"Thermal Characterization Study of Lithium-Ion Cells"
By Doris Britton, Tom Miller and Bill Bennett

Abstract

The primary challenge in designing a full scale lithium-ion (Li-ion) battery system is safety under both normal operating as well as abusive conditions. The normal conditions involve expected charge/discharge cycles and it is known that heat evolves in batteries during those cycles. This is a major concern in the design for high power applications and careful thermal management is necessary to alleviate this concern. An emerging thermal measurement technology, such as the electrochemical calorimetric of batteries, will aid in the development of advanced, safe battery system. To support this technology, several "commercial-off-the-shelf" (COTS) Li-ion cells with different chemistries and designs are being evaluated for different cycling regimes at a given operating temperature. The Accelerated Rate Calorimeter (ARC)-Arbin cycler setup is used to measure the temperature, voltage, and current of the cells at different charge/discharge rates. Initial results demonstrated good cell cyclability. During the cycle testing, the cell exhibited an endothermic cooling in the initial part of the charge cycle. The discharge portion of the cycle is exothermic during the entire discharge period. The presence of an endothermic reaction indicates a significant entropy effect during the beginning of charge cycle. Further studies will be performed to understand the thermal characteristics of the Li-ion cells at the different operating conditions. The effects on the thermal response on cell aging and states-of-charge will also be identified.

Thermal Characterization Study of Lithium-Ion Cells

by

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Characterization of Lithium-ion Cells
Objective & Approach

- Objectives:
    - Apply calorimetry techniques to assess Li ion safe operating conditions.
    - Quantify self-heating rate and temperature limits
    - Investigate new cathode and electrolyte interactions
    - Ascertain failure modes.
    - Understanding of life-limiting mechanisms of Li-ion cells during various electrochemical conditions.

- Approaches:
    - Reproduce published results of commercial off-the-shelf (COTS) cells and components (cathode and electrolyte)
    - Generate data for the next generation materials (high specific energy cathodes, next generation electrolytes, and nanocomposite anodes).
    - Observe cell and component response to thermal and overcharge abuse conditions.

Thermal Analysis Techniques

- Accelerating Rate Calorimeter (ARC) -Thermal Hazards Technology (UK)
  - Adiabatic temperature conditions
  - Measures heat, gas and Onset of Thermal Runaway (OTR)
- Battery Cycler - Arbin Instruments (Texas)
  - Performs battery/cell cycling and measures cell voltage and temperature

The blast enclosure and control rack of the ARC and the Arbin cycler

Part I – Li ion Components

- **Components**
  - Cathode
    - Transition metal (Li) – Ni, Mn, Co
    - Phosphate cathodes
  - Electrolyte
    - Standard - 1M $LiPF_6$ in 1:1 EC:DMC
    - Baseline – 1 M $LiPF_6$ in 1:1:1:3 EC:DEC:DMC:EMC
    - Low Temperature
    - Non-flammable
    - Ester-based
  - Anode
    - New generation carbon or graphite

Thermal Stability of Li ion components

- **Materials studied so far:**
  - Electrolyte:
    - 1M $LiPF_6$ in 1:1 EC:DMC

- **Instrument Used:**
  - ARC = adiabatic calorimeter
  - Test sample holder material = Titanium, 0.8 mm wall diam, 8 g
  - Thermocouple = to measure variation in temperature.

New Ti bomb

Annealed Ti bomb
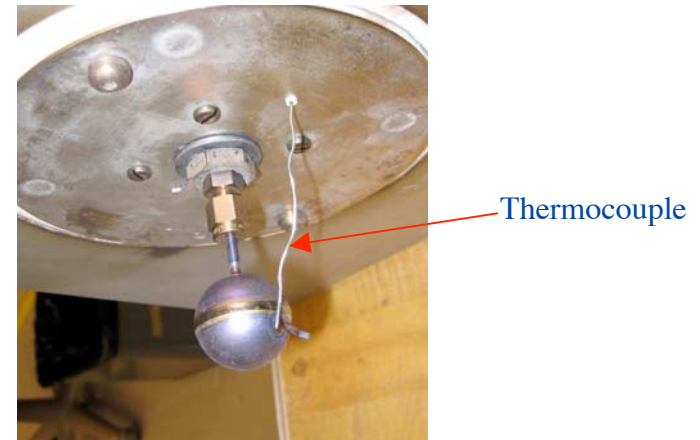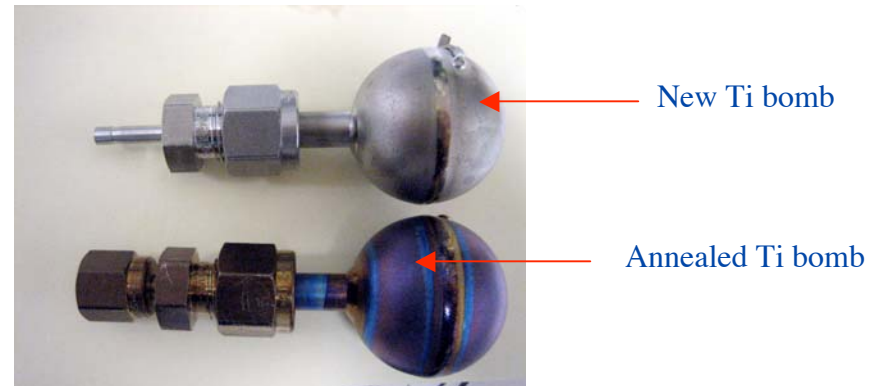
Thermocouple

Sample bomb suspended from the top of the ARC.

Thermal Stability of Li-ion
Procedure

- Measured sample loaded to the Ti bomb
- Thermocouple attached to the bomb to measure variation in temperature
- Controller is programmed to increase the calorimeter's temperature via a predetermined profile.
- Sample temperature increases due to convection and conduction
- If the sample undergoes chemical reactions that generate heat, the sample temperature will rise
- If the self-heating is greater than the threshold level, the ARC proceeds into the exotherm mode
- Self-heating follows until the rate falls below the detection limit or until the end point temperature is reached.
- Adiabatic self-heating rate of the sample is measured as a function of time and temperature.

