Safety of Aged Commercial Lithium-ion Cells

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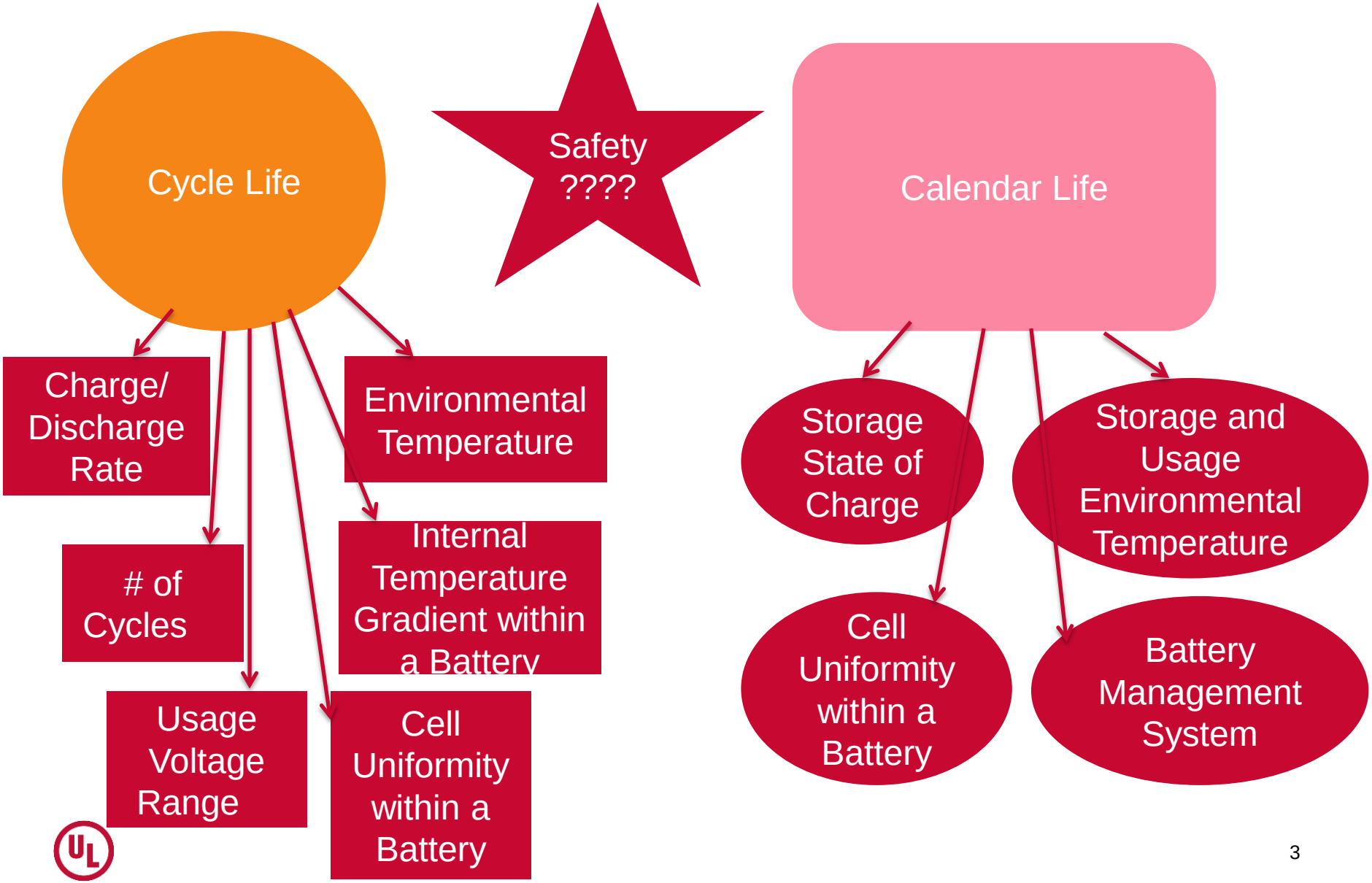
Introduction

- **Lithium ion batteries are being used in automotive applications in various sizes**
- **Introduced into the utility/stationary energy storage industry**
- **Automotive batteries are being repurposed for utility/stationary storage applications**
- **Questions that arise on the safety of used batteries are**
  - Does the safety change with cycle and calendar life (including storage life)?
  - What parameters need to be characterized after first life and before installation in second life?
  - What parameters need to be studied closely during usage in second life?

Factors Affecting Aging and State of Health

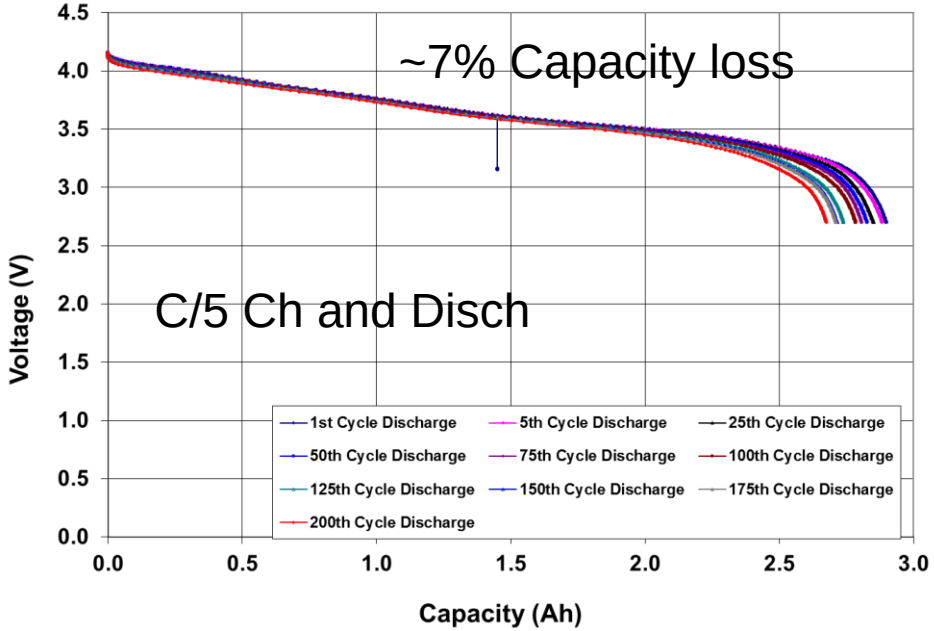


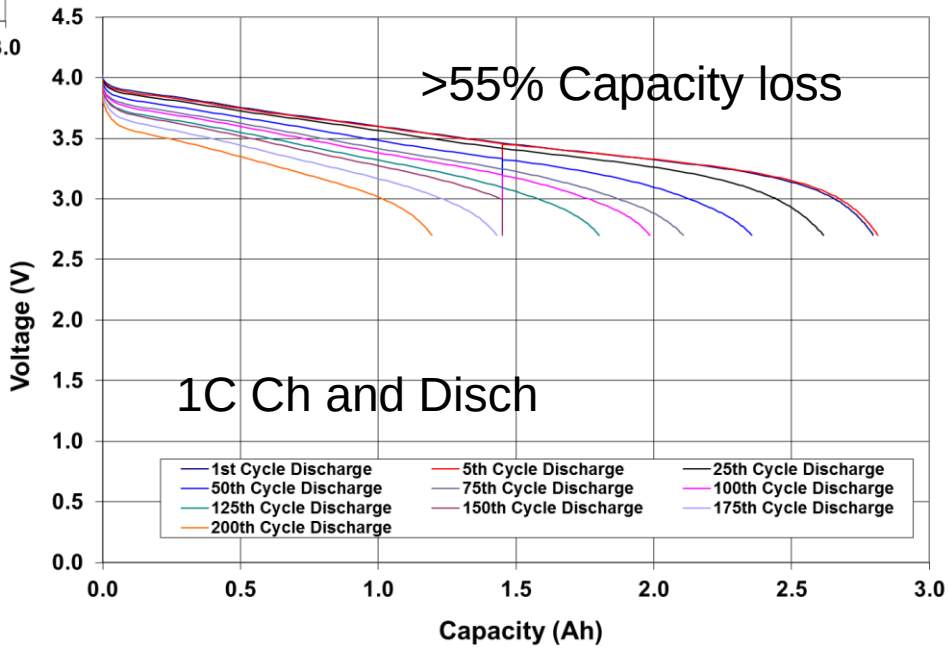
Aging Effects on Cell

- **Lithiation and de-lithiation causes**
  - Anode electrode morphology changes and volume changes – surface can form cracks leading to electrical isolation; delamination from current collector; changes in intercalation kinetics; loss of active lithium inside anode, etc.
- **Decomposition**
  - Binder and electrolyte; SEI decomposition; HF production, li-ion side reaction with electrolyte; etc.
- **Corrosion**
  - Current collector, cell can materials, pouch cell swelling and shorting due to corrosion of pouch material, etc.
- **Cathode changes**
  - Structural disorder, metal dissolution, disproportionation, etc.

