Aging and Safety of Li-ion Cells and Modules of Two Different Formats

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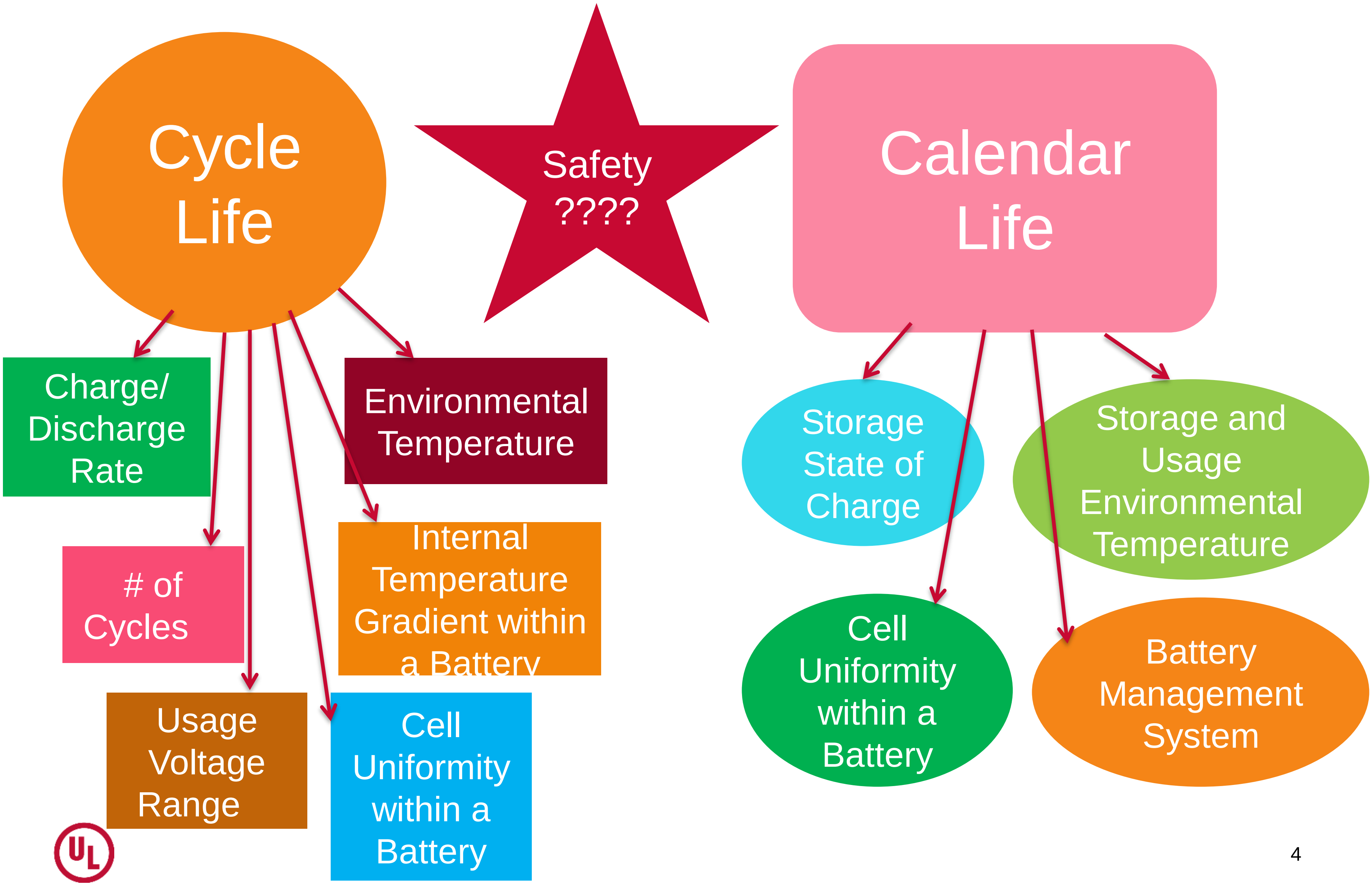
Outline

- Background
- Factors affecting aging
- Past Studies
- Current Studies
- Summary and Recommendations

Introduction

- **Lithium-ion batteries are used in a variety of applications from consumer electronics, automotive and aviation to space applications.**
- **They have been introduced into the Stationary Energy Storage Systems in recent years**
- **Automotive batteries are being repurposed for use in utility/stationary energy 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