Temperature & Pressure Profiles
($1 M LiPF_6$ in 1:1 EC:DMC)
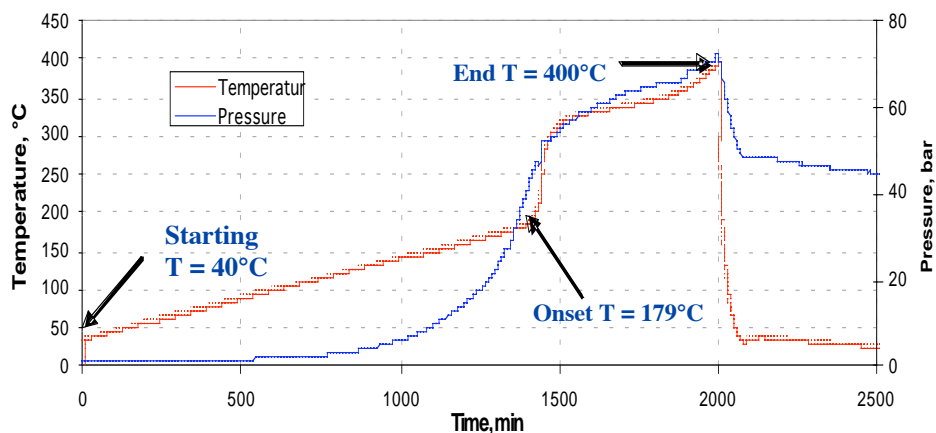
Temperature/Pressure-Time Profile

Starting T = 40°C

End T = 400°C

Onset T = 179°C

Self-heat & Pressure rate profile

T = 266.5°C with max. SHR = 6.95°C/min

Onset T = 179°C at 0.069°C/min
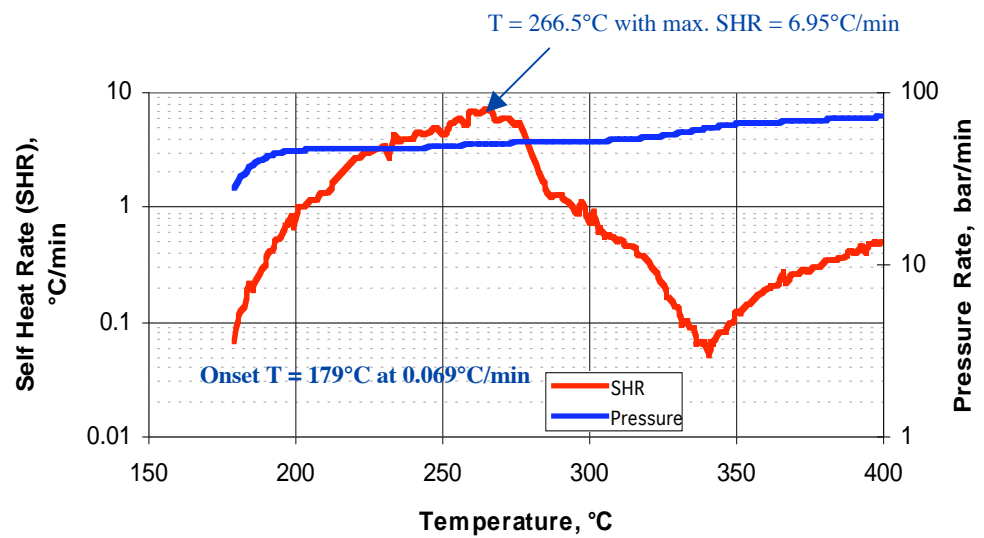
-Sample weight = 2.7 g

-Temp = 40 to 400°C

-Temp step = 5°C; wait time = 15 min

-Sensitivity threshold rate= 0.020 °C/min

Part II - Lithium-ion cells

- Li ion cells
  - COTS 18650 cell
  - Experimental cells
  - Prototype cells with advanced components
  - Other cells

- Electrochemical and thermal profile of Li-ion cells
  - Different charge/discharge cycles

- Thermal profile and runaway of Li ion cells
  - Different depths-of-discharge (DOD) = 20, 40, & 60%
  - Different states-of-charge (SOC) = 0, 25, 50, 75, & 100%