Past Studies

Cycle Life Performance at Different Rates





Rate capability can affect Cycle life performance and health

J. Jeevarajan, NASA Biennial Research Publication; 2011

Cell Studies at Different Storage Conditions for Orbiter Usage Environment (APU Upgrade Study)

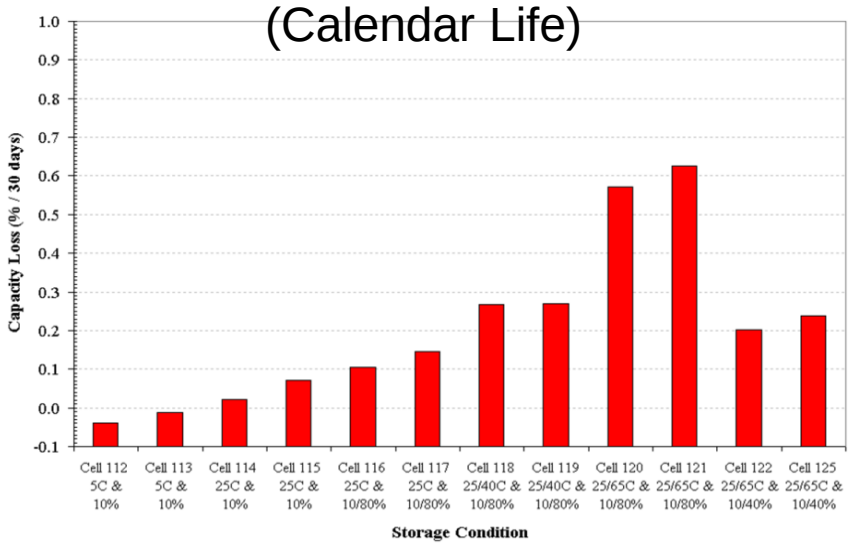
Cell Designation	Condition Description	Storage Temp	Storage SOC	Capacity Check
112, 113	Vehicle Between Missions Cold	5 C (41 F)	5 – 10%	30 days
114, 115	Vehicle Between Missions Nom.	25 C (77F)	5 – 10%	30 days
116, 117	Orbit Cold	25 C (77 F) 25 C (77 F)	5 – 10% 75 – 80% (2.5 mo @ 5-10%, 15 days @ 75-80%, repeat)	0, 2.5, 3 mo (repeat)
118, 119	Orbit Nominal	25 C (77 F) 40 C (104 F) (2.5 mo @ 25C, 15 days @ 40C, repeat)	5 – 10% 75 – 80% (2.5 mo @ 5-10%, 15 days @ 75-80%, repeat)	0, 2.5, 3 mo (repeat)
120, 121	Orbit Hot	25 C (77 F) 65 C (149 F) (2.5 mo @ 25C, 15 days @ 65C, repeat)	5 – 10% 75 – 80% (2.5 mo @ 5-10%, 15 days @ 75-80%, repeat)	0, 2.5, 3 mo (repeat)
122, 125	Post Landing Hot	25 C (77 F) 65 C (149 F) (2.5 mo @ 25C, 1 day @ 65C, repeat)	5 – 10% 75 – 80% (2.95 mo @ 5-10%, 1 day @ 75-80%, repeat)	0, 2.5, 3 mo (repeat)

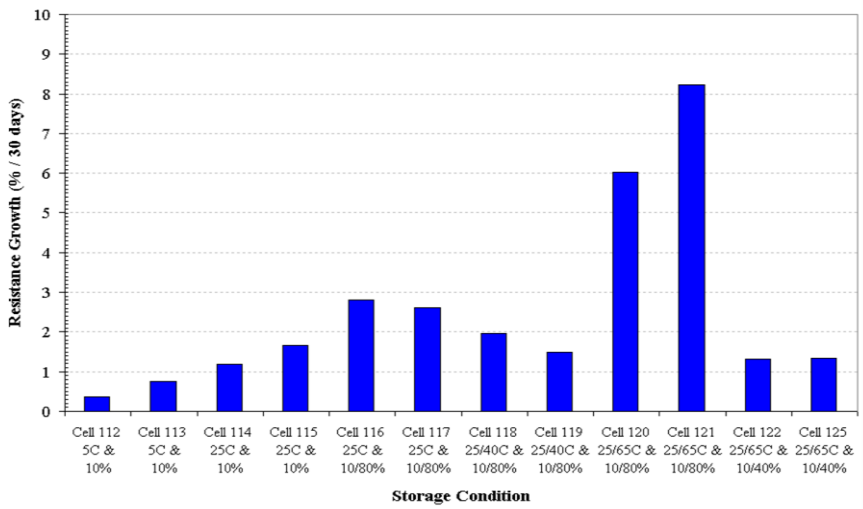
Study Objective: Determine Long Term Effects of "Storage" Temp & State of Charge (SOC) On Cell Capacity & Resistance
(2 cells per condition) Total of 840 days

Jeevarajan, Irlbeck, The 205th ECS Meeting, May 2004

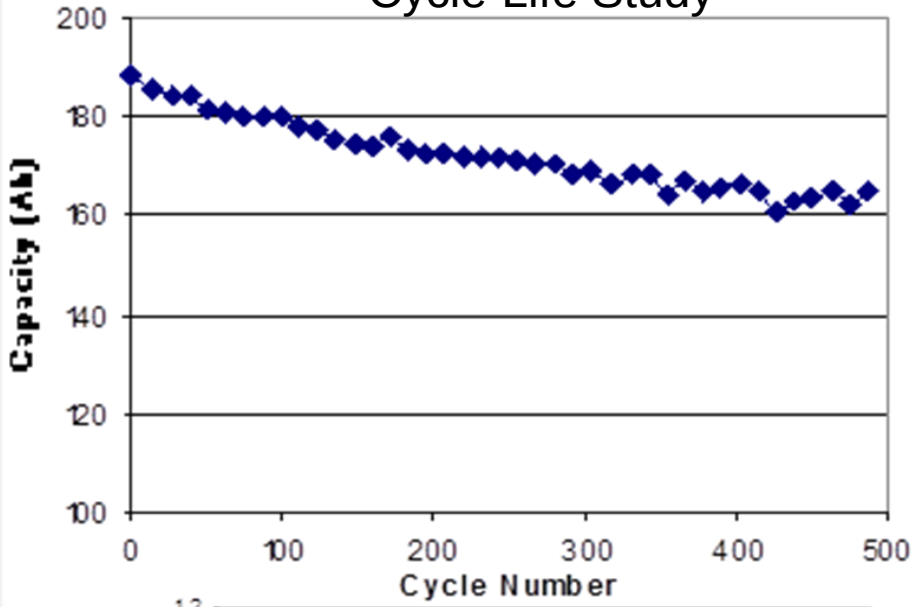
Capacity Loss and Internal Resistance Growth for Cells Used in Orbiter Upgrade Study

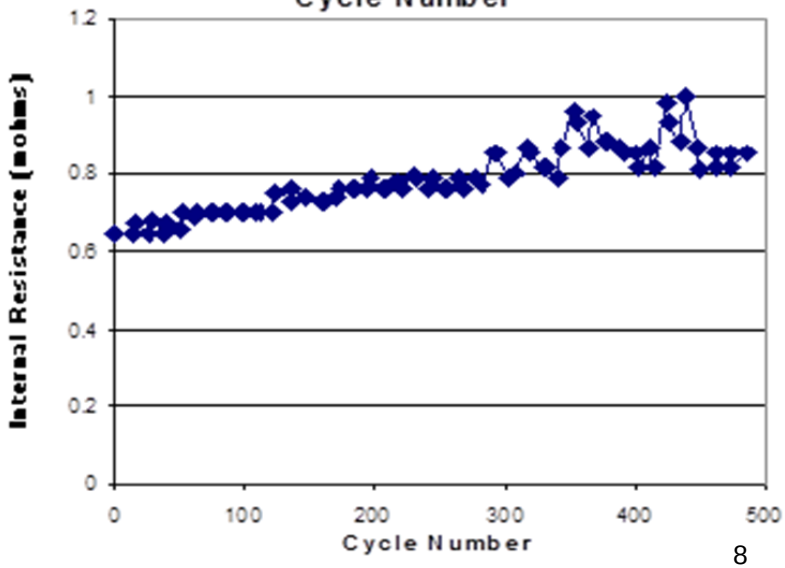
Various SOC and Temperature Storage (Calendar Life)





