Hazards Due to Overdischarge in Lithium-ion Cylindrical Cells in Multi-cell Configurations

Judith Jeevarajan, Ph.D.
NASA-JSC

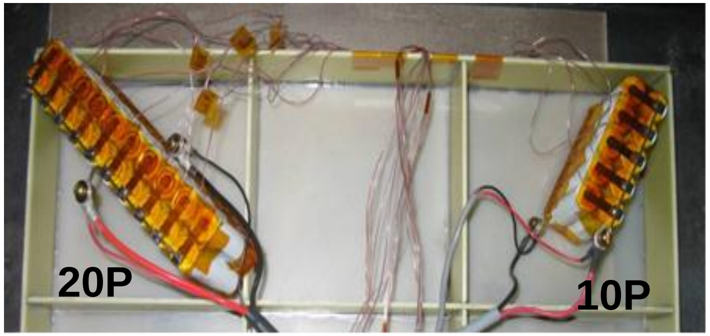
and

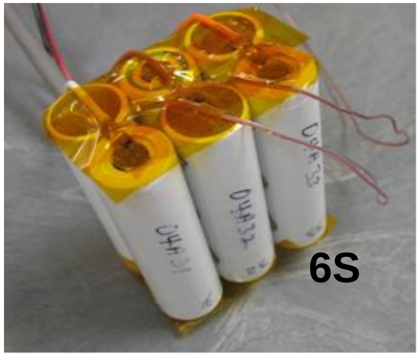
Brad Strangways and Tim Nelson
Symmetry Resources Inc.

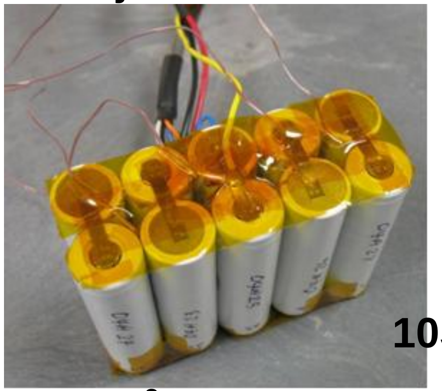
2010 NASA Battery Workshop
November, 2010

Introduction

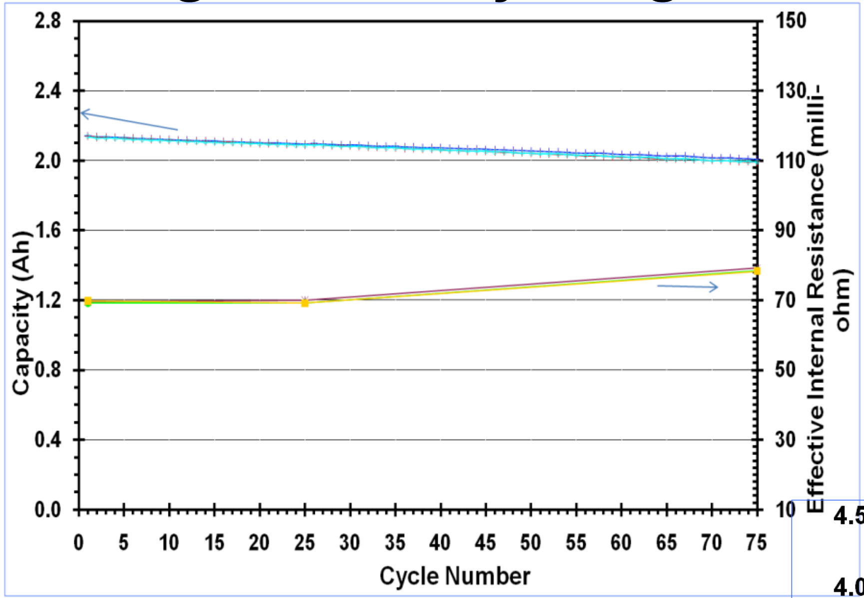
- Lithium-ion cells of the cylindrical commercial-off-the-shelf 18650 design format were used to study the hazards associated with overdischarge.
- The cells in series or in parallel configurations were subjected to different conditions of overdischarge.
- The cells in parallel configurations were all 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.



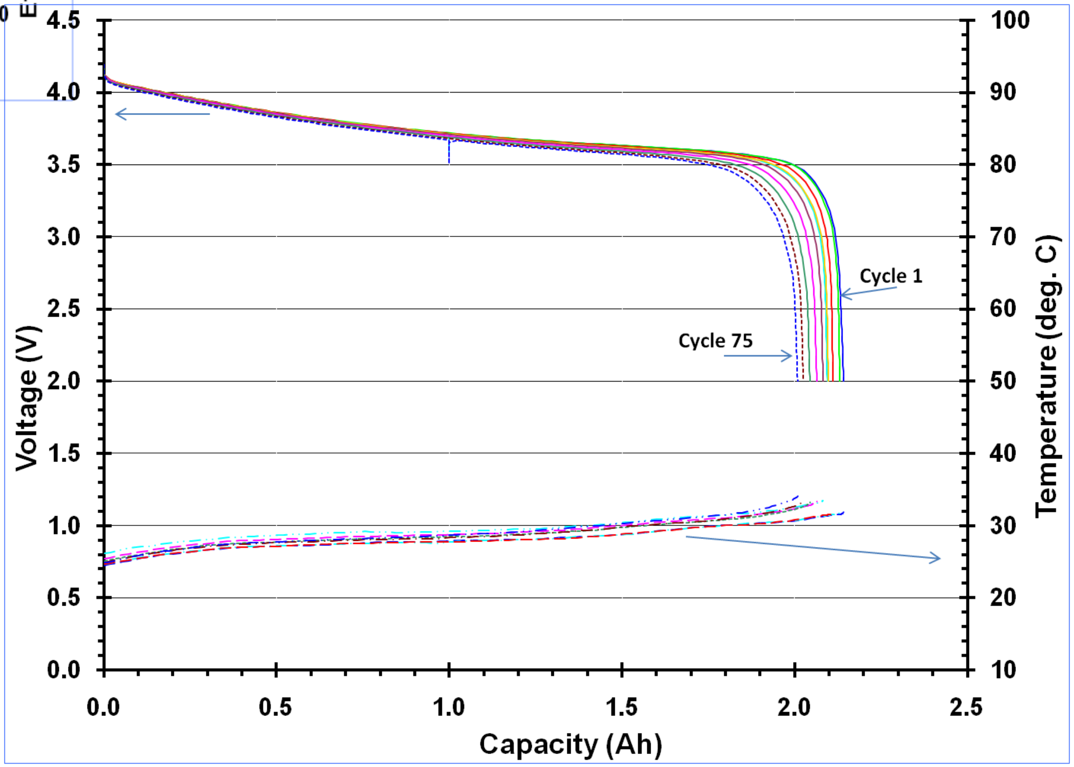




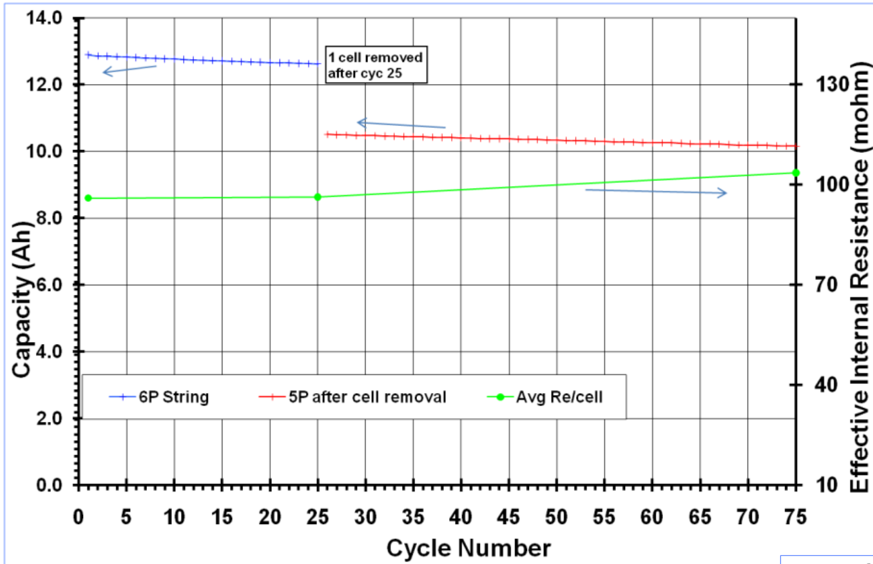
Single Cell Cycling with Continuous Deep Discharge