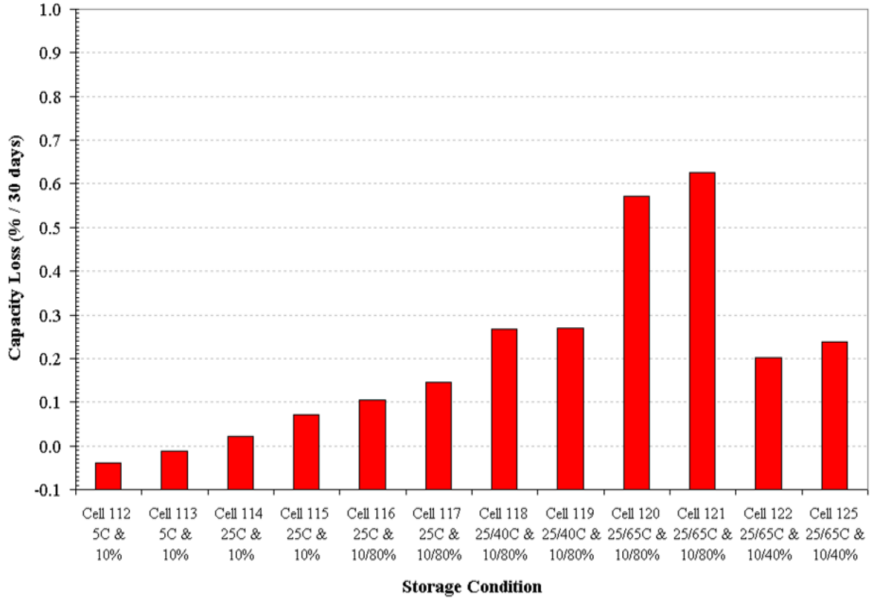
Aging Effects on Cell

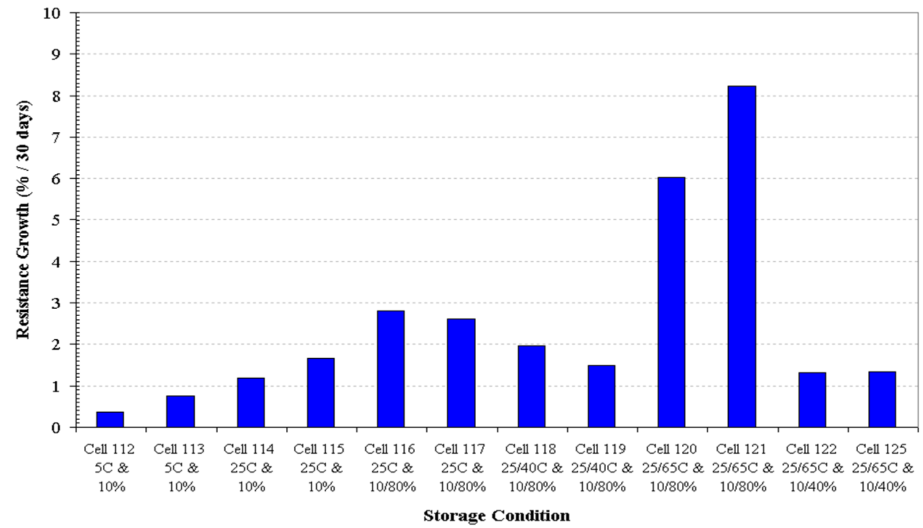
- **Lithiation and de-lithiation causes**
    - Anode electrode morphology changes and volume changes – surface can form cracks leading to electrical isolation; delamination from current collector; changes in intercalation kinetics; loss of active lithium inside anode, etc.
- **Decomposition**
    - 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

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

Various SOC and Temperature Storage
(Calendar Life)





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

Safety after Cycling - Overcharge

3.1 % Capacity loss after 300 Cycles
Cells are of pouch format
Overcharge test has same results on fresh cells and cells that lost ~3% Capacity

J. Jeevarajan, 222nd ECS Meeting, October 2012

Cycle Life Aging and Simulated Internal Short Tolerance

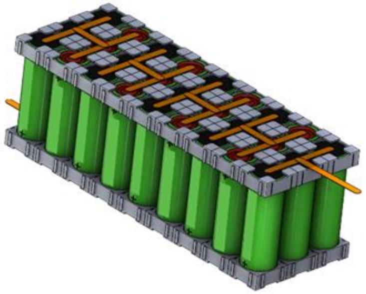
- Cells were cycled at 1C rate of charge and discharge for 1000 cycles
  - Cells lost capacity between 12 to 25%
- Conducted Simulated Internal Short (SIS) tests (Crush test method) - Sample size – 10 cells
  - Tolerance to simulated internal shorts increased with higher loss in capacity– no fire or 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

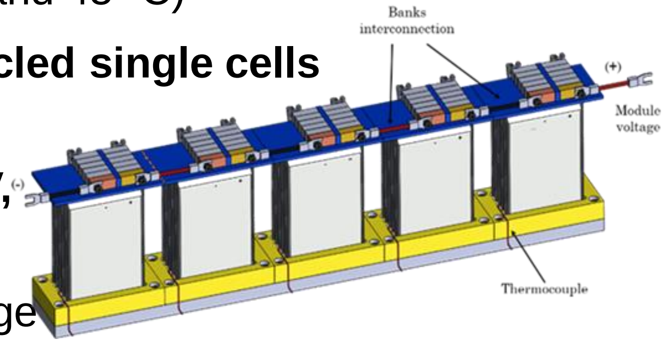
Current Studies

Test Plan – UL/Purdue University



Single Cell Studies – 18650 and pouch formats - ~3.4 Ah capacity

- 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)
- EV Drive cycle profile at 3 temperatures (10 ºC, 25 ºC and 45 ºC)
- **Overcharge and external short test on fresh and cycled single cells**



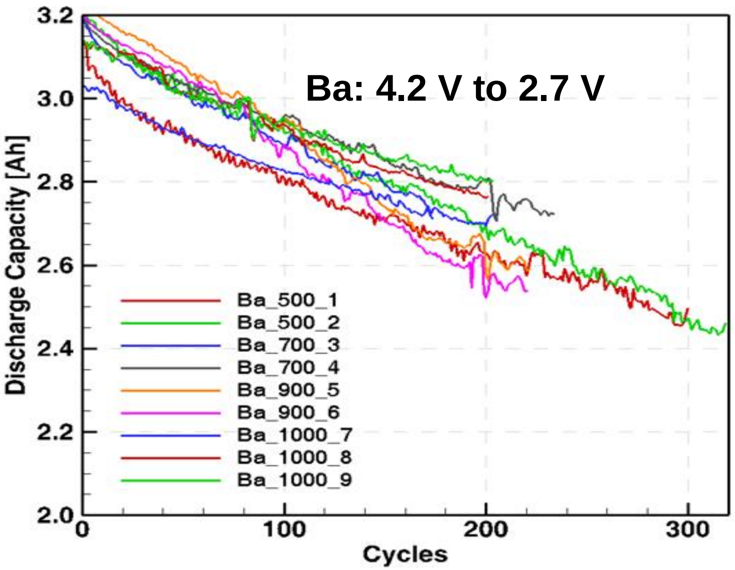
Module (18650 - 3P9S: 33.3 V, 9.9 Ah ; pouch – 5P5S:21V, 16.5 Ah) Studies

- 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 (for 18650 cells and modules only)
- **Overcharge and External short test of fresh modules and overcharge test of cycled modules for 18650 cells; overcharge and external short test for pouch format cells**

Destructive Analysis:

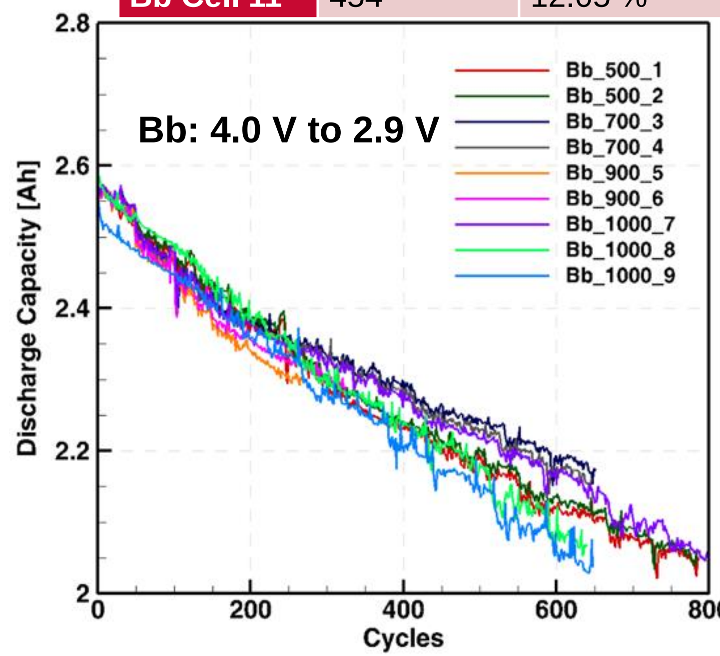
- Fresh cells : un-cycled, externally shorted cell and overcharged cell
- Cycled cells (cells removed after 10%, 15% and 20% capacity loss), externally shorted cycled cells, overcharged cycled cells