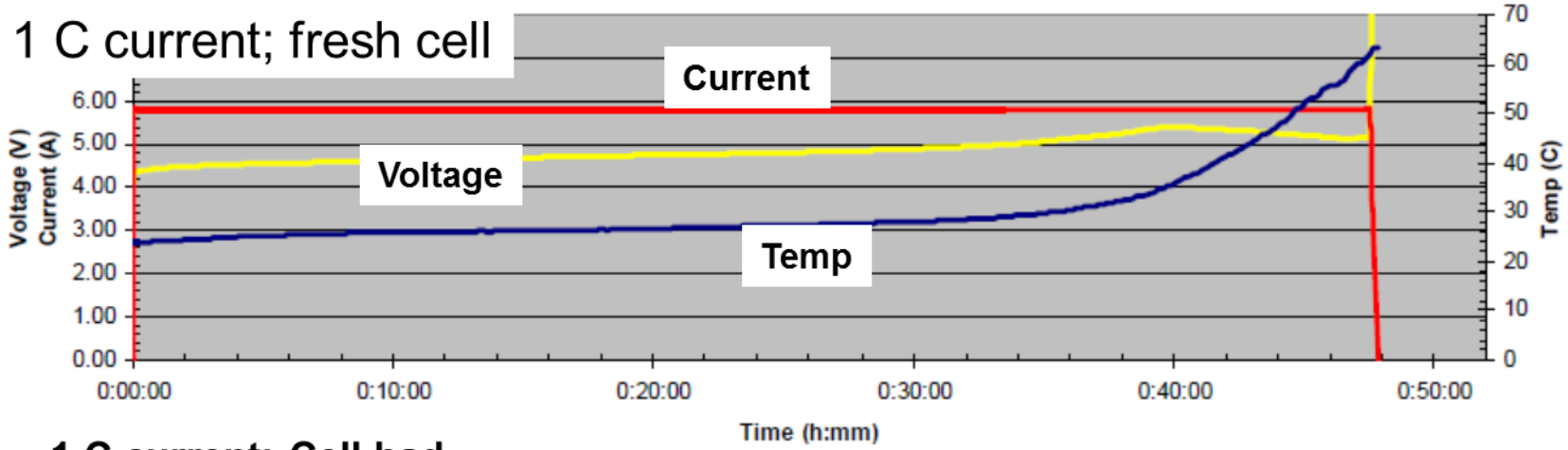
Cycle Life Study

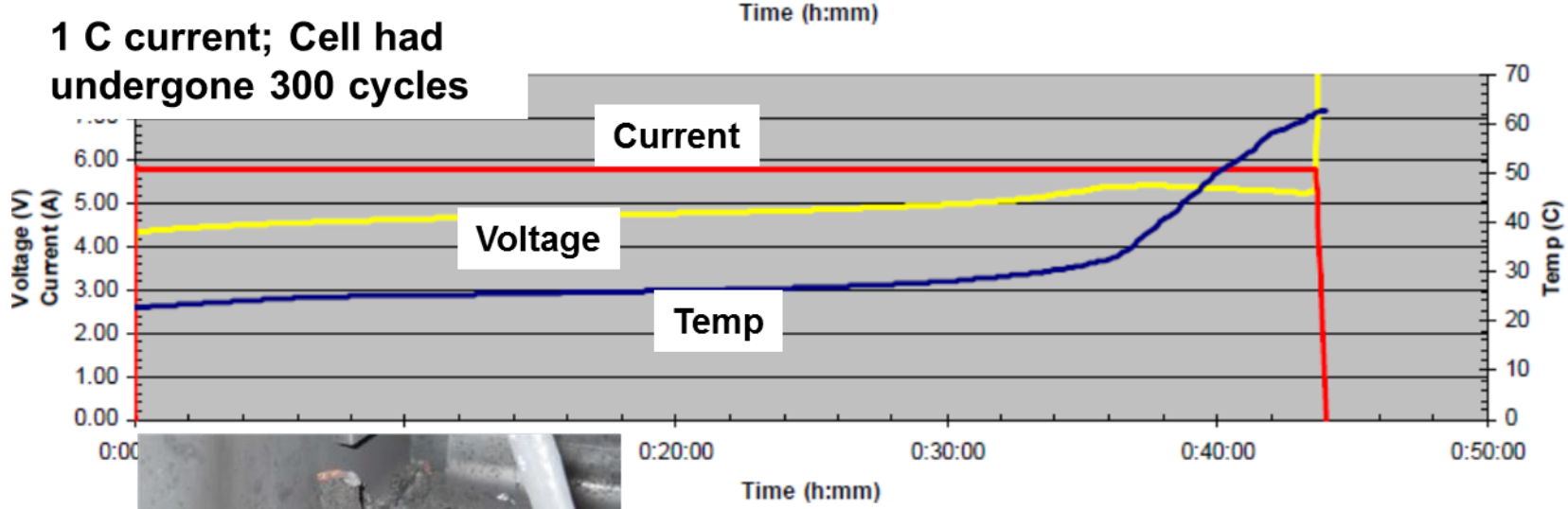




Jeevarajan, Irlbeck, The 205th ECS Meeting, May 2004

Safety after Cycling - Overcharge





3.1 % Capacity loss after 300 Cycles
Cells are of pouch format

J. Jeevarajan, 222nd ECS Meeting, October 2012

Cycle Life Aging and Simulated Internal Short Tolerance

- **Cells were cycled at 1C rate of charge and discharge for 1000 cycles**
  - Cells lost capacity between 12 to 25%
- **Conducted Simulated Internal Short (SIS) tests (Crush test method) - Sample size – 10 cells**
  - Tolerance to simulated internal shorts increased with higher loss in capacity– no fire or thermal runaway observed even with cells that lost greater than 19% capacity (SIS performed at 100% SOC); cells that lost between 12 to 16% capacity went into thermal runaway (SIS performed at 100 % SOC)

Note: All fresh cells at 100 % SOC when subjected to simulated internal short went into thermal runaway

Jeevarajan, *et.al*, The 2011 NASA Battery Workshop
Jeevarajan, *et.al*, Battery Safety 2012

Current Studies

Test Plan – UL/Texas A&M University

- **Single Cell Studies**
  - Cycle life with continuous cycling at normal voltage range
  - Cycle life with continuous cycling with reduced voltage range (200 mV less from both ends of voltage range)
  - HEV profile at 3 temperatures
  - **Overcharge and external short test on fresh and cycled single cells**

- **Module (3P9S: 9.9 Ah, 33.3 V) Studies**
  - Cycle life with continuous cycling at normal voltage range
  - Cycle life with continuous cycling with reduced voltage range (200 mV less from both ends of voltage range)
  - HEV profile at 3 temperatures (10 ºC, 25 ºC and 45 ºC)
  - **Overcharge and External short test of fresh and cycled modules**

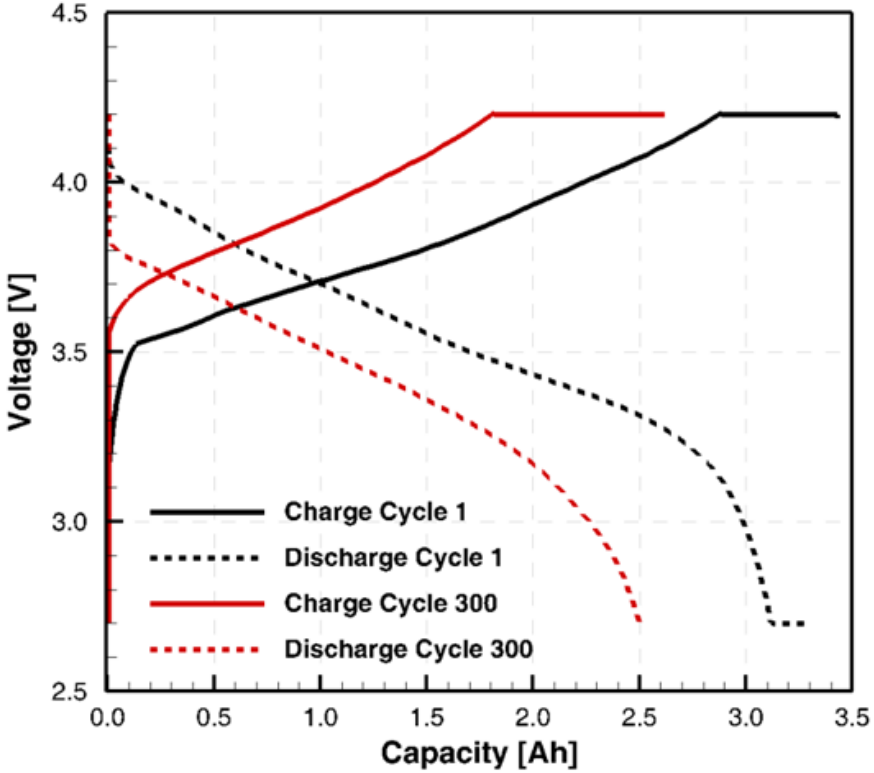
Destructive Analysis:

Fresh cells : uncycled, externally shorted cell and overcharged cell

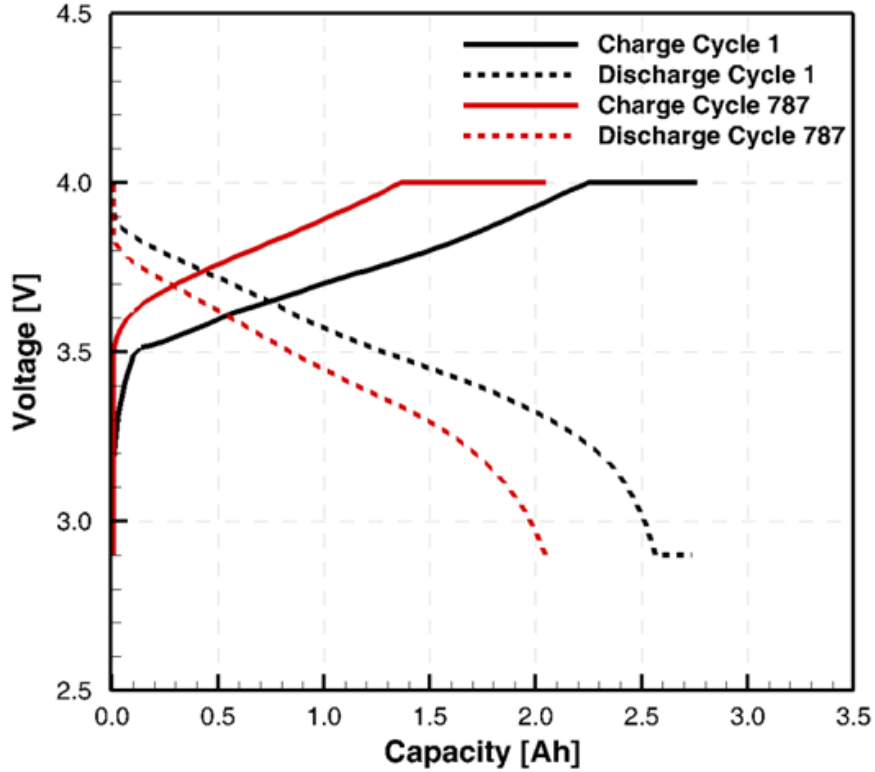
Cycled cells: cycled (cells removed after set number of cycles), externally shorted cycled cells, overcharged cycled cells

