Internal Shorts in Li-Ion Cells – What Does it Take to Cause One that is Catastrophic?

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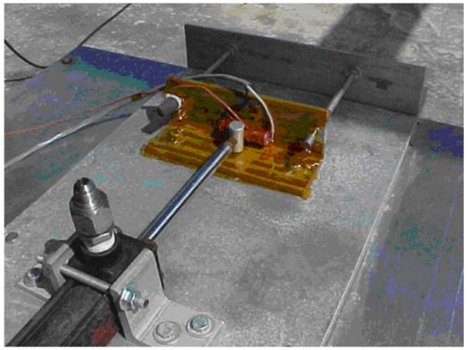
Background

- Simulation of internal shorts using a crush test method has been used for more than 14 years at NASA-JSC
- The equipment used a hydraulic press with manual operation.
- Initial tests were carried out with crushing until voltage fell to 0 V; then later changed to 500 mV drop in voltage
- Not easy to control; but repeatable results obtained
  - Cells of different chemistries (NiMH vs Li-ion; cobaltate vs spinel vs phosphate)
  - Cells tested at different states of charge
  - Results were repeatable and reproducible

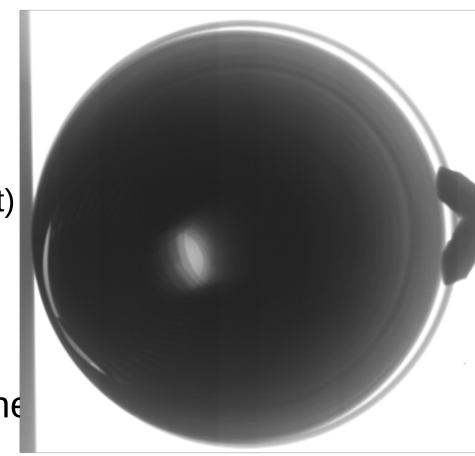


- UL involvement started from the standards working groups and presentation of NASA-JSC data at the meetings.
- Other methods and techniques were also under review such as the BAJ and the UL Blunt Nail Crush (BNC) test.
- Since the UL test is similar to NASA-JSC method, UL was interested in a collaboration.
- A Space Act Agreement was signed between NASA and UL to carry out the work.
- A test plan was provided by NASA as part of the agreement.
- UL provided the test equipment as part of the agreement.
- Several other objectives and tasks were also included such as DPAs, X-ray, CT, etc.

Work Plan

The following plan was formulated with several variables to be studied.

- Cells were subjected to different test protocols before crushing with the blunt rod.
  - Fresh cells (2 cycles only)
  - 200 cycles
  - 500 cycles
  - 1000 cycles
  - Cells rejected from a battery manufacturer
  - Cells cycled at low temperatures
  - Cells cycled at 2 C charge rates
  - Cells cycled to high voltages (4.5 V)
- All cells X-rayed to mark the location of current collector tab.
- Variables:
  - Rod diameter
  - Radius of curvature of the rod tip
  - Rate of displacement (0.1 mm/sec to 0.01 mm/sec)
  - Orientation of cell (location of Al current collector versus location 90 degrees to that)
  - Cell SOC
  - Voltage change for test stoppage (100 mV vs 500 mV)

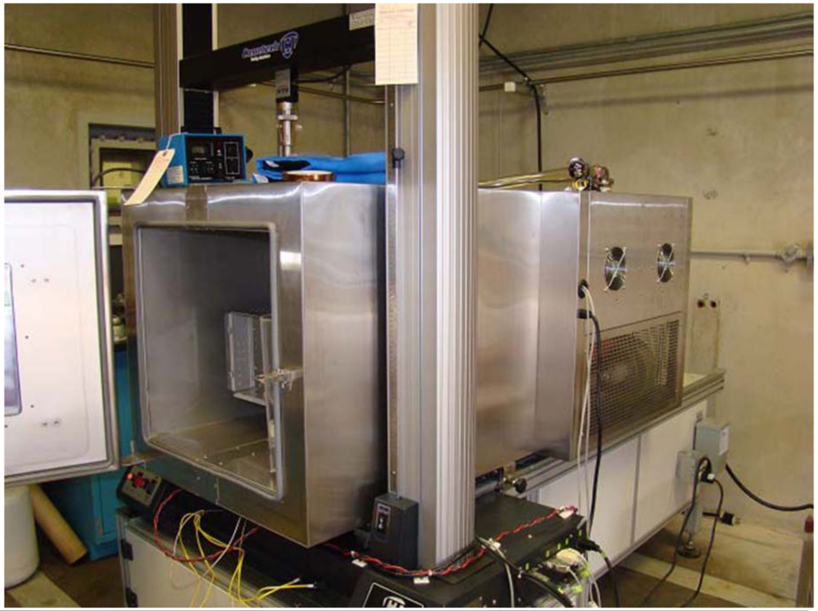


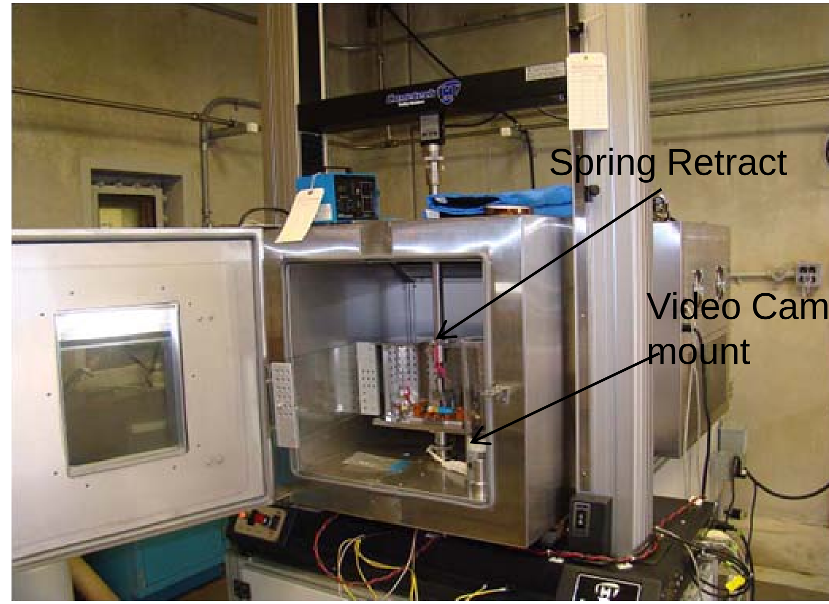
2010-2011: All cells were Sony 18650 cells except two sets used at the start of the
optimize the diameter of the rods and rate of displacement.

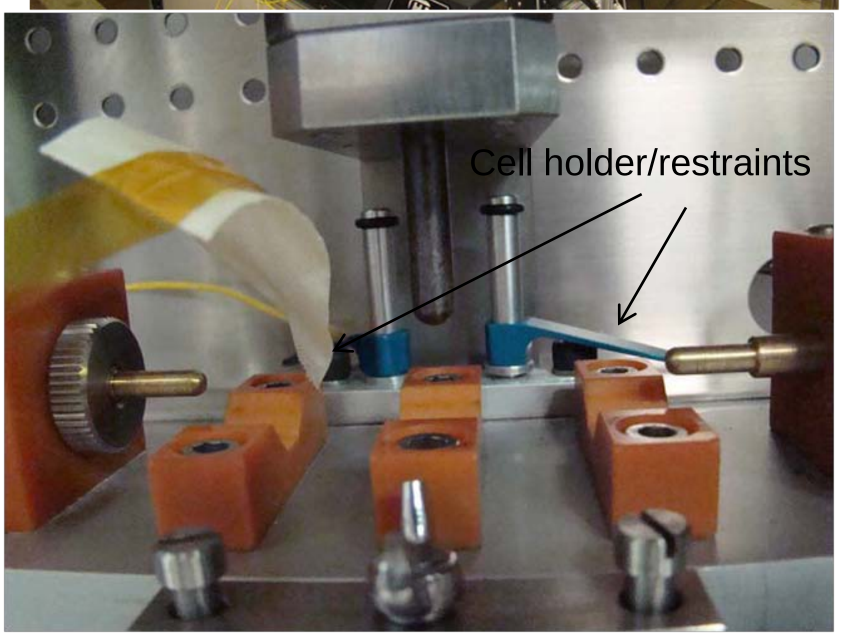
2011 -2012: Boston Power 4400 and Sanyo 1.9 Ah spinel cells.