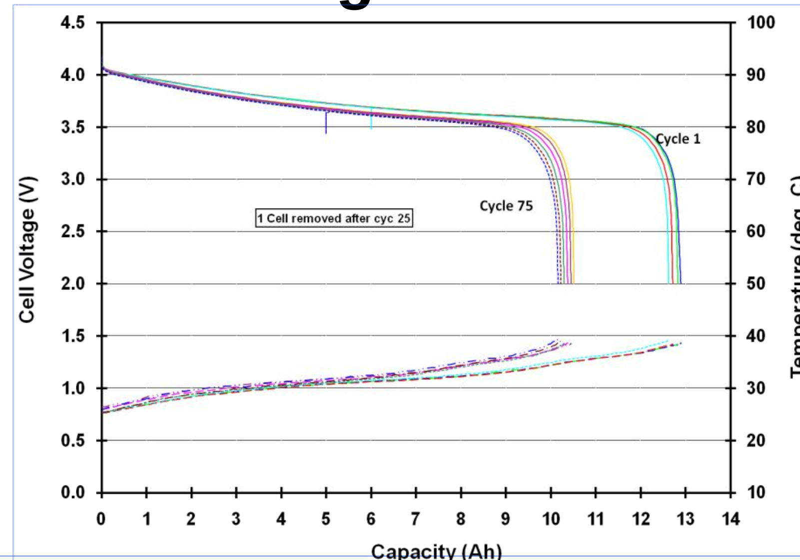


Charge: C/2 to 4.2 V
Discharge: C/2 to 2.0 V

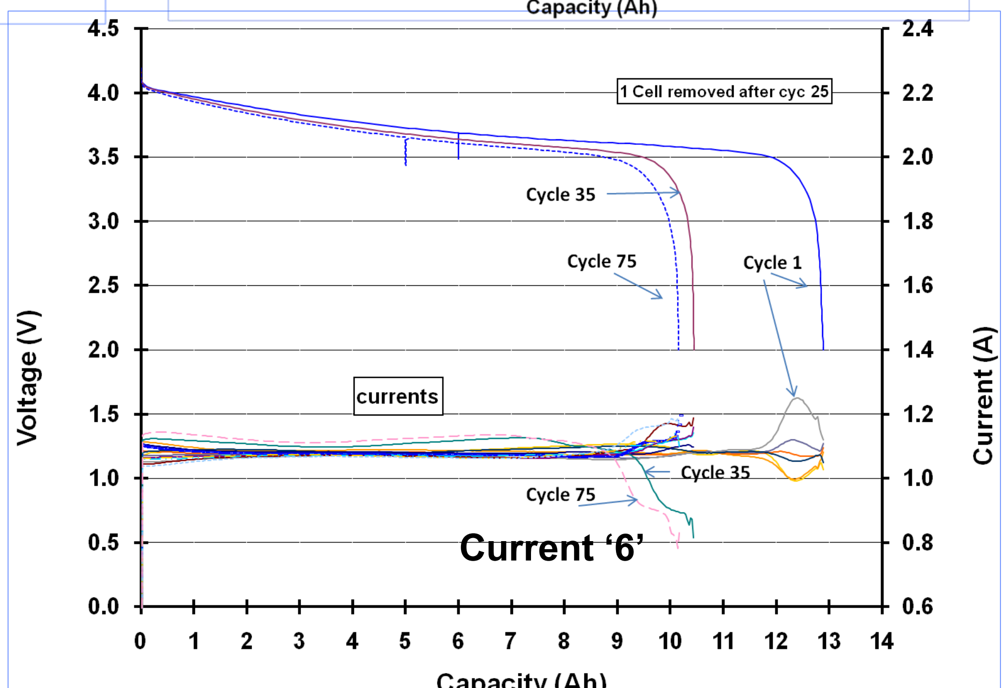


Cycle Life Test for a 6P Lithium-ion Module with Continuous Overdischarge

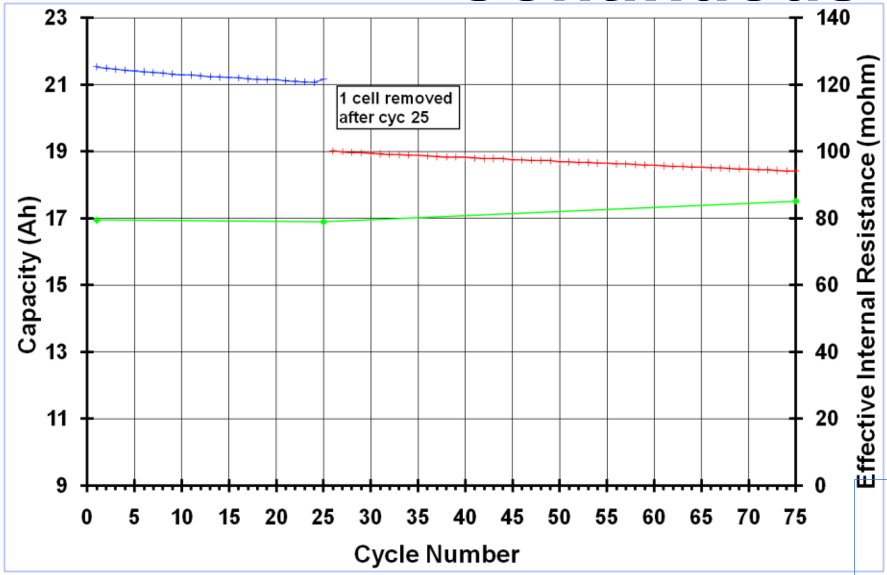




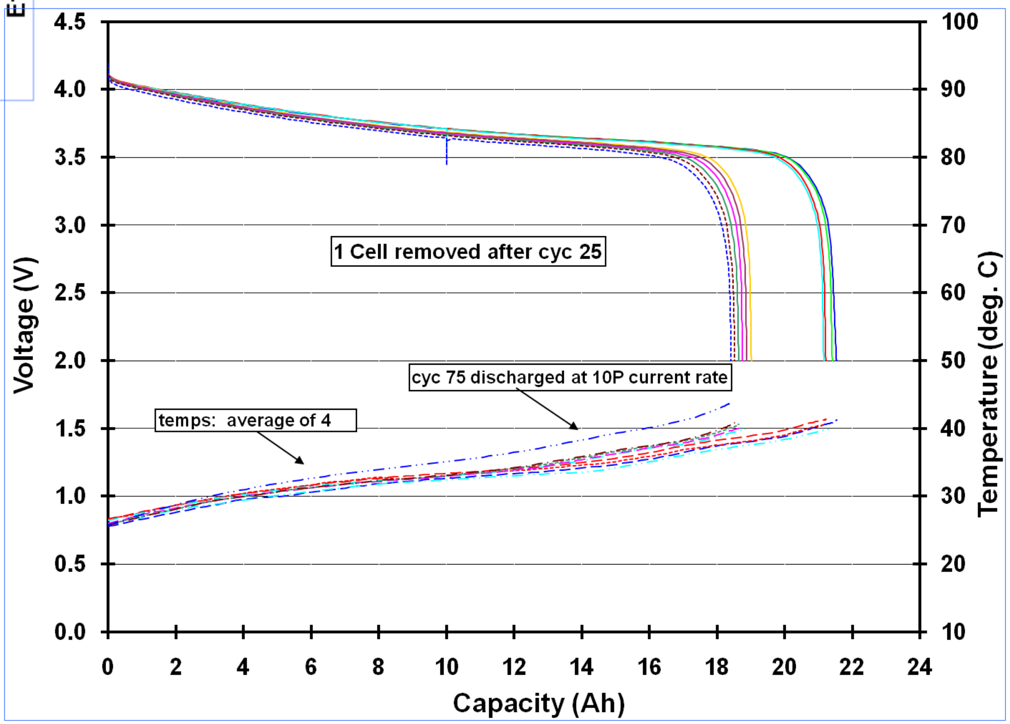
Charge: C/2 (1.08 A); EOCV: 4.2 V
Discharge: C/2 A; EODV: 2.0 V



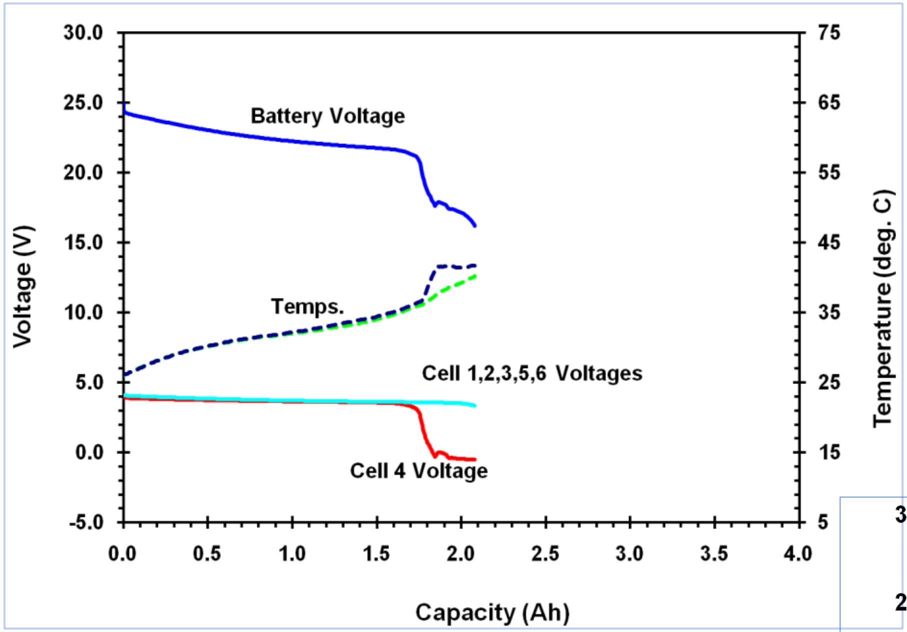
Cycle Life Test for a 10P Lithium-ion Module with Continuous Overdischarge



