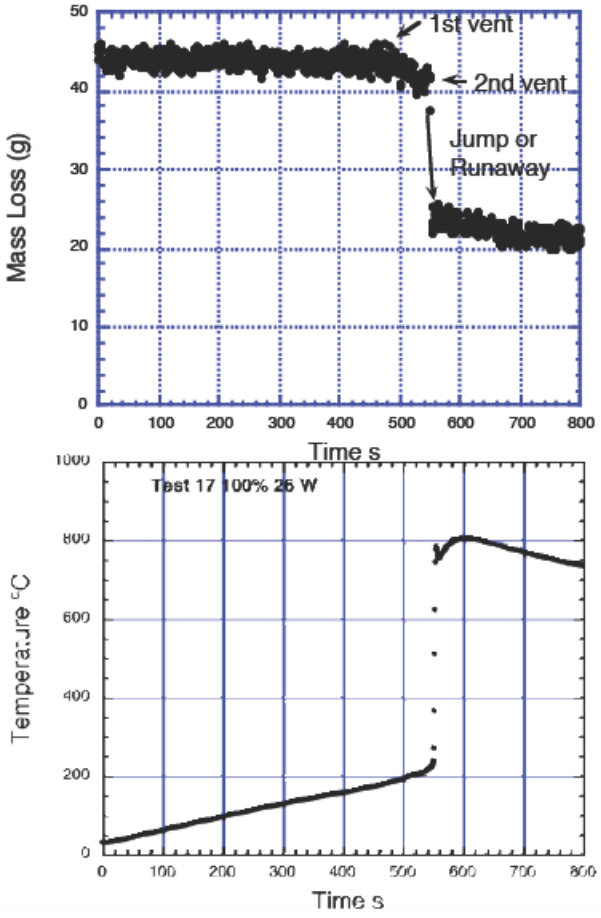
- **Calorimeter with known heat input built**
- **18650 characteristics**
  - **2.6 Ah @ 3.7 V or 34.6 kJ of electric power available**
  - **Separator softens at 130ºC and melts > 150ºC**
  - **PRV @ ~ 200 psi: white vapor emitted**
  - **~ 250 ºC onset of runaway, jump to ~ 800ºC in seconds**
  - **Gases emitted: CO_2, CO, H_2, CH_4, other HC**
  - **Solids emitted: Cu, Graphite, Molten Al**
- **Chemical – Electrical mechanisms not discerned**

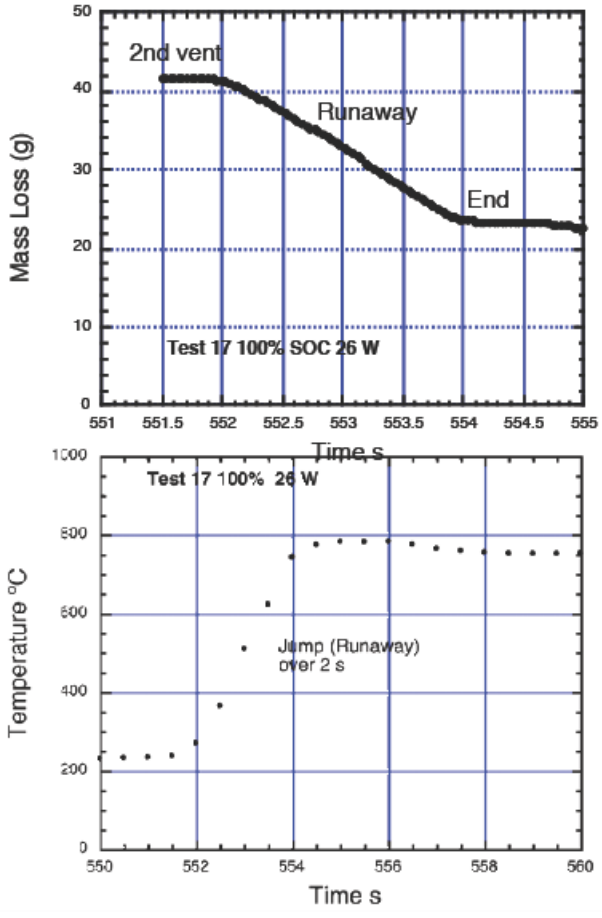




- J.G. Quintiere & S.B. Crowley, Thermal Dynamics of 18650 Li-ion Batteries, The Seventh Triennial International Fire & Cabin Safety Research Conference, Philadelphia, PA, 2013.

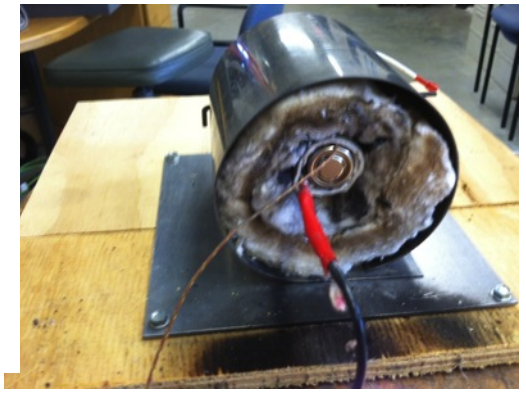
Typical Battery Thermal Runaway 100% SOC