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

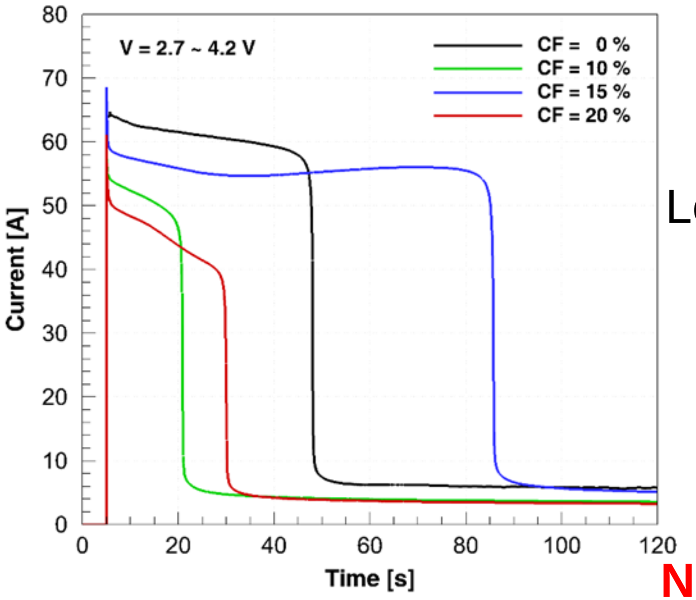


Cell ID	Number of Cycles	Capacity Fade
Ba Cell 2	319	26.70 %
Ba Cell 1	300	24.23 %
Ba Cell 6	221	23.79 %
Ba Cell 5	222	22.97 %
Ba Cell 4	234	18.74 %
Ba Cell 8	201	16.21 %
Ba Cell 10	269	15.49 %
Ba Cell 3	201	15.41 %
Ba Cell 9	204	15.17 %
Ba Cell 7	174	10.59 %

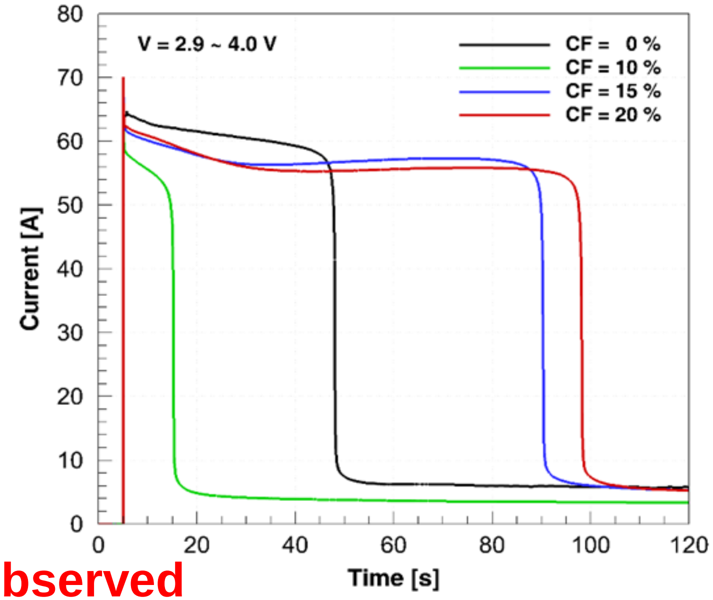
Cell ID	Number of Cycles	Capacity Fade
Bb Cell 1	787	25.30 %
Bb Cell 2	785	25.29 %
Bb Cell 7	800	23.87 %
Bb Cell 8	640	20.11 %
Bb Cell 9	648	20.09 %
Bb Cell 10	616	15.65 %
Bb Cell 4	647	15.50 %
Bb Cell 6	324	15.44 %
Bb Cell 3	651	15.26 %
Bb Cell 5	267	14.94 %
Bb Cell 11	454	12.05 %



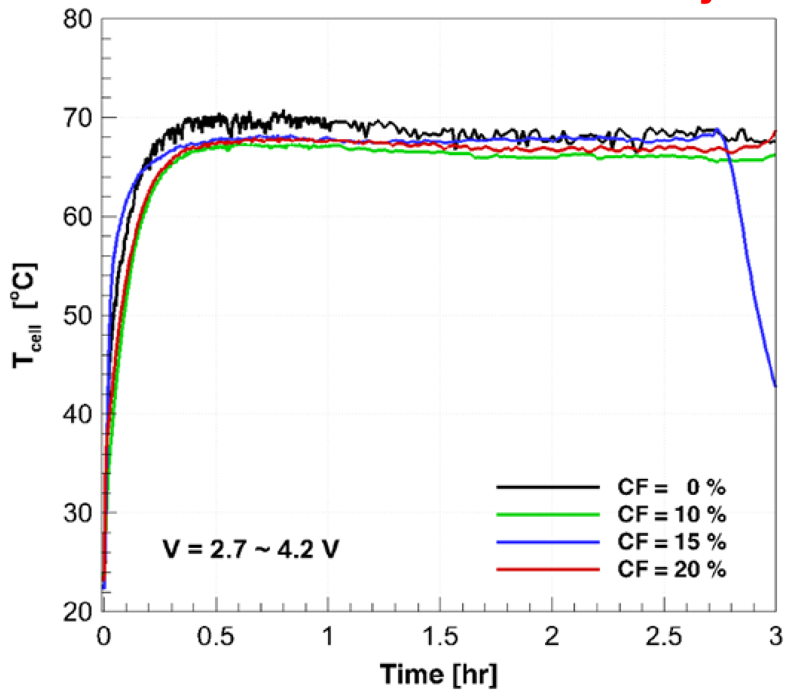
Safety Trend: External Short Test – 18650 Li-ion Cell