Similar test on a 20P module was carried out and the max temperature recorded during the cycle life test was 45 deg C

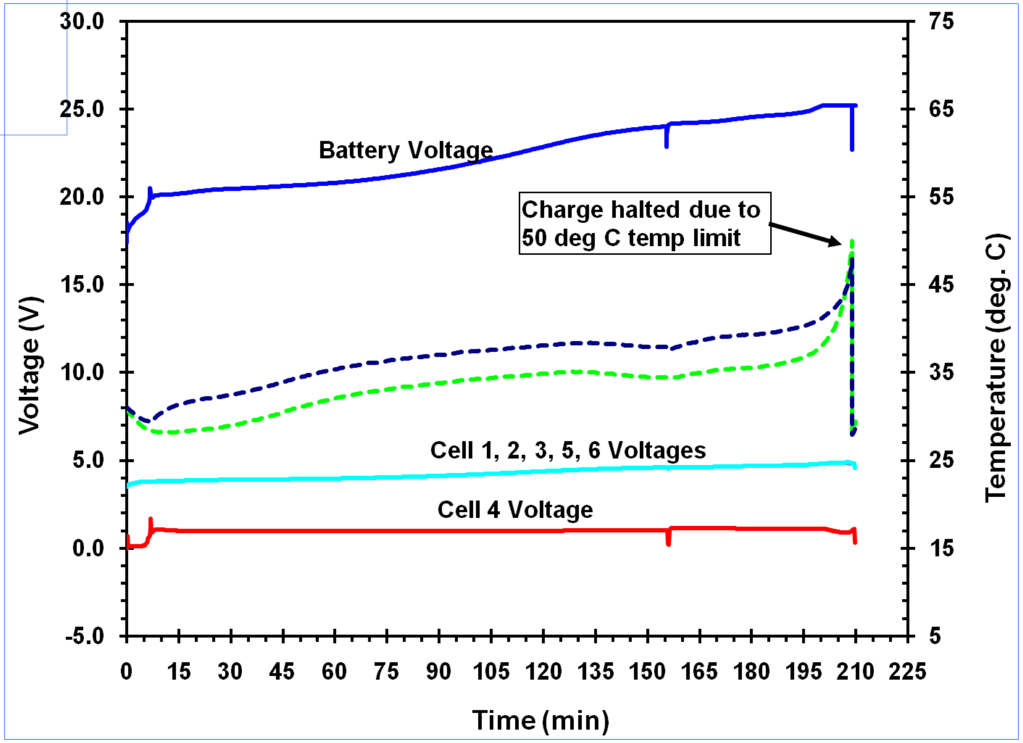


Overdischarge Test on 6S Unbalanced Cell Module

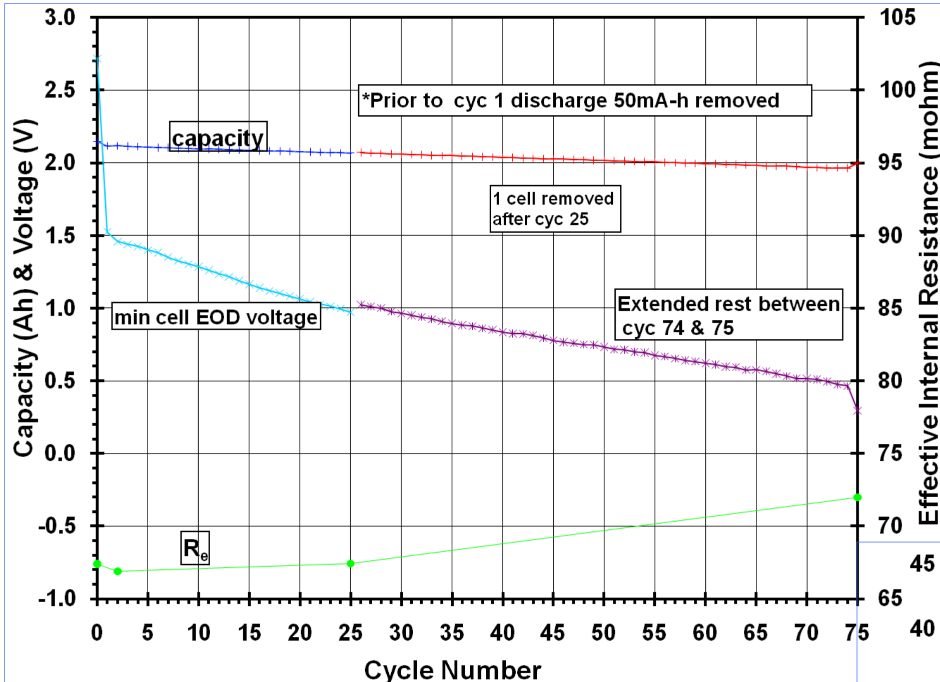


~150 mAh capacity removed from cell 4 (70 mV drop in voltage)

