

Safety Limitations Associated with Commercial 18650 Lithium-ion Cells

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Introduction

- In the past decade, NASA-JSC battery group has carried out several tests on the safety of li-ion cells, modules and battery packs
- The hazards associated with using commercial li-ion cells in high voltage and high capacity batteries have been determined to be different from those associated with the use of the same cells in low voltage, low capacity packs (less than 15 V and 60 Wh)
- Tests carried out included overcharge, overdischarge, external and internal short circuits with destructive physical analysis included in most cases.
 - Chemical analysis, X-rays and in some cases CT scans were used for post-test analysis

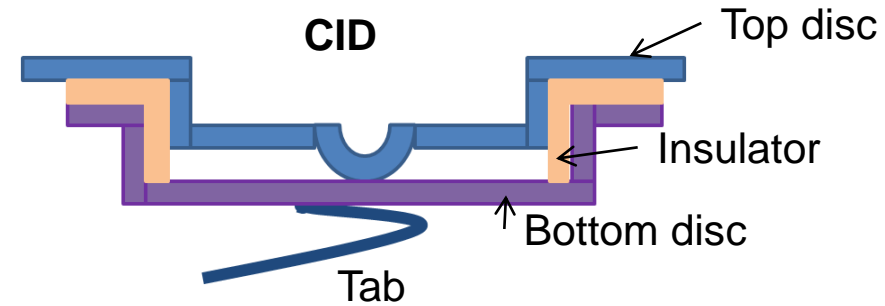
Outline

- Limitations of internal protective devices such as the PTC and CID in 18650 li-ion cells
- Safety of the 18650 li-ion cells in a vacuum environment
- Overdischarge test results for 18650 li-ion cell modules
- Safety of Matrix pack design for 18650 li-ion cells
- Internal short hazards in li-ion cells

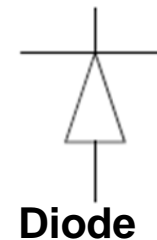
Data and information for these topics has been presented at earlier conferences and the references will be presented under each section

Background

- Lithium-ion cells, whether cylindrical, prismatic, elliptical, etc. have different forms of internal protective devices
 - PTC
 - CID
 - Tab/lead meltdown (fusible link type)
 - Bimetallic disconnects
 - etc.



- External protective devices used in lithium-ion battery designs are
 - Diodes
 - PTC/polyswitch
 - Thermal fuses (hard blow or resettable)
 - Circuit boards with specialized wire traces
 - etc.



- Manufacturing quality will be discussed with respect to internal short hazards – cell quality as well as uniformity of cell performance is very critical

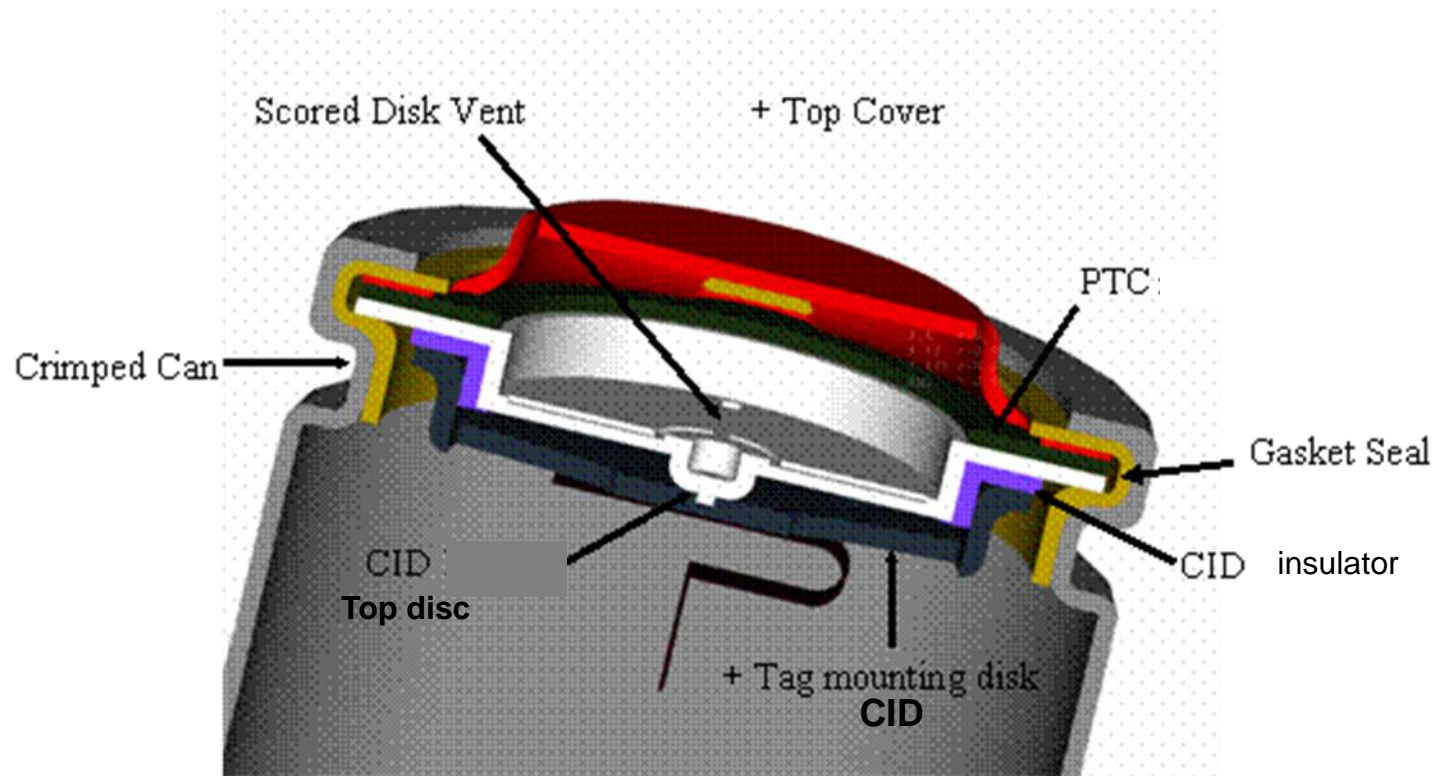
Limitations of Internal Protective Devices in 18650 Li-ion Cells

Limitations of Internal Protective Devices in 18650 Li-ion Cells

(Data presented at Power Sources 2008)

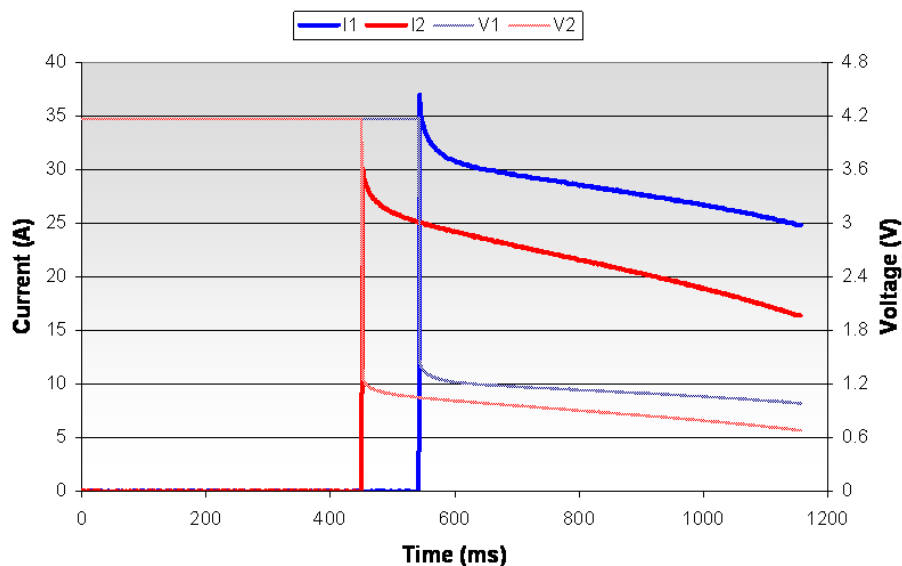
- Test programs in the past decade indicated that internal protective devices (such as the PTC and CID) in small cylindrical COTS (commercial-off-the-shelf) Li-ion cells failed to protect when the battery module designs included multi-cell series and/or parallel configurations. However, a definite set of tests were not carried out to characterize these limitations.
- In this test program, the tests were carried out with cells in series and/or cells in parallel
- The tests carried out were off-nominal and were carried out under worst-case conditions to determine the worst-case failures that could occur.
- Cells used for these test programs were only test vehicles to provide data for the issue being discussed and also due to ease of availability. The test results do not infer any type of endorsement and are presented for information purposes only.

Schematic of Cell Header Portion

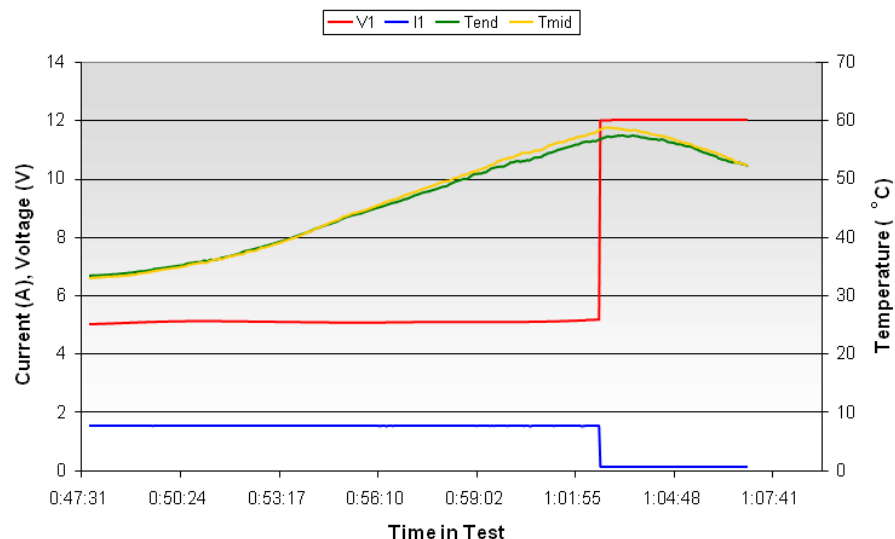


External Short and Overcharge on Single 18650 Li-ion Cells (low voltage)