1st vent @ 470 s
Lose ~ 2 - 3 g
~ 200 °C

2nd vent @ 552 s
Runaway ~ 2 s
Lose ~ 17 g
T: ~ 250 °C to ~ 800 °C



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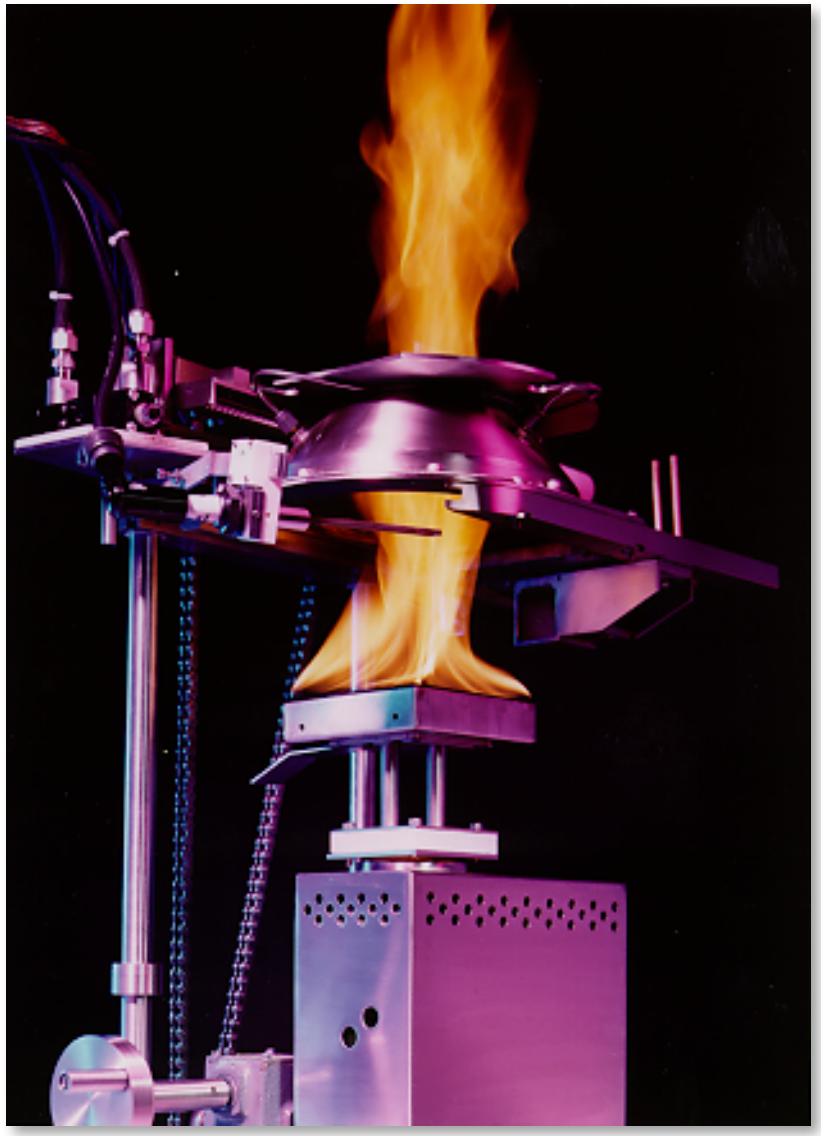
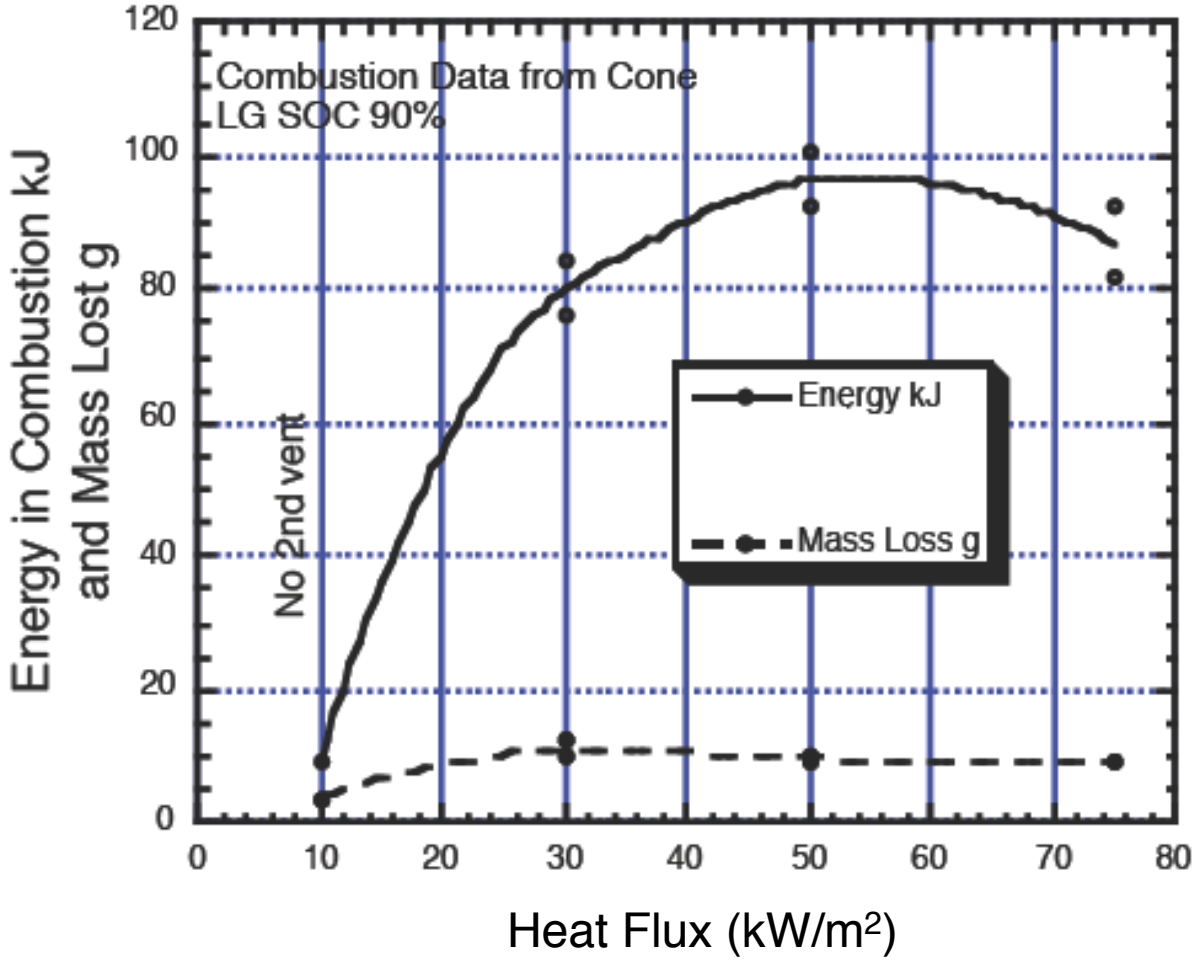
Cone Calorimeter

- **ASTM E1354**
  - **Flaming combustion test that measures heat release by O_2 consumption calorimetry.**
  - **Peak HRR**
  - **Total HR**
  - **Mass Loss Rate**
  - **Time to Ignition**
  - **Time to Peak**