Charge: C/2 (1.08 A); EOCV: 4.2 V/cell
Discharge: C/2 A; EODV: 3.0 V/cell

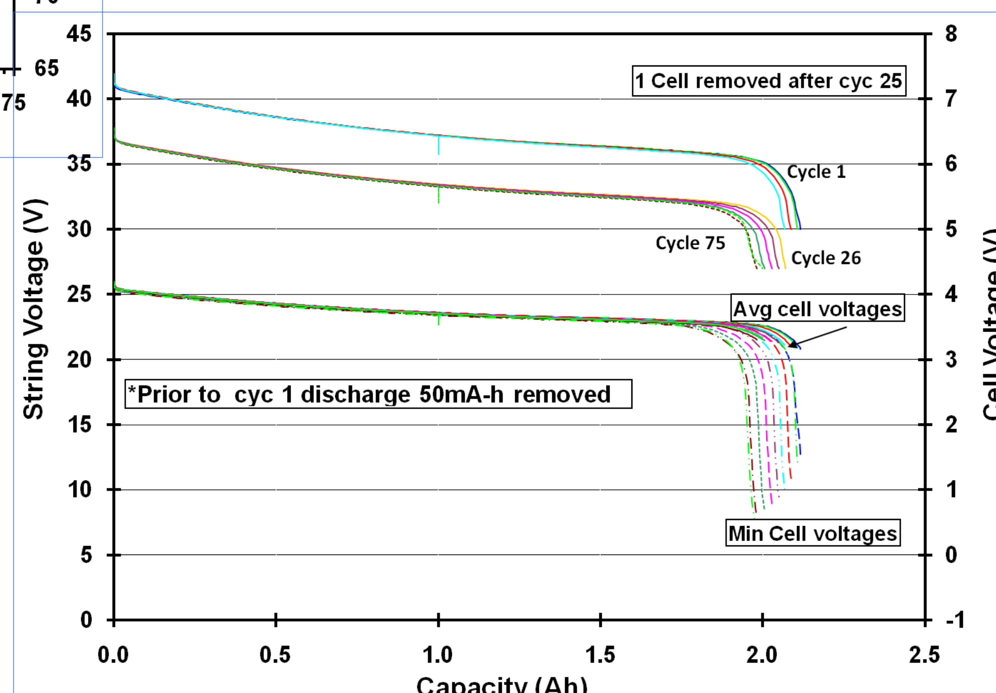


Overdischarge Test on 10S Unbalanced Cell Module



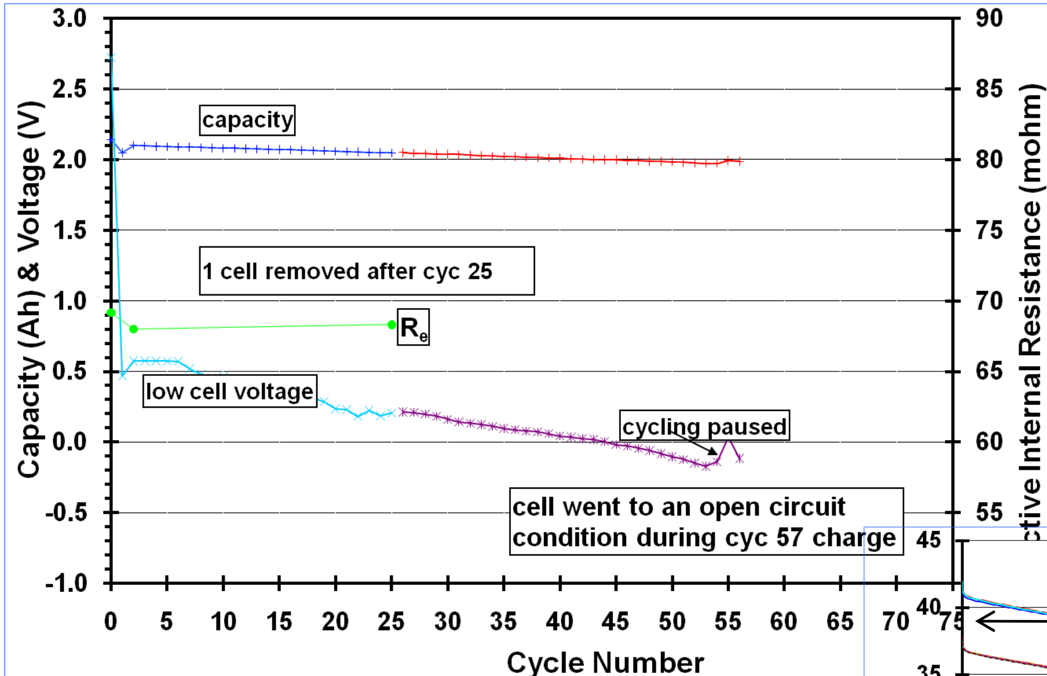
50 mAh capacity removed (20 mV change in voltage) from one cell and placed back in the string before cycling was initiated

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



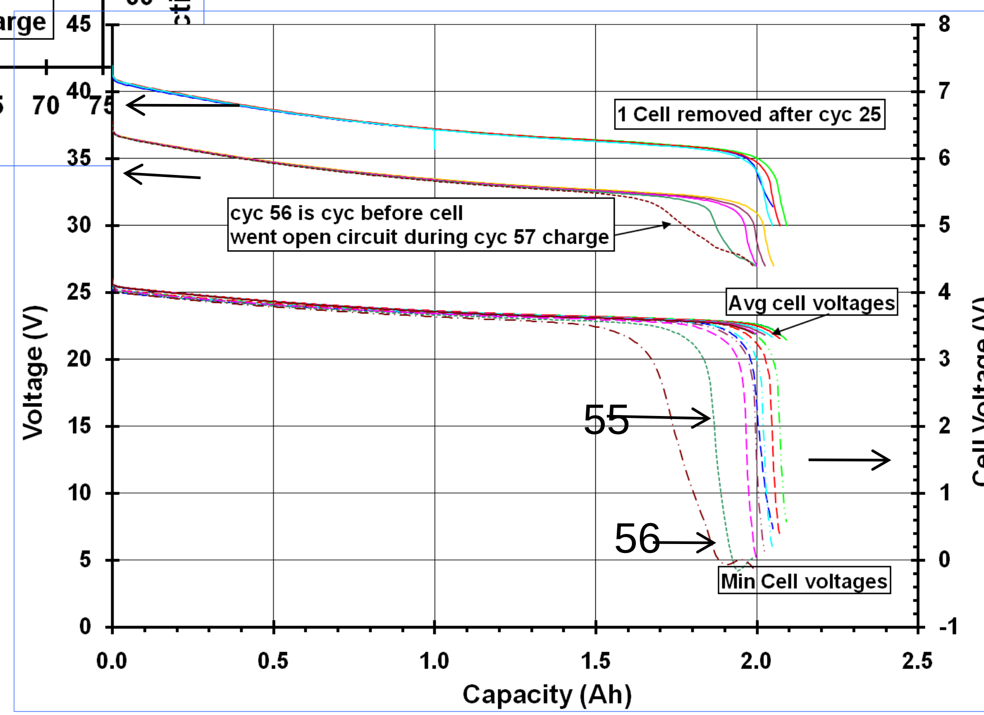
R_e increase is 7 %

Overdischarge Test on 10S Unbalanced Cell Module



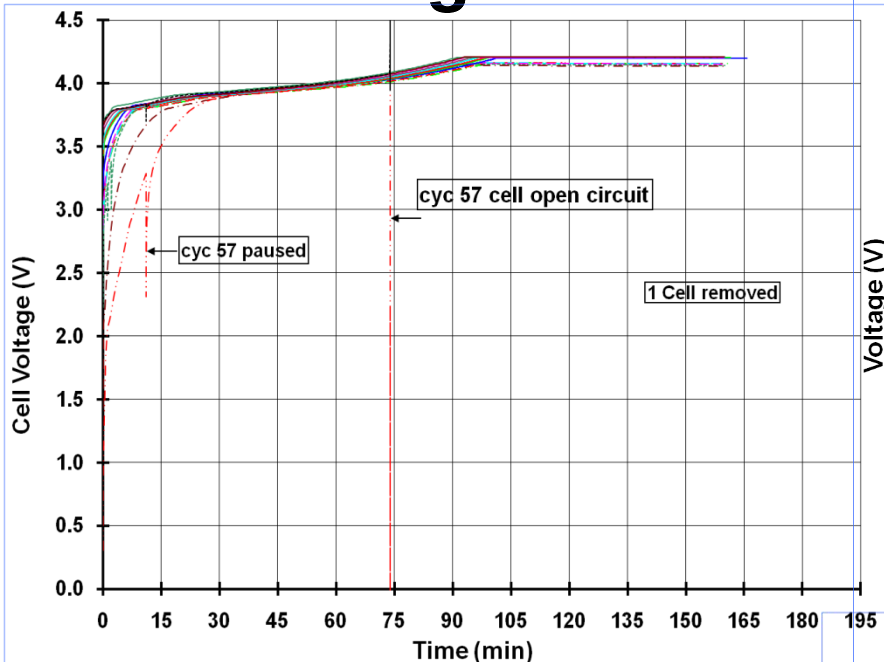
100 mAh removed
(50 mV change in voltage)

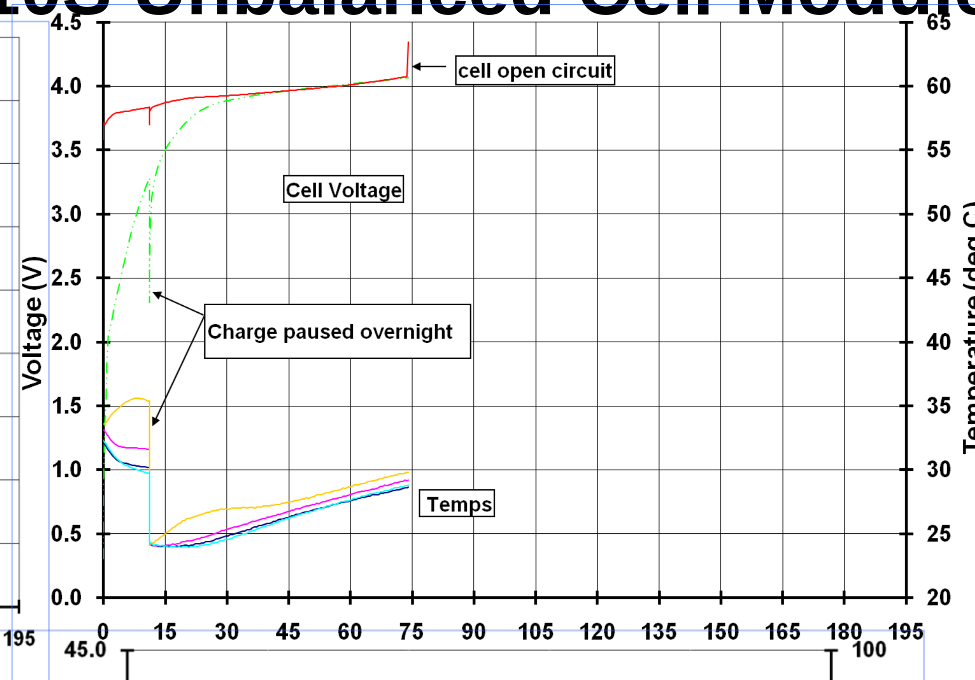
Prior to cyc 1 discharge 150mAh removed from cell 25.
***Cycle 1 discharge terminated to prevent extreme min cell voltage.**
***During cyc 2 charge, the charge was halted and 50 mAh added to the cell for a net 100 mAh removed from cell 25.**