N2-360-1A, Samples 1 and 2, 50mOhm SC, 18Oct07



N2-360-2A-11, 12V 1.5A Overcharge, Single Cell, 19Oct07



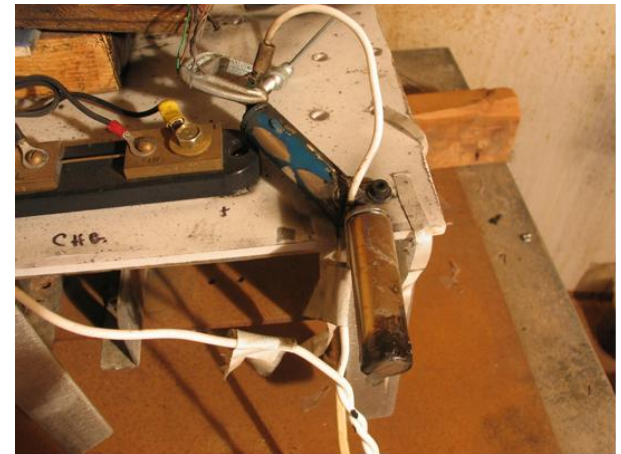
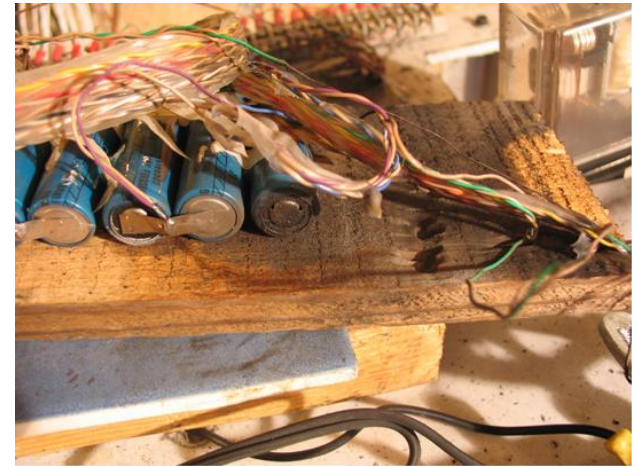
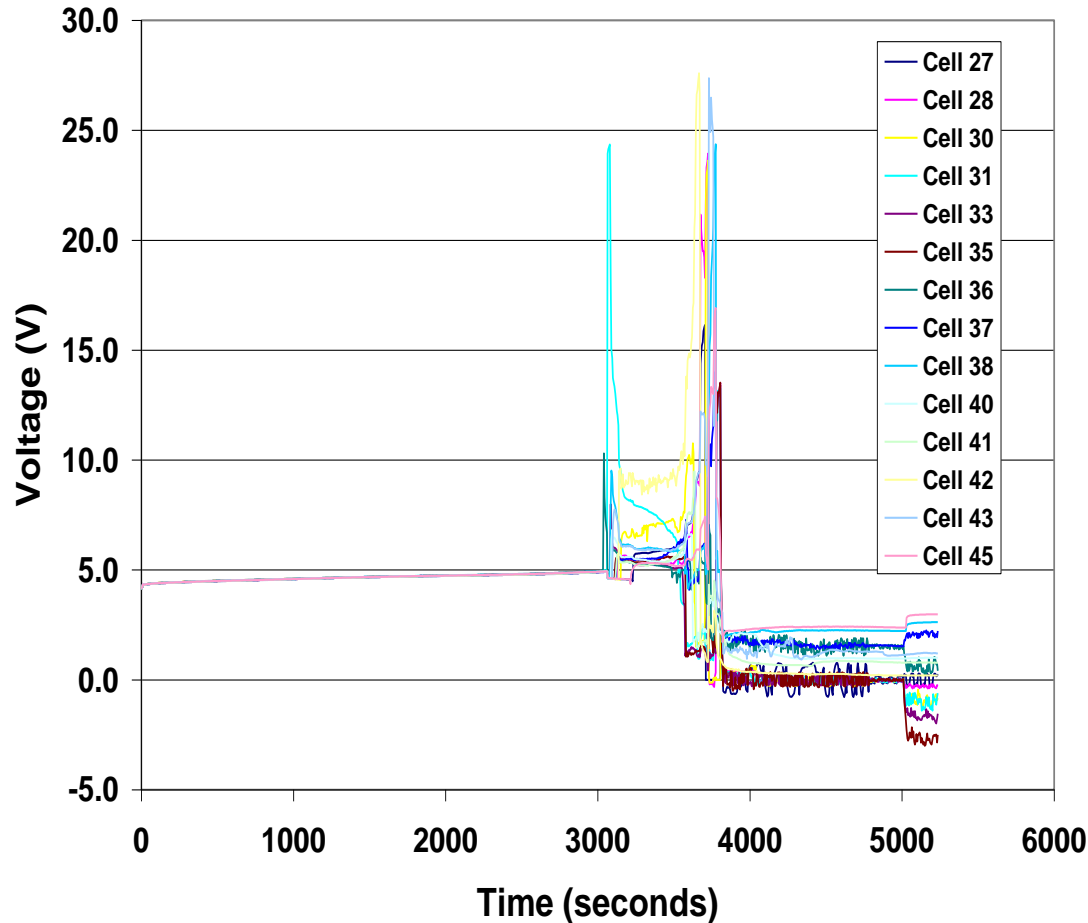
	Peak Current (A)	Peak Temp (°C)
N2-360-1A-1	37	78
N2-360-1A-2	30	82

Operation consistent with typical 18650 cell PTC performance

	Sample Temp. at CID Open (°C)
N2-360-2A-11	59
N2-360-2A-12	73

CID devices activated in both samples at 1 hour and 2 minutes into the overcharge.

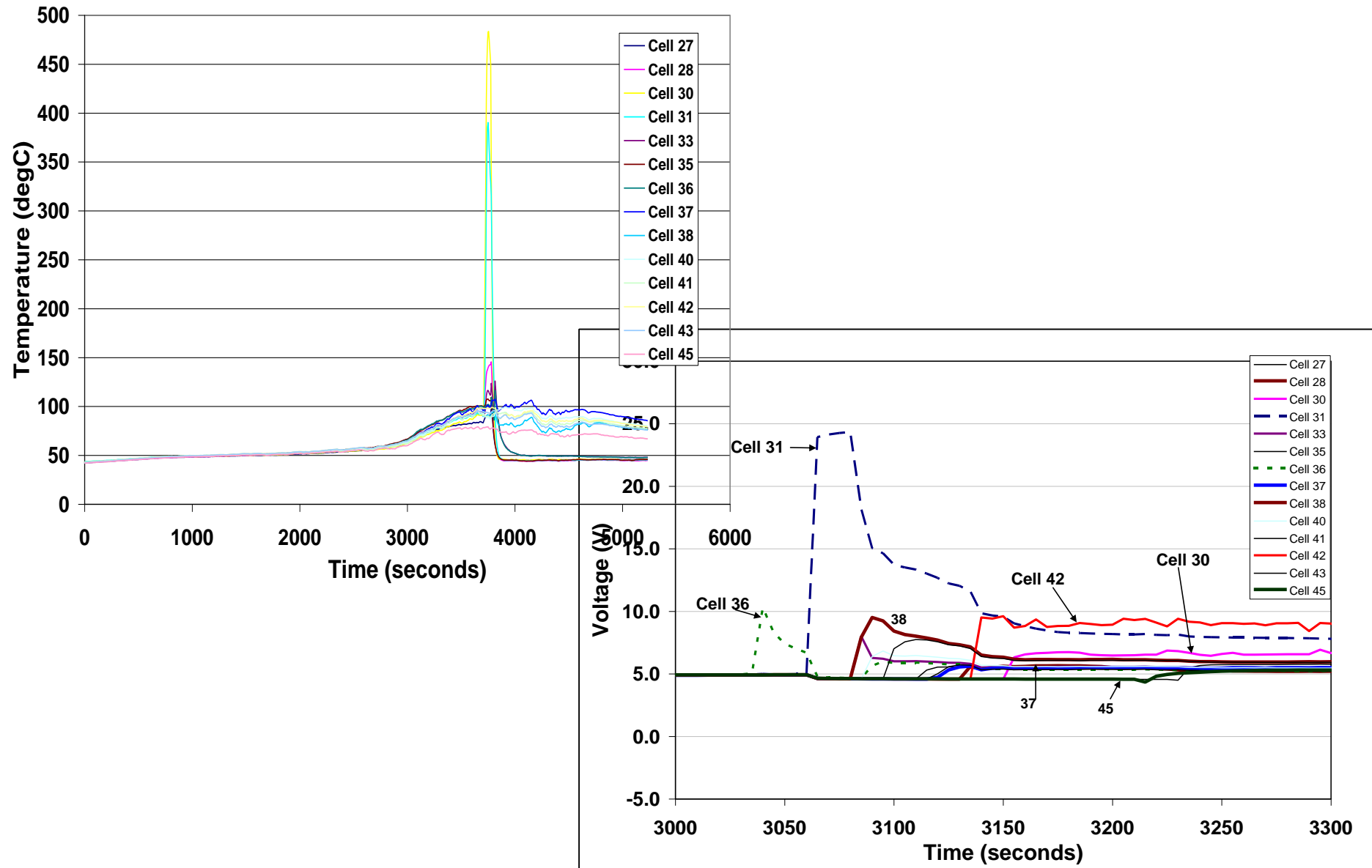
Overcharge Test on a 14-Cell String Showing Cell Voltages for the 18650 Li-ion Cells (High voltage)