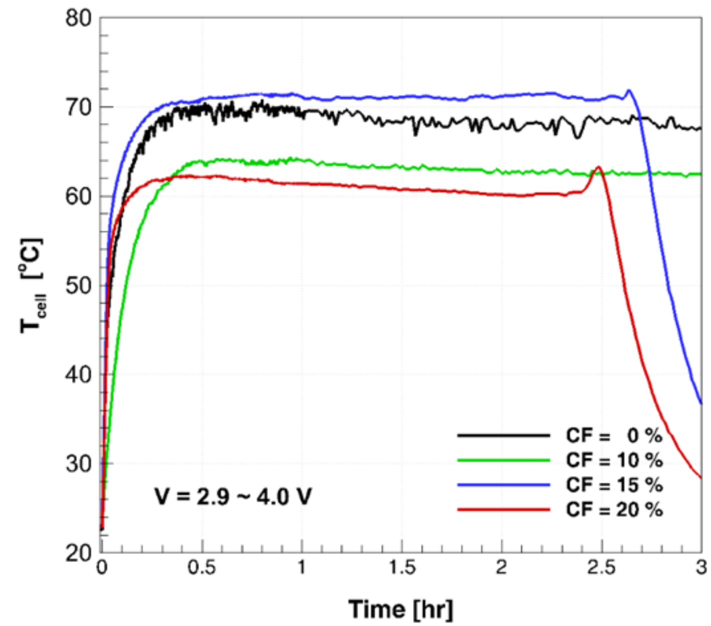


Load: 50 mohm



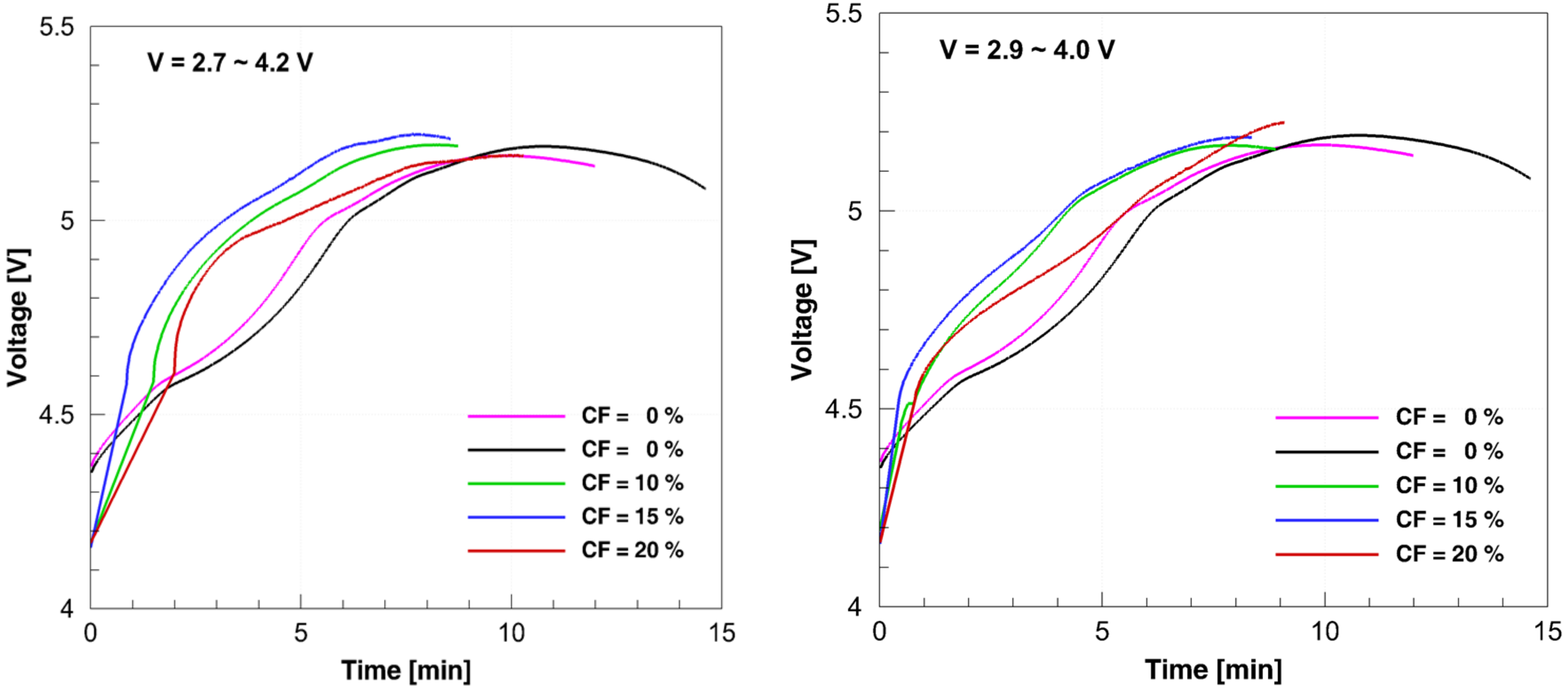
No Major trend observed





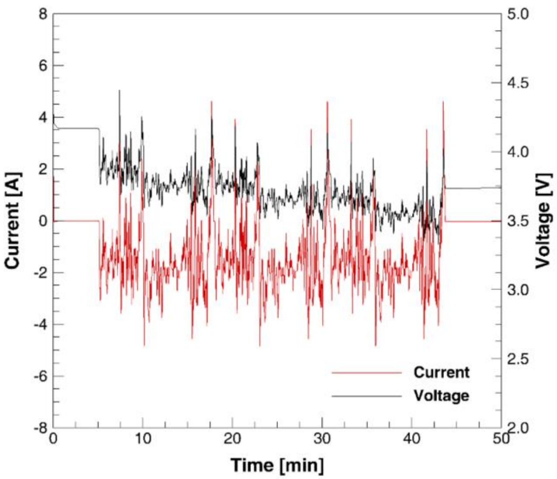
Overcharge Test

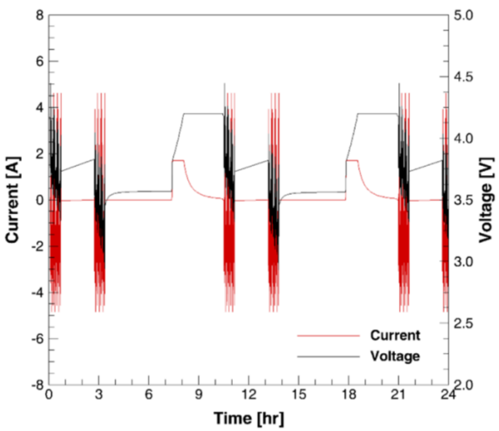
Overcharge current: 1C rate to 12V limit



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



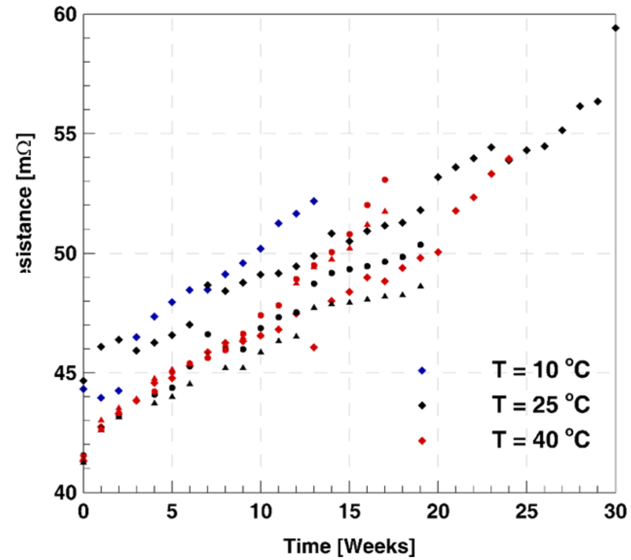


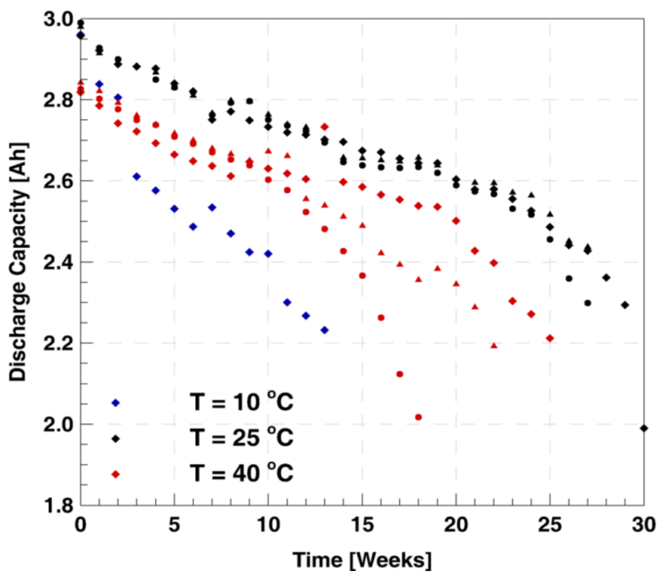
2-hr rest period between cycles;
Normal capacity checks once a week