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

Overdischarge Test on 10S Unbalanced Cell Module

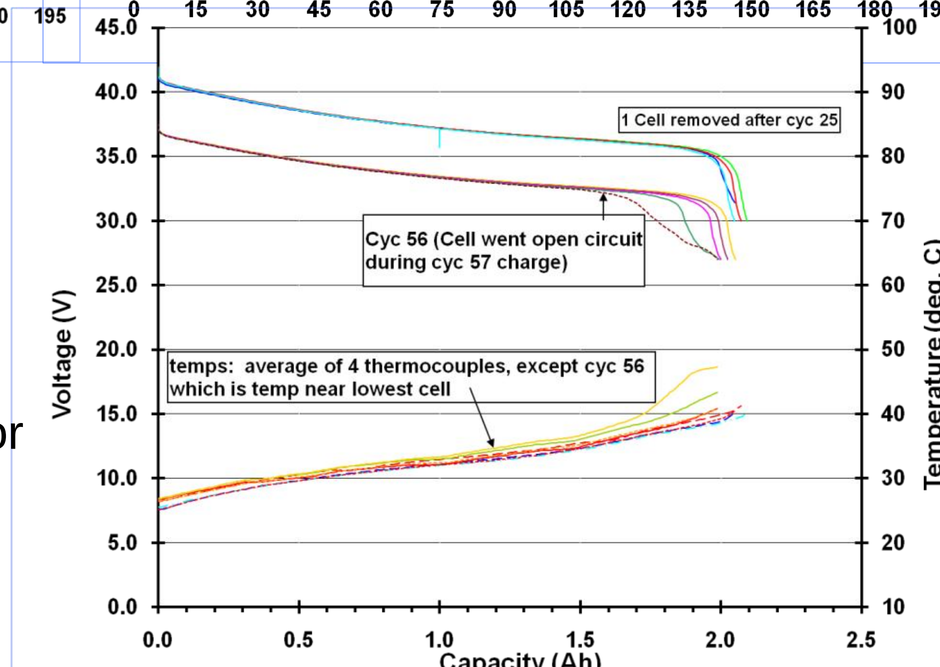




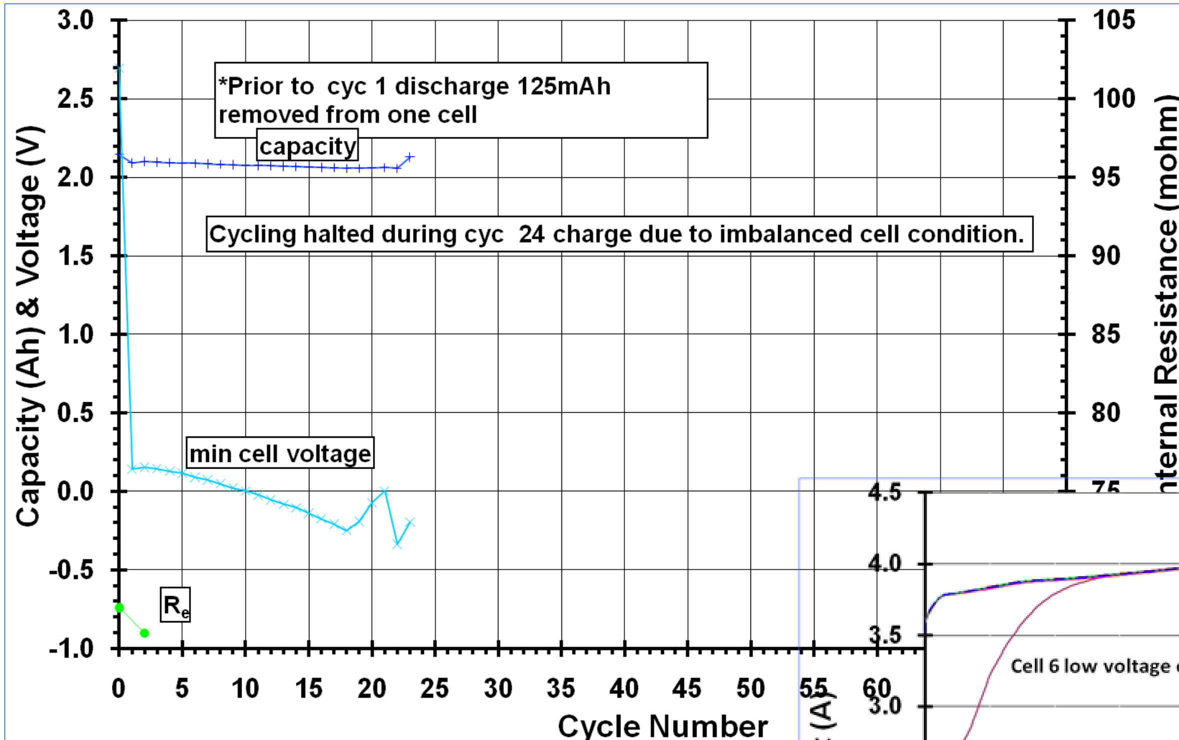
Charge: 1.08 A; EOCV: 4.2 V/cell
Discharge: 1.08A; EODV: 3.0 V/cell

Temp not high; but unstable string;
Test equipment showed erratic behavior

100 mAh removed



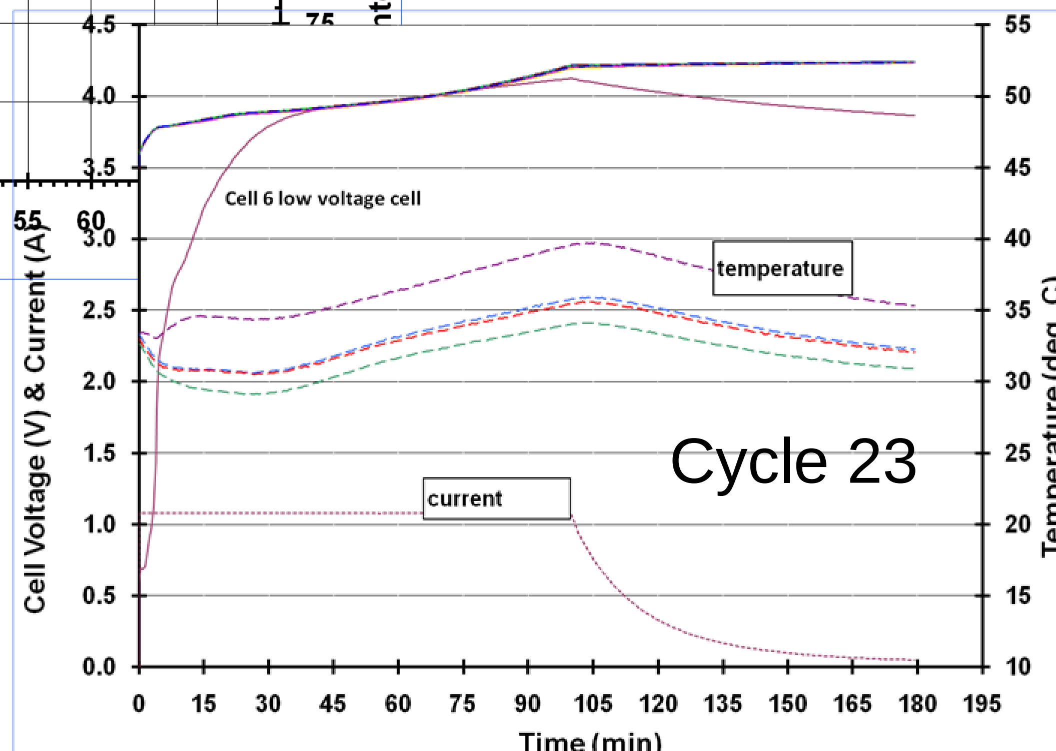
Overdischarge Test on 10S Unbalanced Cell Module