Cone Calorimeter 90% SOC - Varying Heat Flux

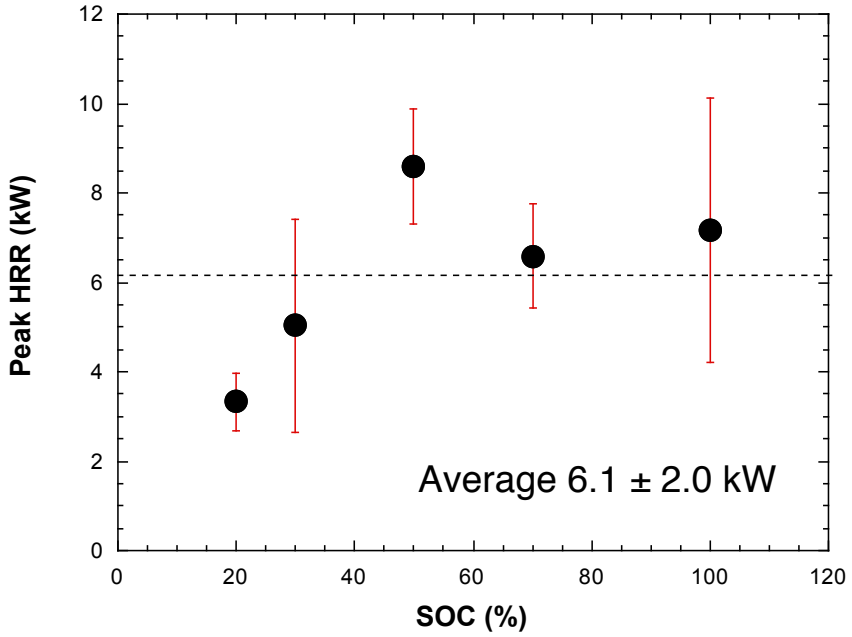


Total heat release and mass lost independent of heat flux

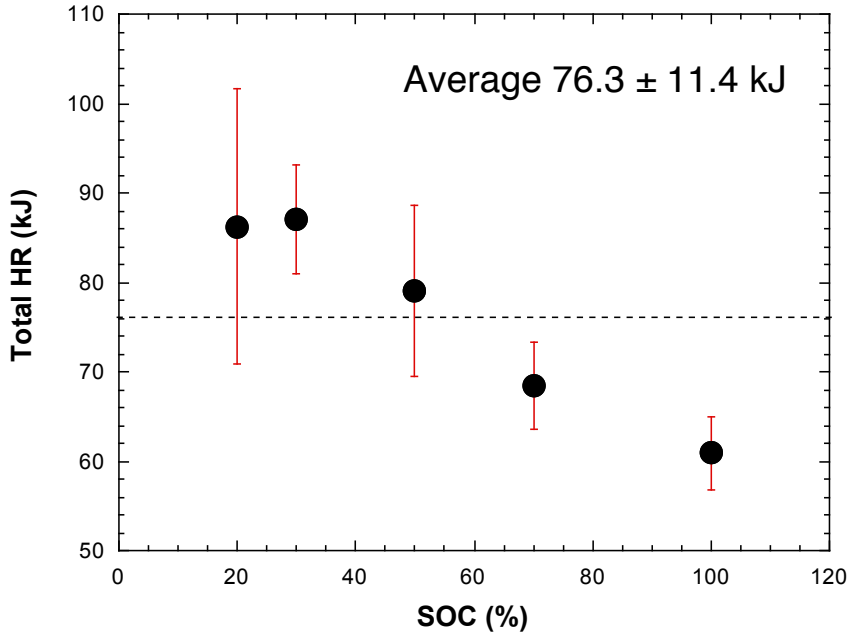
- J.G. Quintiere & S.B. Crowley, Thermal Dynamics of 18650 Li-ion Batteries, The Seventh Triennial International Fire & Cabin Safety Research Conference, Philadelphia, PA, 2013.

Cone Calorimeter 50 kW/m² - Varying SOC

Peak HRR



Total HR



- **Peak and total heat release independent of SOC**
- **Combustion products evolved do not change**
- **Chemical heat release not detected in cone calorimeter**

18650 Li-Ion Batteries Tested at FAA

3.7 V Li-Ion Batteries

- Range of Capacities

- **Samsung** **1500 mAh**
- **Tenergy** **2600 mAh**
- **Panasonic** **3400 mAh**
- **UltraFire** **5000 mAh**

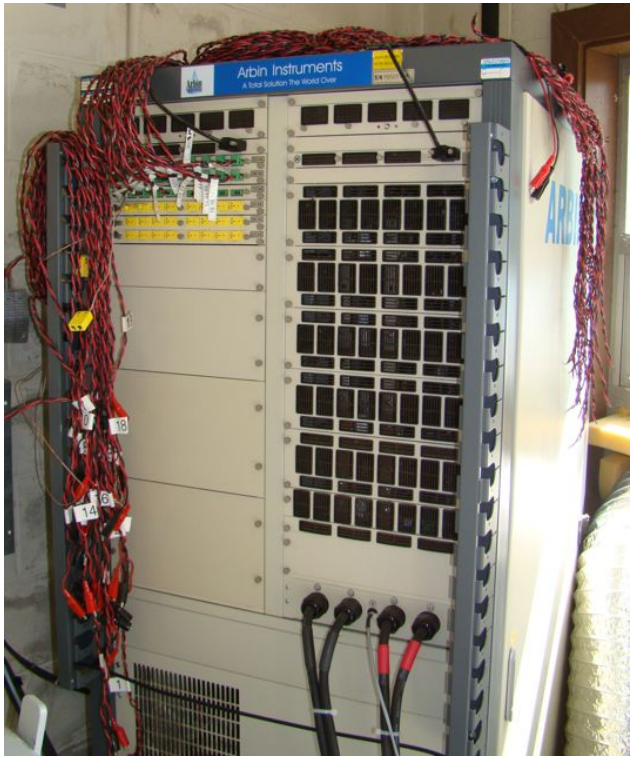
(~1000 mAh Actual)

Big Battery Charger

Arbin Systems BT2000

- **Voltage Range of 10-100V**
- **Max Charge / Discharge Current 400A**
- **Individual Cell Monitoring Capabilities**