Effect of charging and discharging on thermal stability of Panasonic 18650 Li ion cell
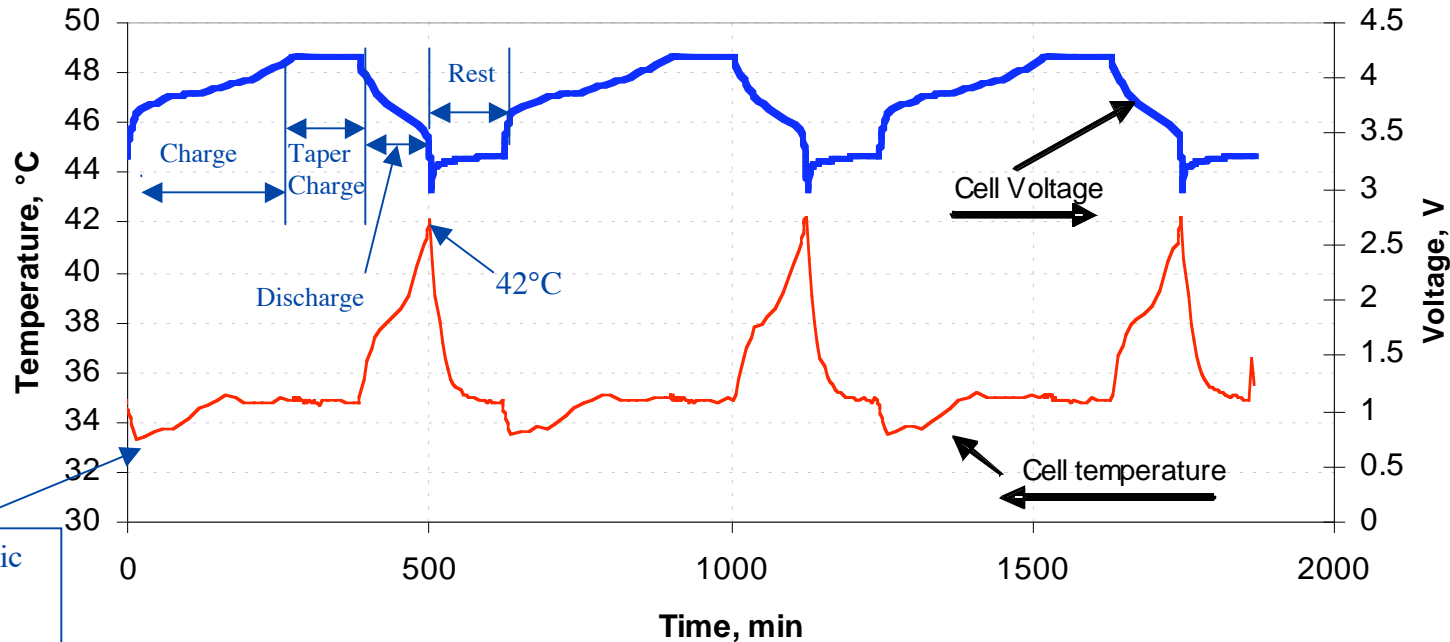
Cycling conditions

- Charge @ C/5 rate to 4.2V

- Taper charge C/50 current or 8 hours

- Discharge @ C/2 to 3.0V

- Rest for 2 hours

ARC conditions

- Isothermal mode

- Start T = 35°C (kept at that temperature until cycling is terminated)

- Temperature rate sensitivity = 0.1 °C/min

Temperature during first charge/discharge cycle
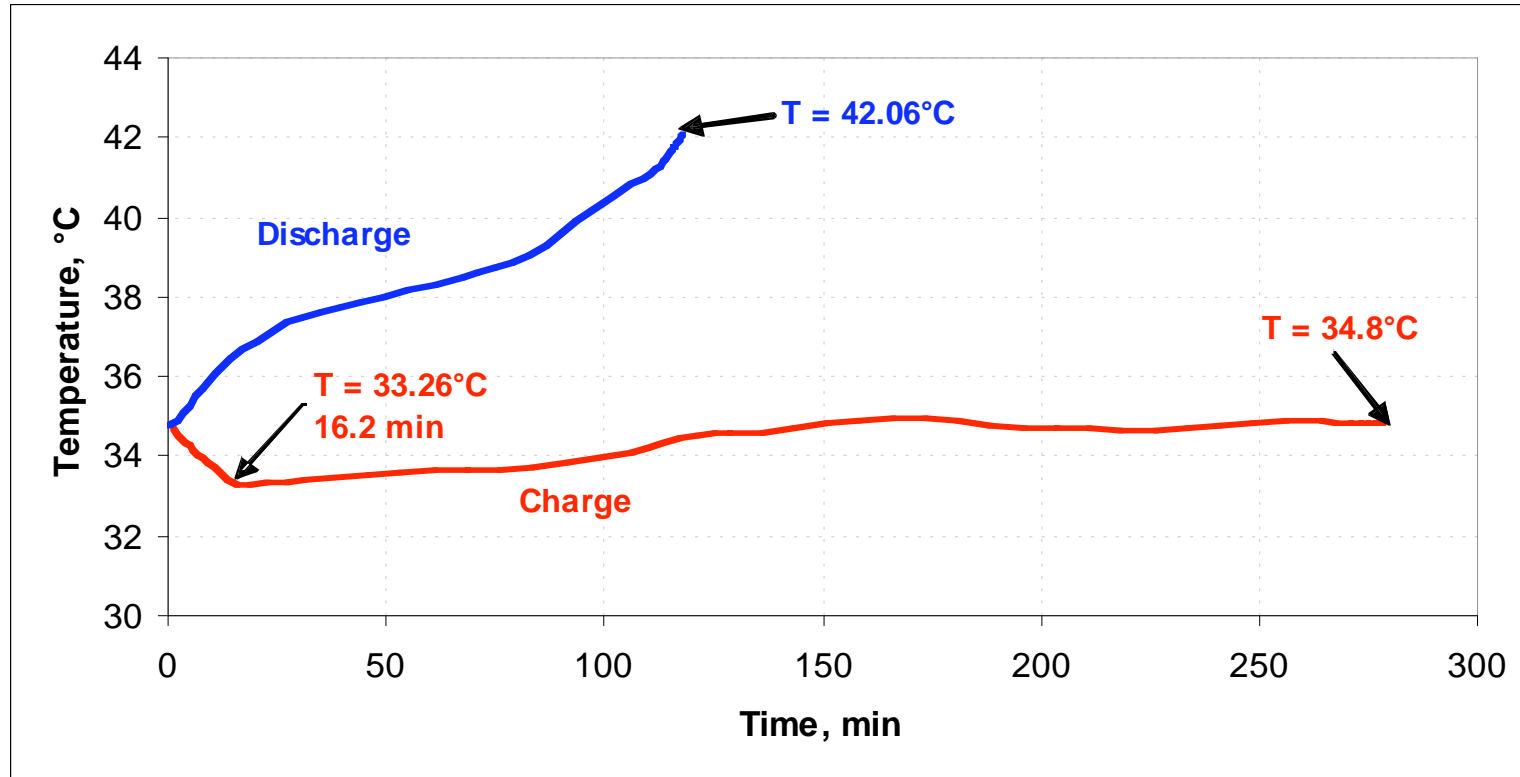
Temperature profiles of 18650 cell as a function of DOD (LEO cycling regime)