Comparison of Charge and Discharge Profiles of fresh and cycled cells

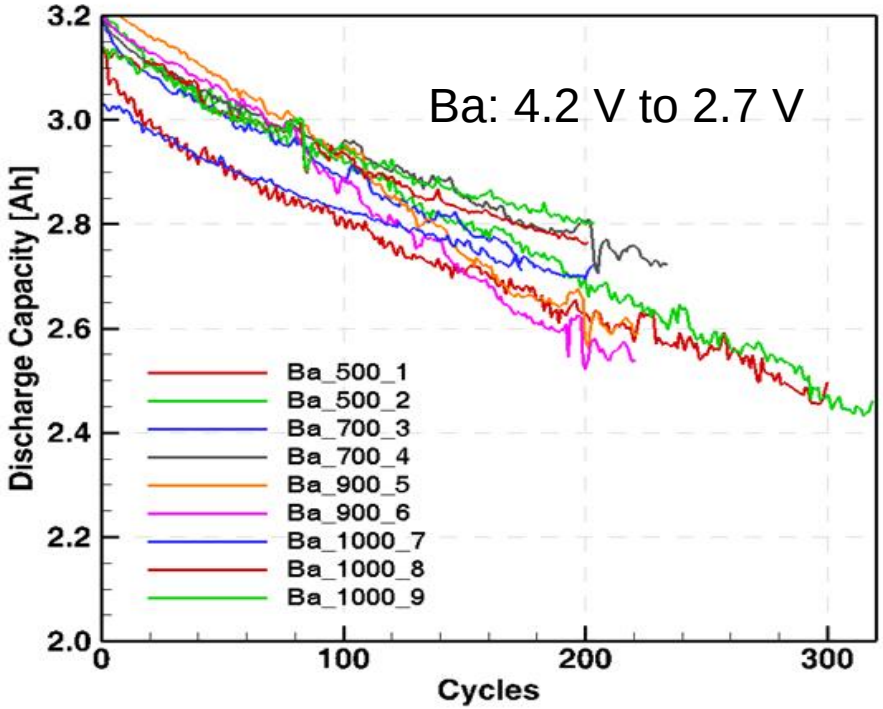
4.2 V to 2.7 V



4.0 V to 2.9 V

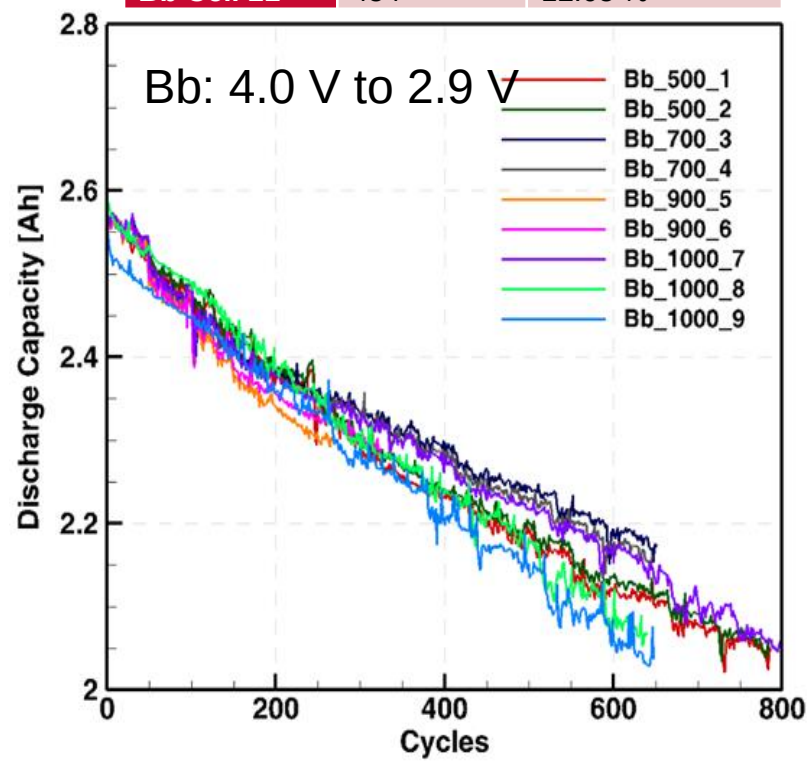


Cycle Life Testing on Single 18650 Li-ion Cells- Capacity Trend

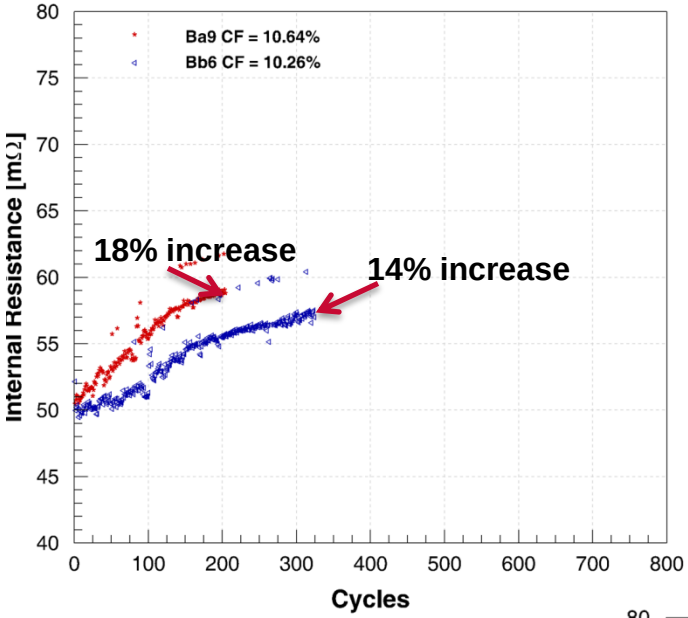


Cell ID	Number of Cycles	Capacity Fade
Ba Cell 2	319	26.70 %
Ba Cell 1	300	24.23 %
Ba Cell 6	221	23.79 %
Ba Cell 5	222	22.97 %
Ba Cell 4	234	18.74 %
Ba Cell 8	201	16.21 %
Ba Cell 10	269	15.49 %
Ba Cell 3	201	15.41 %
Ba Cell 9	204	15.17 %
Ba Cell 7	174	10.59 %

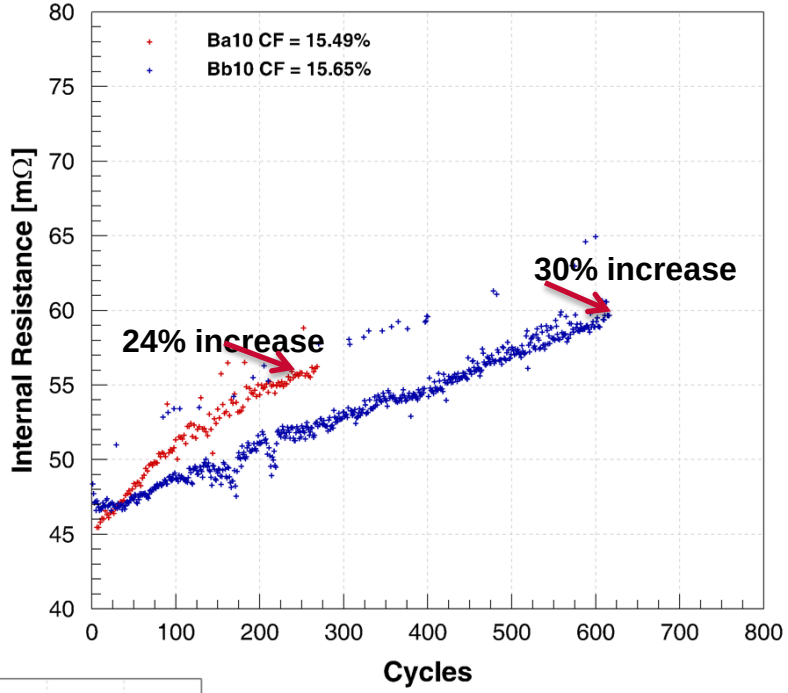
Cell ID	Number of Cycles	Capacity Fade
Bb Cell 1	787	25.30 %
Bb Cell 2	785	25.29 %
Bb Cell 7	800	23.87 %
Bb Cell 8	640	20.11 %
Bb Cell 9	648	20.09 %
Bb Cell 10	616	15.65 %
Bb Cell 4	647	15.50 %
Bb Cell 6	324	15.44 %
Bb Cell 3	651	15.26 %
Bb Cell 5	267	14.94 %
Bb Cell 11	454	12.05 %