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

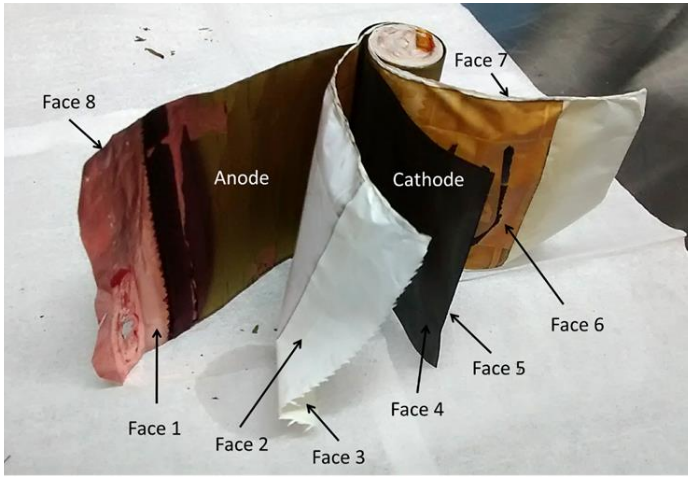
Cell at 25 ºC: 25% Capacity Fade (29 weeks)
(33% increase in internal resistance)

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%

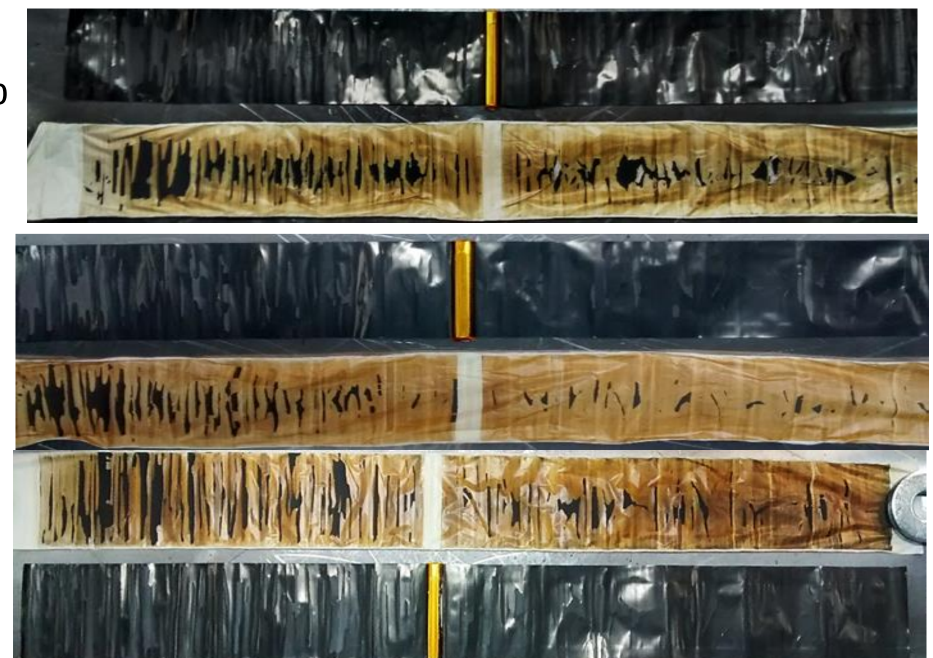
20%

Cathodes

10%

15%

20%



DPA of cells that underwent Cycle Life tests only

DPA after safety tests on cycled cells - Cathodes

External Short

Ba10%

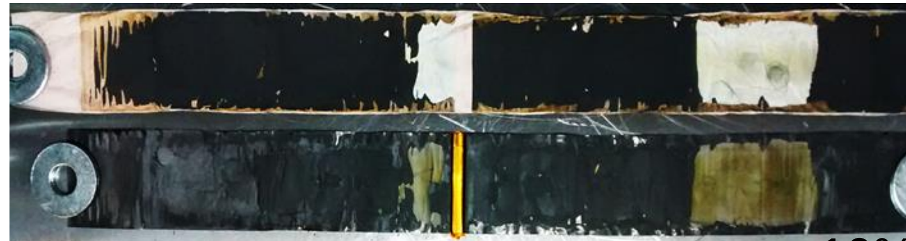
Ba 20%

Bb10%

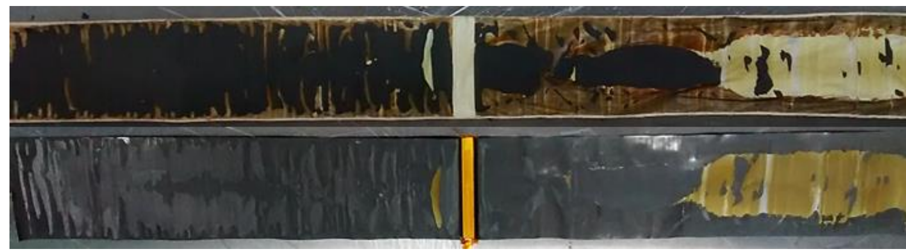
Bb 20%

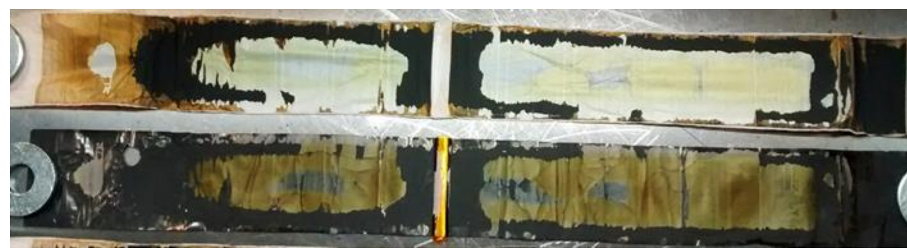
Overcharge

DPA below shows both sides of electrode

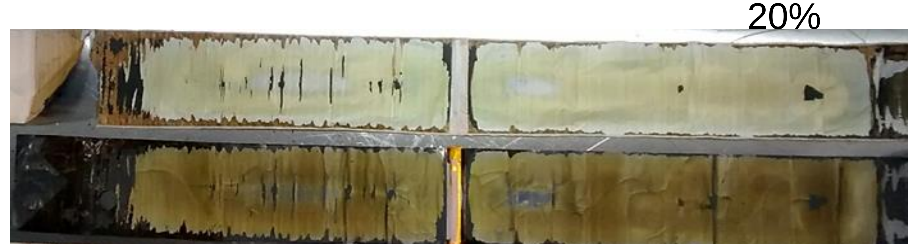


10%





20%



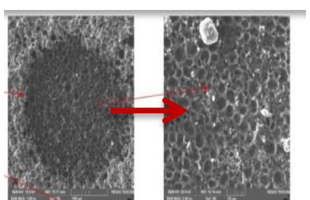