20% DOD
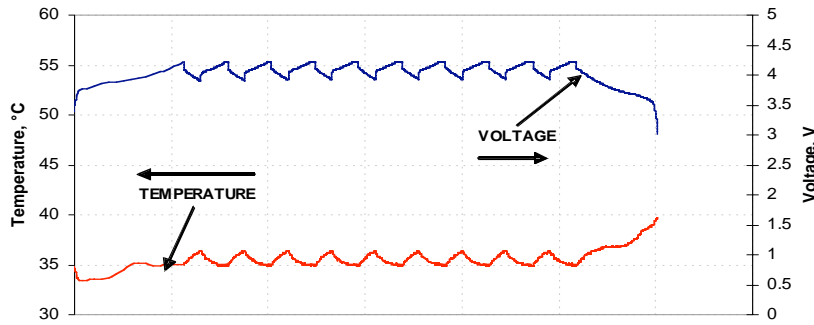
40% DOD
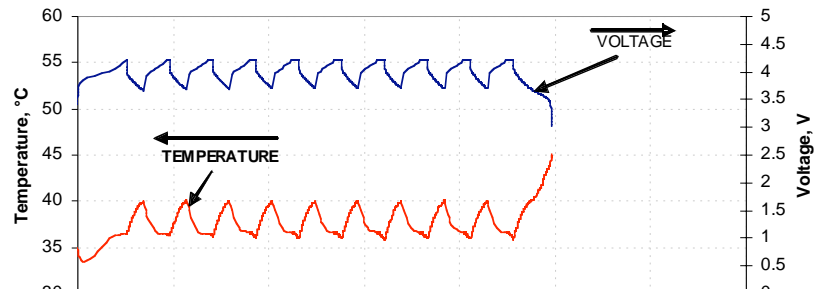
60% DOD
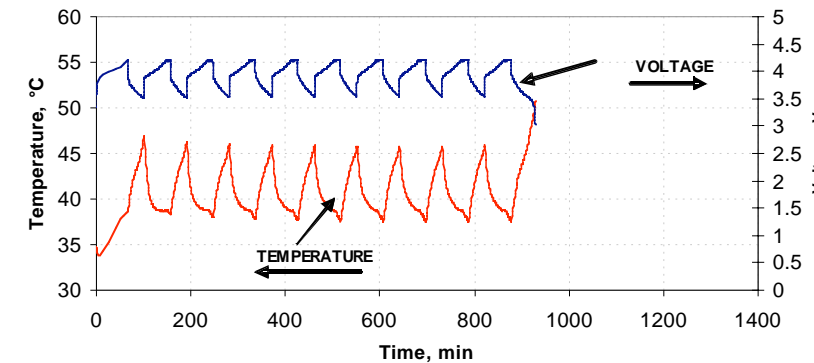
Operating Temperature = 35°C

- Net cooling effect during charge

33°C at beginning of charge

-Highly exothermic effect during discharge (LEO regime)

20% DOD = 36°C

40% DOD = 40°C

60% DOD = 46°C

**Significant temperature rise at increasing DOD.**

Thermal Runaway of Li ion cell

- Thermal testing of cell to determine the self heating thermal runaway of the cells under different conditions.

- ARC conditions:
  - Temperature = 35 to 160°C
  - Temperature rate sensitivity = 0.020 °C/min
  - Temperature step = 5.0°C

- Different conditions:
  - 0%, 50%, 75%, 100% SOC
  - Different aging conditions (temperature & days in OC)