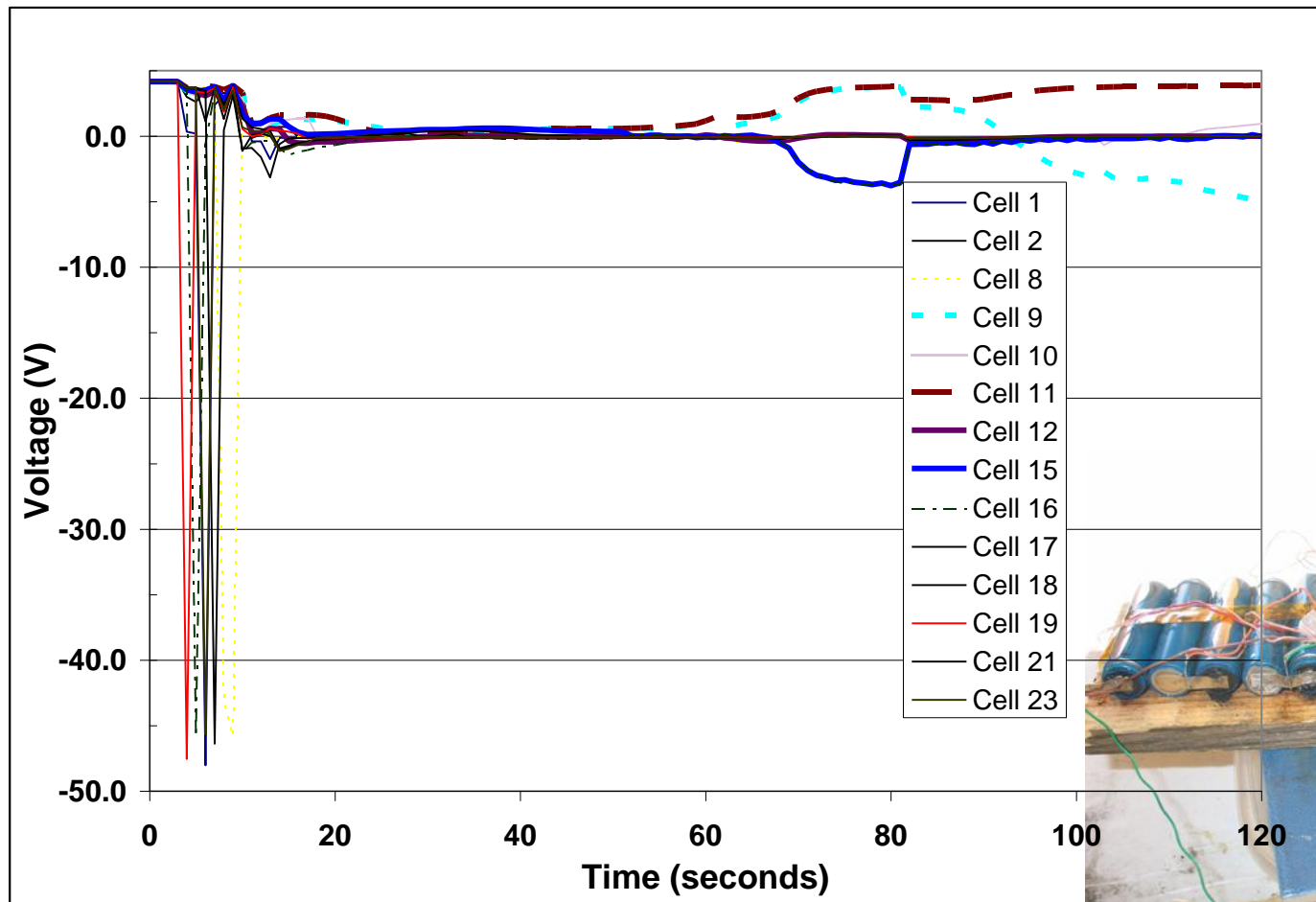
Cells missing from 14-cell string on test table after test event : 27, 28, 30 and 31

**Cells 37, 38 and 45 showed no visible
Signs of venting**

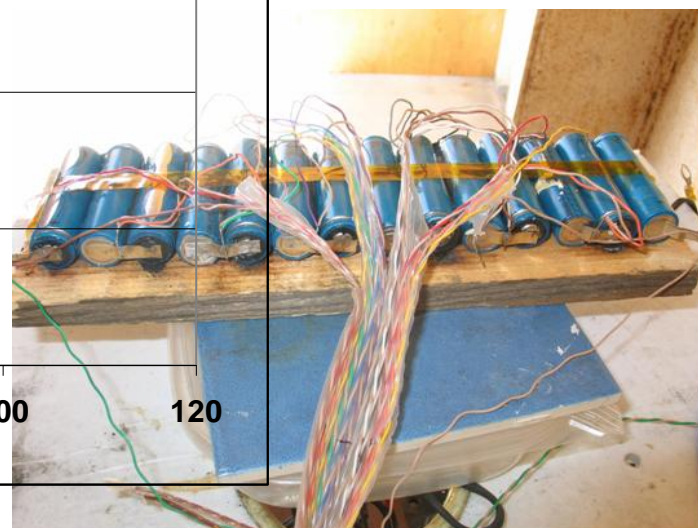
Overcharge Test on 14S set of 18650 Lithium-ion Cells (contd.)



14-Cell String Short Circuit Test on 18650 Li-ion Cells (High Voltage)



Only venting observed,
no fire
Cell Voltages in bold –
No visible signs of
Venting or damage,
but no voltage;
All others vented with
Obvious leakage or
discoloration



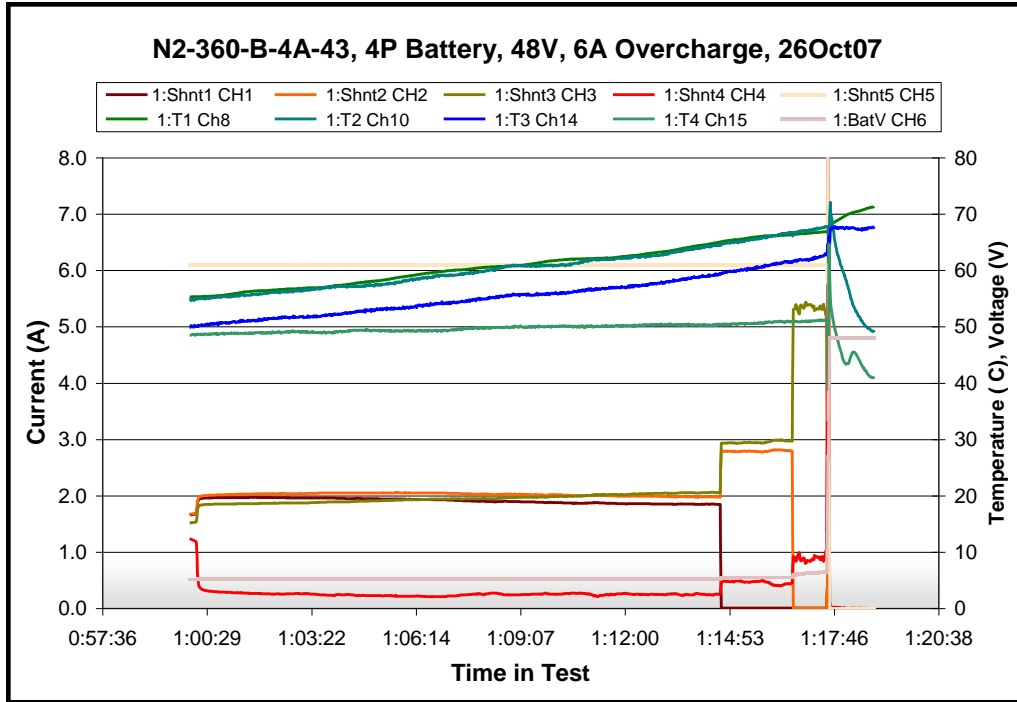
Rapid cell venting within the first 10 seconds

Variable Bank (High Capacity) Size Test Summary Table

Test Code	Date	Old Cells	New Cells	Description	Volts	Amps
1A	18-Oct	2		Single cell short, 2X		
2A	19-Oct	2		Single cell overcharge, 2X	12	6
4A	26-Oct	4		4P overcharge, 48V, 6A	48	6
4A2	24-Oct	4		4P overcharge, 12V, 6A	12	6
4A3	31-Oct	4		4P overcharge, 12V, 4A	12	4
4A4	1-Nov		4	4P overcharge, 12V, 6A	12	6
4B	2-Nov		16	16P overcharge, 48V, 24A	48	24
4A5	15-Nov	4		4P overcharge, 12V, 6A	12	6
4B2	19-Nov		16	16P overcharge, 12V, 24A	12	24
4B3	19-Dec		16	16P overcharge, 12V, 12A	12	12
3B	31-Jan		16	16P short circuit		

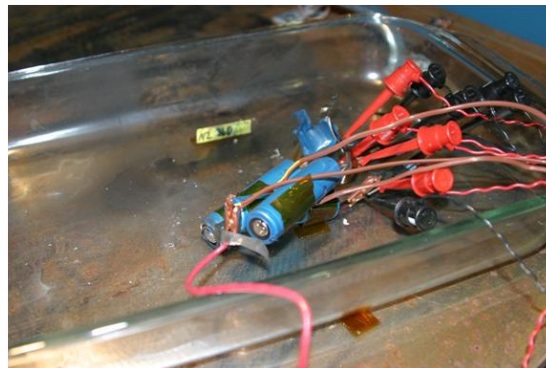
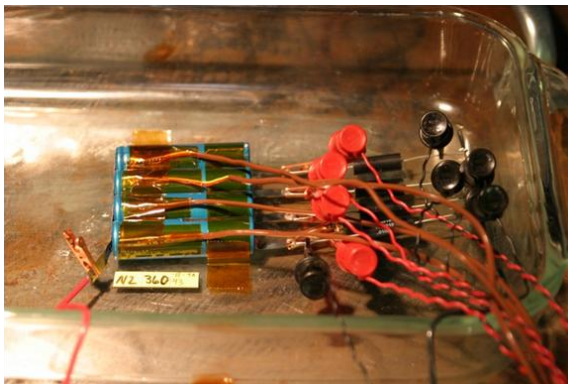
- Test 1A- 50mOhm Short Circuit on Single Cells
- Test 2A- 12V, 1.5A Overcharge on Single Cells
- Test 4A- Overcharge on 4 parallel cells
- Test 4B- Overcharge on 16 parallel cells
- Test 3B- Short Circuit on 16 parallel connected cell battery

Overcharge Tests on 4P 18650 Li-ion Module (High Capacity)