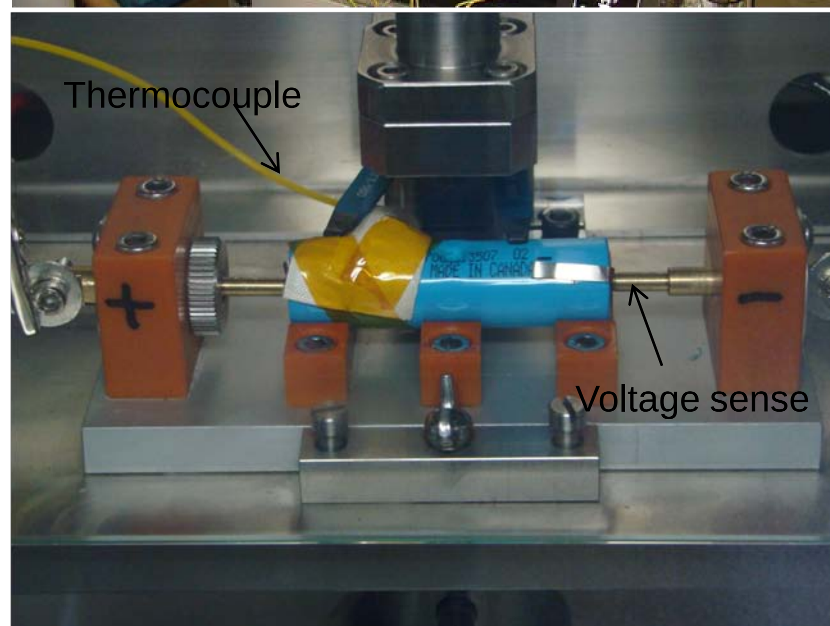
All cells used in this program were only test vehicles and not to be construed as endorsement or problematic.

Simulated Internal Short Test Equipment at NASA-JSC









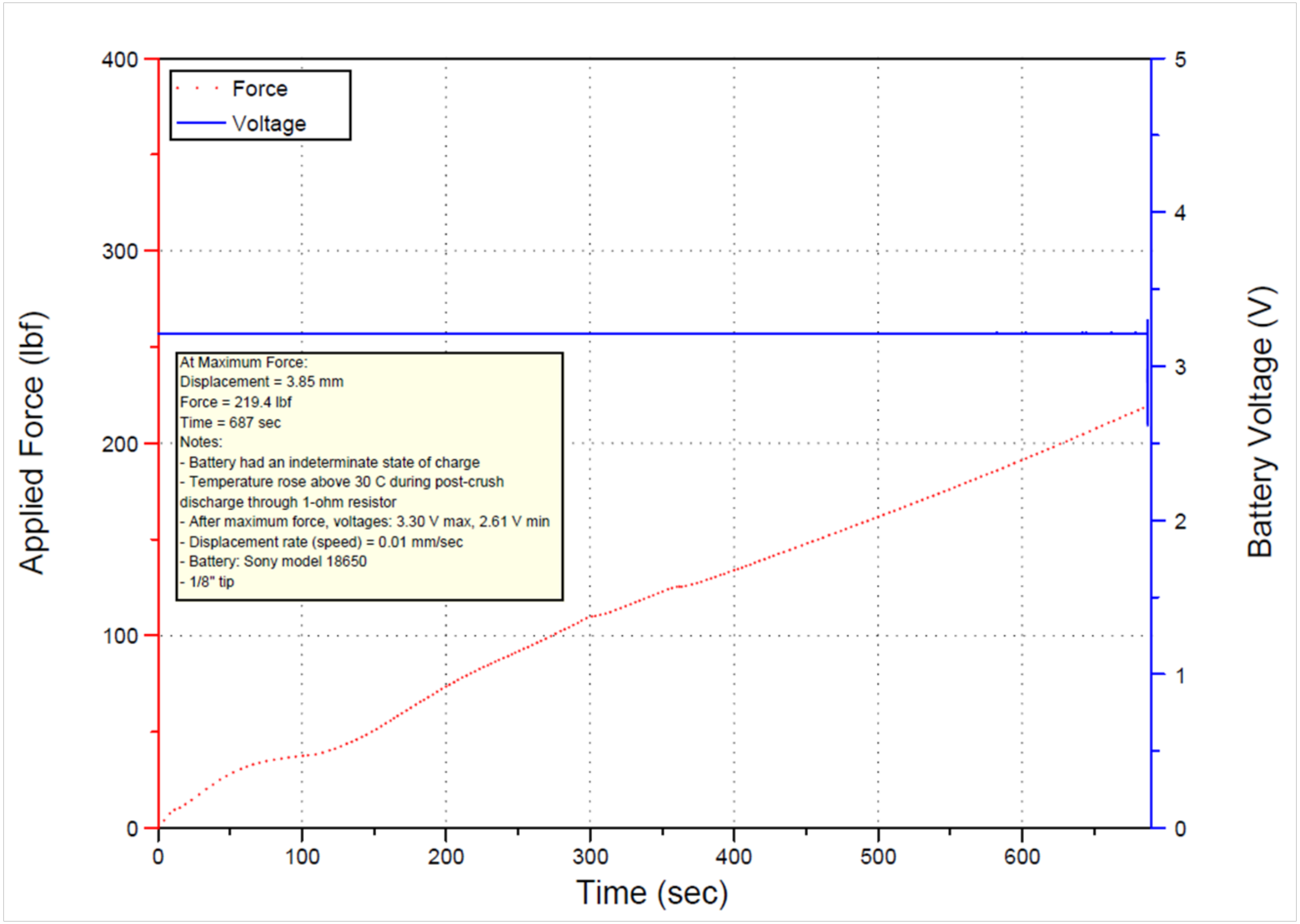
CT Scan Work

- CT scans were carried out on all the cells that were not compromised (that is, no breach of cell can)
  - All cells that did not undergo a vent or disassembly during the simulated short test were discharged after test completion and test chamber purged with inert gas for at least 4 hours. Temperatures were always checked before cells were removed from test stand.
- Each CT slice represents 30 to 50 micron thickness

Initial Tests

- The first trials were carried out on fully discharged cells using a speed of 0.1mm/sec and rods of two diameters namely 1/8” and ¼”.
- We found that the ¼ and 1/8” rod penetrated the can when tested at a speed of 0.1mm/sec.
- The second set of tests involved changing the rate of crush to 0.01 mm/sec. This seemed to provide results that did not cause the compromise of the can.
- Tests were then conducted with 0.01 mm/sec rate of crush with the rods of ¼” and 1/8” diameters.
- Voltage limit was 500 mV drop.

Cell 63



400
300
200
100
0
Applied Force (lbf)
Force
Voltage
At Maximum Force:
Displacement = 3.85 mm
Force = 219.4 lbf
Time = 687 sec
Notes:
- Battery had an indeterminate state of charge
- Temperature rose above 30 C during post-crush discharge through 1-ohm resistor
- After maximum force, voltages: 3.30 V max, 2.61 V min
- Displacement rate (speed) = 0.01 mm/sec
- Battery: Sony model 18650
- 1/8" tip
0
100
200
300
400
500
600
Time (sec)
5
4
3
2
1
0
Battery Voltage (V)