- Arbin cycler monitors cell temperature & voltage
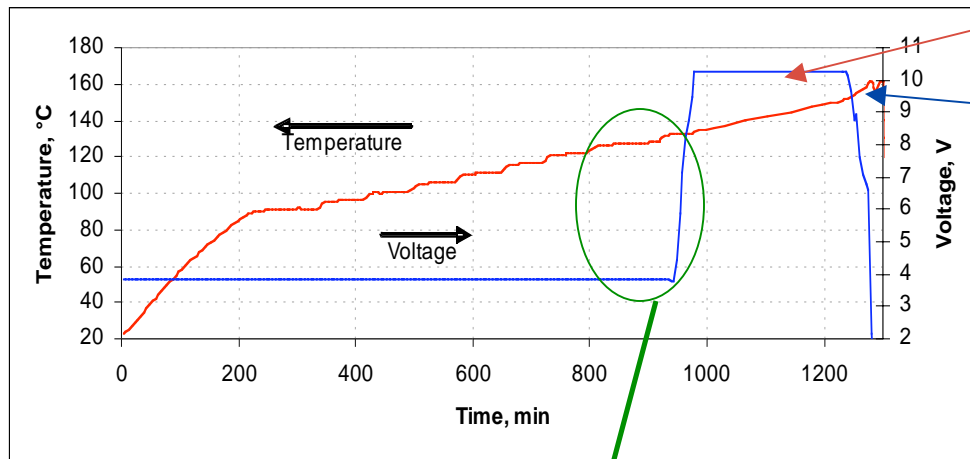
Temperature & Voltage versus Time
(0% SOC)
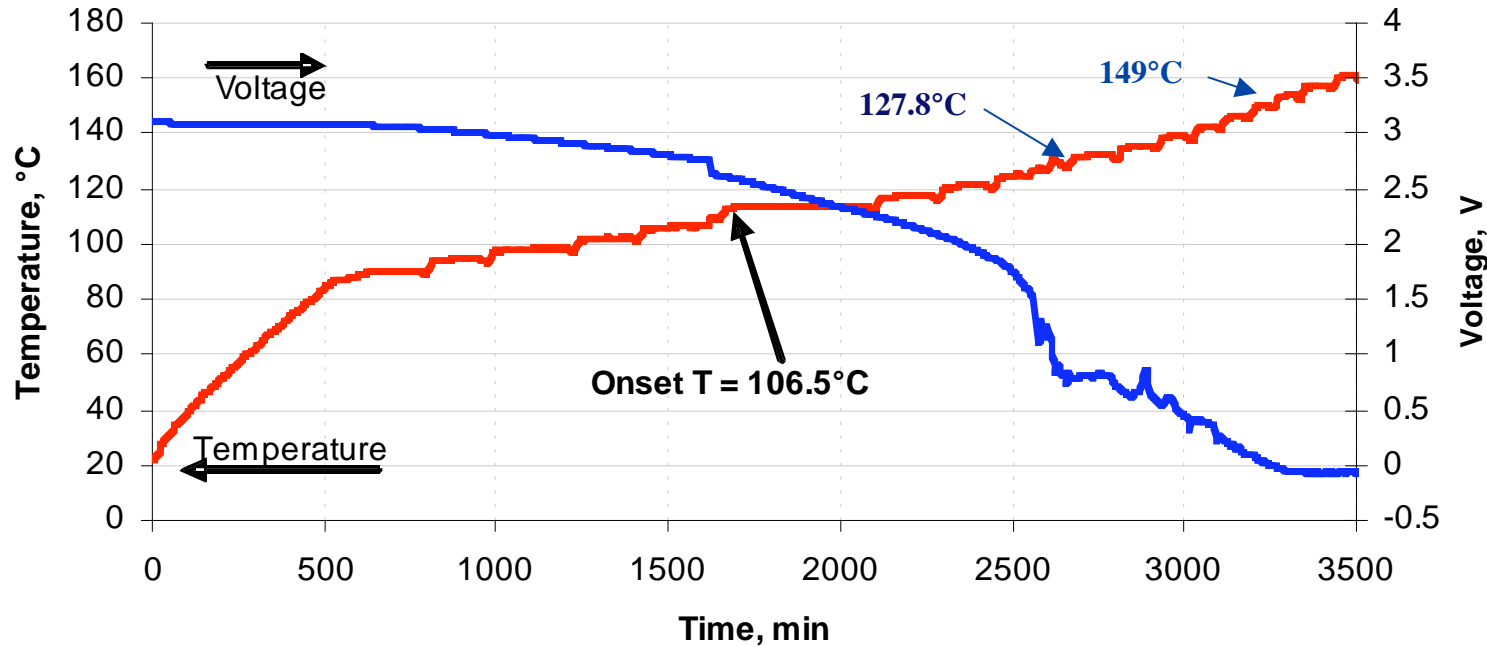
- ARC T = between 35 and 160 C
- Onset T = 106.5°C → voltage started to fall
- Second exotherm after 2652 min, 0.822 V at 127.8°C
- After 3257 min, 0.0 V at 149°C indicating internal cell shorting.
- No runaway before 160°C

Temperature Profiles of Panasonic 18650 cell
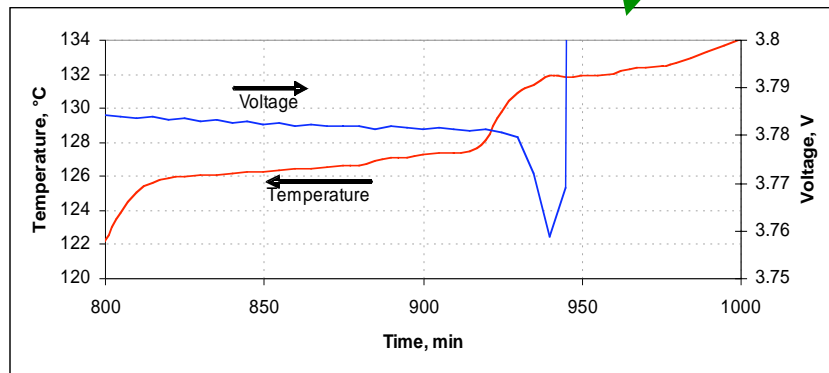## (50% SOC)
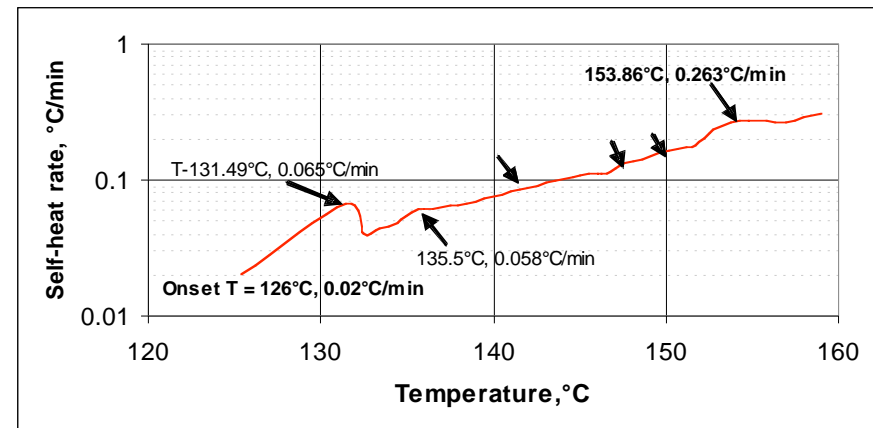
Temperature vs. Time

Arbin malfunction

Thermal runaway

- Onset T= 126°C → Voltage started to fall

-Several peaks corresponding to different reactions involving anode, cathode and electrolyte

-Arbin malfunction, voltage went up to 10V

Expanded view

Self-Heat Rate vs. Temperature

153.86°C, 0.263°C/min

T-131.49°C, 0.065°C/min

135.5°C, 0.058°C/min

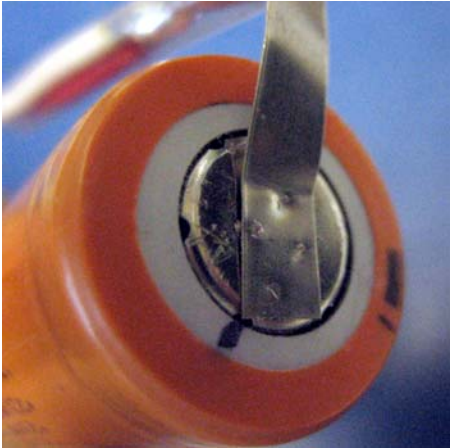Onset T = 126°C, 0.02°C/min

Before and after venting

- Before

After

Heat Generation

Objective:

• calculate internal heat generation for lithium-ion cells

• contrast and compare two different cathode chemistries

    • $LiCoO_2$

    • $LiFePO_4$

• use results to identify operating conditions which can lead to excessive internal temperature increase

Heat Generation

Thermal contributions:

- irreversible heat due to polarization (always positive)

- reversible heat due to entropy change (may be positive or negative)

- entropy, ΔS, can be calculated from cell equilibrium potential/temperature data

- total internal heat generation

$$q_{irrev} = I\left(E_{eq} - E\right)$$

$$q_{rev} = I\frac{T\Delta S}{nF}$$

$$\Delta S = nF\frac{\partial E}{\partial T} \longrightarrow q_{rev} = IT\frac{\partial E}{\partial T}$$
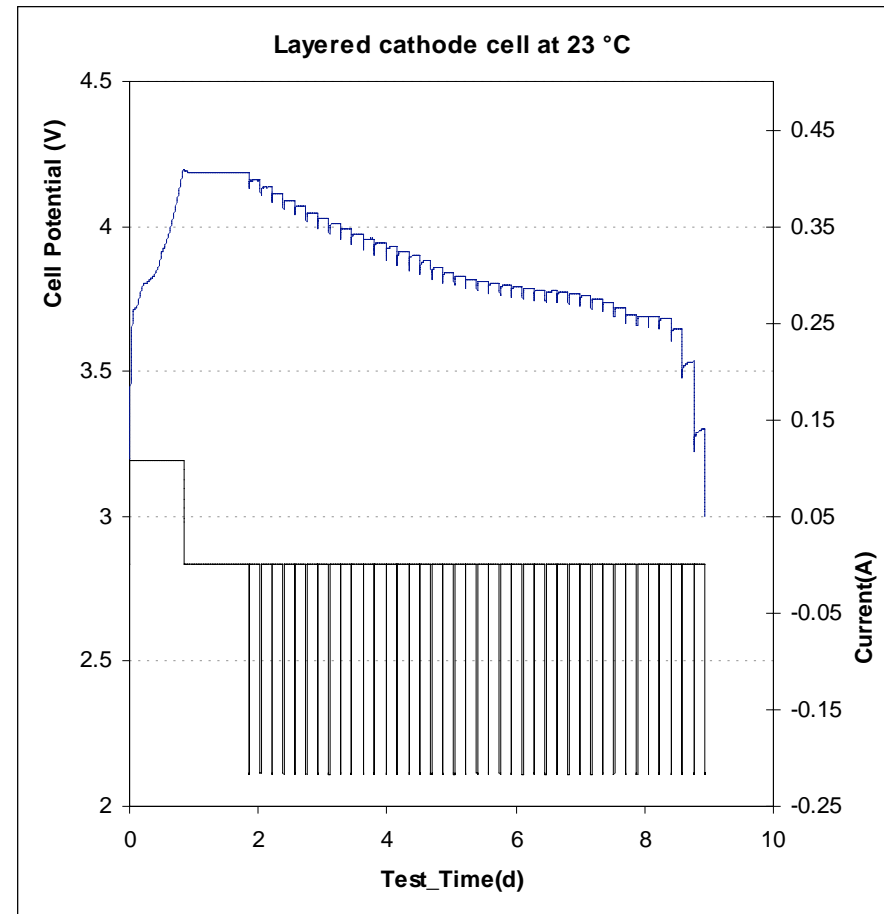
$$q_{total} = q_{rev} + q_{irrev}$$

Heat Generation

Equilibrium potential measurement:

• fully charge cell under "standard" conditions (C/20, 23°C)

• adjust temperature to desired value and equilibrate for 1 day

• use incremental discharge followed by 4-6 hour rest

• use voltage after rest as equilibrium potential

rest time affects accuracy. how long?

Layered cathode cell at 23 °C

Heat Generation

Equilibrium cell potential:

•for $LiCoO_2$ cathode cell, cell potential decreases with increase in temperature

•for $LiFePO_4$ cathode cell, cell potential *increases* with increase in temperature