Used at FAA for charging up to 400 18650 batteries at a time

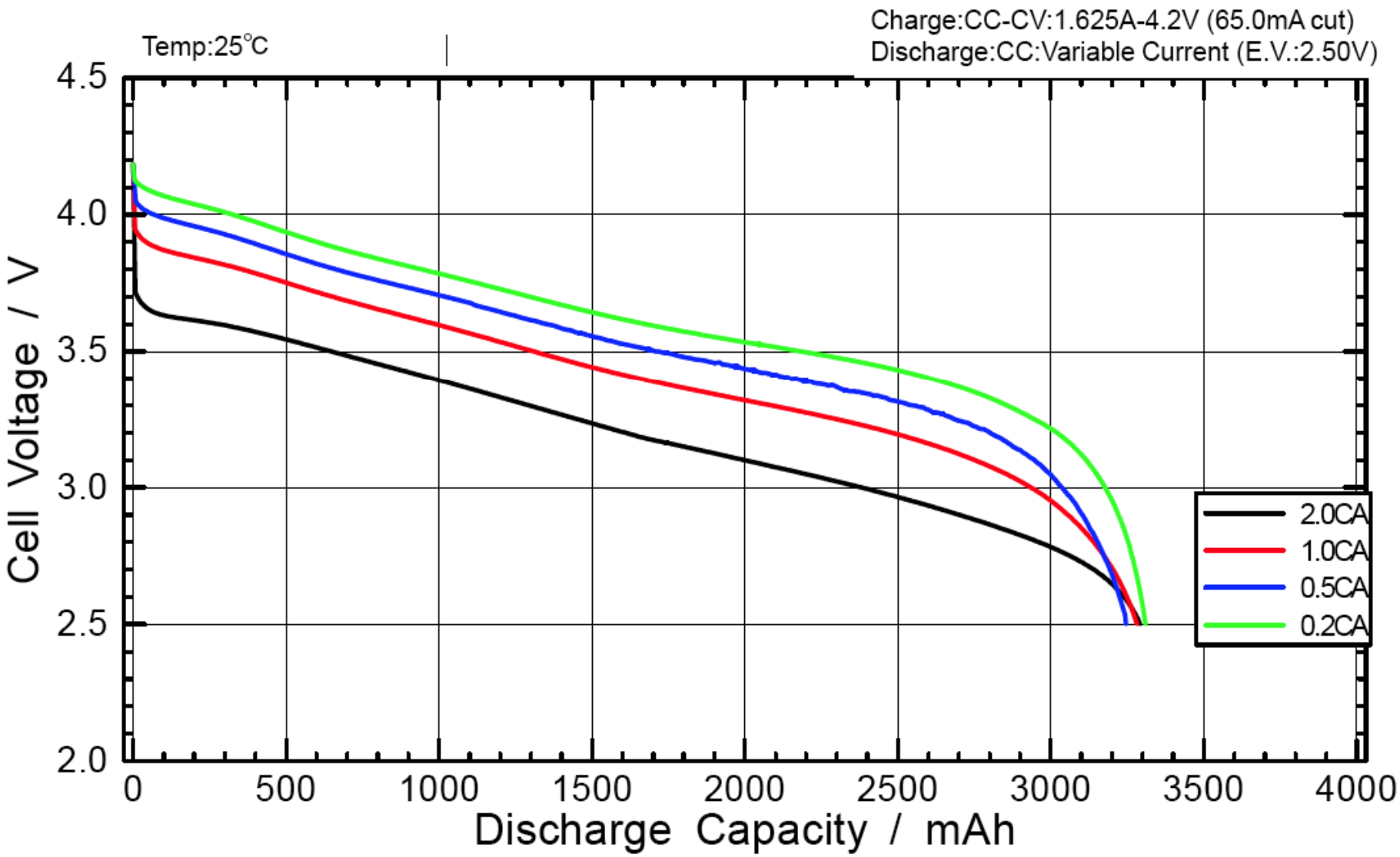


Little Battery Charger

- **HiTec X4AC**
  - **Charge / Discharge 4 batteries at a time individually**
  - **Records charge / discharge capacity**
  - **Programmable for different states of charge**

Battery Capacities

Discharge Rate Characteristics for NCR18650B

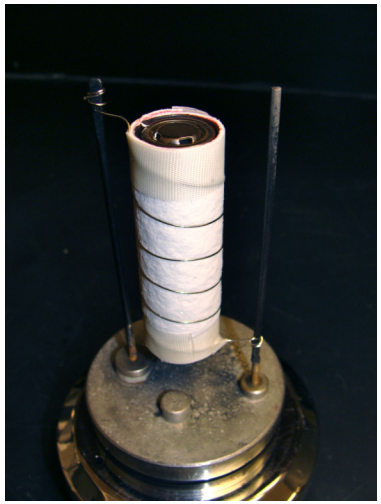


Bomb Calorimeter

Parr Instruments Model 1341 Plain Jacket Oxygen Bomb Calorimeter

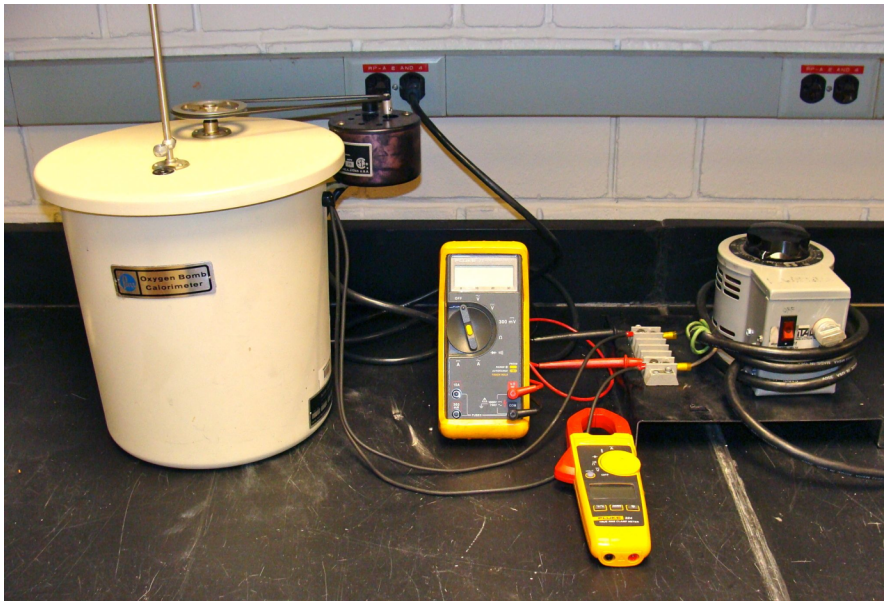
Voltage and current applied to force thermal runaway was the same for all tests

Temperature data logged for all tests



Bomb and other components for 18650 battery tests

Experimental Setup



Chemical Energy Measurements

- **ASTM bomb calorimeter method was modified to measure chemical energy of battery exotherm during thermal runaway**
- **Battery heated in bomb purged with N_2 until thermal runaway occurred (usually @ 10 min)**
- **Energy release calculated from temperature rise of calibrated bomb**
- **Baseline test was run after battery test without disturbing contents to keep mass the same**
- **Chemical energy from reaction at different SOC measured**