CT images
Cell 63 1/8” rod

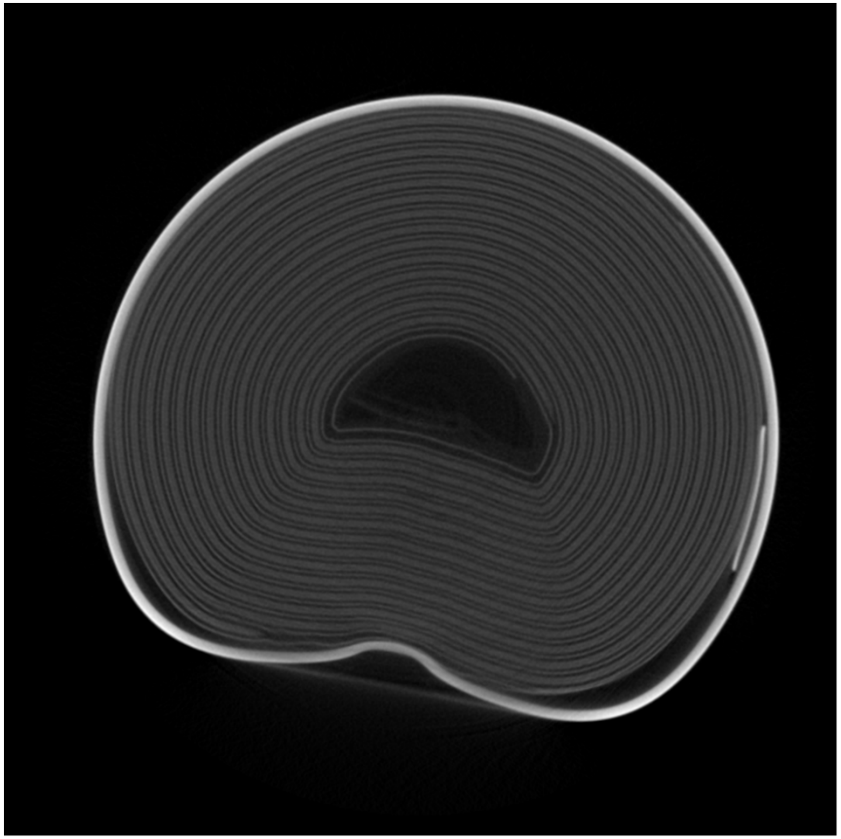


Image 570

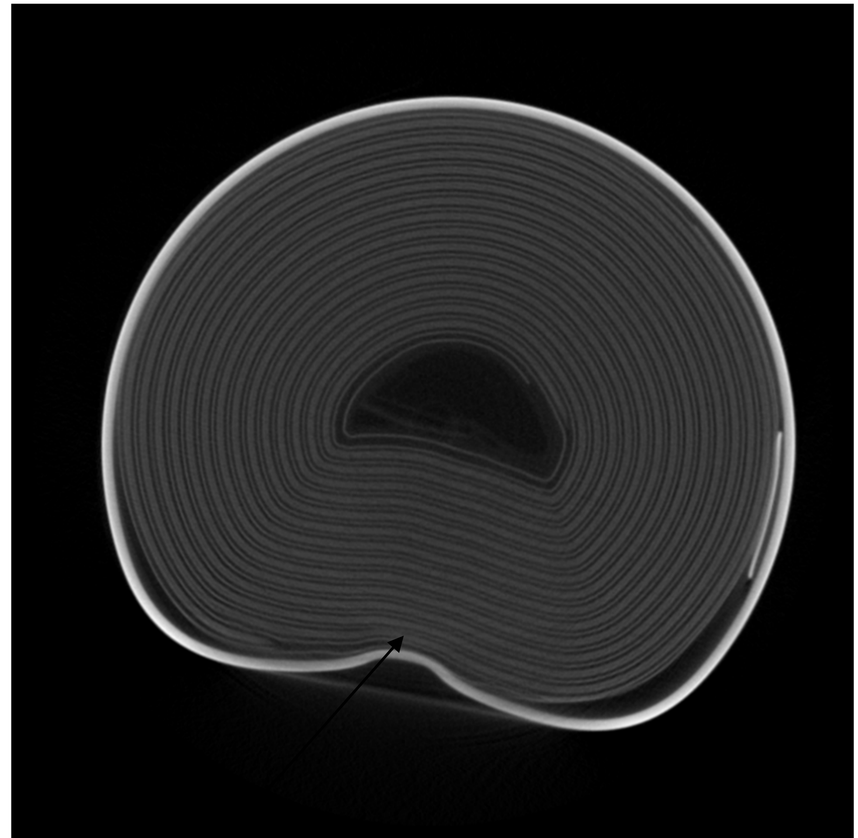
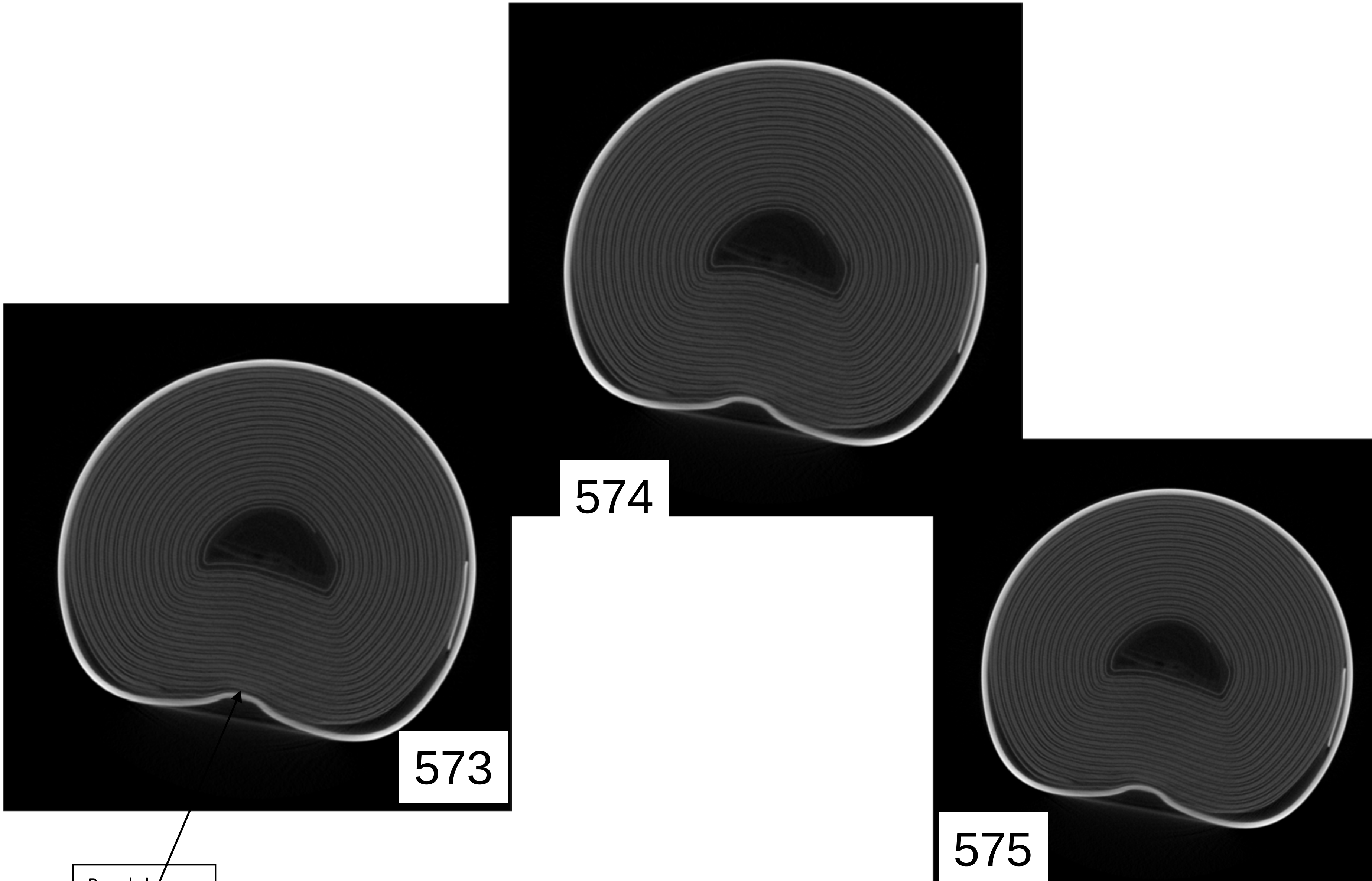