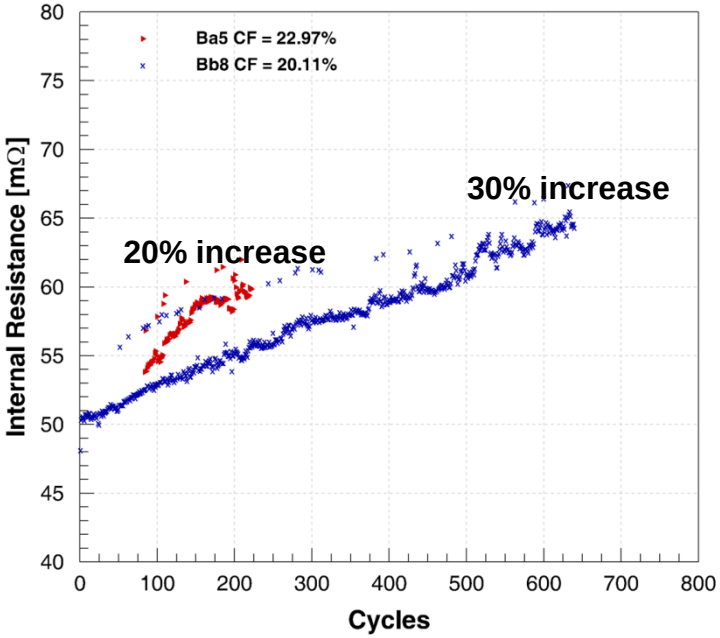


Cycle Life Testing on Single 18650 Li-ion Cells - Internal Resistance Trend



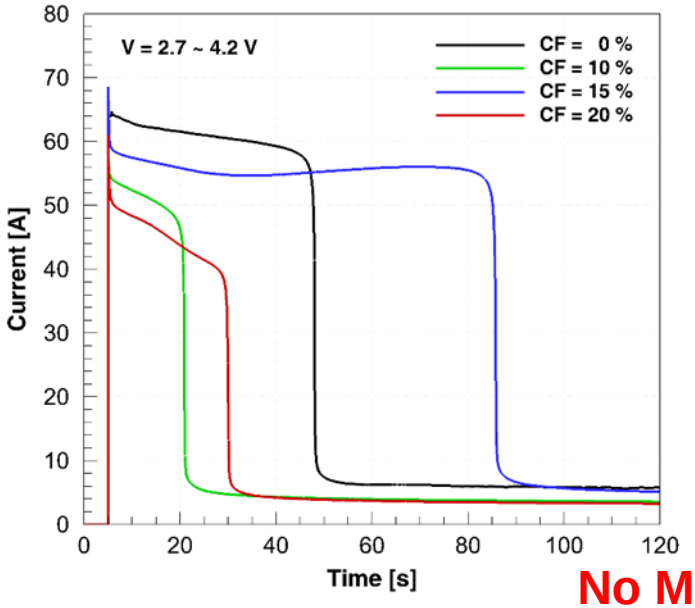
Ba: 4.2 V to 2.7 V
Bb: 4.0 V to 2.9 V

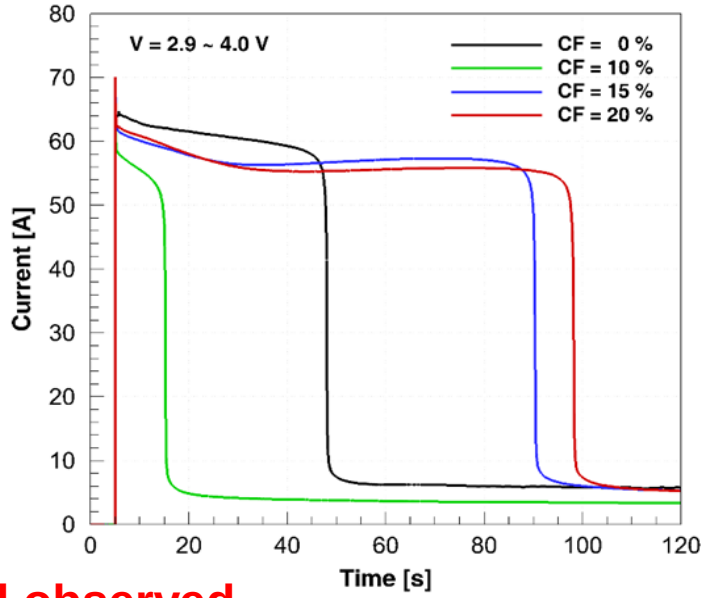




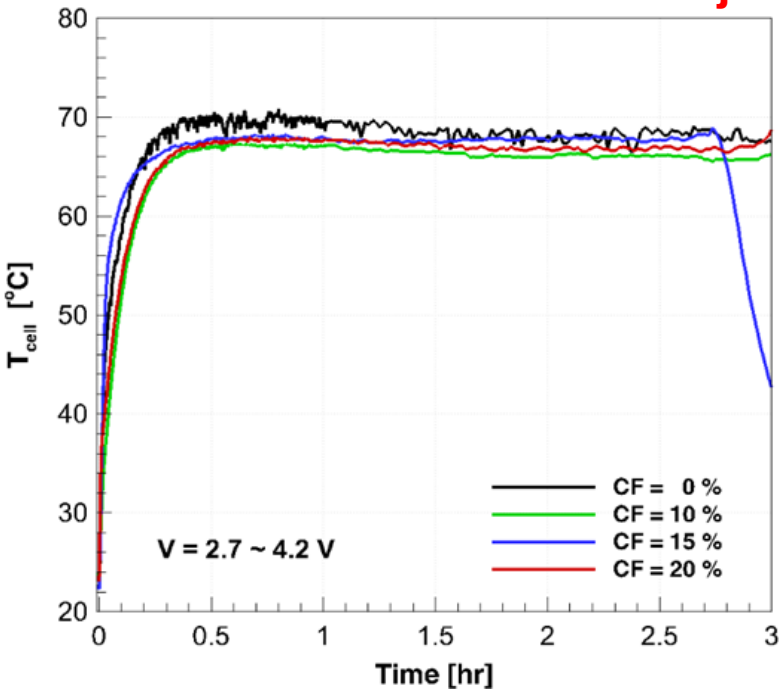
Safety Trend: External Short Test

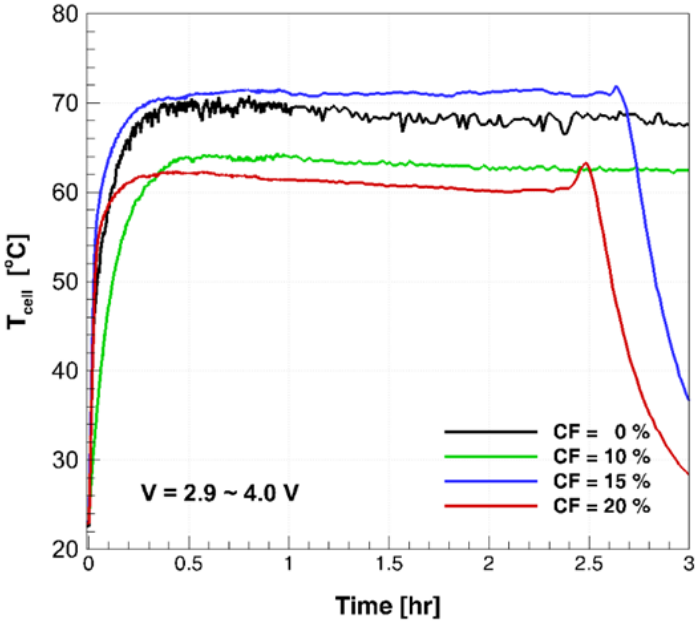
Load: 50 mohm





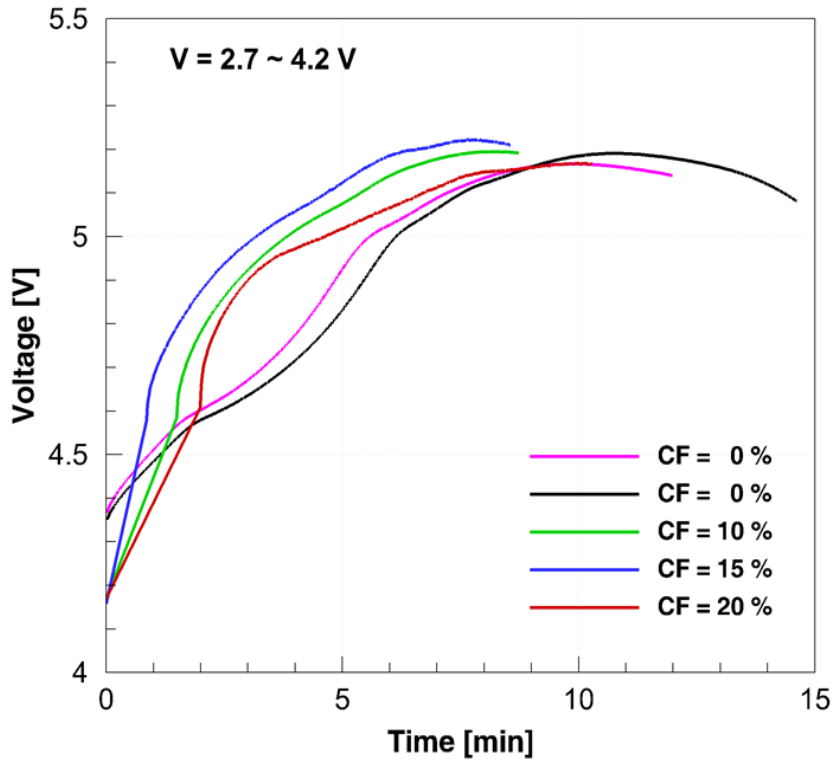
No Major trend observed

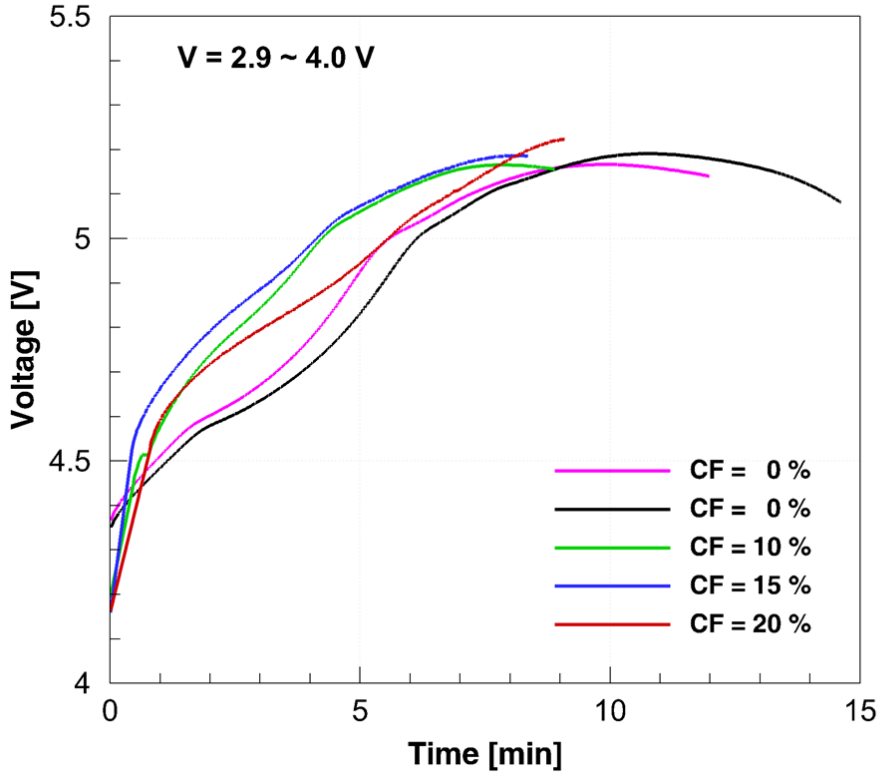




Overcharge Test

Overcharge current: 1C rate to 12V limit





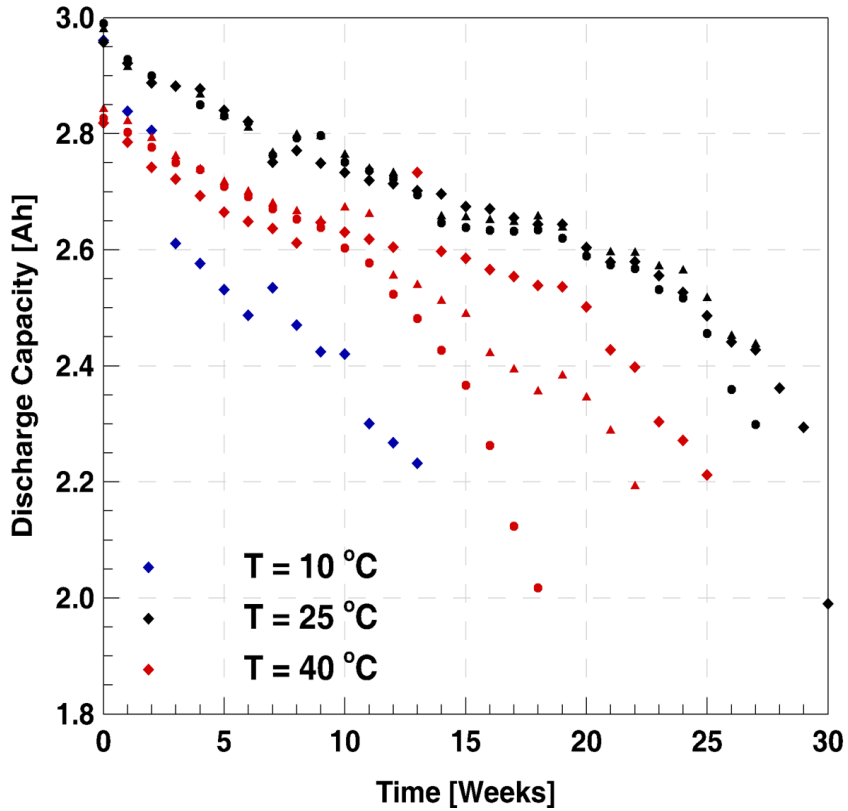