- The current on cell 4 in the parallel battery dropped low at ~1 hour into the overcharge; 14 minutes later the three other cells began to trip CID devices (a pop was audible) in sequence
- When the 3 cells dropped out, cell 4 was left carrying the 6A charge current.
- Cell 4 ruptured with flame (explosion); The cell can was split; temperature of the cell at the time of the event was 51°C

Test 4A- 48V 6A Overcharge on 4P Battery



High Voltage/High Capacity Limitation Studies - Summary Of Tests and Results

Description	Volts	Amps	Load (Ohms)	Notes
Single cell overcharge, 2X	12	1.5		CID operates; Canon / fresh
4P overcharge, 48V, 6A	48	6		Thermal runaway; Canon
4P overcharge, 12V, 6A	12	6		CID operates; fresh
4P overcharge, 12V, 6A	12	6		Thermal runaway / Canon
4P overcharge, 12V, 4A	12	4		CID operates / Canon
16P overcharge, 48V, 24A	48	24		Thermal runaway / fresh
16P overcharge, 12V, 24A	12	24		Thermal runaway / fresh
16P overcharge, 12V, 12A	12	12		CID operates /fresh
16 P external short			2	No thermal runaway /Canon
Single Cell external shorts				No failures; PTC trips / Canon
4S External short			50	No failures; PTC trips / Canon
14S External short			50	PTC fails; venting and sparks / Canon
4S Overcharge	48	1.5		No failure; CID activates / Canon
14S Overcharge	84	1.5		Thermal runaway / Canon

Limitations of Internal Protective Devices in 18650 Li-ion Cells

Summary

- The PTC characteristics varies from manufacturer to manufacturer in their trip currents as well as withstanding voltages. The withstanding voltage of the PTCs implies that they have a voltage limitation.
- Tripping cell PTCs irreversibly increases their electrical resistance by up to a factor of two. Compromised or high-resistance PTCs cause catastrophic failures under overcharge conditions.
- The CID did not protect or underwent incomplete opening and reset under some overcharge conditions.
 - Cell internal heating causing separator damage, PTC ignition before CID opening, etc.
- In cell banks, two major factors dictated the reaction of the cells to overcharge conditions. These were the charge current and voltage of the cell string or voltage limit set on the equipment. For example, 16 cells in parallel went into a thermal runaway under 48 V, 24A conditions as well as 12V 24A conditions. But they did not go into a thermal runaway under 12 V, 12 A test condition.
- The complete data set can be obtained from the presentation at the Power Sources 2008.

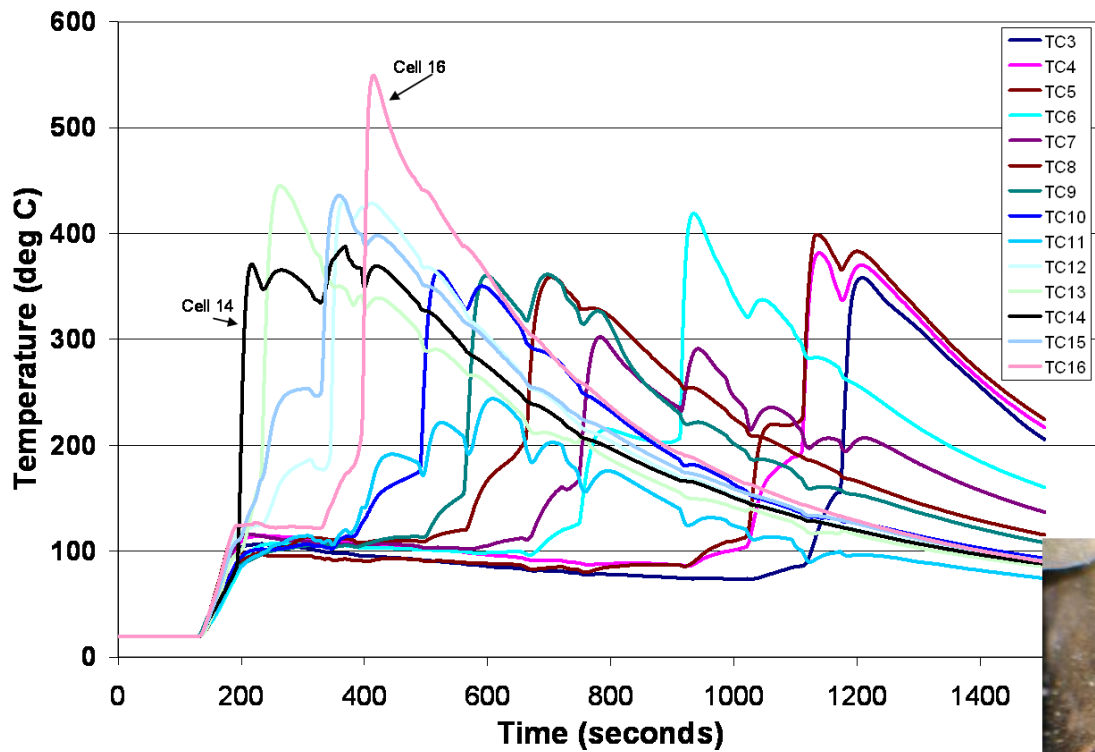
Overcharge and External Short Tests for High Voltage 18650 Cell Strings under Vacuum Conditions

Overcharge and External Short Tests for High Voltage 18650 Cell Strings under Vacuum Conditions

(Data presented at NASA Battery Workshop 2008)

- Li-ion batteries are used in various environments in space including vacuum
- It is important to determine the safety of the high voltage li-ion cell modules in a vacuum environment under conditions of overcharge and external short circuit to help design the modules safely
- A summary of the results from this test program will be presented here
- For more details, refer to paper presented at NASA Battery Workshop 2008

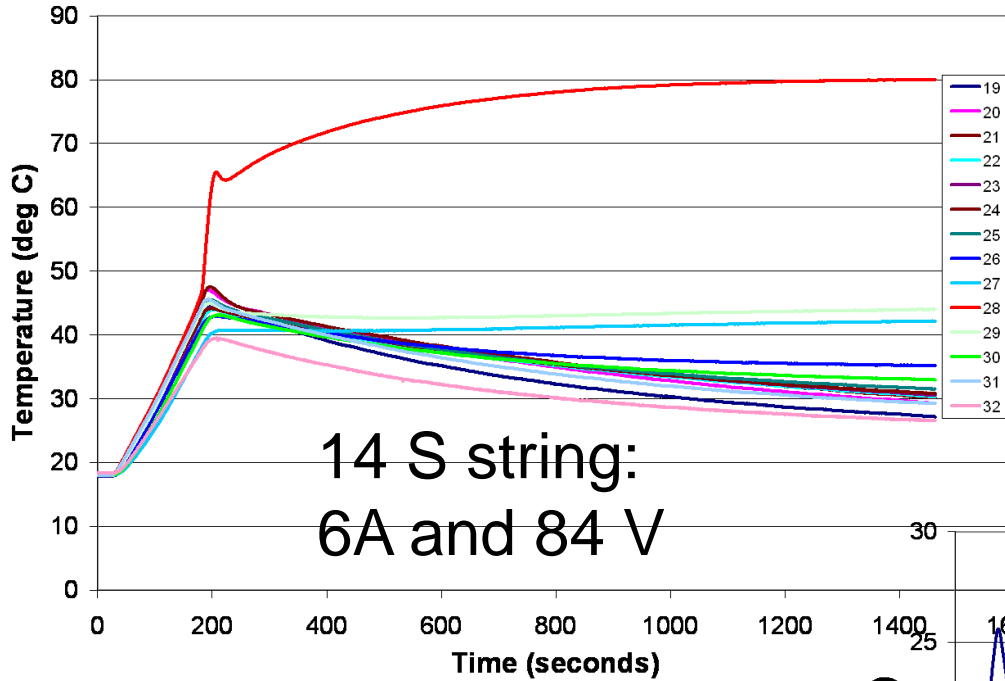
External Short under Vacuum Conditions (High Voltage 14S string)



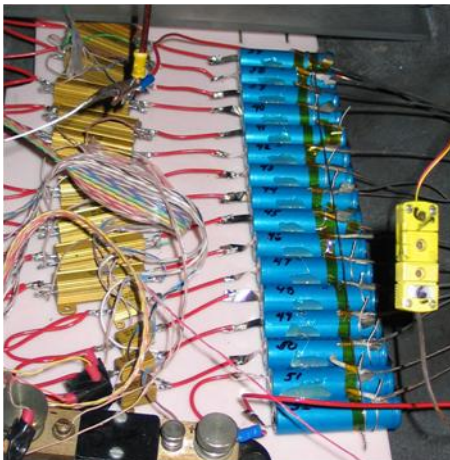
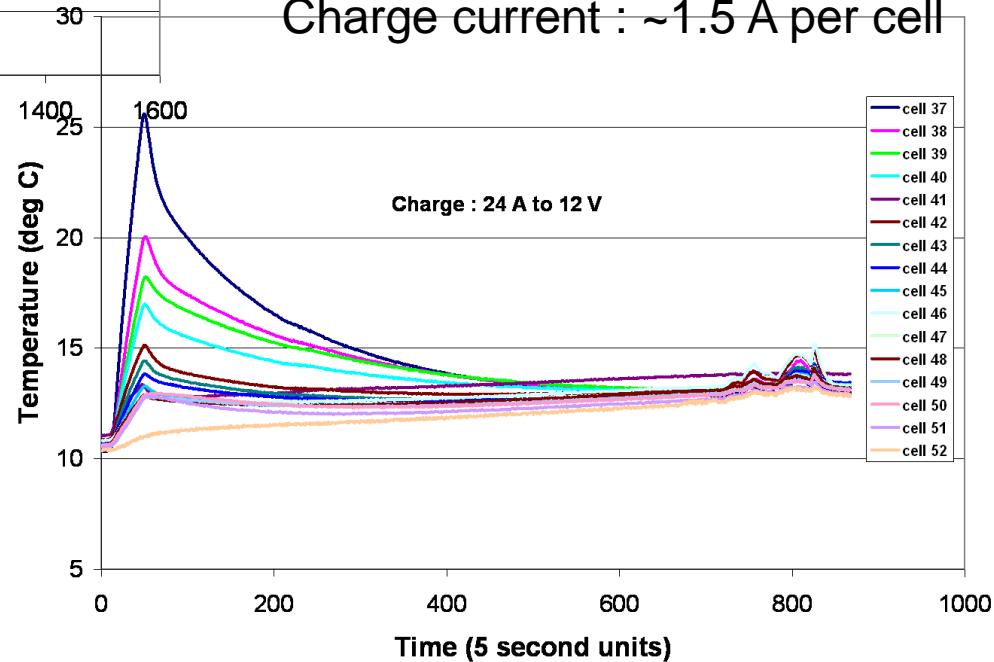
50 mohm