Image 572

Start of
Breakdown

Cell 63 1/8” rod

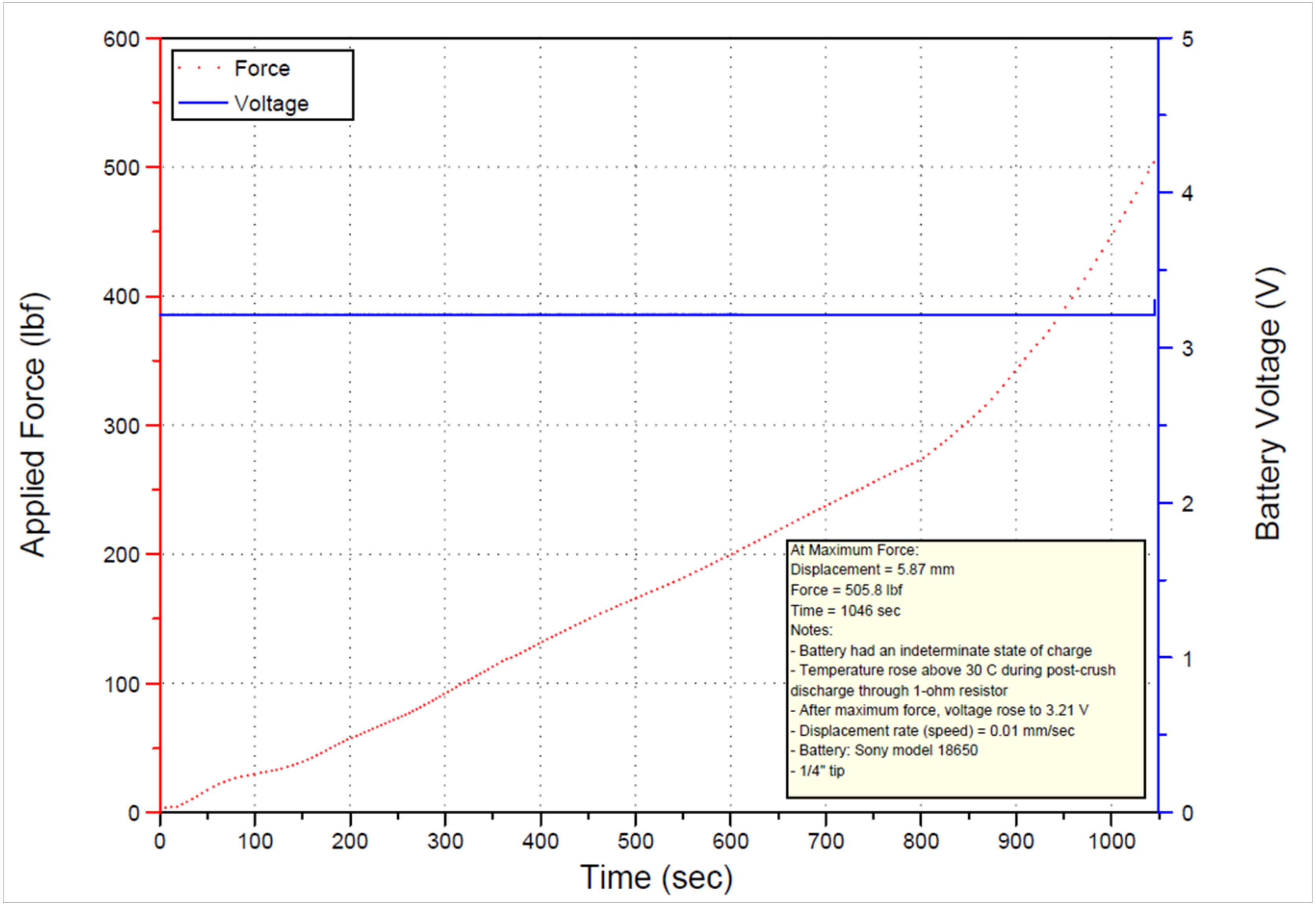


Breakdown point

Distinct electrode separation observed again in this.

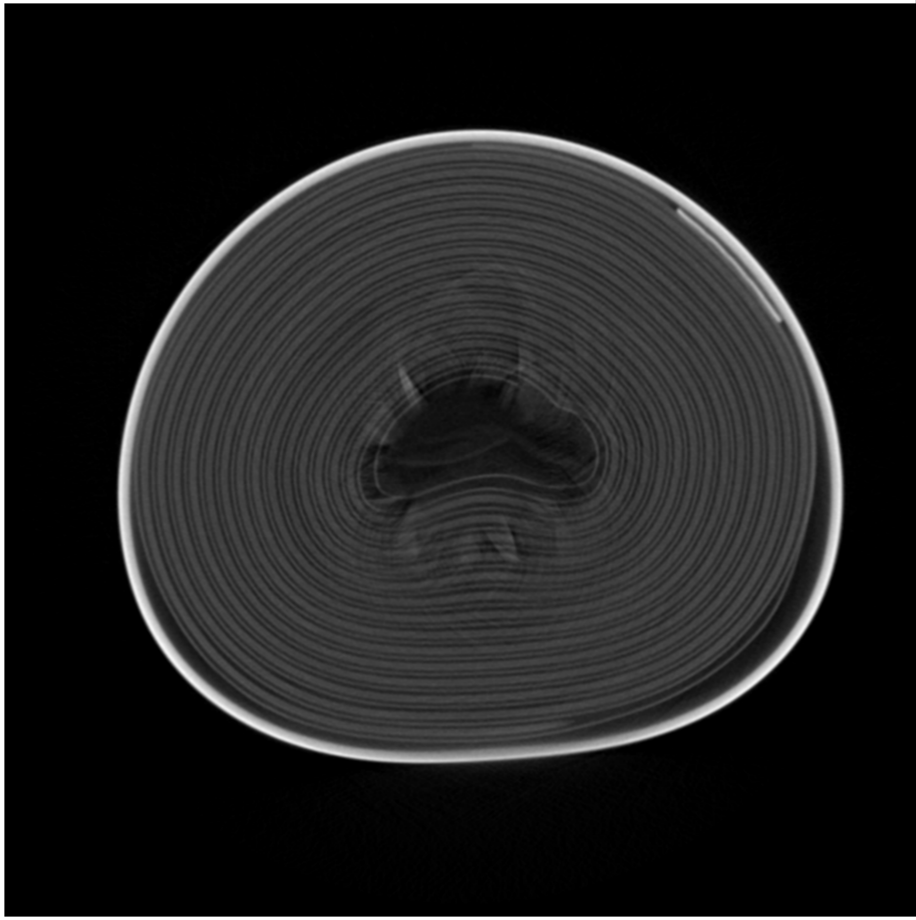
DPA Cell 63 Photos

Cell 64



600
500
400
300
200
100
0
Applied Force (lbf)
Force
Voltage
0
100
200
300
400
500
600
700
800
900
1000
Time (sec)
5
4
3
2
1
0
Battery Voltage (V)
At Maximum Force:
Displacement = 5.87 mm
Force = 505.8 lbf
Time = 1046 sec
Notes:
- Battery had an indeterminate state of charge
- Temperature rose above 30 C during post-crush discharge through 1-ohm resistor
- After maximum force, voltage rose to 3.21 V
- Displacement rate (speed) = 0.01 mm/sec
- Battery: Sony model 18650
- 1/4" tip

Cell 64 ¼" rod



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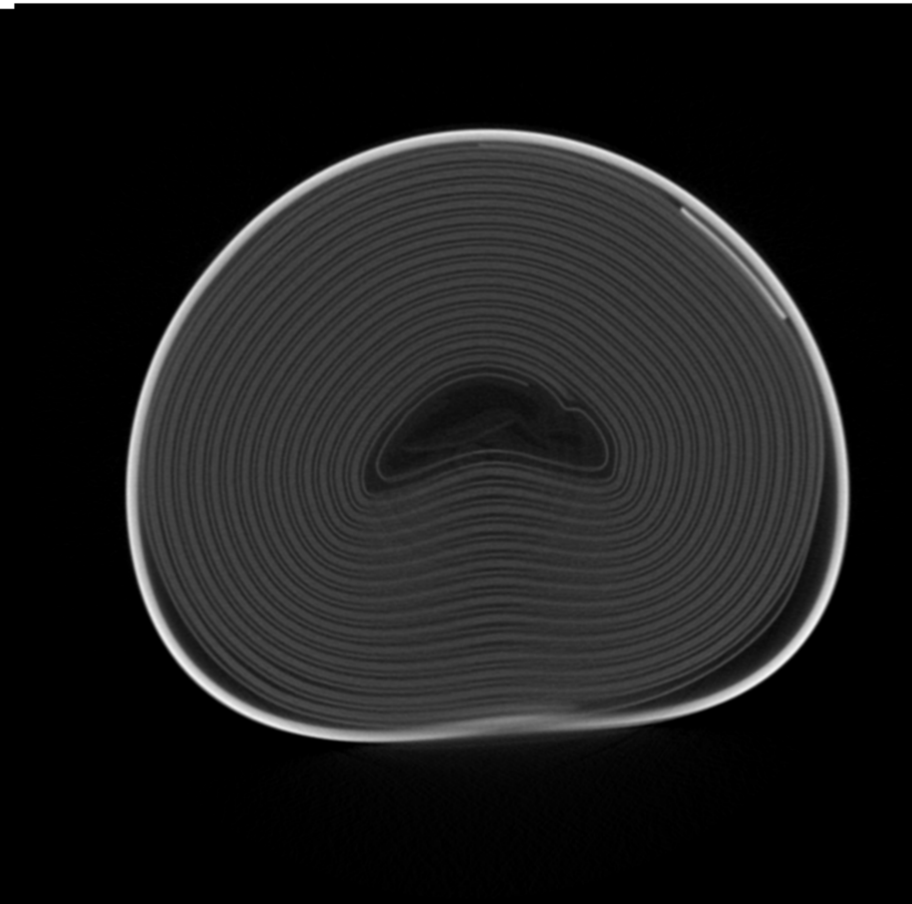