Fresh cells take longer to exhibit CID activation
Cycled cells exhibit shorter times to CID activation possibly due to formation of gases and accumulation of pressure as cells are cycled

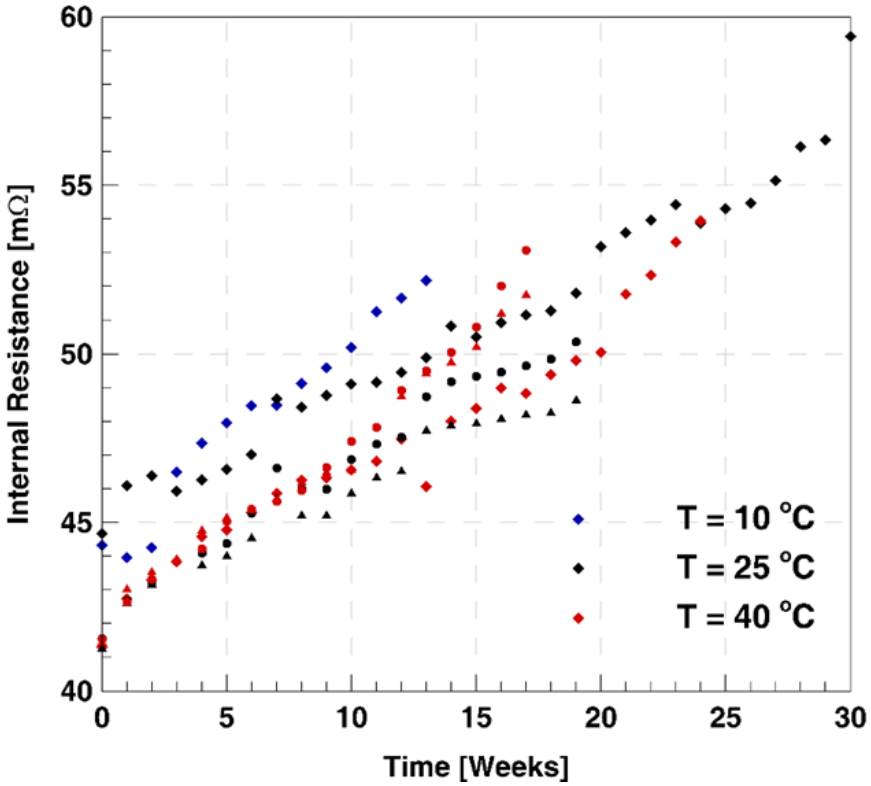
Capacity and Internal Resistance Trend for HEV profile cycles

Cell at 10 ºC: 25% Capacity Fade (13 weeks)
(18% increase in internal resistance)

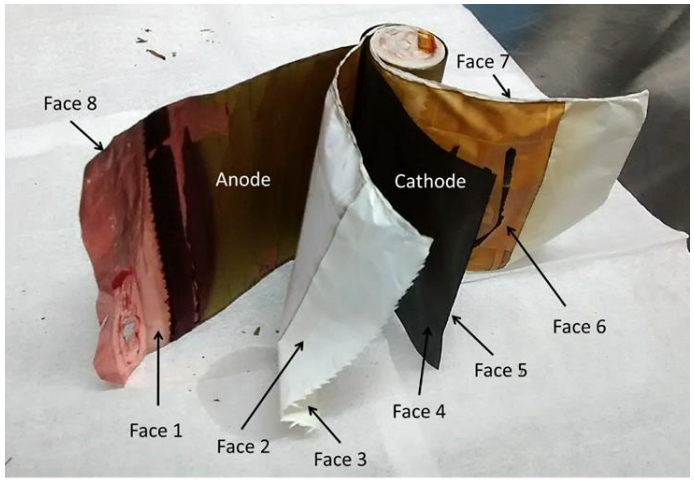
Cell at 25 ºC: 25% Capacity Fade (29 weeks)
(33% increase in internal resistance)

Cell at 40 ºC: 25 %Capacity Fade (24 weeks)
(29% increase in internal resistance)