(ceramic coating is typically on surfaces of separator facing cathode – see graphic on slide 19); in cells that underwent safety tests the coating is stuck on the electrode surface

Electric Vehicle Drive cycle – Single cells

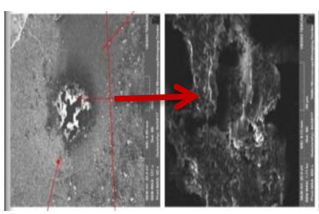
	Cycling
Section Ca (25 °C) Ambient Temperature	**Cell Ca 2** CF = 23.11 % Weeks = 27 Cycles = 3126
Section Cb (10 °C) Low Temperature	**Cell Cb 1** CF = 24.56 % Weeks = 13 Cycles = 1347
Section Cc (40 °C) High Temperature	**Cell Cc 1** CF = 21.52 % Weeks = 25 Cycles = 2730

Electrodes after Cycling

Electrodes after Cycling + External Short



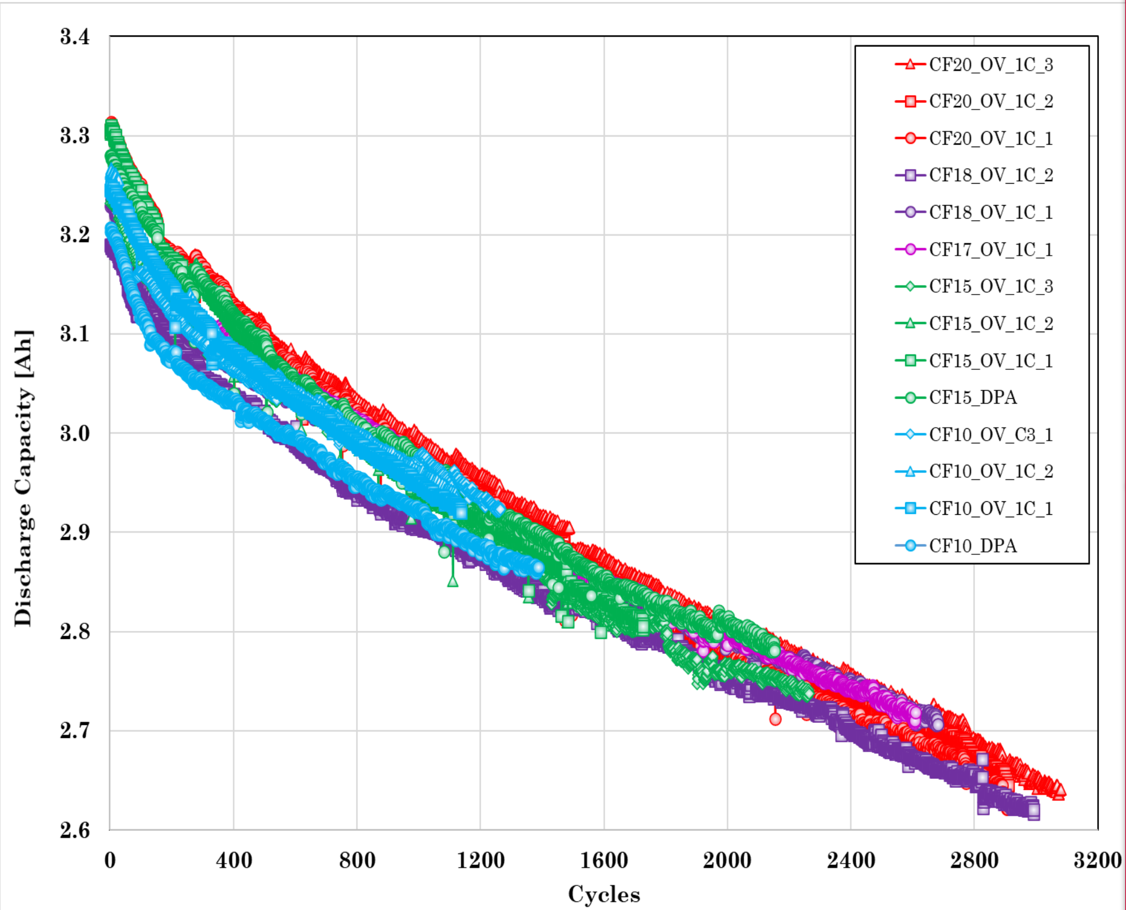
SEM of cycled cathode at ambient temperature



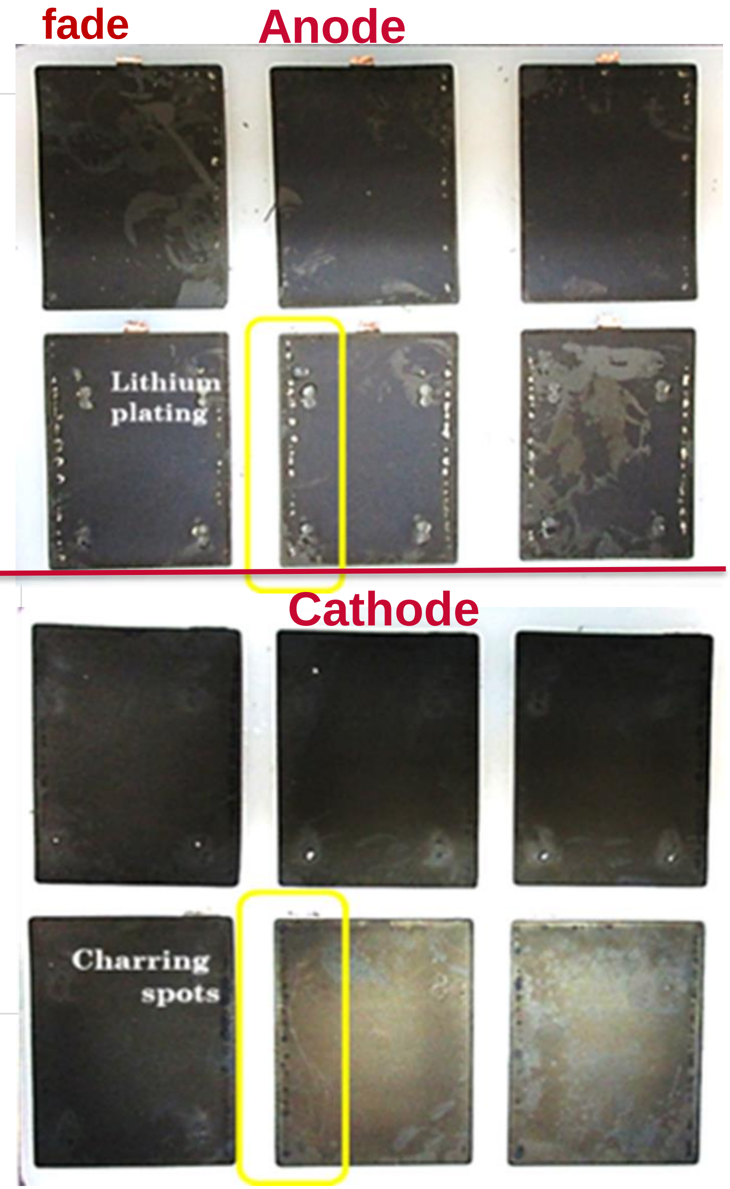
SEM of cycled anode at ambient temperature (after solvent added)