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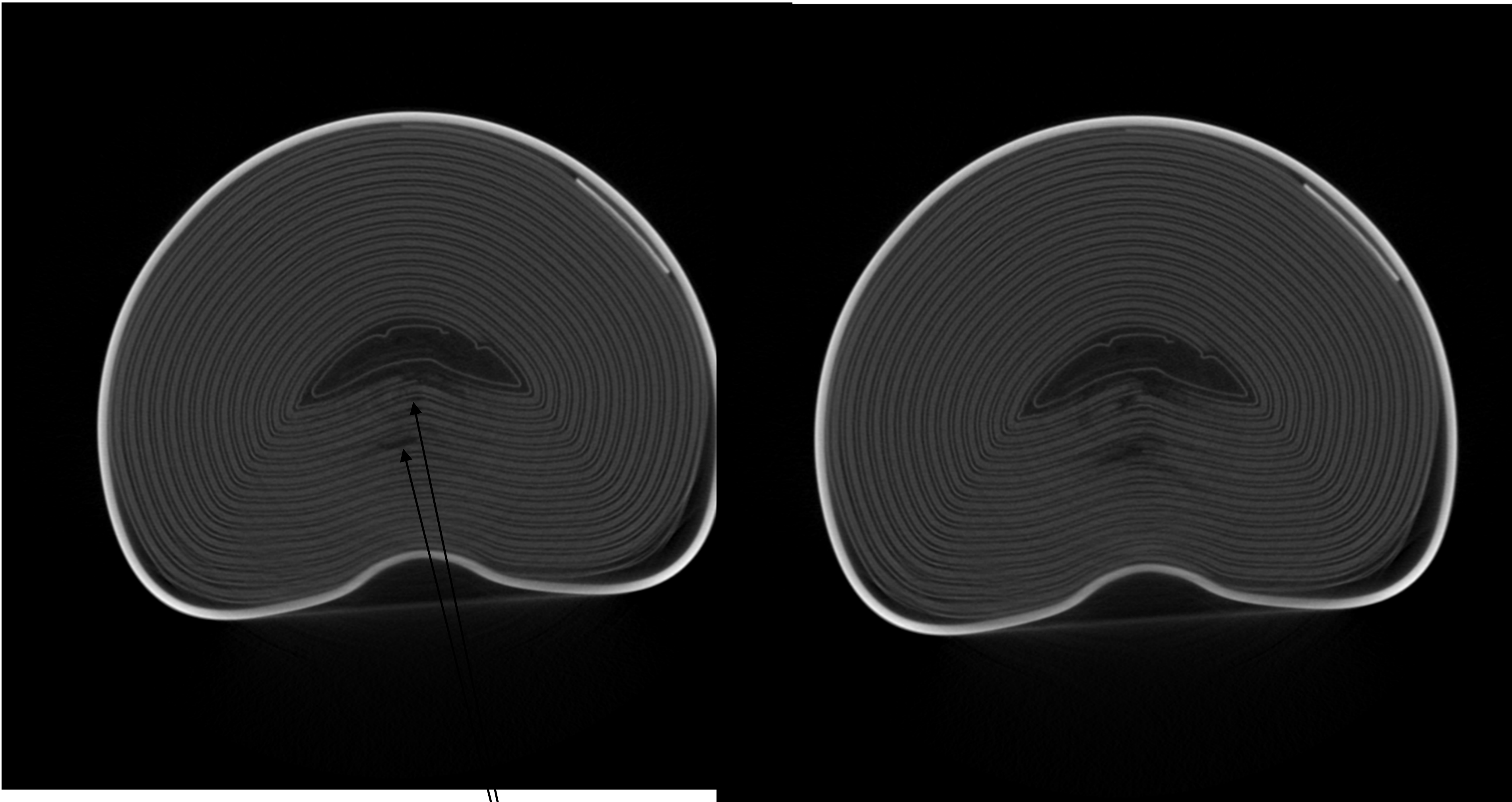
Note more shape change internal to the electrode roll than external to the roll.

Cell 64 ¼” rod



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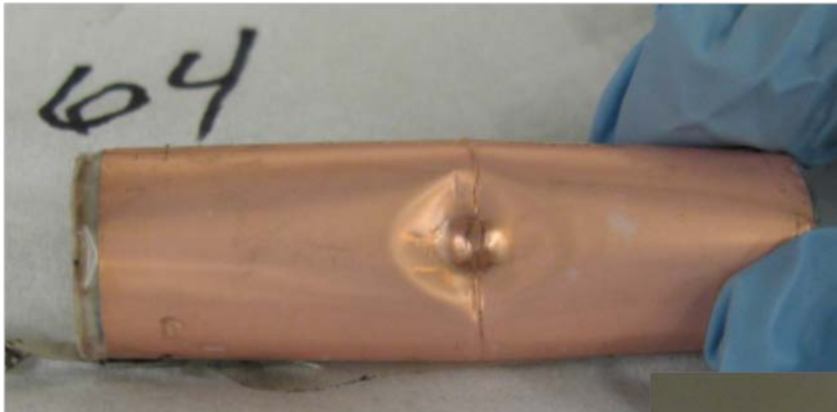
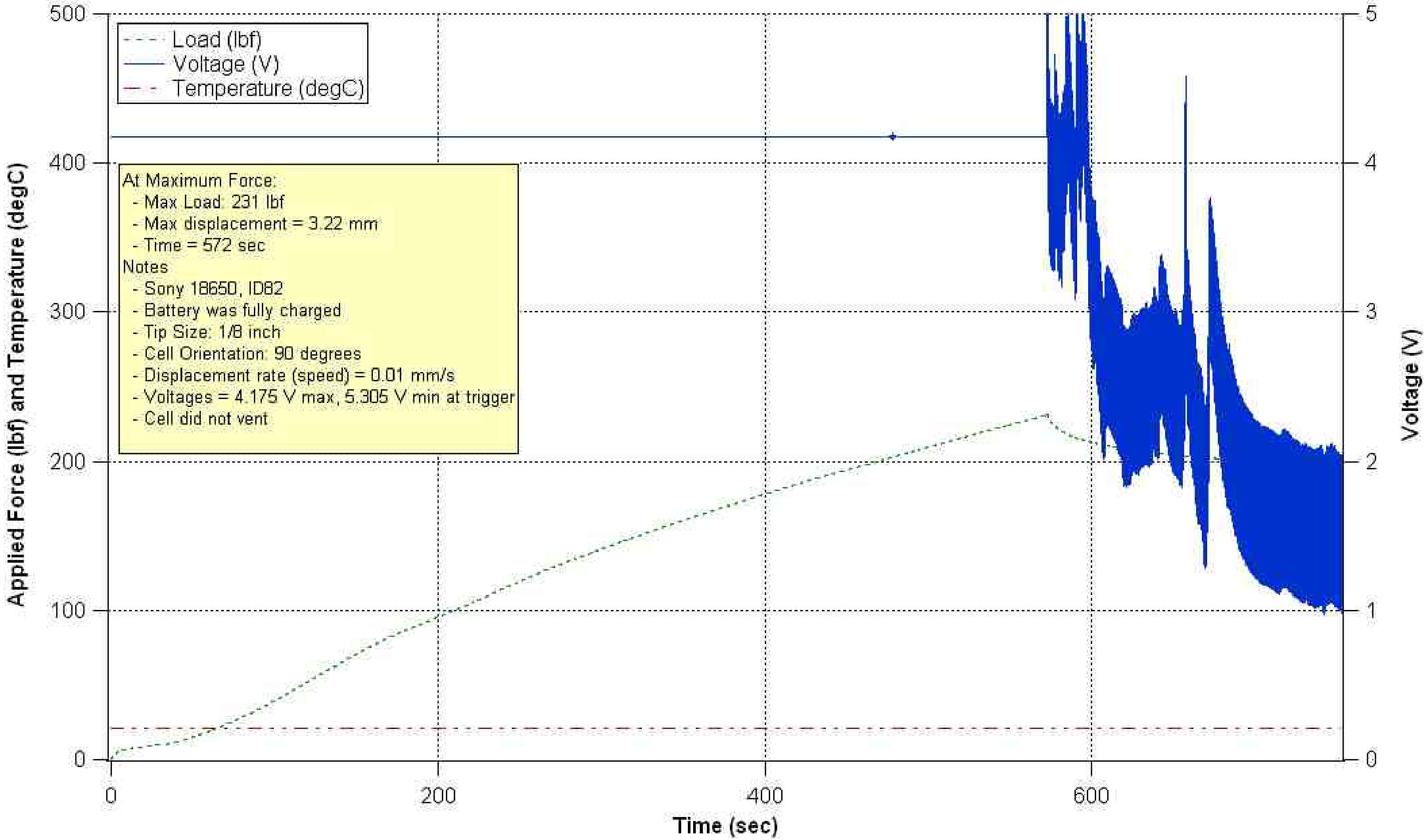
DPA Cell 64 Photos