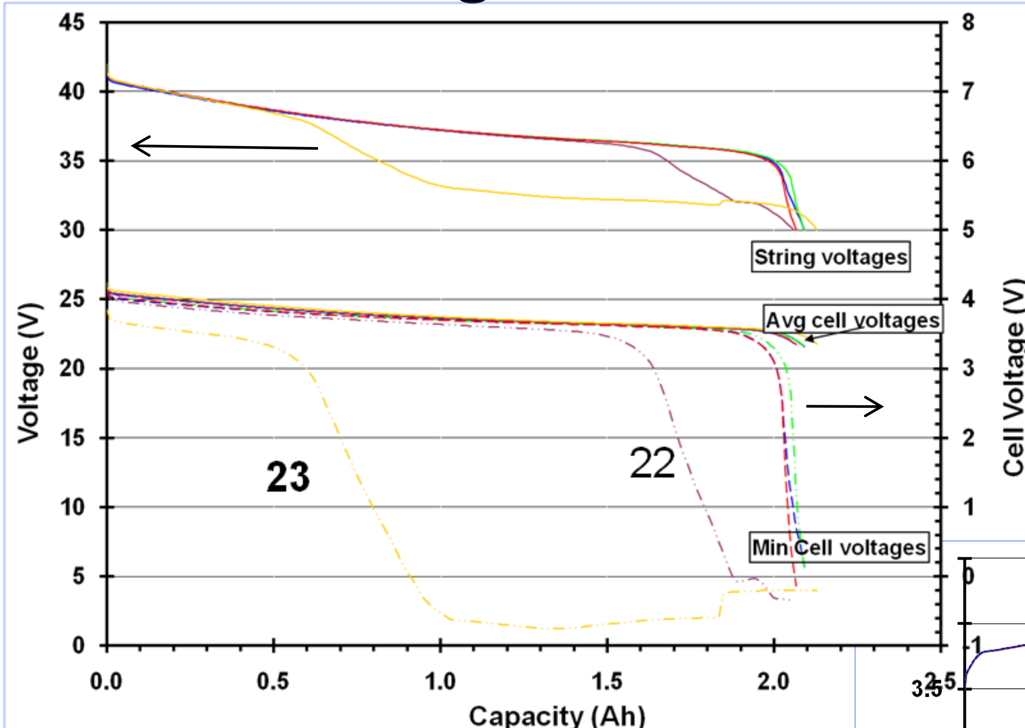
125 mAh removed (60 mV change in voltage)

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

R_e change in 25 cycles: 3 %

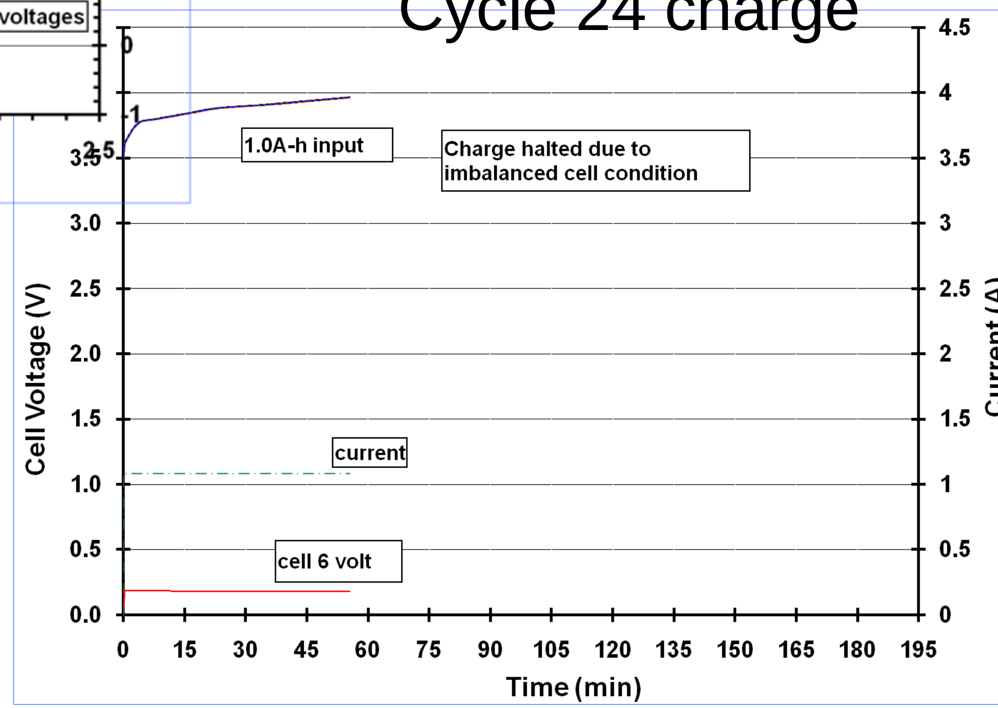


Overdischarge Test on 10S Unbalanced Cell Module



125 mAh removed (60 mV change in voltage)

Cycle 24 charge

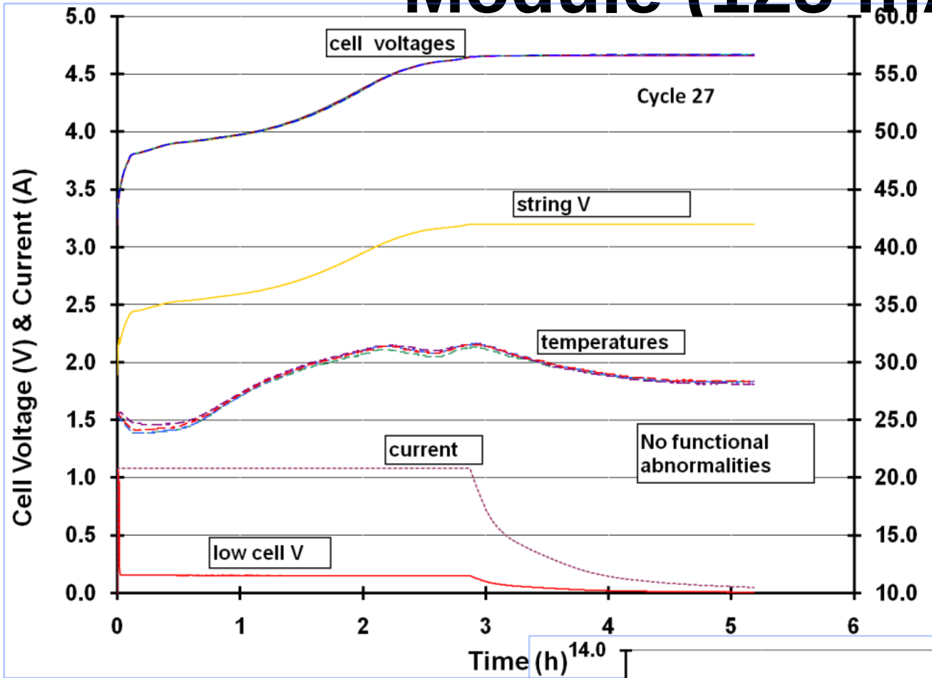


Charge: 1.08 A; EOCV: 4.2 V/cell
Discharge: 1.08A; EODV: 3.0 V/cell

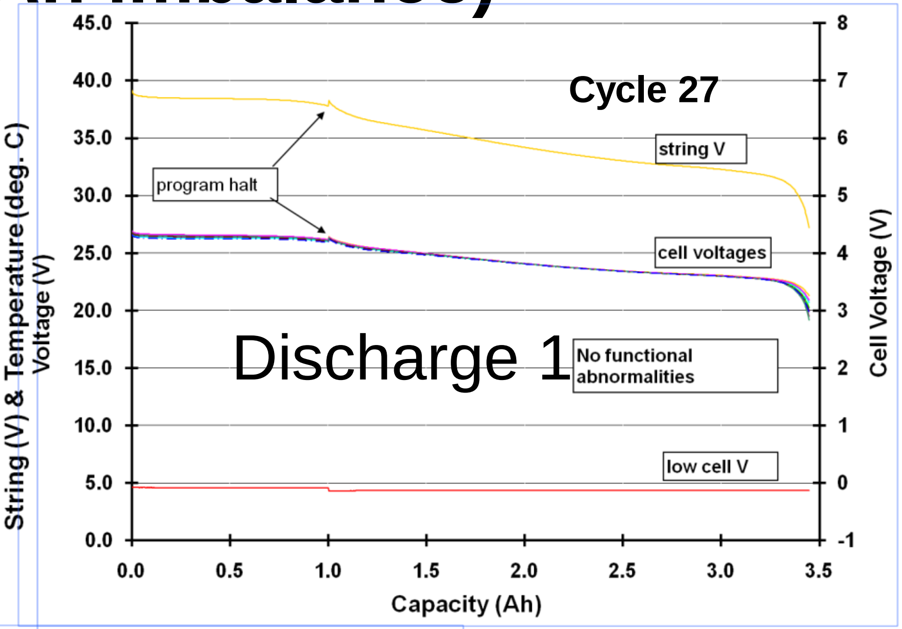
Overdischarge Test on 10S Unbalanced Cell Module (125 mAh imbalance)

- Test Protocol for module with a single cell that had 125 mAh capacity removed was modified.
- Cell 6 (low voltage) was at 0.179 V at the end of Cycle 24 charge (1 Ah input).
- A rest period of 1 week was provided.
- String was charged and discharged and then charged again.
- Second charge resulted in CID opening in one cell.