Overcharge Test on High Voltage Li-ion Cell String (14S) Under Vacuum Condition



16P Bank (12 V and 24 A)
Charge current : ~1.5 A per cell



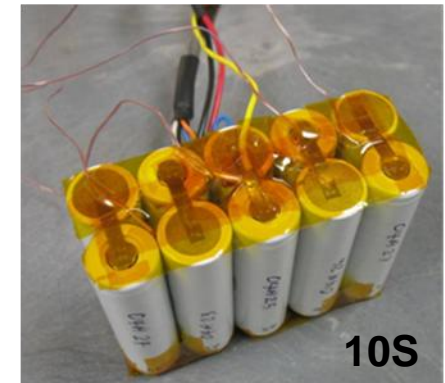
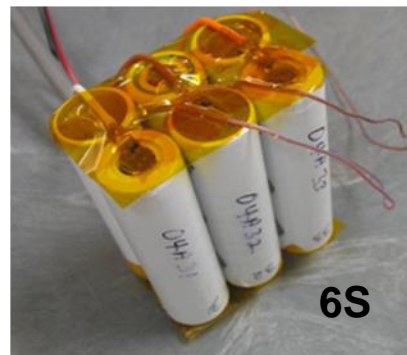
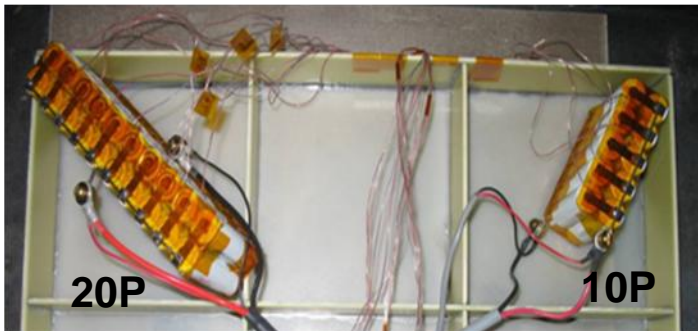
Overcharge and External Short Tests for High Voltage 18650 Cell Strings under Vacuum Conditions Summary

- Under Vacuum conditions, the external short test caused thermal runaway in all the 14S (14 series) cells, but the overcharge condition in the series and parallel configurations did not result in a thermal runaway.
 - These results are the opposite of that seen at ambient pressure environments
- It is critical to test under the relevant environment to understand the worst case hazards encountered with the high voltage strings

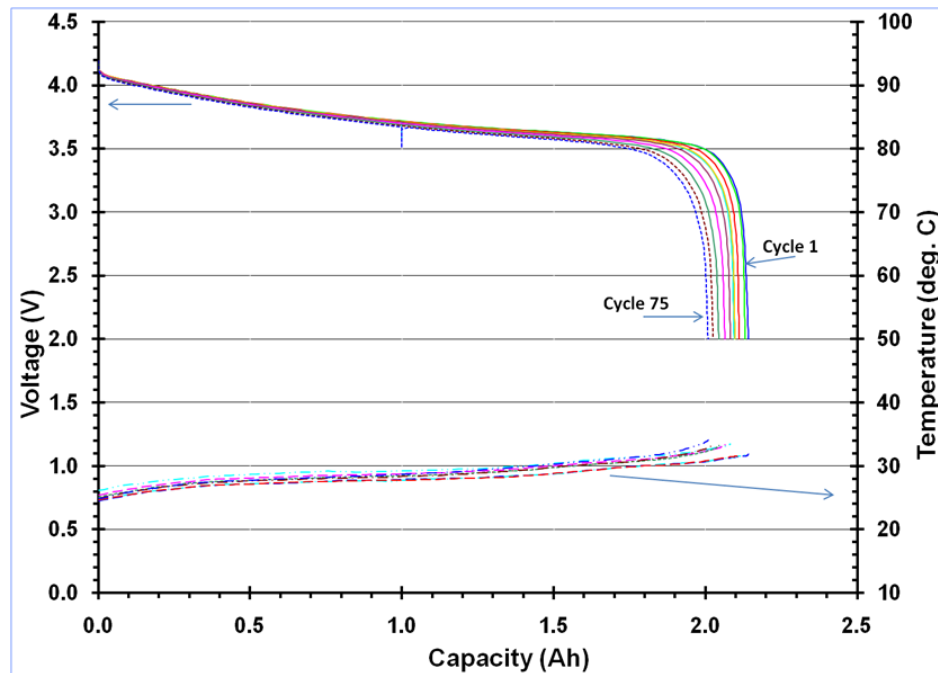
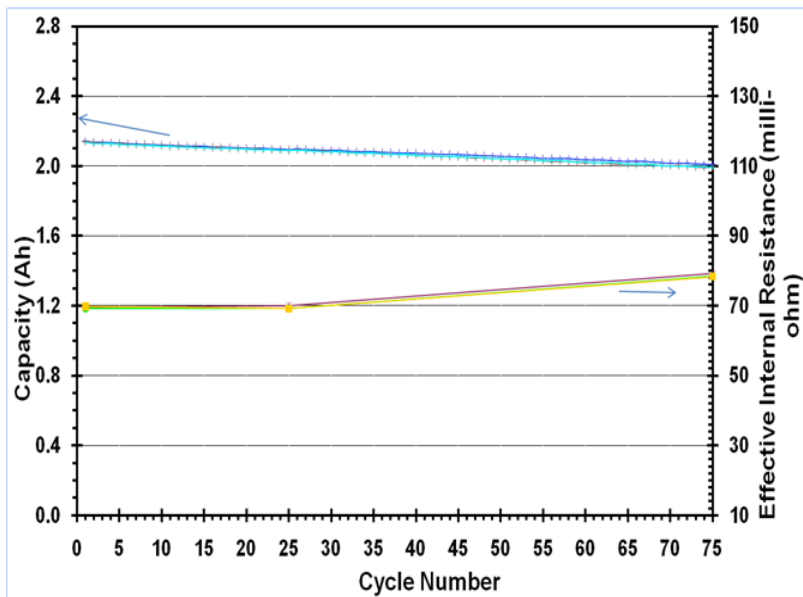
Overdischarge Test Program on 18650 Li-ion Modules

Overdischarge Test Program on 18650 Li-ion Modules (Power Sources 2010)

- Lithium-ion cells of the cylindrical commercial-off-the-shelf 18650 design format were used to study the hazards associated with overdischarge.
- The cells in series or in parallel configurations were subjected to different conditions of overdischarge.
- The cells in parallel configurations were all overdischarged to 2.0 V for 75 cycles with one cell removed at 25 cycles to study the health of the cell.
- The cells in series were designed to be in an unbalanced configuration by discharging one cell in each series configuration before the start of test. The discharge consisted of removing a pre-determined capacity from the cell. This ranged from 50 to 150 mAh removal. The cells were discharged down to a predetermined end-of-discharge voltage cutoff which allowed the cell with lower capacity to go into an overdischarge mode.
- The cell modules that survived the 75 cycles were subjected to one overvoltage test to 4.4 V/cell