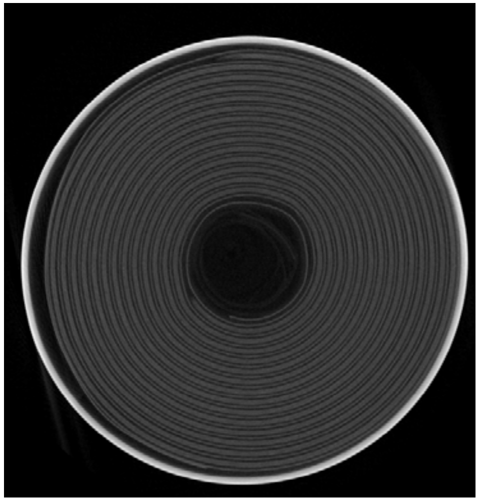
Cell 82



500
400
300
200
100
0
Applied Force (lbf) and Temperature (degC)
Load (lbf)
Voltage (V)
Temperature (degC)
At Maximum Force:
- Max Load: 231 lbf
- Max displacement = 3.22 mm
- Time = 572 sec
Notes
- Sony 18650, ID82
- Battery was fully charged
- Tip Size: 1/8 inch
- Cell Orientation: 90 degrees
- Displacement rate (speed) = 0.01 mm/s
- Voltages = 4.175 V max, 5.305 V min at trigger
- Cell did not vent
0
200
400
600
Time (sec)
5
4
3
2
1
0
Voltage (V)

Cell 82 (1/8”) no vent

⊥ 90 deg to tab
500 cycles



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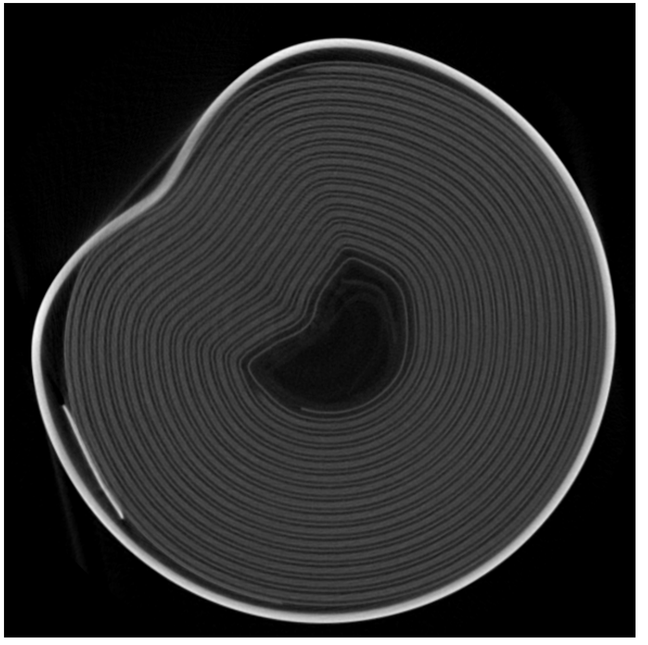
No internal short was observed due to the rod losing its polished tip



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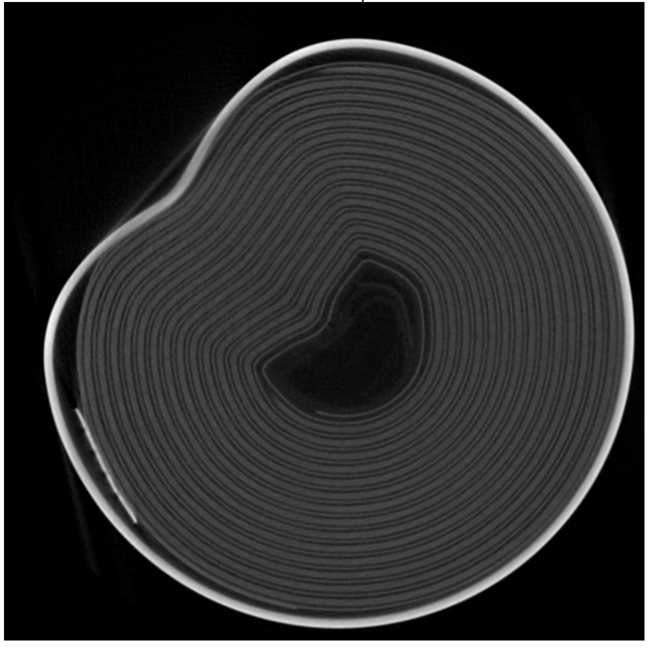

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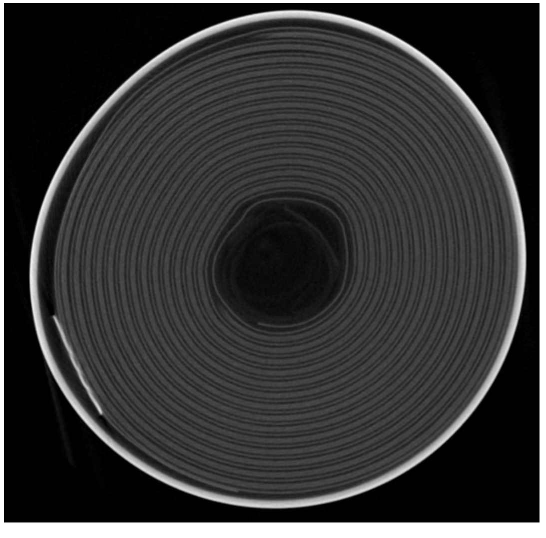

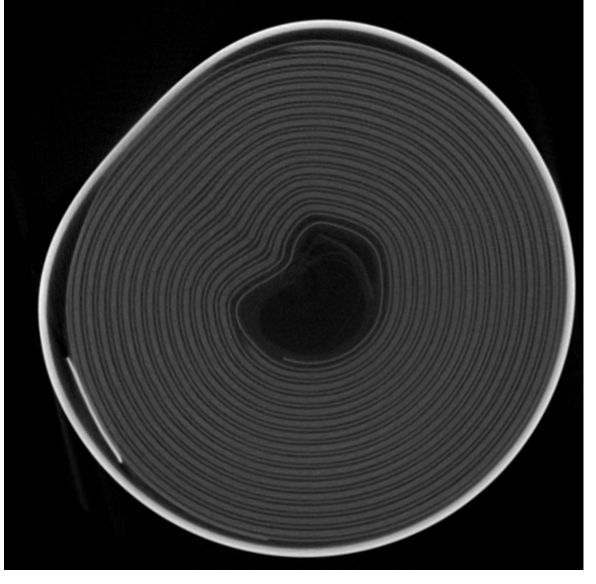

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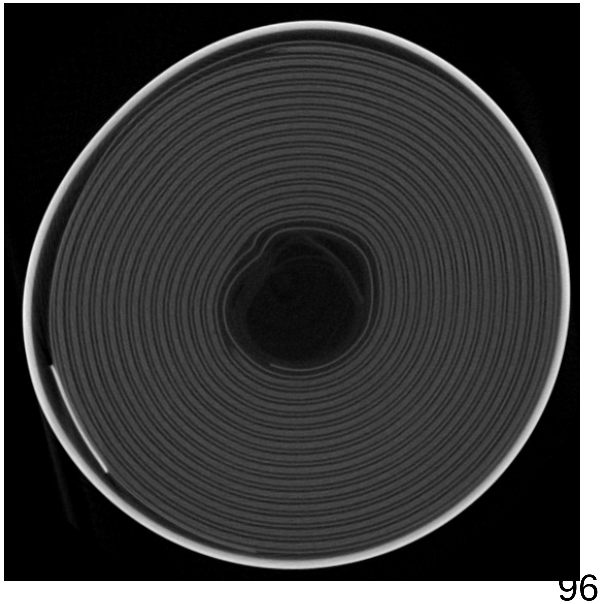