Equilibrium potential is used to compute polarization

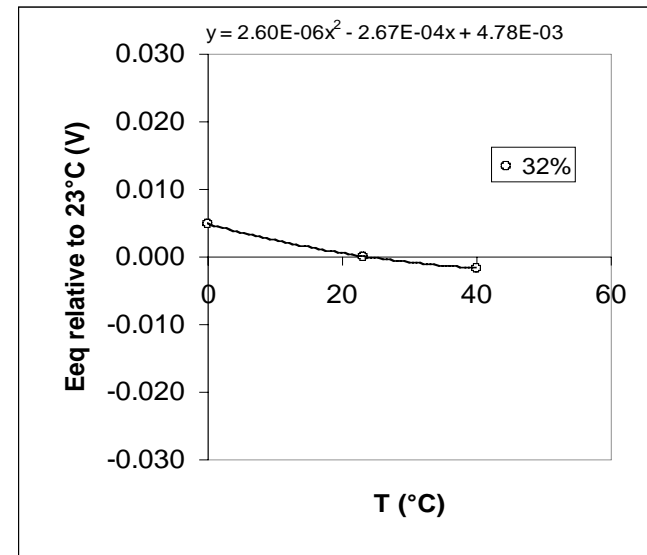Change in equilibrium potential with temperature is used to compute entropy
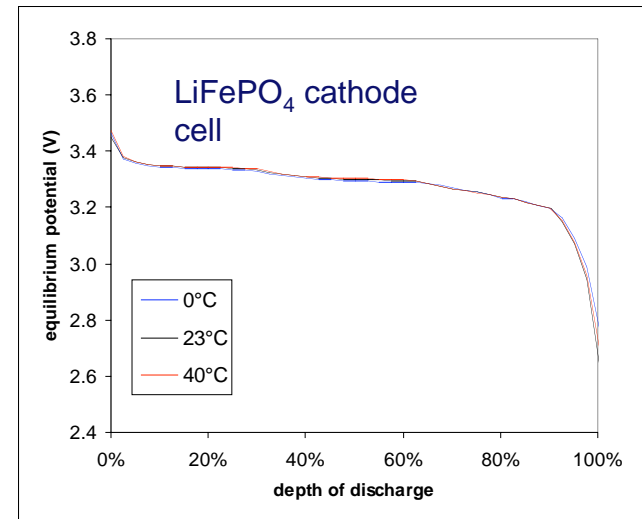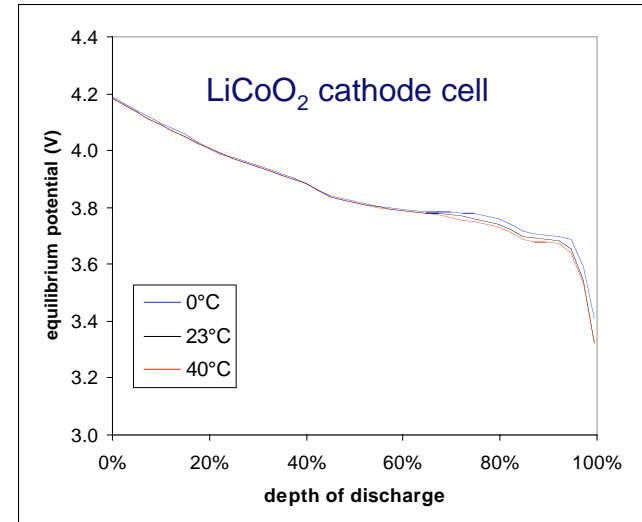
Heat Generation

Compute derivative:

• plot potential versus temperature at a given state-of-charge

• fit curve and compute slope (quadratic used here)

• repeat at other states-of-charge

LiCoO$_2$ cathode cell at 32% DoD

$y = 2.60E\text{-}06x^2 - 2.67E\text{-}04x + 4.78E\text{-}03$
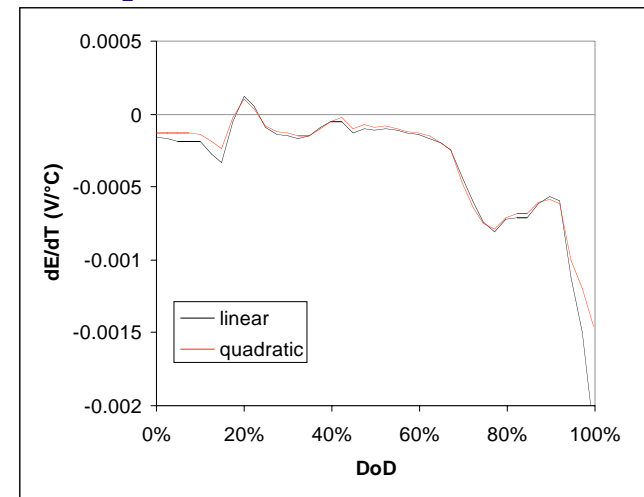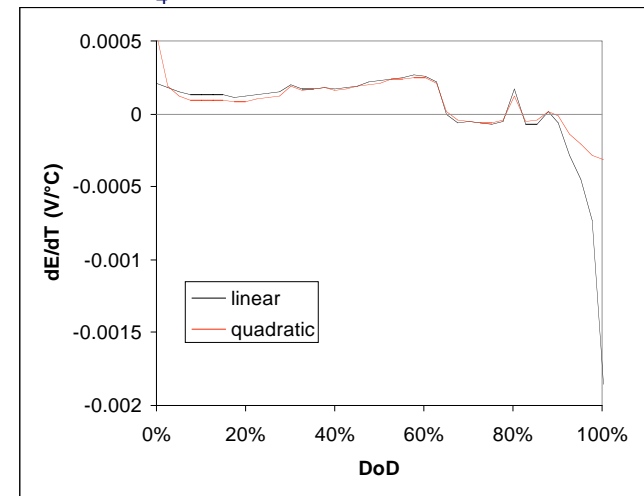
Heat Generation

Computed derivatives:

• pronounced negative derivative for $LiCoO_2$ cathode at DoD > 50% (heating effect on discharge)

• for $LiFePO_4$ cathode, derivative is generally closer to zero, positive at <50% DoD