Electrodes after Cycling + Overcharge

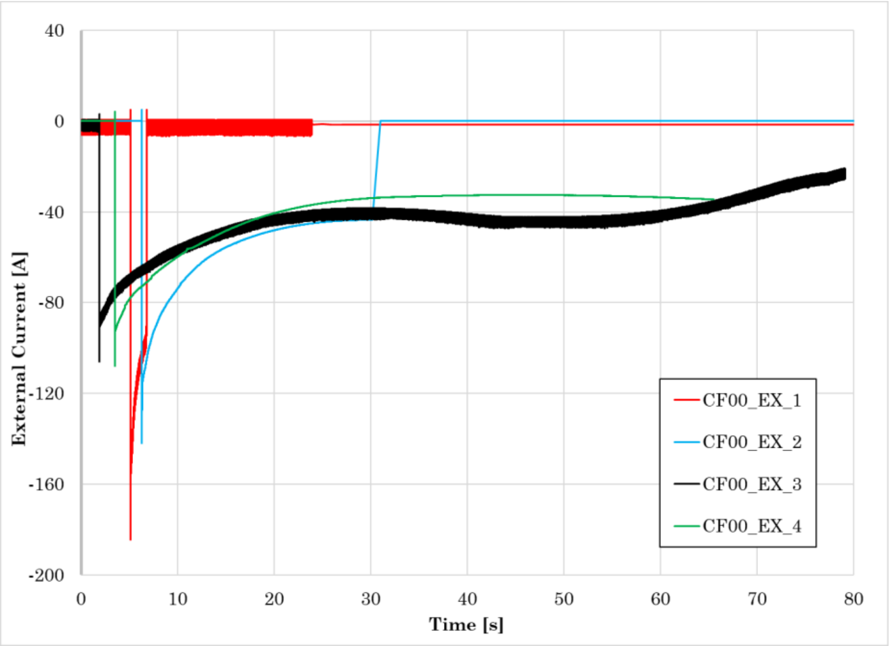
Discharge Capacity – Pouch Format - Single Cells



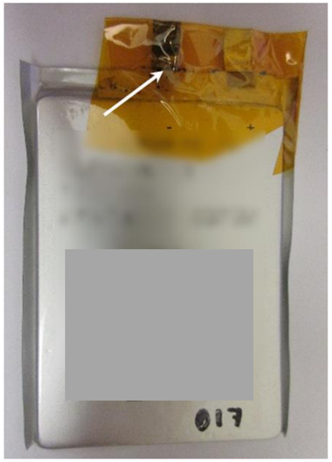
Electrodes in Li-ion Pouch Format Cells after 20% capacity fade

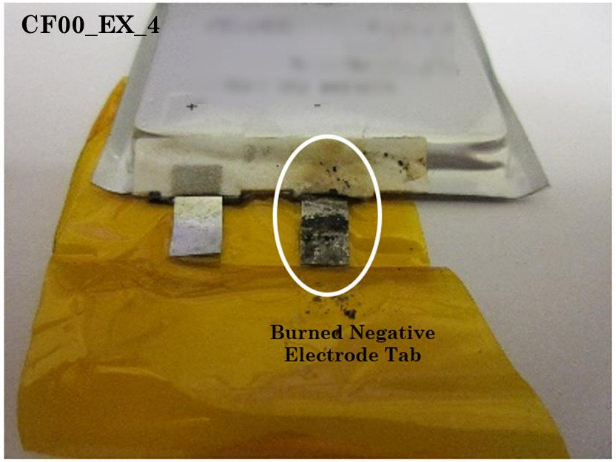


External Short – Pouch Format Cells – Fresh



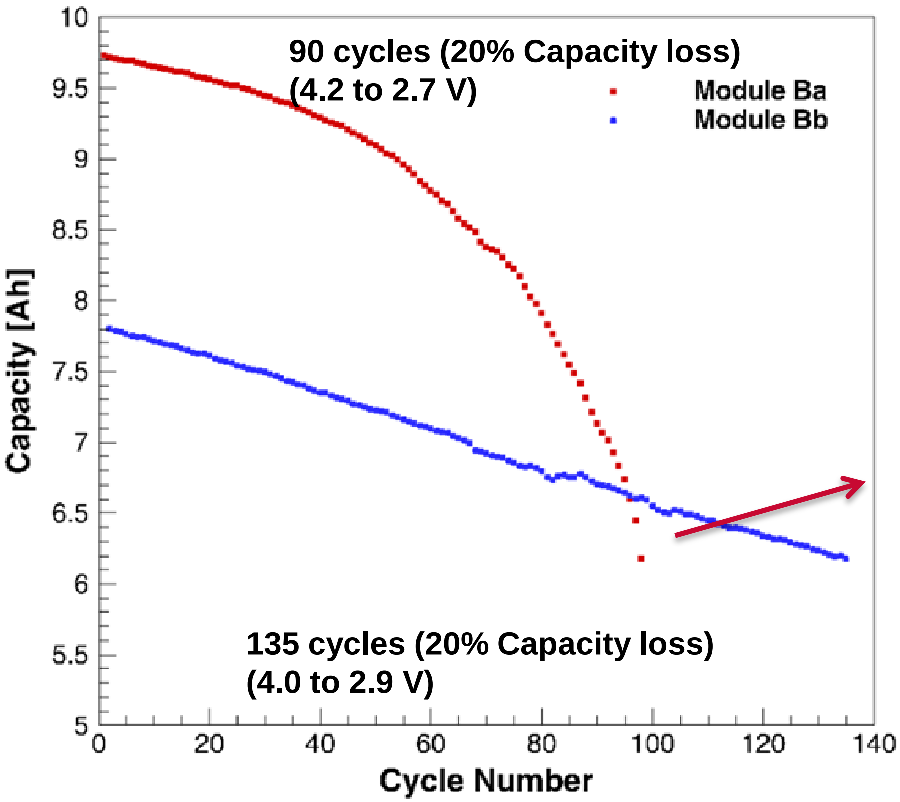
Postmortem analysis of fresh cell externally shorted before the pouch removal. No swelling; negative tab burned off