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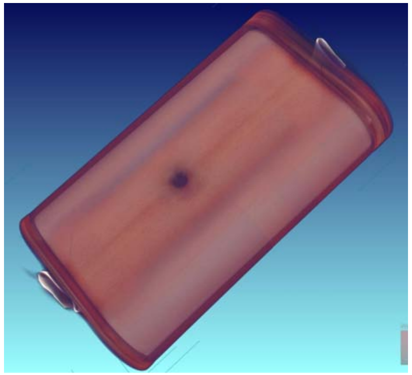
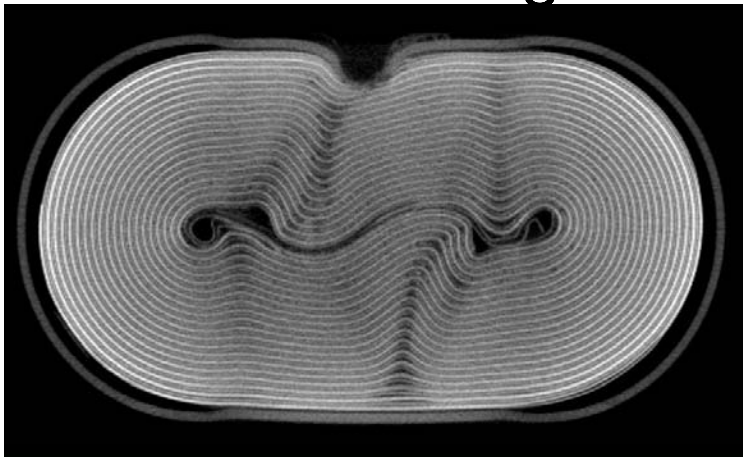
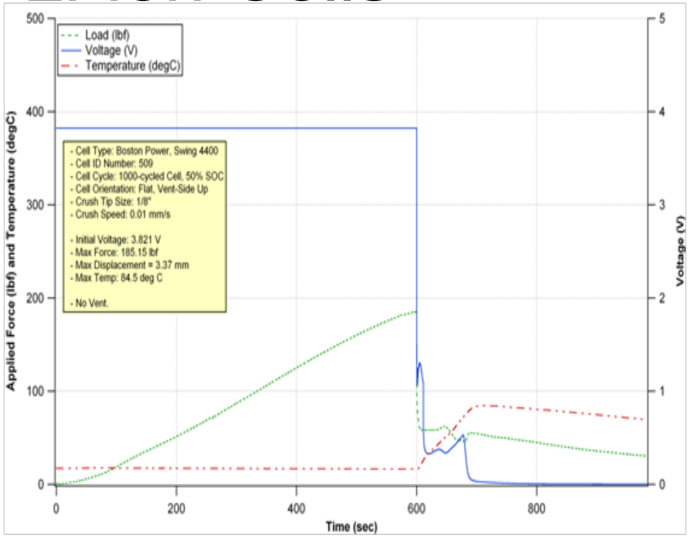
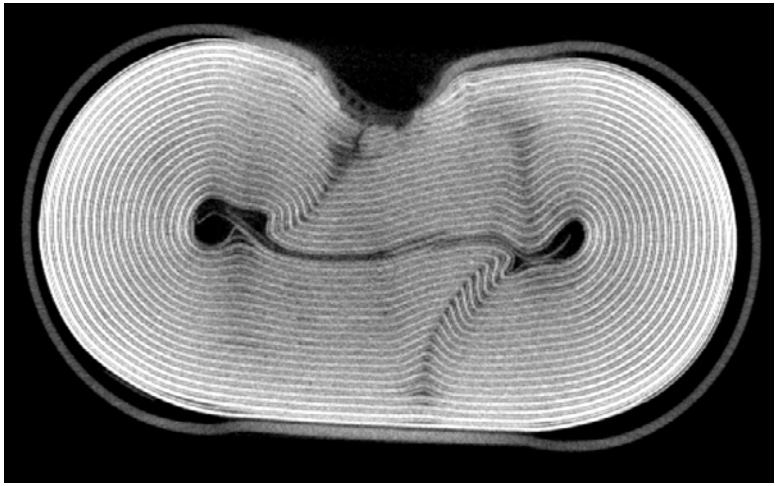
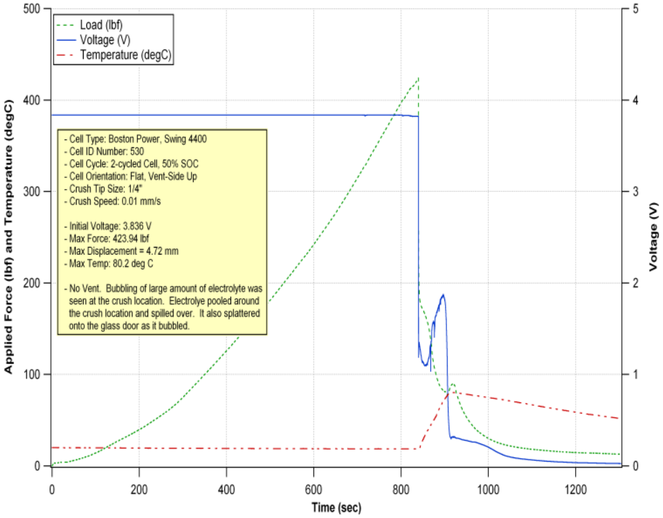
Boston Power Swing 4400 Li-ion Cells







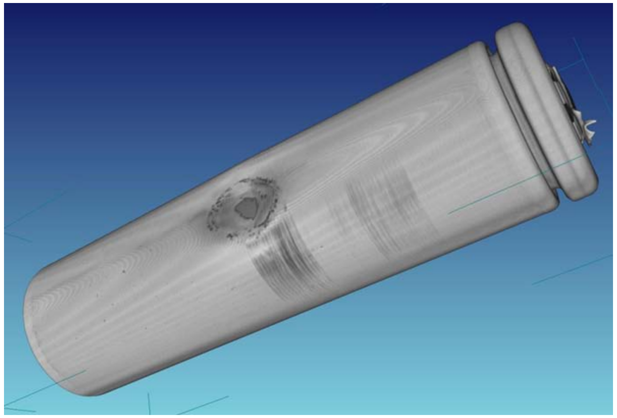


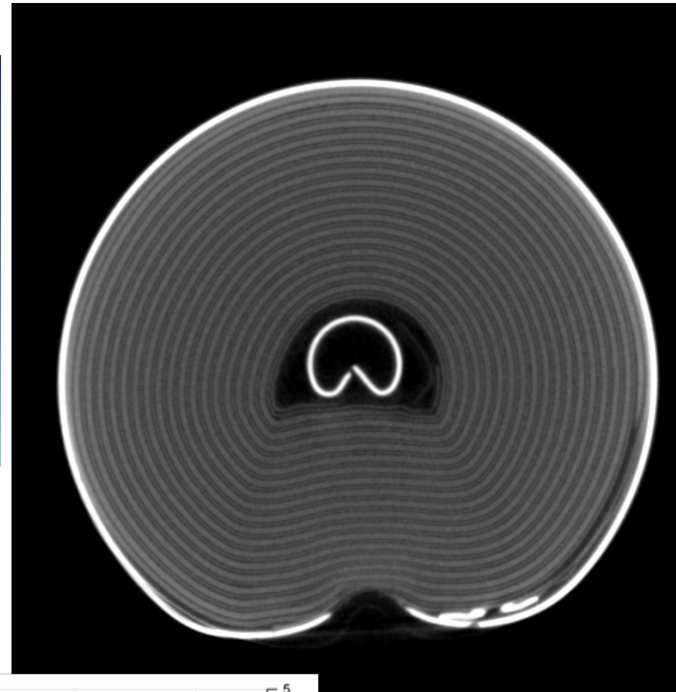


Boston Power Simulated Internal Short Test Summary

- Cell casing was breached in several cells during the Simulated Internal Short crush test but this did not have an impact on the nature of the results.
- Most cells vented a lot of electrolyte.
- No fires were observed at all. Smoke was observed in cells that went over 150 °C and cells looked charred at the end of the venting period, but no fires were observed. Maximum temperature recorded was 520 °C.
- Cells vented through the crush location if there was cell can penetration; in all other cases of venting, it occurred slowly through the vents in the cell.
- Fresh cells at 100 % SOC exhibited temperatures between 400 and 500 °C while fresh cells at 50 % SOC did not go over 90 °C.
- Cells that underwent 1000 cycles lost about 20 % of the original capacity and exhibited venting of electrolyte even at 50 % SOC, but the maximum temperature recorded with the cells at 50 % SOC was not greater than 104 °C.