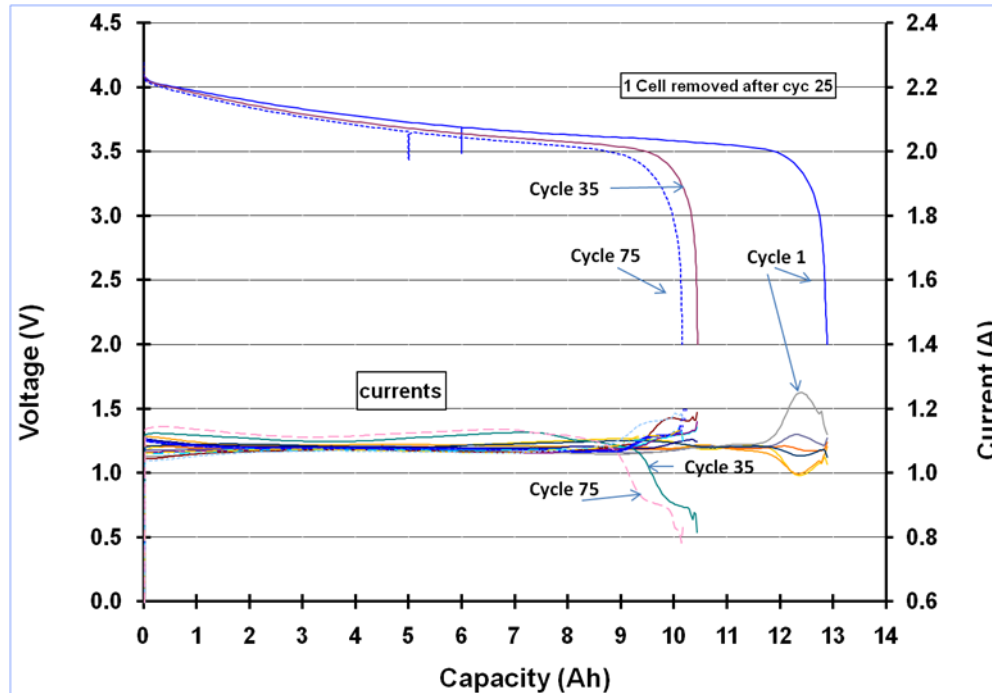


Single Cell Cycling with Continuous Deep Discharge



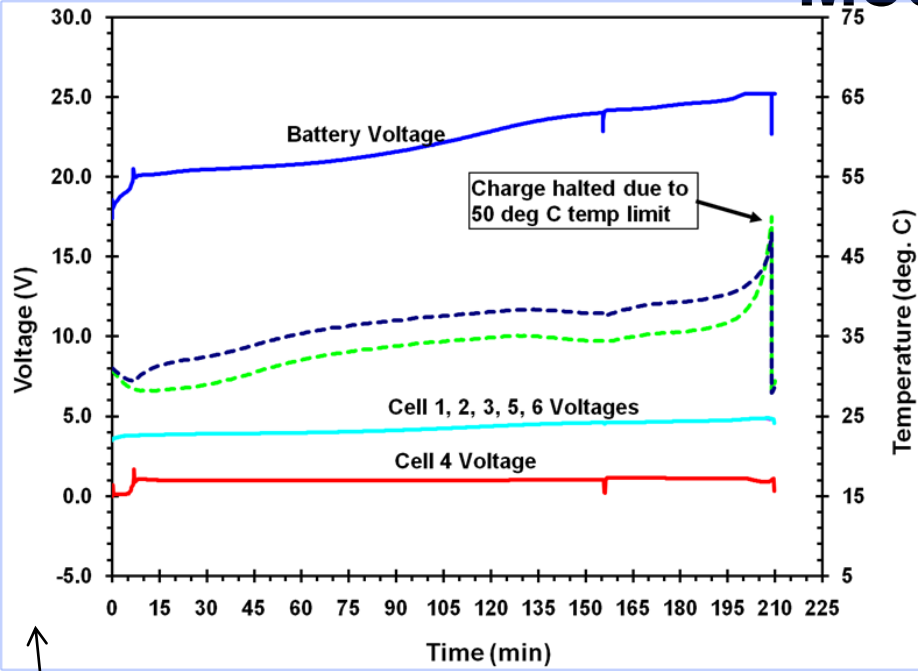
Charge: C/2 to 4.2 V; Discharge: C/2 to 2.0 V

Cycle Life Test for a 6P Lithium-ion Module with Continuous Overdischarge



Charge: C/2 (1.08 A); EOCV: 4.2 V
Discharge: C/2 A; EODV: 2.0 V

Overdischarge Test on 10S Unbalanced Cell Module

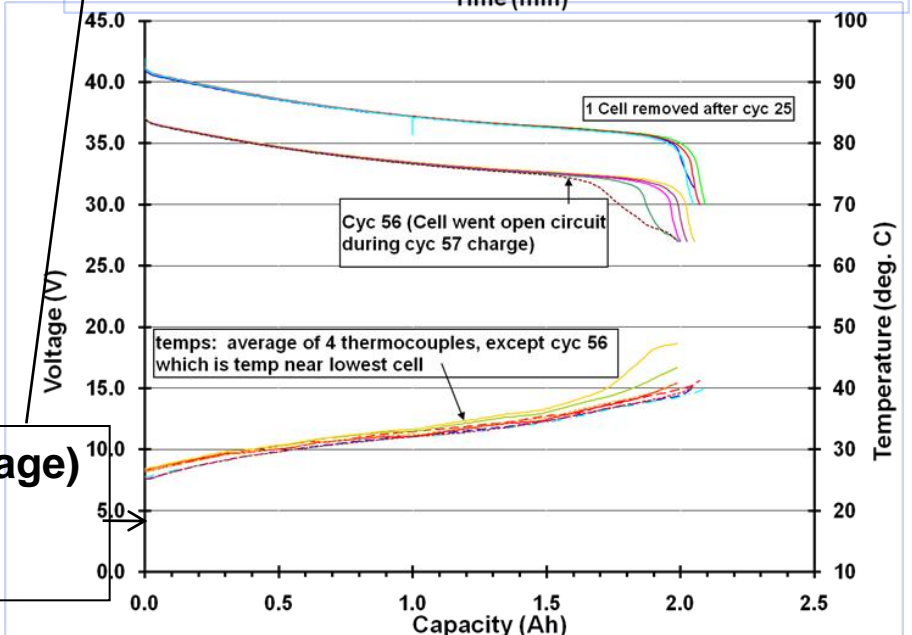
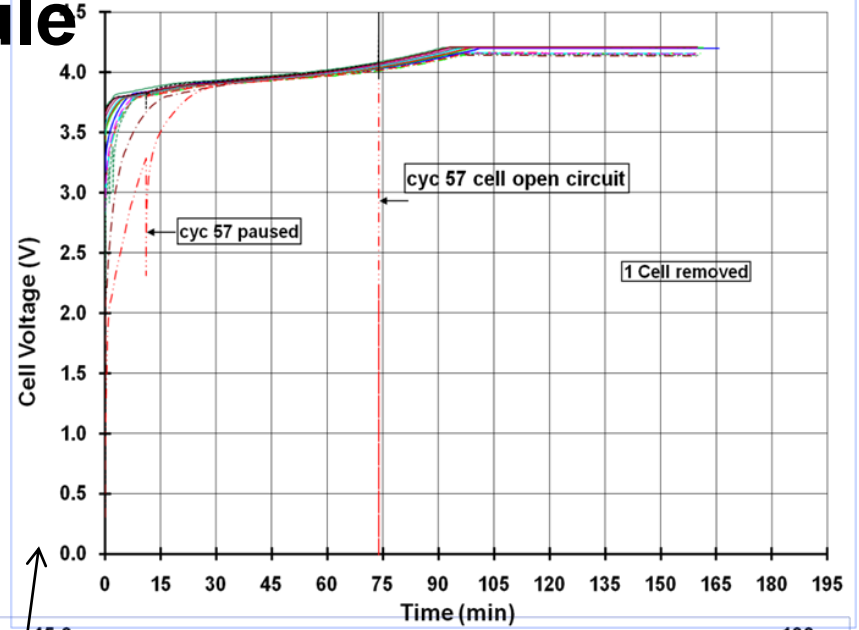


~150 mAh capacity removed from cell 4 (70 mV drop in voltage)

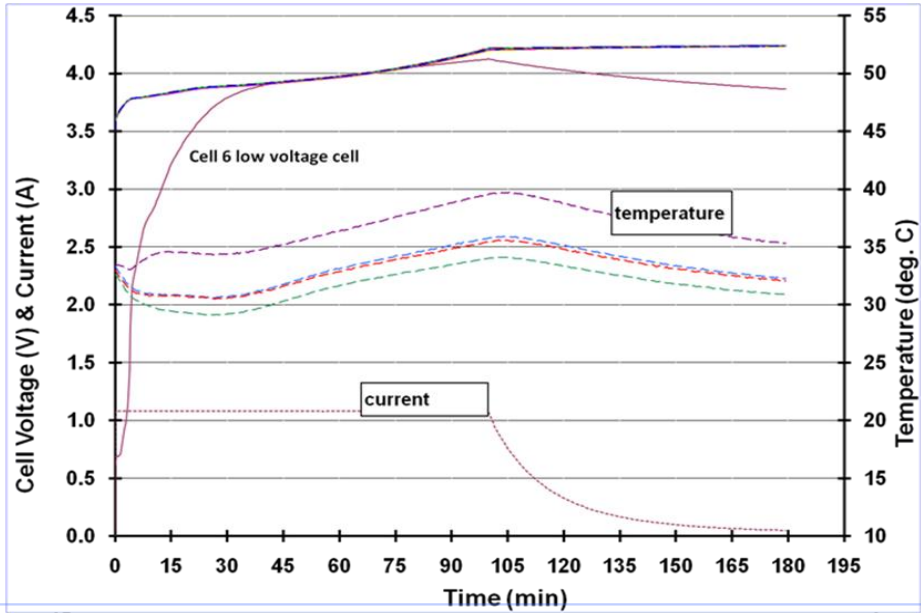
Charge: 1.08 A; EOCV: 4.2 V/cell
Discharge: 1.08A; EODV: 3.0 V/cell

100 mAh removed (50 mV drop in voltage)
 Temp not high; but unstable string;
 Test equipment showed erratic behavior

Module

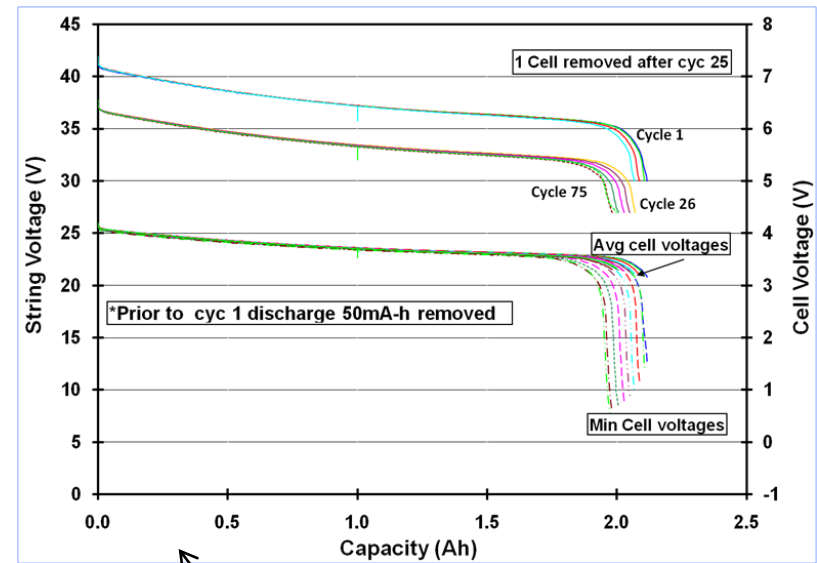
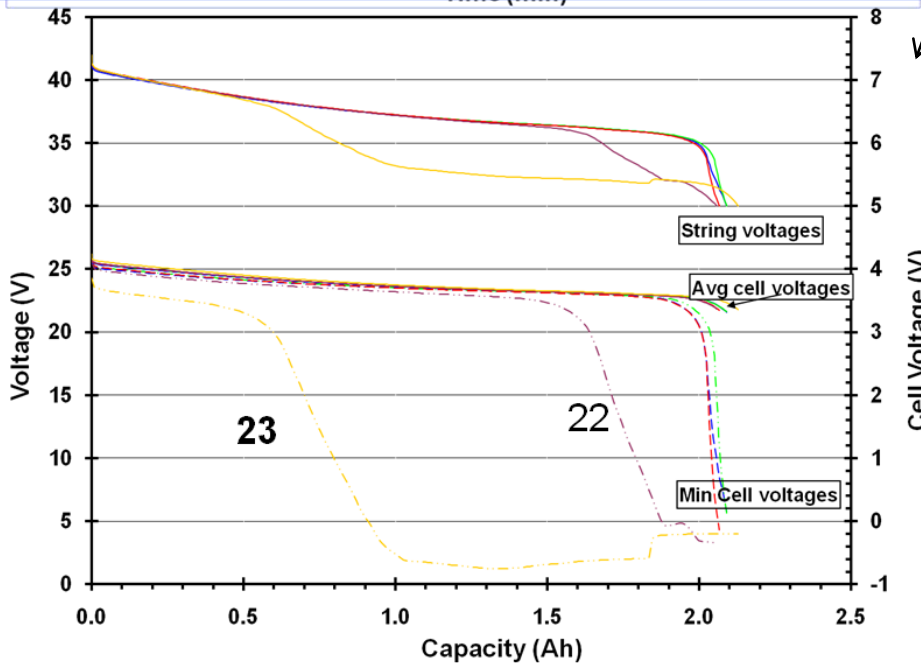