Module Cycle life Trend – 18650 and Pouch Format

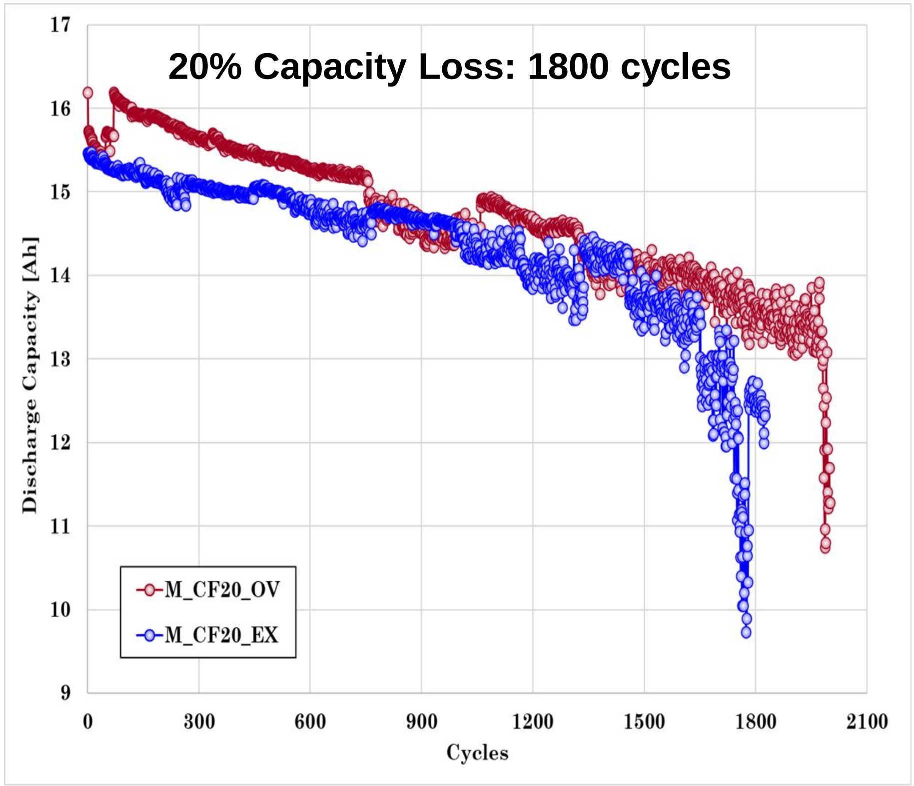
18650 Cell Modules



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

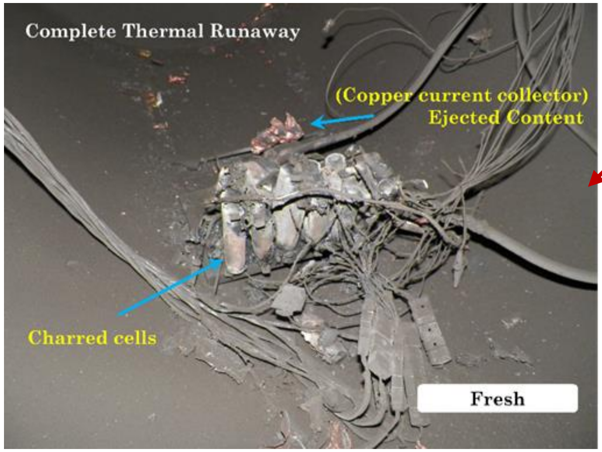
Pouch Format Cell Modules

5P5S Module
4.2 V to 2.7 V per bank



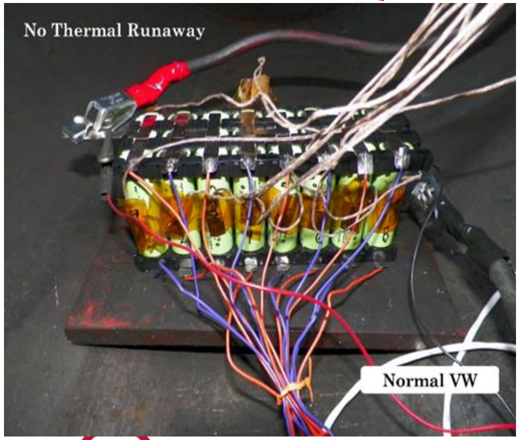
Safety of Cycle-Life Aged Modules - Overcharge Test

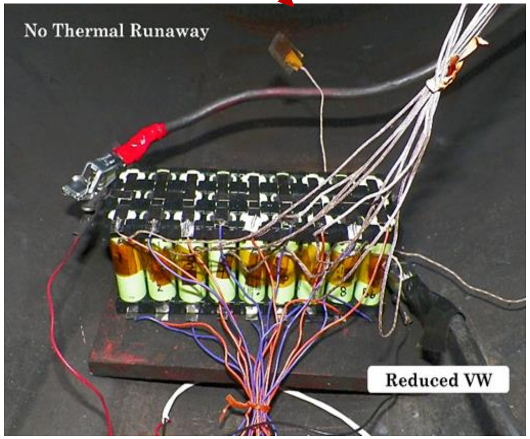
Cylindrical 18650 Cell Modules – Post Test



Fresh Module

Cycled Modules – 20% capacity loss





Pouch Format Cell Modules- Post Test

Fresh Module

Cycled Module- 20% capacity loss

Summary

Lithium-ion cells and modules undergo capacity degradation at different rate depending on several factors

- The cell design which includes the internal construction and the amount of electrolyte as well as the rate capability of the cells play an important role in the degradation.

- It was observed with the cylindrical cells that in spite of the internal protective features activating under off-nominal conditions of overcharge and external short circuit, heat is produced internally and hence physical degradation and changes to the electrodes and separator are observed in both the fresh and the aged cells.
- Cylindrical cells and modules aged to 20% or higher capacity fade are more benign than the fresh cells under the off-nominal conditions tested.
- The pouch format cells are still reactive at 20% capacity fade under the overcharge conditions but experience tab burning under the external short conditions.
- Single cell abuse tolerance does not translate to module or battery level tolerance.

Questions

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

- 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 **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 are recommended
- **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

Carry out initial as well as periodic cell to cell interconnects' integrity tests, complete visual inspection and voltage measurements on each cell /cell bank

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

UL 1974 – Standard for Second Use of Lithium-ion Batteries

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