Bomb Calibration

- **10 tests over 3 days with varying sample size**

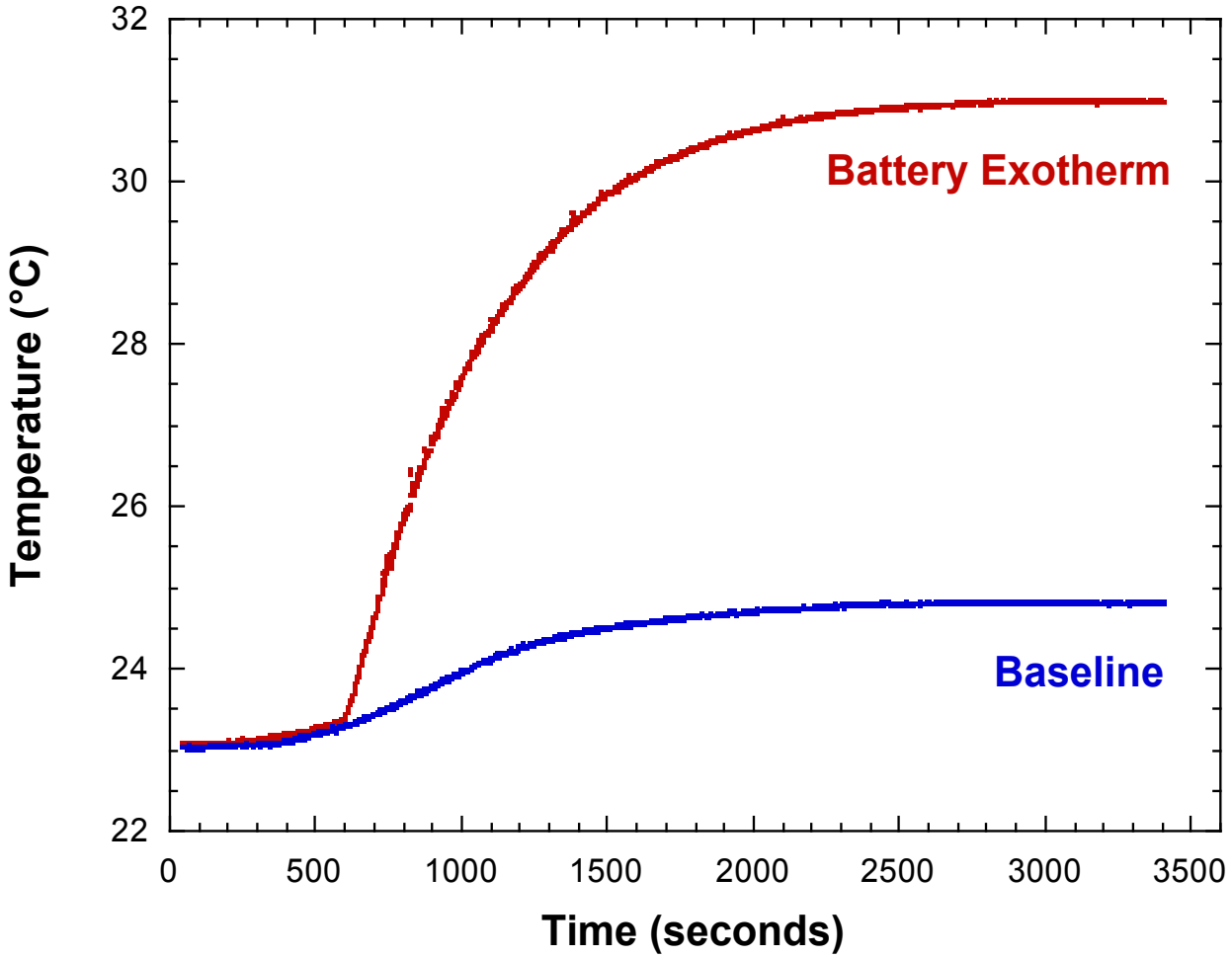
Bomb Calibration -10.285 kJ/°C

0.098903106

Benzoic Acid -26.453 kJ/g
Fuse Wire -5.863 kJ/g

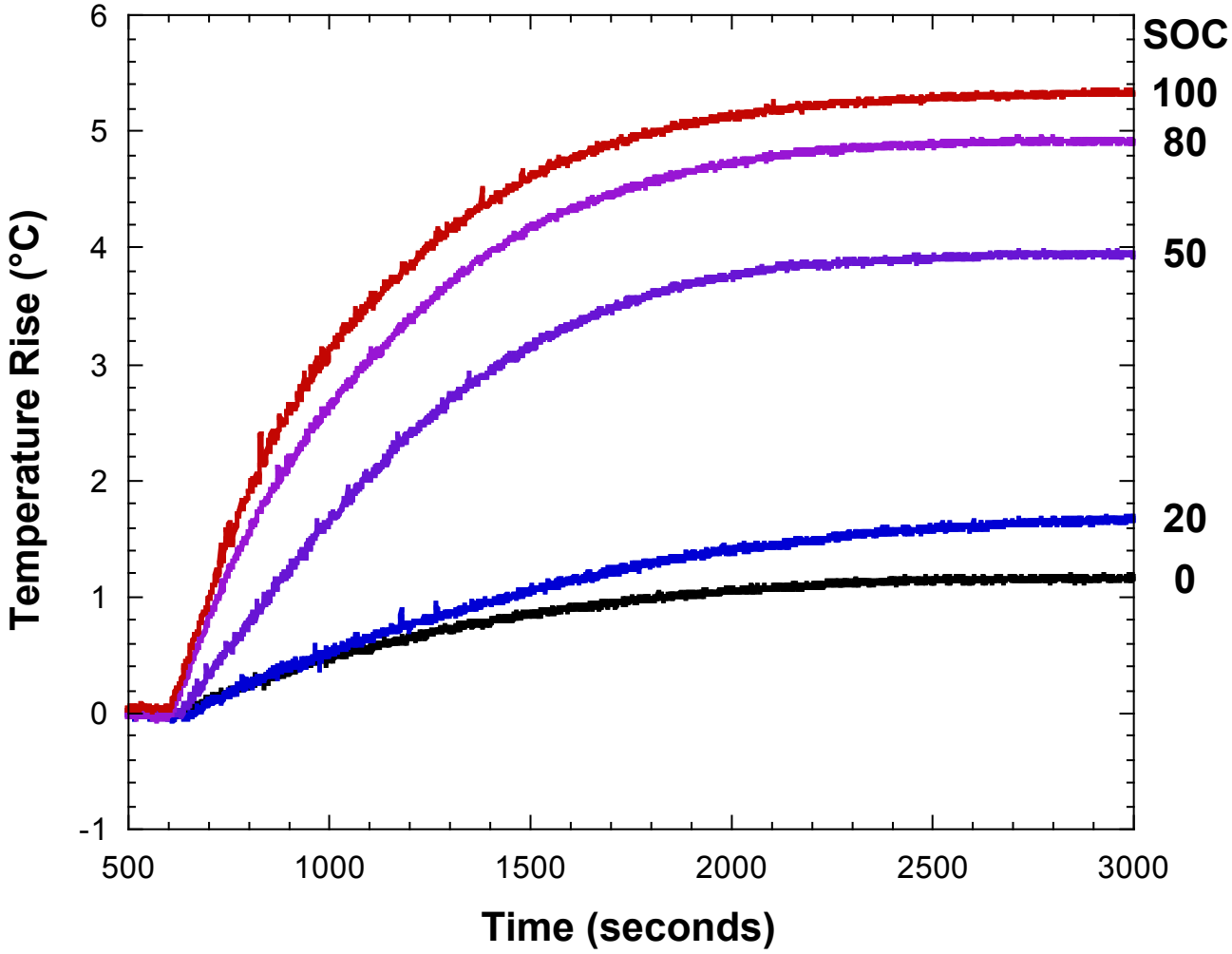
Test	Benzoic Acid (g)	Wire (g)	Remaining Wire (g)	T_0 (°C)	T_f (°C)	ΔT (°C)	E (kJ/°C)
1	0.966	0.0156	0.0076	22.37	24.85	2.48	-10.32278306
2	0.9728	0.0169	0.0067	22.77	25.3	2.53	-10.19497273
3	0.9913	0.0165	0.005	22.77	25.36	2.59	-10.15068857
5	1.5616	0.0159	0.0086	23.34	27.36	4.02	-10.28651858
6	1.0069	0.0158	0.0069	24.03	26.62	2.59	-10.30413375
7	1.5678	0.0164	0.0045	22.76	26.82	4.06	-10.23221259
8	1.3899	0.0154	0.0083	24.34	27.9	3.56	-10.33950899
9	0.999	0.0159	0.0089	23.98	26.5	2.52	-10.50301111
10	1.5028	0.0157	0.0073	22.39	26.29	3.9	-10.20585067
11	1.451	0.0159	0.0045	22.53	26.26	3.73	-10.30834885
4	1.3771	0.015	0.005	23.52	27.37	3.85	-9.477157481