Overdischarge Test on 10S Unbalanced Cell Module (125 mAh imbalance)

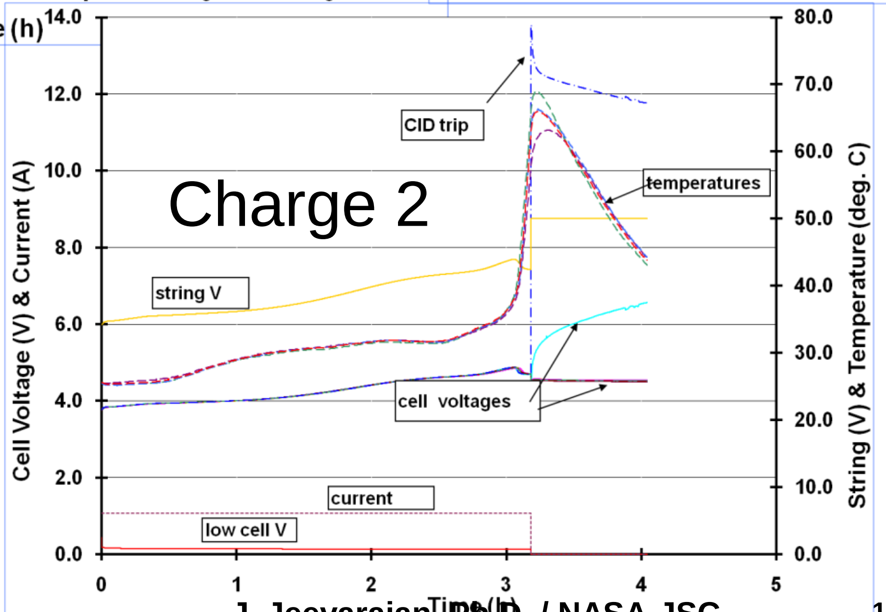


Charge 1



Discharge 1

Low Cell still reading V, one cell with CID open, one cell at 6.1 V



Charge 2

DPA and Chemical Analysis

- Destructive Physical Analysis (DPA) was carried out on several cells of which two are of particular interest.
- One cell that had undergone deep discharge and shown reversal in the very first discharge step (with 150 mAh imbalance) showed that the can itself had a lot of corrosion and had a dark reddish brown color in the separator. The bottom of the can tore off easily during the DPA. This indicates that severe corrosion of the cell can had occurred after the overdischarge into reversal had occurred on this particular cell. The cell had been in storage for at least two months after the test before the DPA had been carried out on it.
- Chemical analysis confirmed the presence of iron in the separator.

Photo 9 – Cell 32, Red discoloration on edges of separator

Photo 8 – Cell 32, weak case bottom

DPA and Chemical Analysis

- The second cell was one that had gone into overcharge condition and was suspected to have its CID activated. The cell voltage during post-test analysis indicated that the CID had not activated and provided about 85 % of the rated capacity. This cell showed several interesting features:

1. Discoloration of the insulator in the upper header area
2. Holes in the separator observed in the SEM; possibly due to lithium dendrites.
3. Negative lead separated from the jelly roll when jelly roll was being removed from the dissected can, atypical of that seen with a normal cell; only one nugget observed from the normal four welds.

Photo 10 – Cell 36, Negative lead with copper nugget

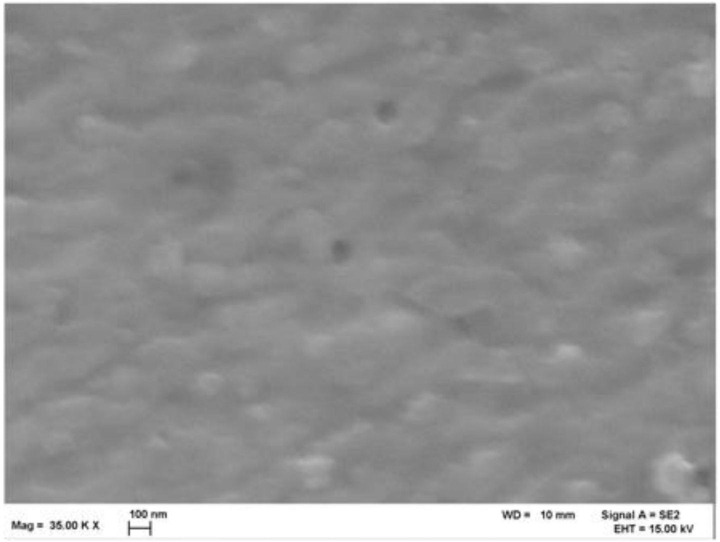
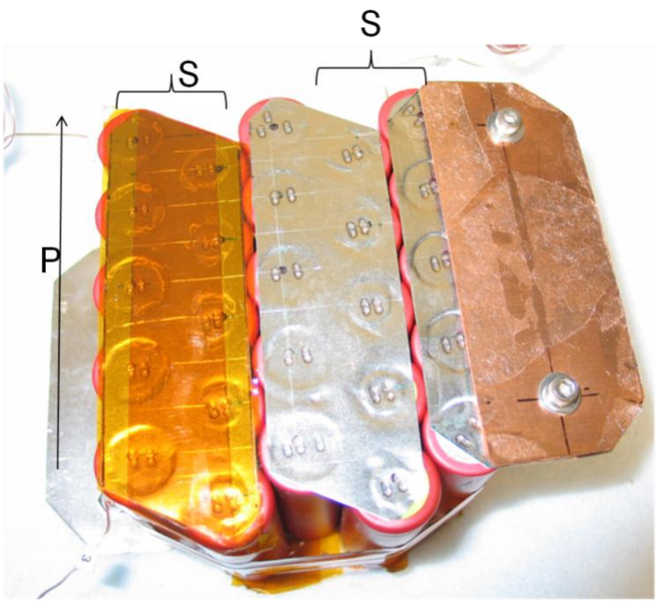


Photo 12 – Cell 36, Circular holes, probable dendrite locations

Matrix Pack with Imbalanced Li-ion Cells

- A matrix pack was tested under a different program where one cell was disconnected from the pack and 100 cycles were carried out.
- No major change in performance was observed in spite of one cell not participating in the cycling process. This data is shown for comparison with the imbalanced traditional pack configuration test data provided in this presentation.