Overdischarge Test on 10S Unbalanced Cell Module



125 mAh removed
(60 mV change in voltage)

Charge: 1.08 A; EOCV: 4.2 V/cell
Discharge: 1.08A; EODV: 3.0 V/cell



50 mAh capacity removed
(20 mV change in voltage)

Overdischarge Test Program Summary

- The single cells as well as the cells in parallel design configurations did not display any anomalous behavior. There was a very slight increase in resistance with the deep discharges (EODV is 2.0 V) that they were subjected to.
- The series configuration test modules with the unbalanced cells displayed different behavior. If the capacity removed from the unbalanced cell was 100 mAh or greater (50 mV or greater imbalance), the cells did show internal shorting at some point and this caused instability in the whole string or abnormal behavior in some.
- If the imbalance in the cell strings was in the range of 50 mAh or less, no significant changes in cycling behavior were observed even though the imbalanced cell went to very low voltages (less than 1.0 V) throughout the program.

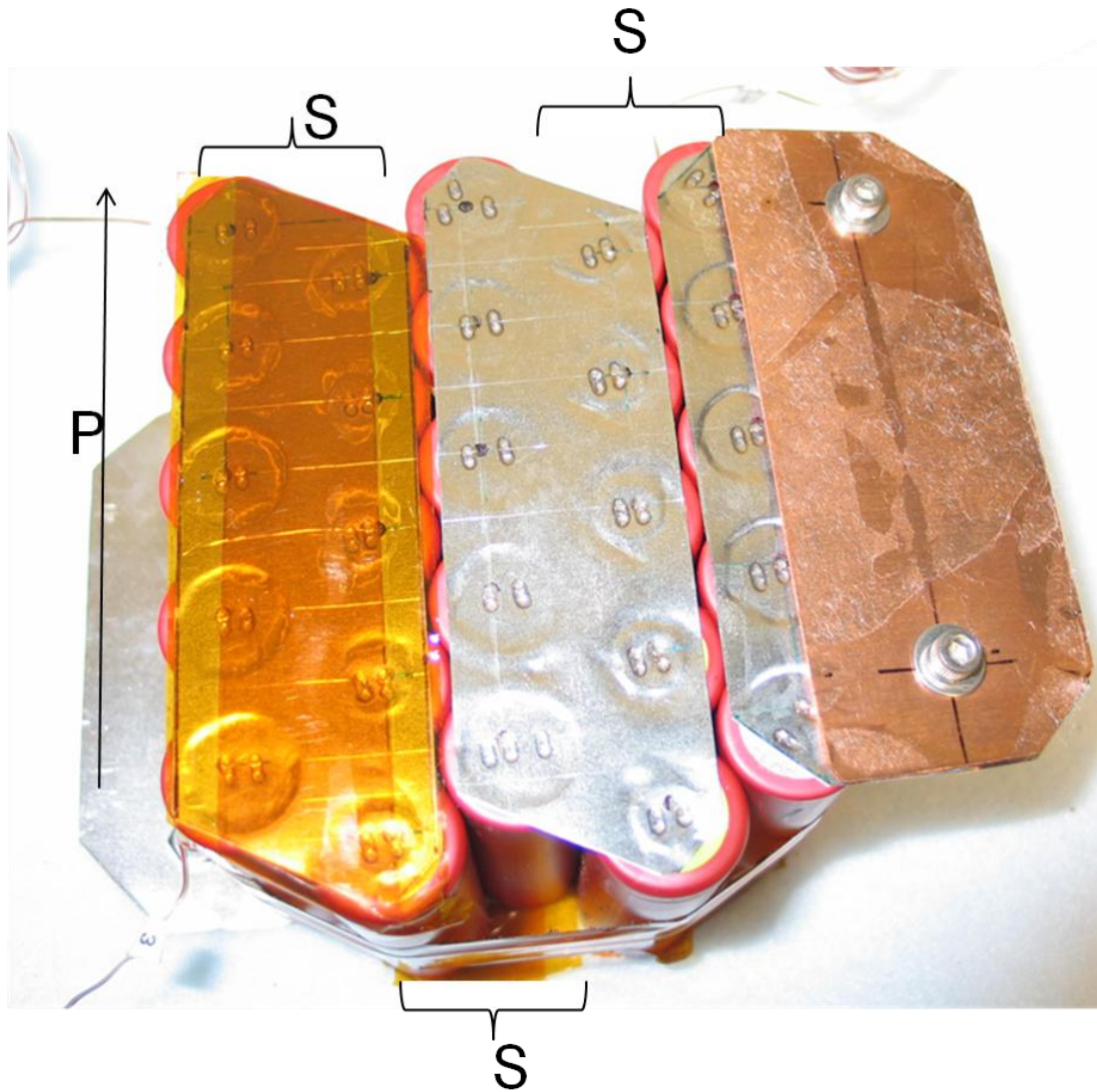
Matrix Design Safety for Li-ion Cell Modules

Matrix Design Safety for Li-ion Cell Modules (Space Power 2010)

- Commercial lithium-ion batteries in portable electronic equipment have been used by NASA for space applications since 1999.
- Latest Lenovo Thinkpad Battery has cells in a matrix configuration.
- Used Quallion matrix packs to understand the performance as well as safety
- Test Articles:
 - Two 5X5 Matrix Packs (One with Heat Absorbent Material (HAM) and one without)
 - One 8X8 Matrix Pack (without HAM)Cells are from Sanyo (cobaltate in the 8X8 and spinels in the 5X5)
- Tests:
 - Short term cycle life: 100 cycles (all three packs)
 - Additional 100 cycles with one cell disconnected (5X5 packs only)
 - Overcharge Test : 5X5 packs
 - External Short: 8X8 pack