Test Data from 100% SOC



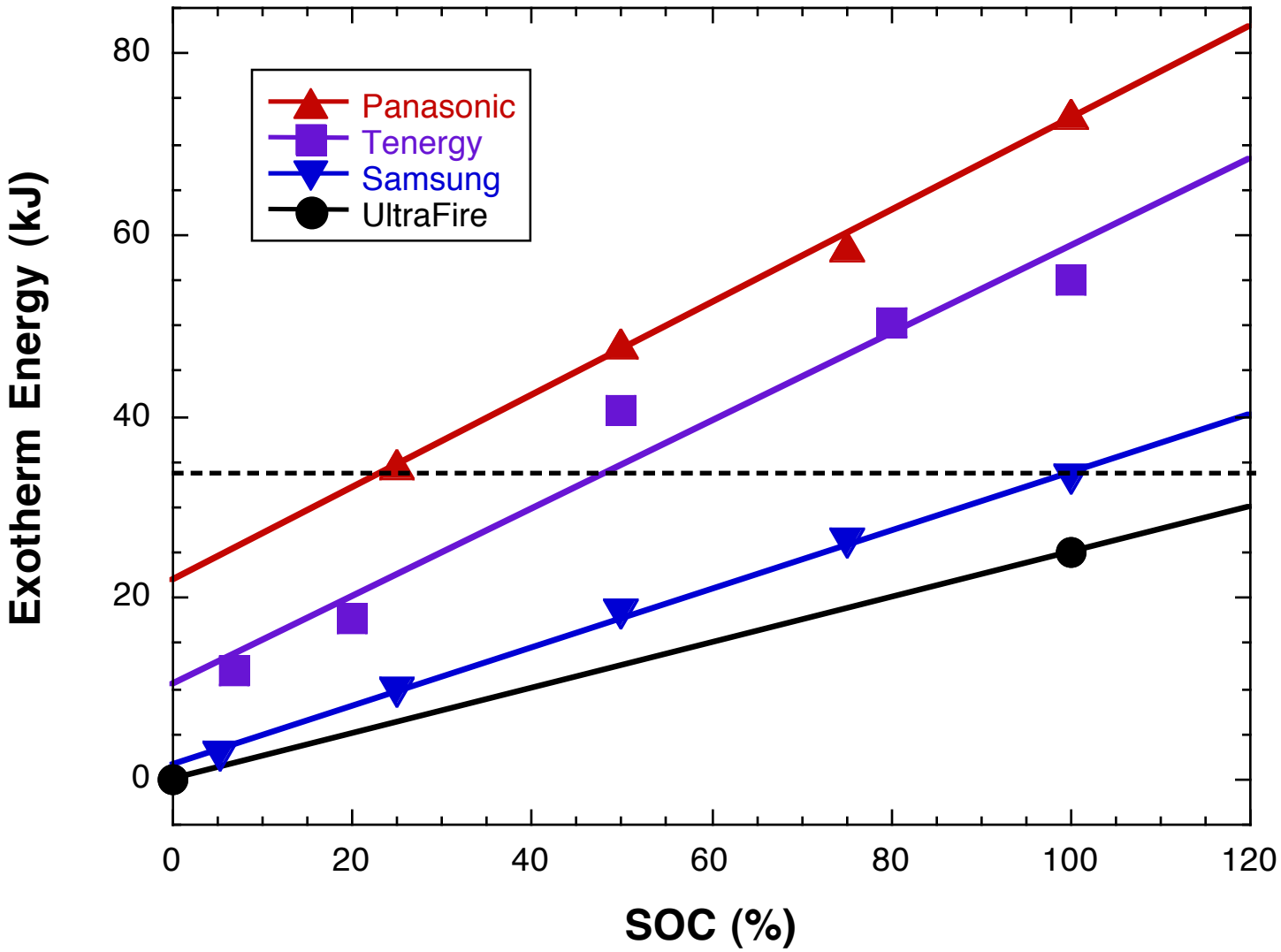
Baseline from heater subtracted from battery exotherm to get temperature rise from battery only