DPA



Faces 6 and 3 of the separator that faces the cathode have ceramic coating

Anodes

10%

15%

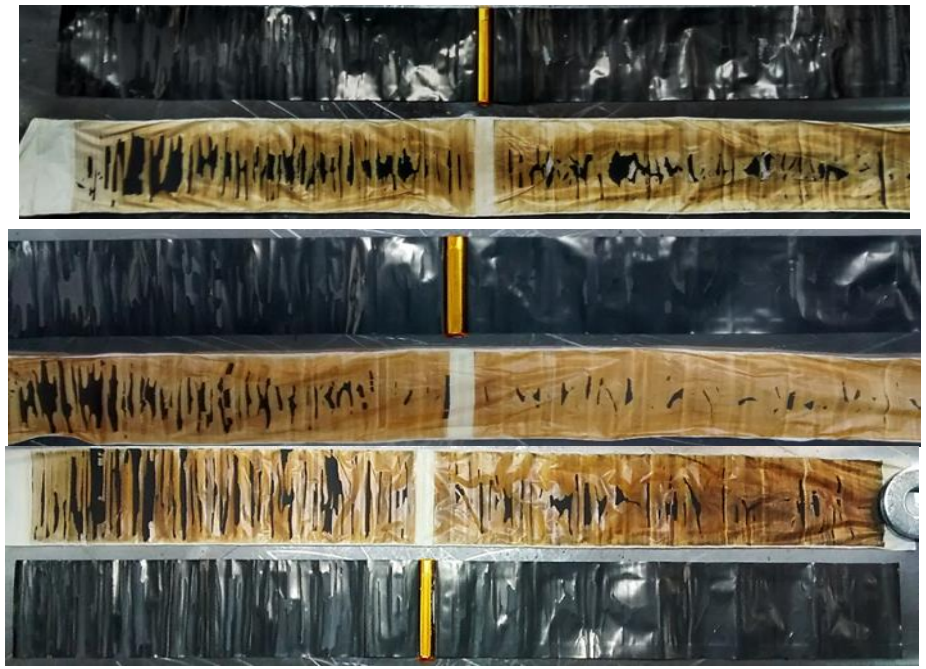
20%

Cathodes

10%

15%

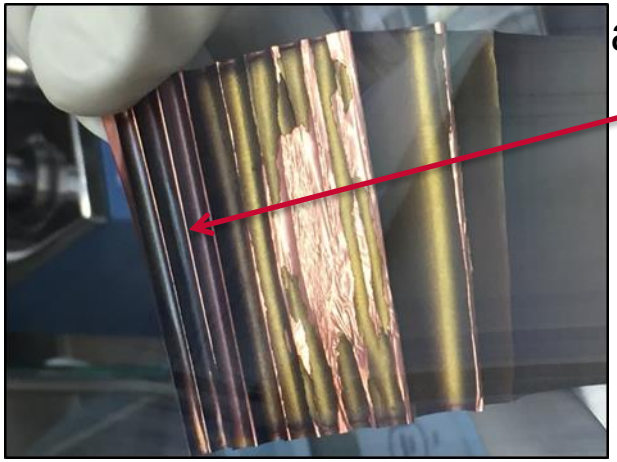
20%

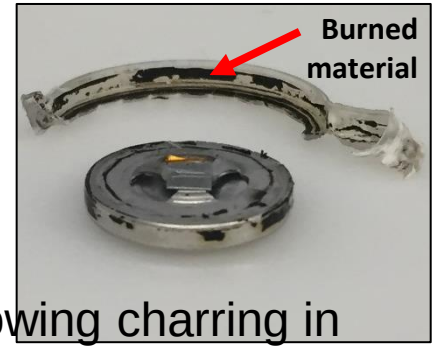


DPA of cells that underwent Cycle Life tests only

Challenges with Cell Safety Features – Safety tests on fresh cells

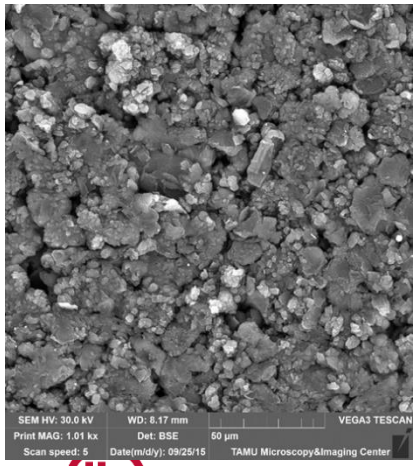
Overcharged cell (fresh cell) with CID activation showing charring of electrodes





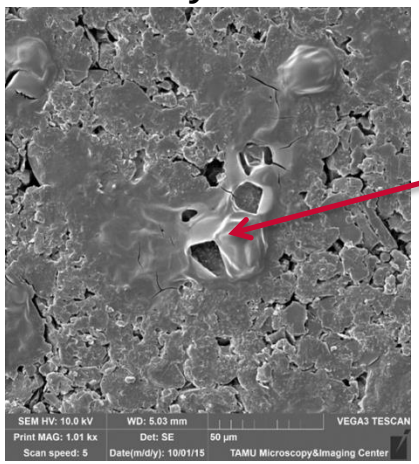
Cell header (underside) showing charring in overcharged fresh cell with CID activation (CID activation is fail-safe mode)

Anode of Fresh cell



Cells exhibited PTC and CID activation under external short and overcharge conditions respectively

Anode surface of fresh (not cycled) externally shorted and overcharged cells



Melt-down on Surface of electrode

DPA after safety tests on cycled cells - Cathodes

External Short

Ba10%

Ba 20%

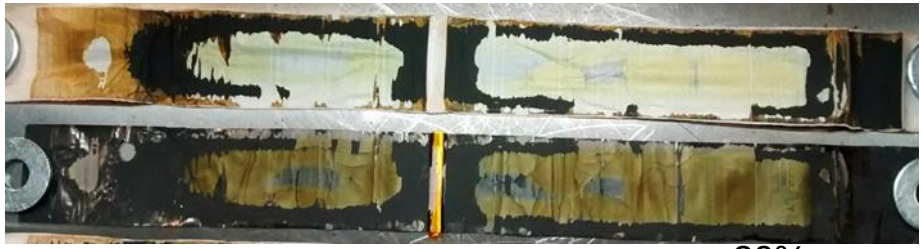
Bb10%

Bb 20%

Overcharge

DPA below shows both sides of electrode

10%

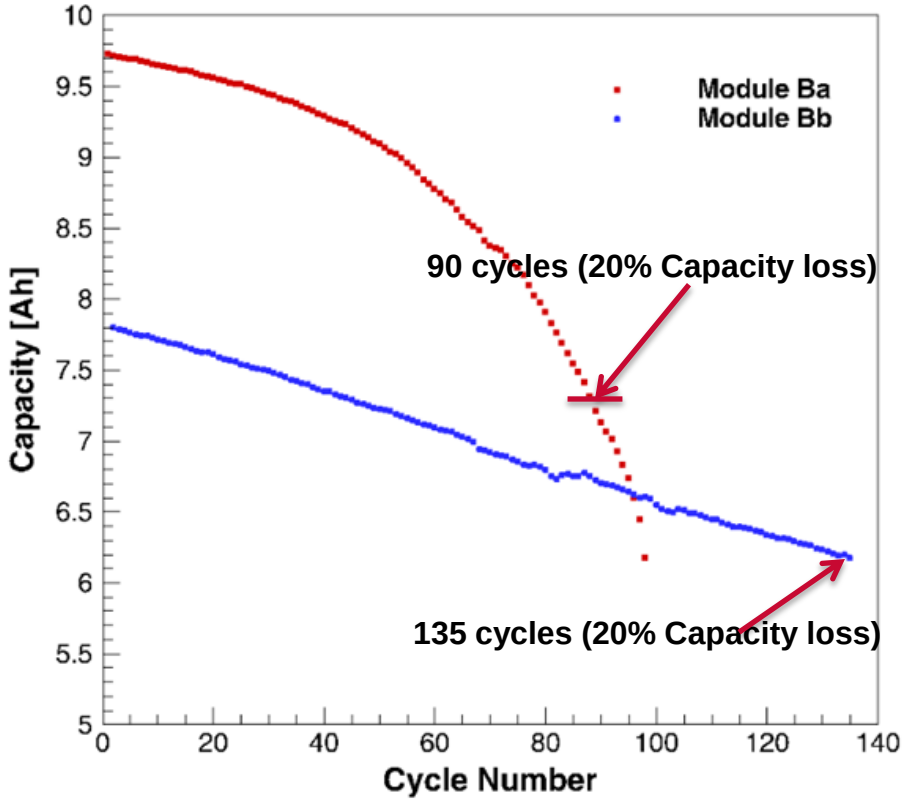


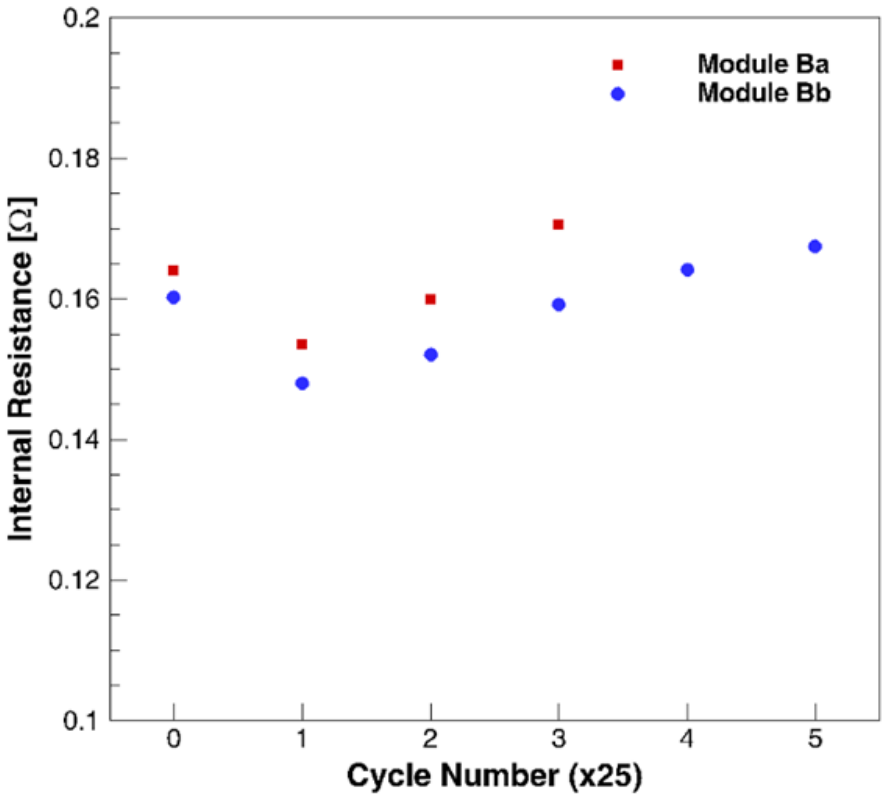
20%

(ceramic coating is typically on surfaces of separator facing cathode – see graphic on slide 19); in cells that underwent safety tests the coating is stuck on the electrode surface