These results show that the reversible heat of the LiFePO4 produces a slight effect on discharge.
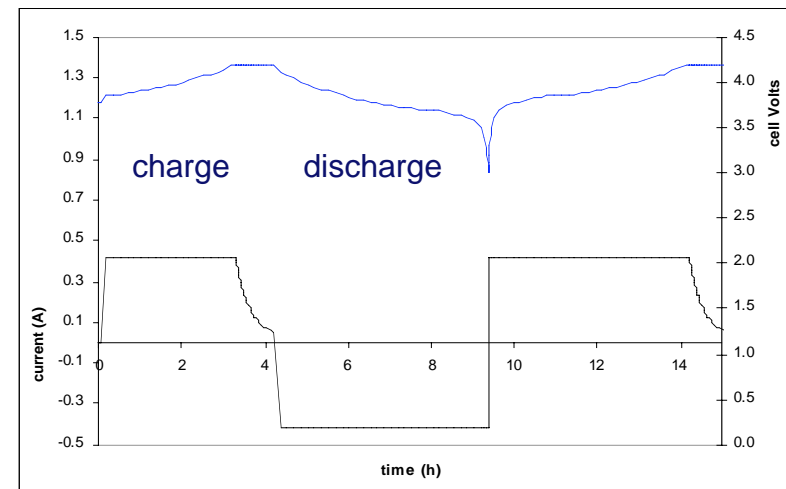
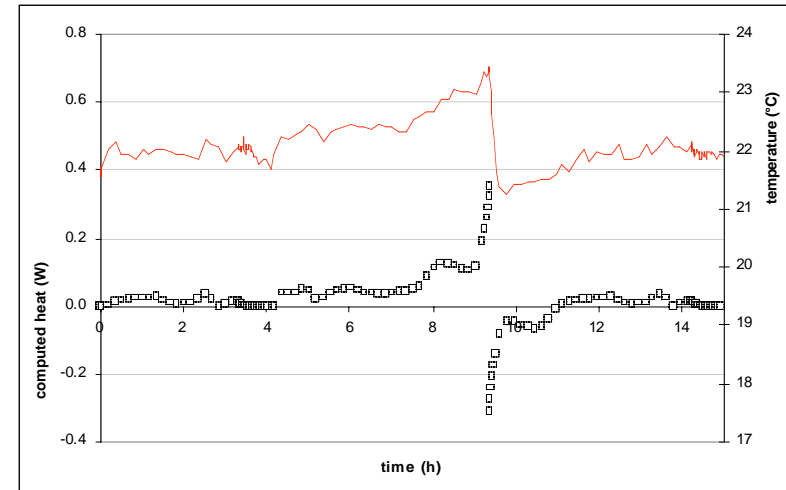$LiCoO_2$ cathode

$LiFePO_4$ cathode

Heat Generation

Compare heat generation calculation with measured cell temperature of $LiCoO_2$ cathode cell:

- computed heat generation correlates well with temperature

- gradual heating begins immediately on discharge
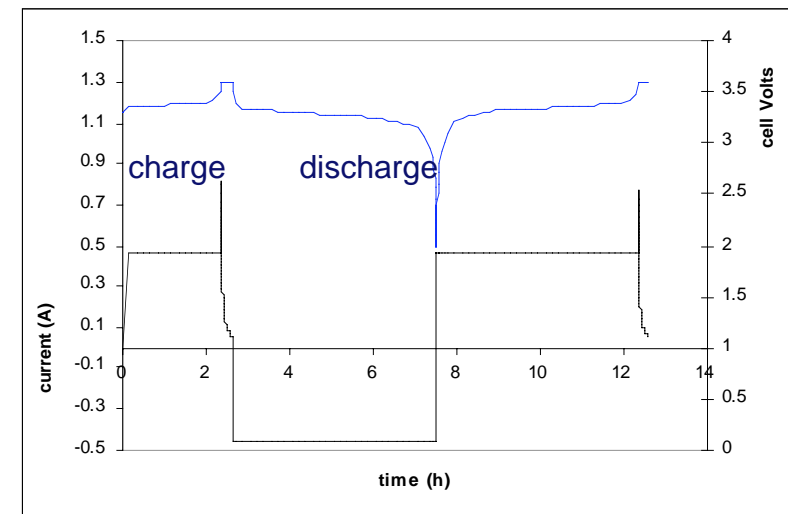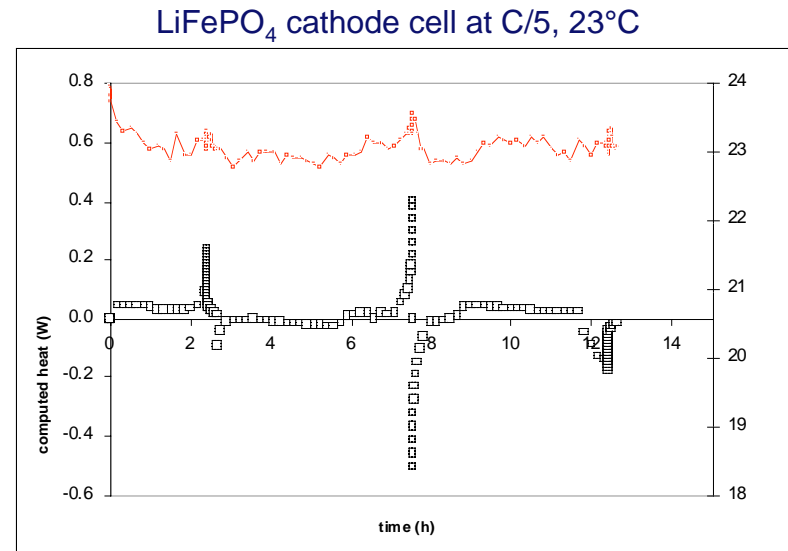
$LiCoO_2$ cathode cell at C/5, 23°C

Heat Generation

Compare heat generation calculations with measured cell temperature of LiFePO$_4$ cathode cell:

• computed heat generation correlates well with temperature

• little temperature change with pronounced temperature rise at end of discharge

LiFePO$_4$ cathode cell at C/5, 23°C

Summary

- ARC is used to determine the temperature ranges where cell starts self-heating and goes into thermal runaway

- Thermal stability studies as functions of DOD and SOC using the ARC were initiated.

- ARC in combination with an Arbin battery cycler is currently used to evaluate and study the performance and thermal behavior of Li-ion cells.

- Significant temperature rise with increasing DOD

- Results will provide a fundamental database for cell safety from a proper thermal management

- Heat generation correlates well with temperature

- Change in equilibrium potential with temperature is used to calculate entropy.

Future Research Work

- Continue thermal study of other Li-ion components (anodes, cathodes & electrolytes).

- Continue thermal behavior study of Li-ion cells at different conditions – SOC, aging, etc.

- Continue to understand the thermal stability and heat generation from decomposition and exothermic reaction of the materials within the cell.

- Initiate study of next generation cells and components.

- Verify heat generation calculation at higher rate of discharge/charge.