Temperature Rise In Bomb

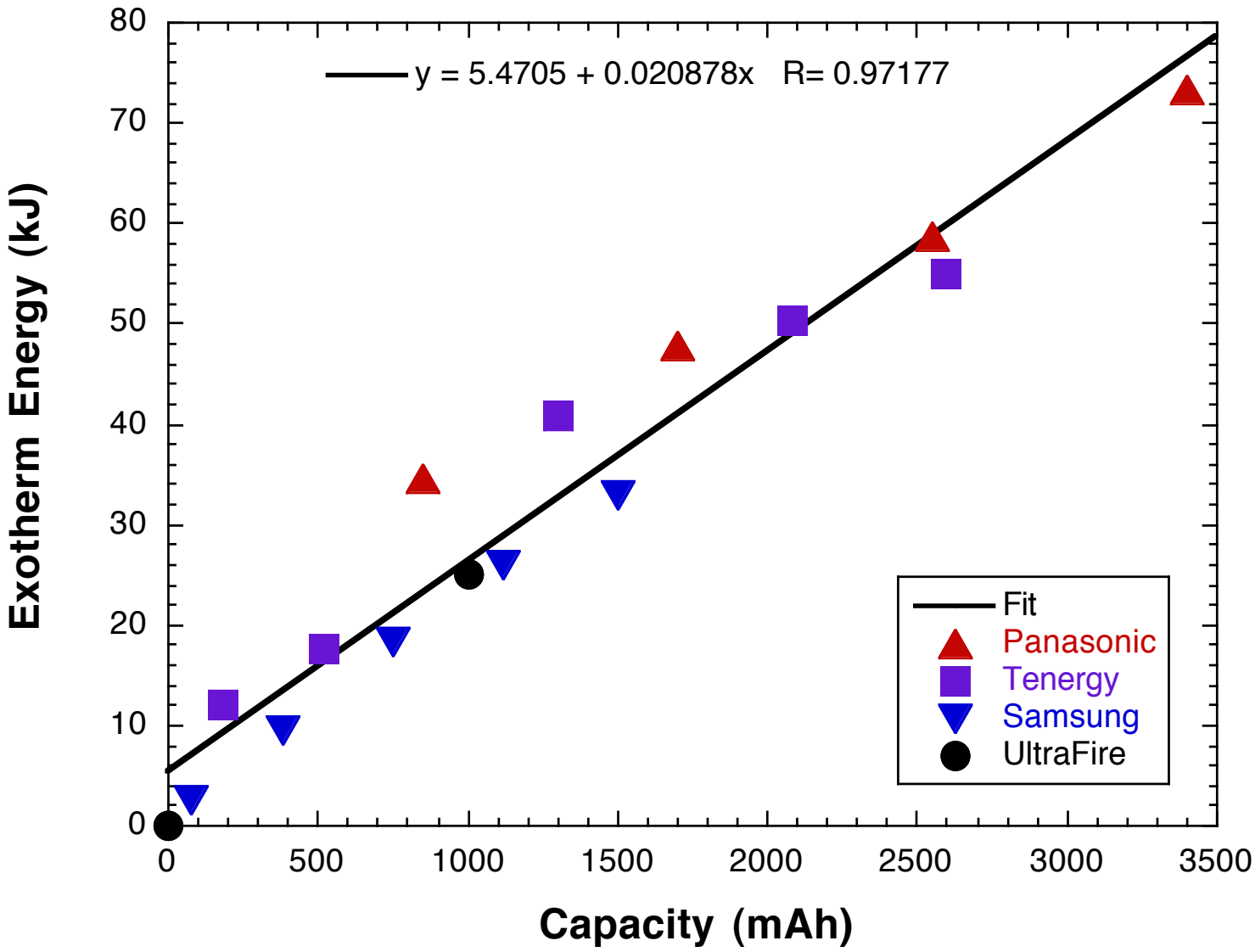


Baseline corrected temperature rise data

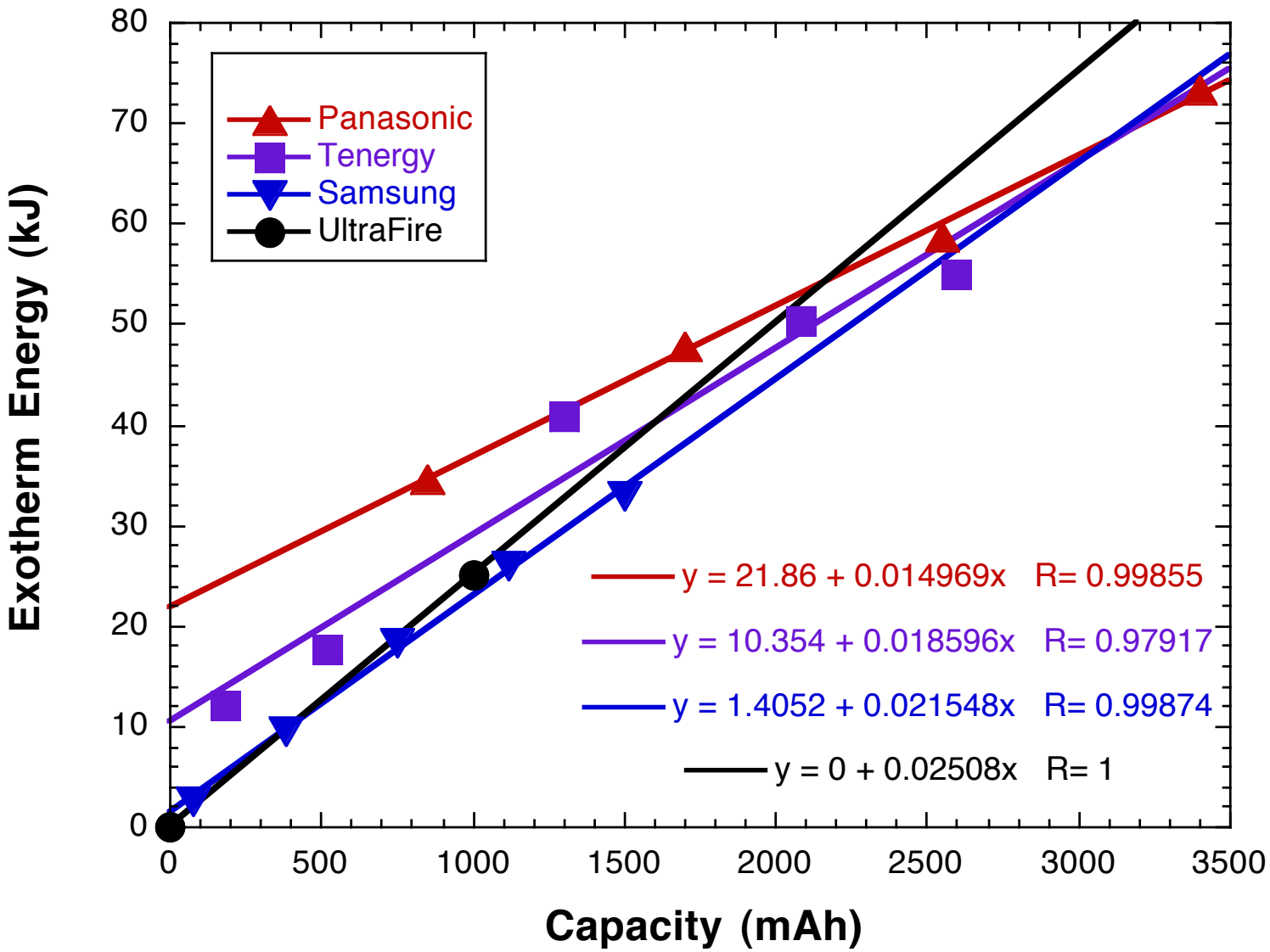
Chemical Exotherm Energy



Chemical Exotherm Energy



Chemical Exotherm Energy

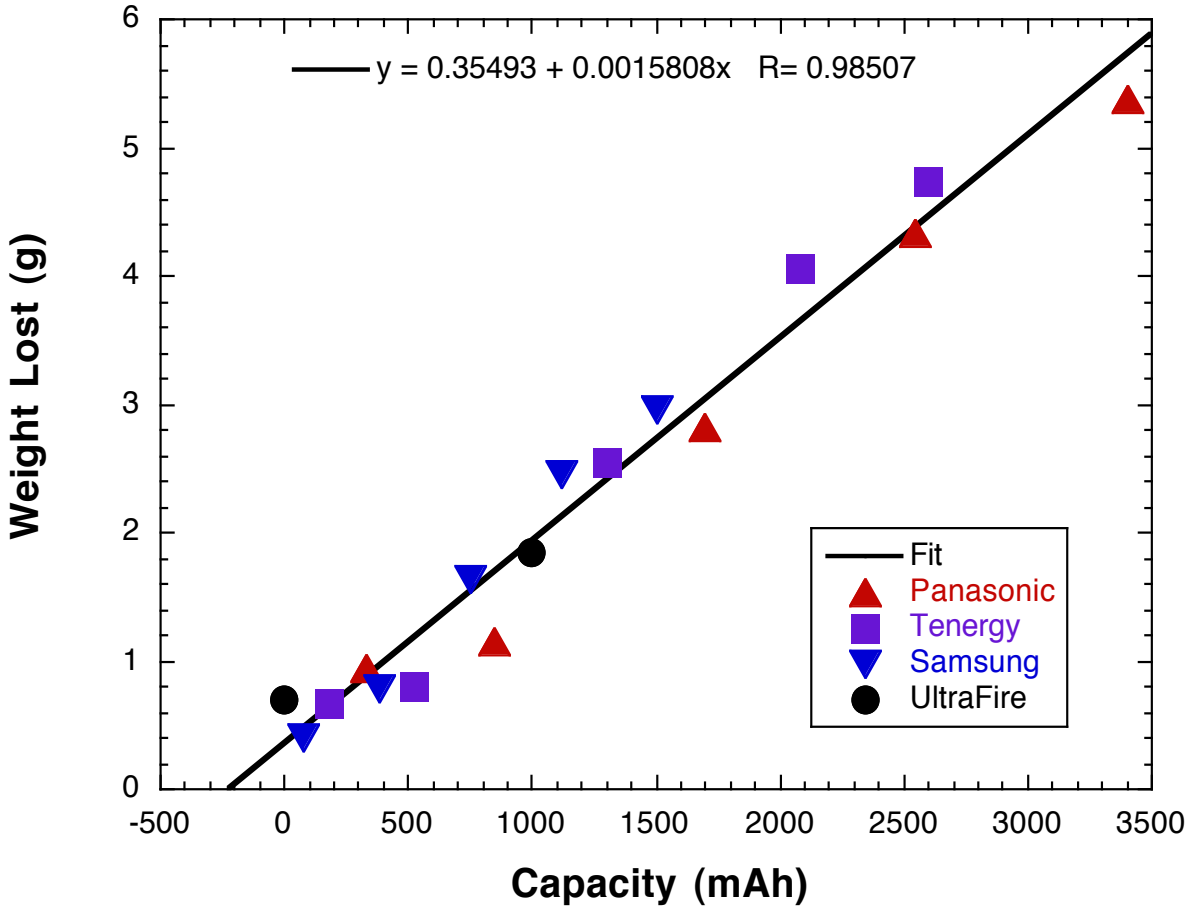


Li-Ion 18650 Batteries - Post Test

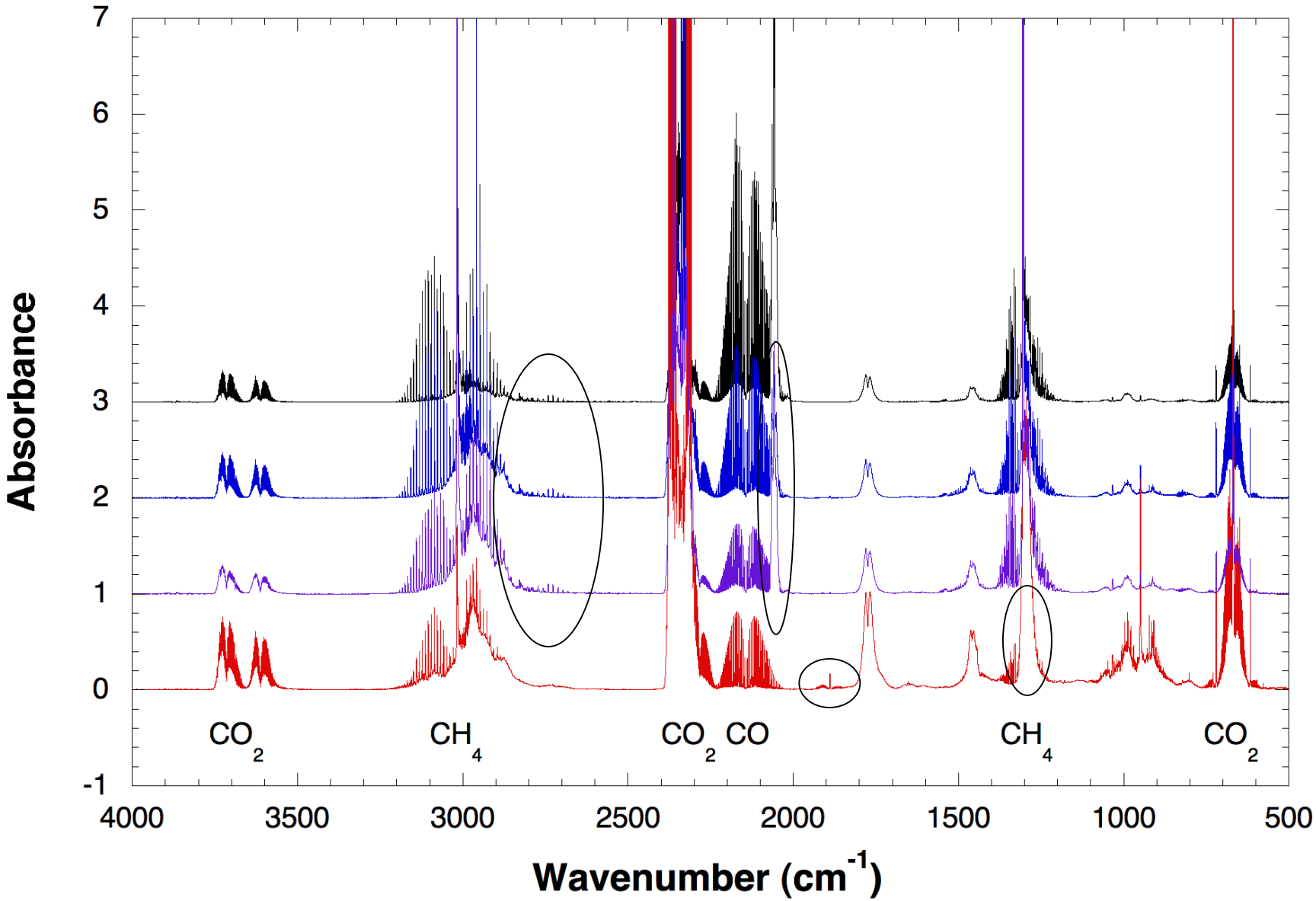
Discharged **50% Charged** **100% Charged**

Gravimetric Analysis

Weight lost per SOC



Infrared Gas Spectra



Findings

- **Bomb**
  - **Total amount of heat released from chemical reactions quantified**
  - **Exothermic runaway energy increases from 5 to 75 kJ with SOC**

- **In General**
  - **Runaway results most dependent on SOC**
  - **Combustion energy doesn't vary much with SOC and heat flux (Cone Calorimeter)**
  - **Temperatures of battery and exit debris increase from about 600 to 1000ºC with SOC**
  - **Duration of runaway ~ 2 s**
  - **Duration of flaming ~ 10 s**

Future Work

- GC of gases
- Interpret FTIR to identify other gaseous components
- Measure pressures generated in bomb
- Test more batteries at different states of charge
- Examine energy from combustion more closely
- Energy balance calculations (reversible - irreversible)
- Modeling work for safer transport of Li ion batteries

Acknowledgement

- **Thank you to Steve Summer and Tom Maloney, FAA, for supplying and charging some of the batteries**

- **Thank you to Dr. James Quintiere, UMD, for data and helpful discussions**