Module Cycle life and Internal Resistance Trend

3P9S Modules
Module Ba: 4.2 V to 2.7 V per bank
Module Bb: 4.0 V to 2.9 V per bank





Li-ion Battery Designs and Challenges

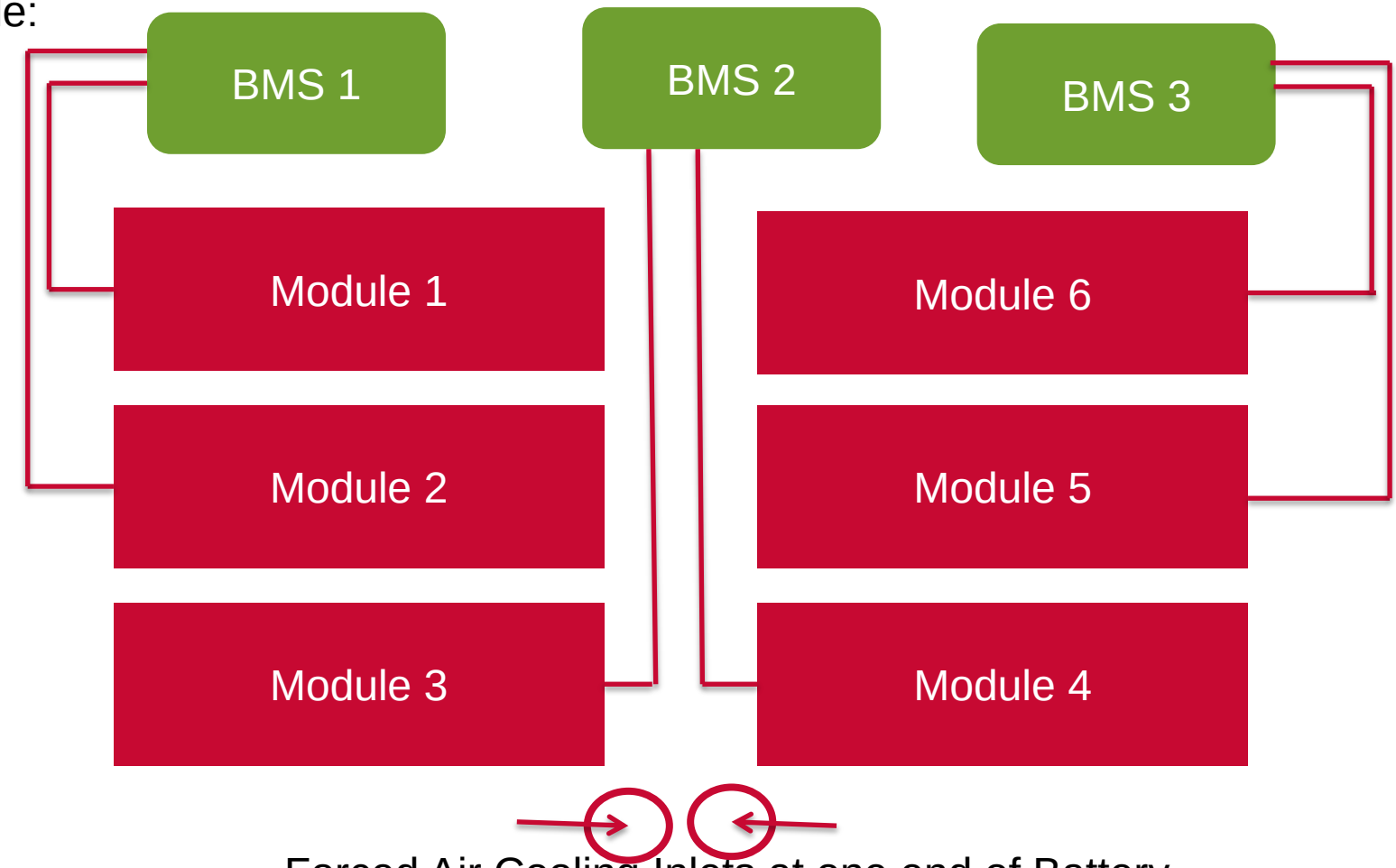
Thermal Gradient and Safety are major Challenges

High Voltage/High Capacity

Challenges with Large Battery Designs

Thermal Gradient → Deviations: Voltage, capacity, internal resistance/impedance Eventually safety is ?

Example:



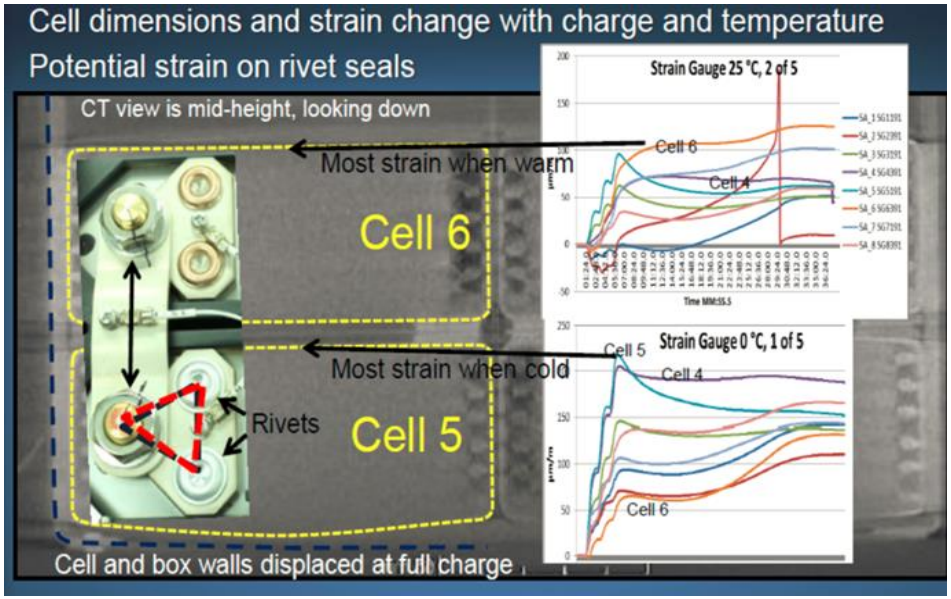
Cell Design Concerns

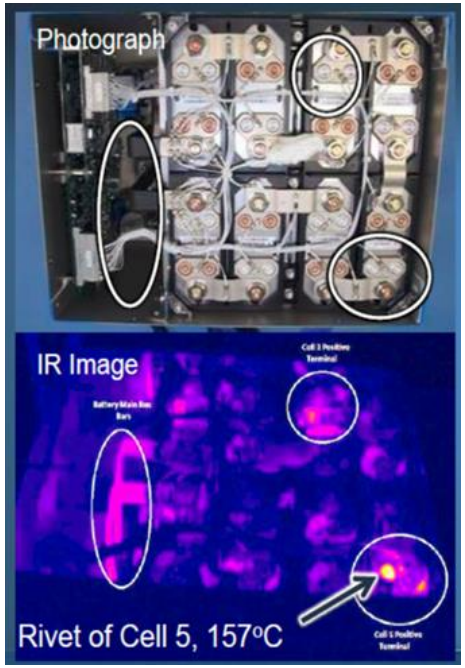
DPA of Fresh Overcharged cell ~5 V with CID activation; uniform lithiation with smooth golden color on anode surface observed (UL- TAMU studies)

DPA of cell under normal use (no record of overcharge; may have been charged at low temperatures in use; shows lithium metal dendrites in electrode crevices and lack of lithiation (dark areas) in the electrode. (Photo from NTSB report on Boeing 787 investigation)

Other Challenges

- Cell to cell interconnect integrity through life of battery; non-uniform stresses on interconnects
- Terminal Connections - integrity
- Temperature tolerance and lifetime stability of cell to cell connections; tab integrity (oxidation/corrosion of tab surfaces and connection points)
- Interconnects' current carrying capability – is it fully understood?
- Can cause cell swelling; loss of terminal seal, etc.





Summary

Is safety of used batteries a concern?

Yes

Can used batteries be repurposed safely?

Yes, if done meticulously

Methods to Determine Module Health Before Second Life

Destructive Analysis:

- Using high fidelity thermal analysis for the battery/module design, the module exposed to worst case thermal deviations should be chosen for testing (as it will not be reused)
- Carry out voltage, capacity and internal resistance/ac impedance tests
- Carry out cell to cell interconnects' integrity tests, complete visual inspection and voltage measurements on each cell /cell bank
- Disassembly of module followed by measurement of cell voltage, capacity of individual cells, internal resistance and ac impedance tests
- Disassembly of cells to study electrodes and electrolyte; three electrode cell studies
- Safety tests at the module and cell level to study any variations in safety characteristics between used and baseline values (inclusion of ARC along with electrical safety tests will add value)

Methods to Determine Module Health Before and During Second Life

For Modules to be reused:

- Visual inspection (should include internal component inspection), voltage, capacity, internal resistance/ac impedance
- Functional checks for proposed new second-use application and environment – run profiles in the relevant environment to confirm that module can perform as required
- Functional checks through complete process of assembly and after assembly into stationary energy storage configuration for utilities.
- Continuous monitoring of health of the cells, modules, battery and system to look for anomalies – allows for early problem detection
- Confirm that charger is suitable for the age of the battery

Future Studies

Carry out module level safety test

Carry out aging tests on li-ion pouch cell format

Acknowledgment

Texas A&M University team for current collaborations with UL:

Prof. Partha Mukherjee

Daniel Robles

Chien-Fan Chen

THANK YOU.