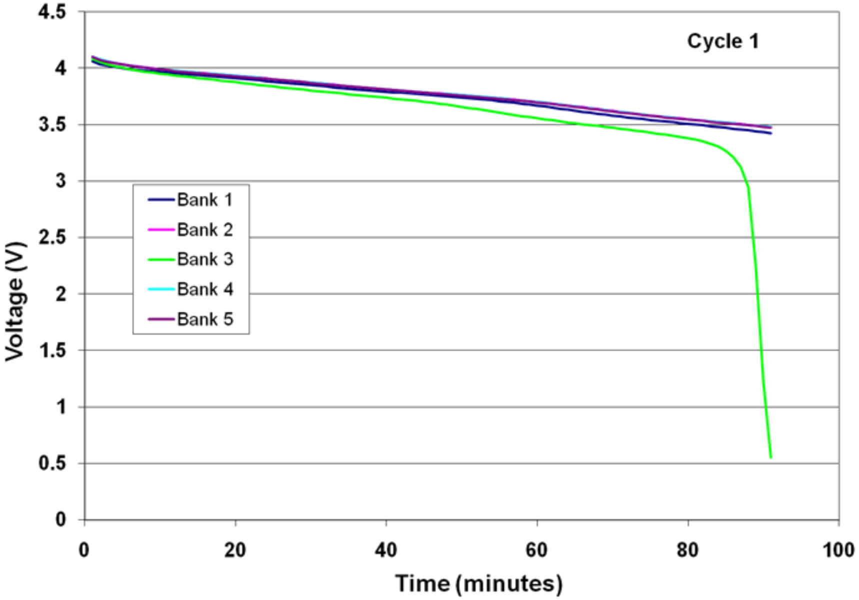


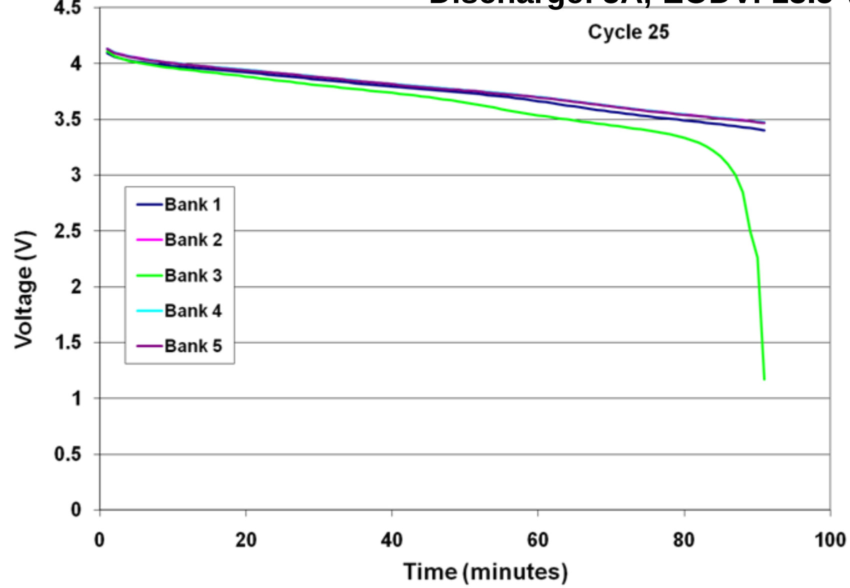
Matrix 5X5 Configuration

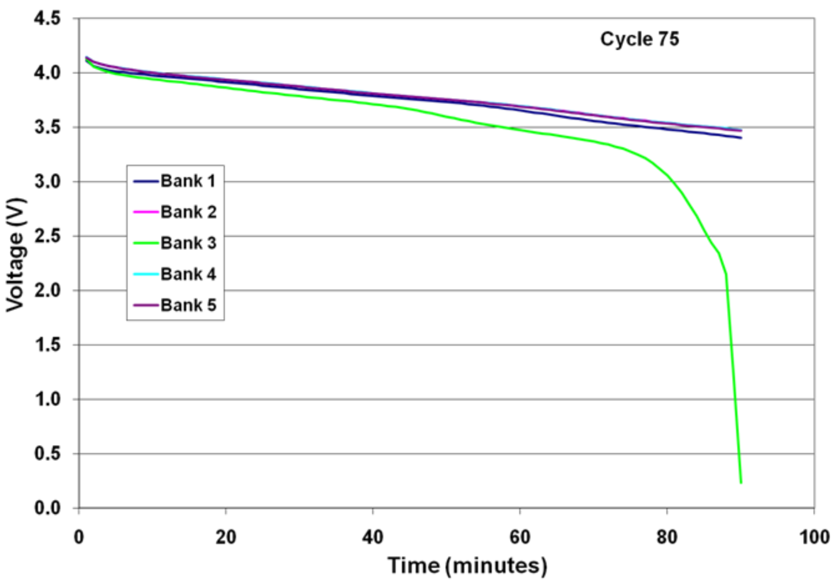
Matrix 5X5 pack showing disconnected cell

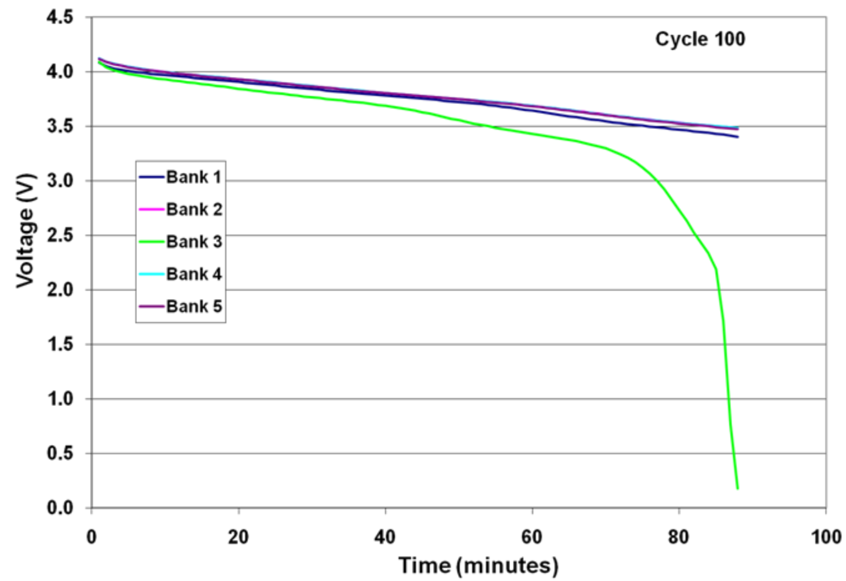
Cycle Life Test for 5X5 Lithium-ion Matrix Pack With One Cell Disconnected

Charge: 5 A; EOCV: 21 V
Discharge: 5A; EODV: 13.5 V

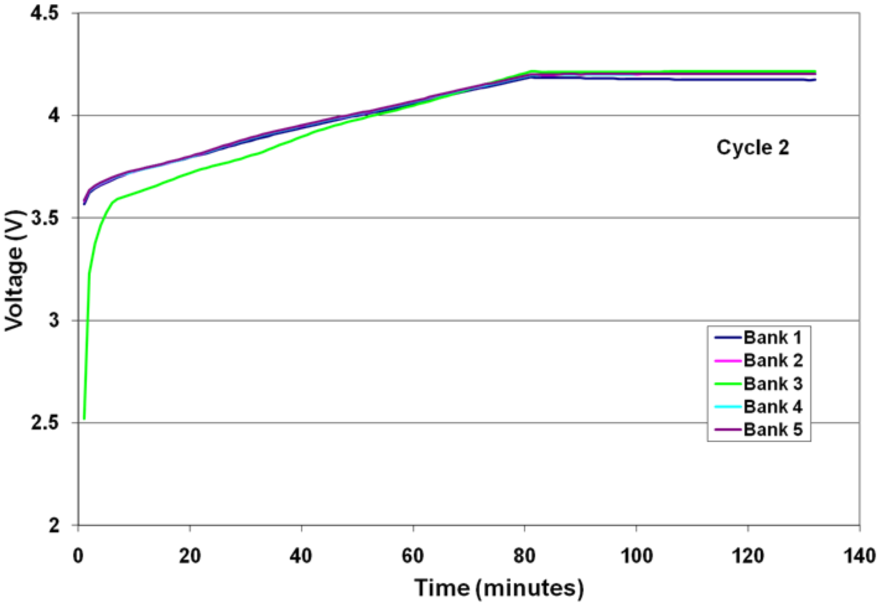






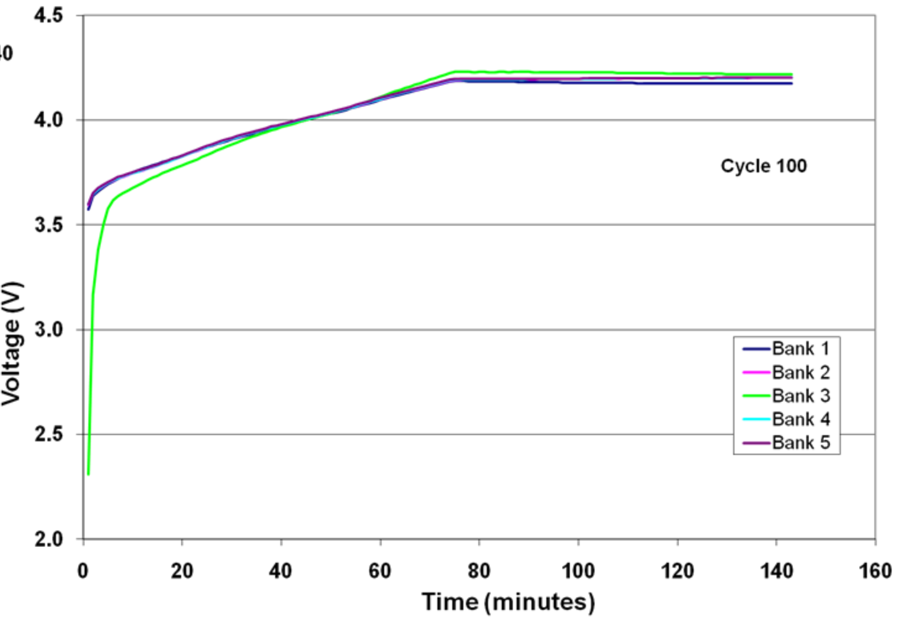


Cycle Life Test for 5X5 Lithium-ion Matrix Pack With One Cell Disconnected



At 2nd Cycle:
Max volt difference: 38 mV
Diff between two of the lower voltage banks is 25 mV

At 100 cycles:
Max volt difference: 55 mV
Diff between two of the lower voltage banks is 25 mV



Summary and Conclusions

- **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 that they were subjected to.**
  - **The observations may be due to the fact that the discharges were not deep enough (EODV was 2.0 V per cell) to cause significant dissolution of copper that would in turn cause internal shorts to develop with cycling.**
- **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, the cells did show internal shorting at some point and this caused instability in the whole string or abnormal behavior in some.**
  - **CID opening in high voltage strings is not a reliable occurrence and PTC failures can be induced in high voltage/high capacity modules (43rd Power Sources Conference)**
- **If the imbalance in the cells strings was in the range of 50 mAh, 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.**

Summary and Conclusions

- **The 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 and balancing, or it would be difficult to capture deep discharge or voltage reversal of one or more cells.**

- **In the matrix design configuration, disconnection of cells 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.**

- **Balancing during discharge may be more critical than during charge (!)**

Acknowledgment

SRI for the flexibility in changing the test program based on the results obtained throughout the test.

API: for carrying out the matrix pack test that is referenced in this presentation.