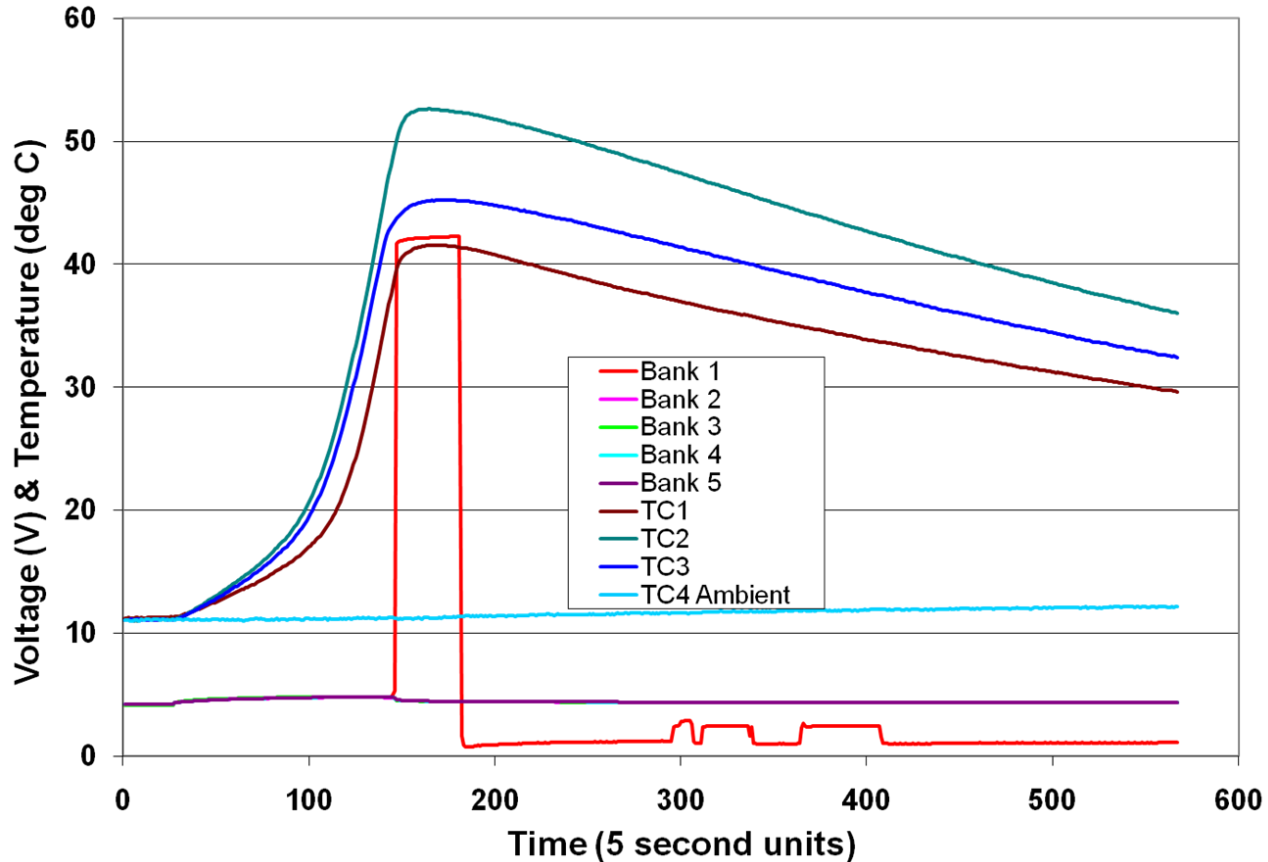
Matrix Design Configuration



Lenovo Li-ion
Battery (ISS)
Matrix Design

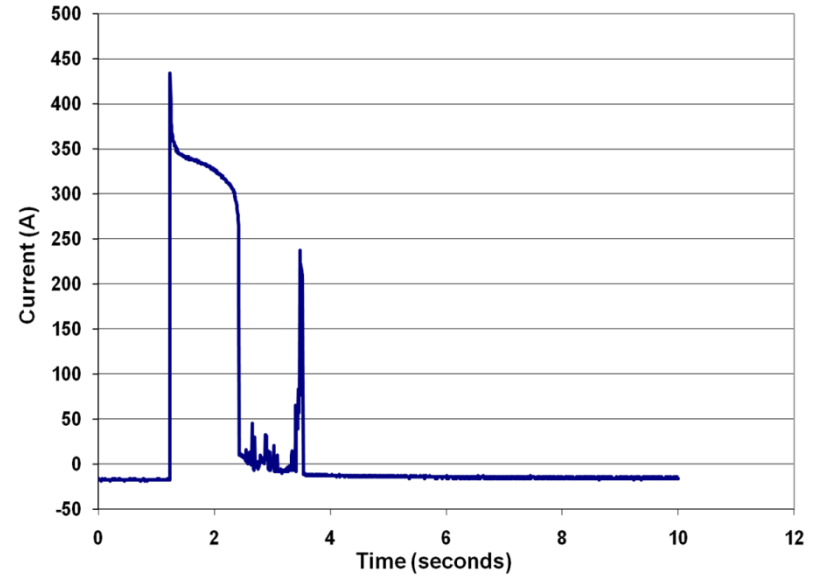
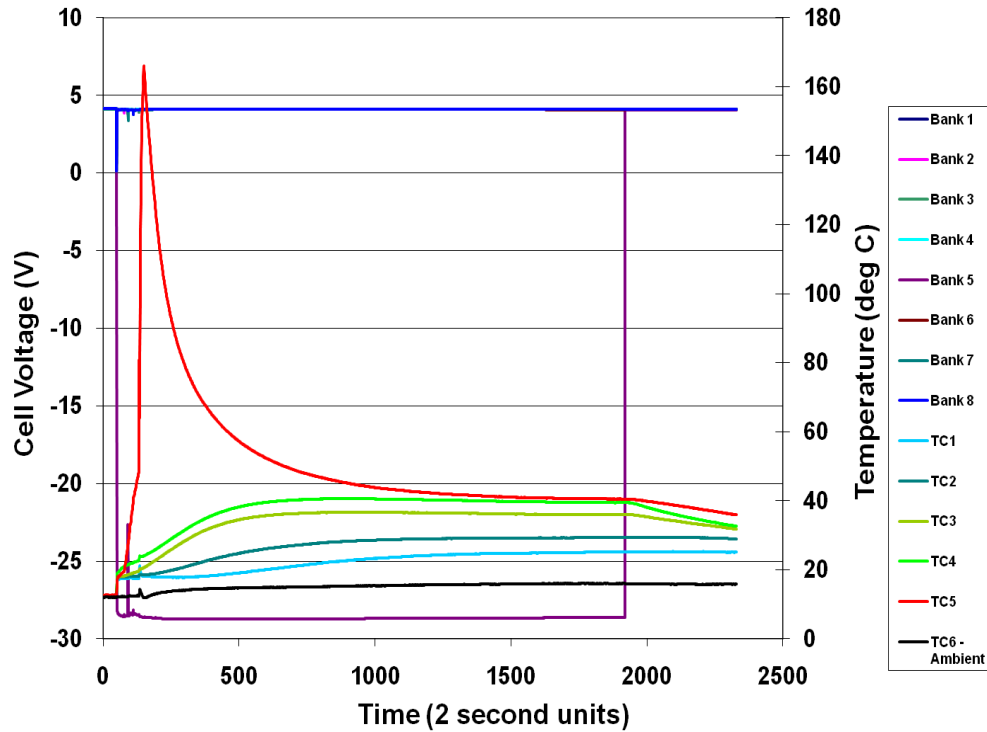
Overcharge Test for 5X5 Matrix Pack (no HAM)

(Overcharge at 10 A)

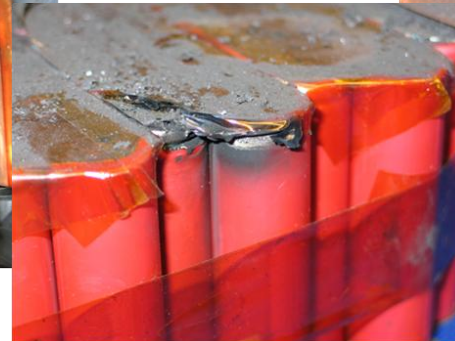


**Bank 1 behaves like a soft-shortened bank;
has one cell with a CID activation**

External Short on 8X8 Matrix Pack



Load: 10 mohms



Matrix Design Safety for Li-ion Cell Modules

Summary

- Disconnection of any one cell in matrix design configuration packs has almost no influence on the performance of the packs and does not show any abnormal thermal changes for the 100 cycles obtained in this test program. Longer cycle life may influence the performance especially if the low voltage cell bank goes into reversal.
- Overcharge leads to CID activation of cells. If the matrix configuration has a larger number of cells in series, (more than 5S configuration) and had the PTCs, the limitations of protective devices may manifest itself irrespective of it being in a matrix configuration.
- External short circuit causes a fire with expulsion of content from some cells. The fire does not propagate itself laterally, but if there was cell module stacking, then the fire would cause the cells above it to also go into flames/thermal runaway. Limitations of protective devices are observed in this case as the PTCs in the cells did not protect under this abusive condition.
- Matrix configurations can provide protection against lateral propagation of fire and flame.

Internal Short Hazard

(Presented at NASA Battery Workshop 2008)

- Frank Zhao at 2007 IEEE PSES (Product Safety Engineering Society) Symposium presented the following data:
 - Anode Film ↔ Cathode Film (<120 °C)
 - Anode Film ↔ Al Foil (thermal runaway)
 - Cathode Film ↔ Cu Foil (< 100 °C)
 - Al Foil ↔ Cu Foil (< 80 °C)
- COTS Li-ion cells are produced in millions and if the quality control is not stringent, there is a higher possibility of getting internal cell shorts due to the presence of impurities such as metal particles, burrs, etc.
- NASA is more concerned about the impurities manifesting an internal short by dislodging and piercing the separator, during launch.

Causes for Internal Shorts

- Manufacturing defect –
 - manifests during assembly line or during the formation process (foreign object debris, lithium deposits, uneven electrode or separator during winding process; uneven wetting)
 - Manifests as latent defects during its calendar or cycle life
- Induced internal shorts in the field
 - Due to usage (charge/discharge cycling) and/or storage in extreme thermal environments (hot and cold)
 - Due to usage outside manufacturer's voltage and current specifications
 - Due to high thermal gradients within a high voltage/high capacity pack
 - Due to dried out areas resulting from lack of accommodation of electrode swelling with bad cell designs

Summary: High quality control of cells is necessary and usage should be within manufacturer's specifications for all parameters.

Summary of all Safety Test Programs

Conclusions and Recommendations

- Determine, by testing, the PTC withstanding voltage and trip current for the cell to be used in battery design. Cells from different manufacturers will have different PTC ratings and this information is not provided in a cell specification.
- The cell PTC should not be compromised (activated or subjected to a condition that causes a rise in its resistance), if needed to be used as safety control. Cell screening for battery build for engineering, qualification as well as flight testing should not cause inadvertent activation of the PTC. Any cells in which the PTC may have been inadvertently tripped should not be used in the fabrication of flight batteries.
- The CID cannot always be depended upon as safety control in multicell series/parallel battery designs. To prevent cells from going into an overcharge condition, voltage monitoring should be implemented at a level that would allow reliable and accurate detection and prevention of an overcharge condition of even a single cell.
- Confirm that the CID safely activates and protects the battery from overcharge catastrophies in the actual flight battery configuration, if the CID is used as a level of safety control. Tests should be run at the module size that the CID is being used as a safety control.

Conclusions and Recommendations

- The charge current used to charge a string or a bank should be as low as possible. For charging of cell banks, the total charge current should be limited to a value that would not cause PTC activation in any single cell in the event that the CIDs of all the other cells have opened.
- In general, all electronic components have limitations -Environments can change their characteristics due to factors such as temperature gradients, distribution of current, imbalanced voltages, etc. which can make these devices ineffective
- The overdischarge test results indicate that several factors have to be taken into consideration while using cells in series and parallel configurations.
 - Cell matching should be stringent and based on capacity as well as internal resistance of the cells and not just the Open circuit voltage (Voltage versus capacity should be characterized for each cell design)
 - Cell modules should have an undervoltage cutoff to prevent cells from going into very low voltages especially if they are not stringently matched.
 - Have cell balancing to prevent one or more cells from being significantly imbalanced from the others.
 - Provide monitoring or it would be difficult to capture deep discharge or voltage reversal of one or more cells.
- Balancing during discharge may be more critical than during charge.

Conclusions and Recommendations

- The thermal environment is an important criteria –
 - Thermal signature of a large pack may indicate that there are huge gradients due to unbalanced internal resistances with cycle and calendar life which can in turn lead to overdischarge or overcharge due to imbalance as well as change the properties of protective devices.
- Modeling studies have shown that if the temperature is controlled to a reasonable value (below 55 °C was used in NASA-JSC studies), then the hazards do not manifest themselves into a thermal runaway condition.
- Tests have shown that for ease of monitoring and control, high voltage/ high capacity batteries are built with a P-S topology. However, the limitation of having too many in parallel should be understood. If there is a weak cell, all the current from the neighboring cells will feed into the weak cell.
 - 4 cells in parallel is maximum recommended design for medium-rate cell designs (provided the charge current is also controlled) based on available test data.
 - If more need to be paralleled, the limitations of the cell module needs to be determined and safety controls at the appropriate levels need to be incorporated.
- **Use high quality cells with manufacturing control wherever possible.**
 - Destructive Physical analysis and X-ray of sample cells of every new lot. X-ray of every cell that is used in a high capacity/ high voltage battery pack (field/flight unit) will be a benefit.
- Test as you fly – i.e., in the relevant environment

Acknowledgment

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Mobile Power Solutions, Symmetry Resources Inc. and Applied
Power International for the all the work performed