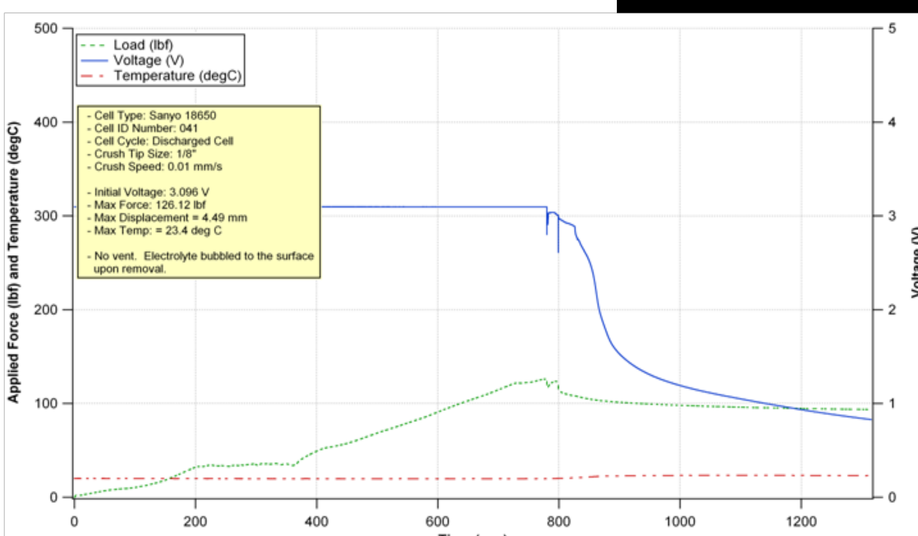
Sanyo Li-ion Spinel 1.9 Ah Cylindrical Cells

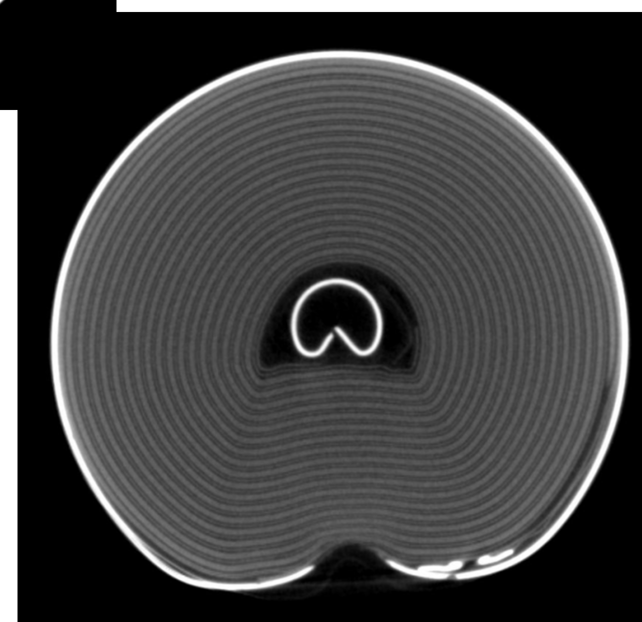




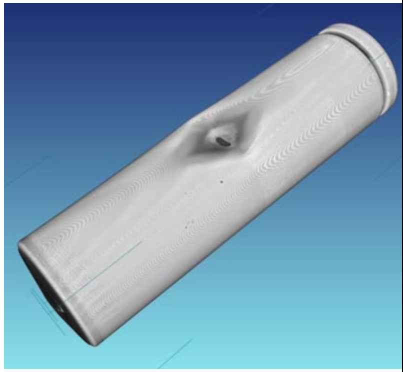
Overdischarged Cell

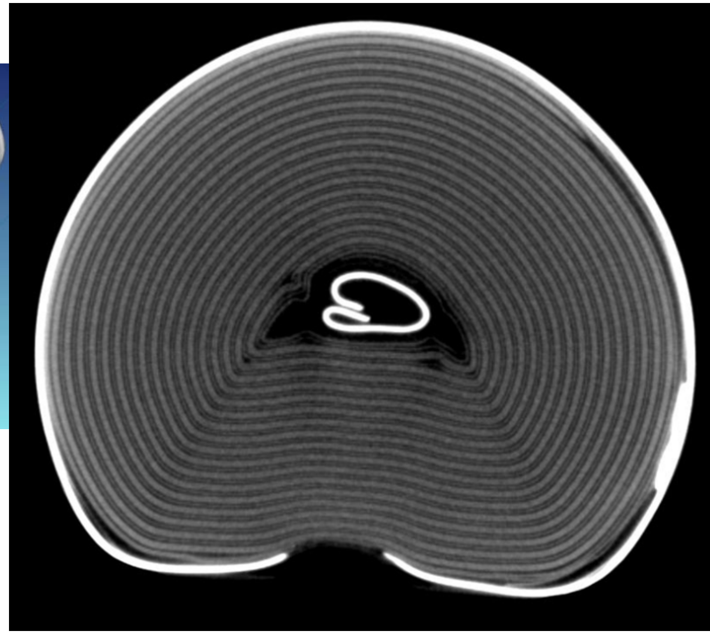
1/8” Tip Blunt rod





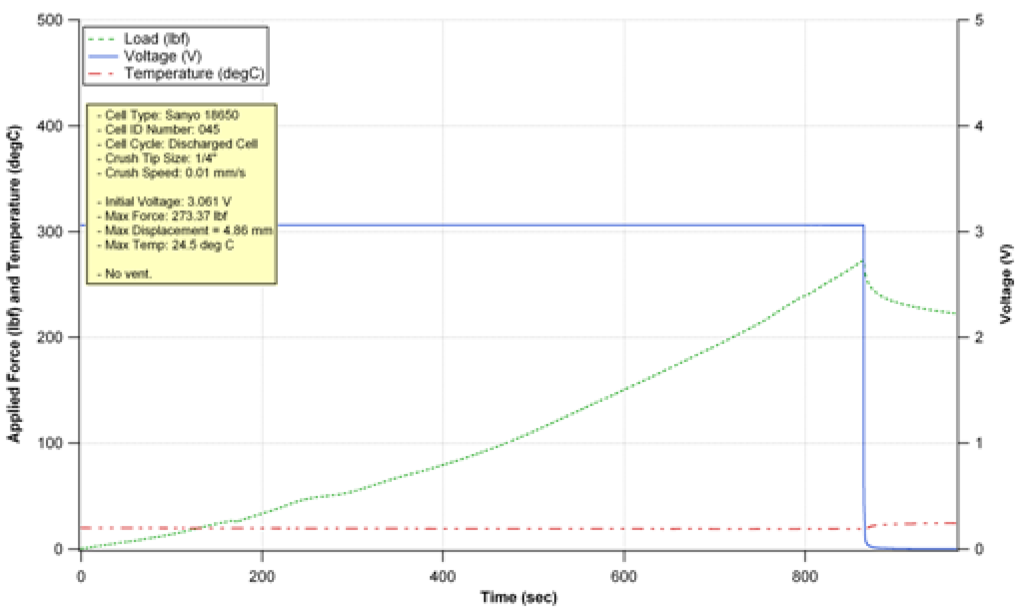
Sanyo Li-ion Spinel1.9 Ah Cylindrical Cells

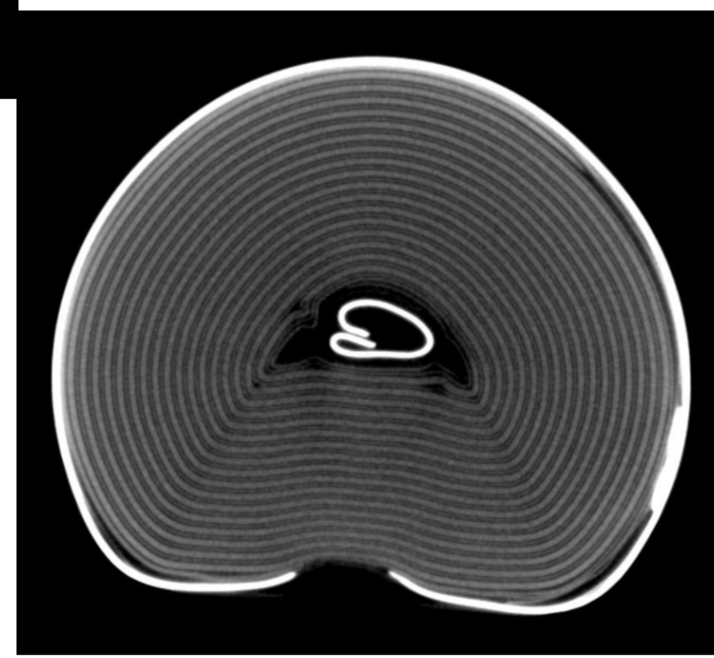




Overdischarged Cell

1/4” Tip Blunt rod





Sanyo Li-ion Spinel 1.9 Ah Cylindrical Cell Summary

- Cells exhibited a maximum temperature of 120 C during the crush test.
- No thermal runaway was observed with any of the cells tested.
- Crush test data is consistent with previous results obtained with JSC's old primitive test equipment.
- Cell metal can was breached in some cases but the results did not vary.
- Cells are inherently safer under simulated internal short conditions compared to a pure cobaltate cathode cell.

What makes an internal short catastrophic?

- Internal shorts are caused in two ways
  - Manufacturing defects
  - Field failures due to misuse or going beyond recommended cell/battery specifications
- Manufacturing defects undetected during acceptance testing can later become problematic as they can be prone to the development of dendrites that can then turn into latent defects that are catastrophic
- Soft shorts such as blackening of the separator, very tiny halos, etc. are observed even in the most pristine cells; cells with lithium metal deposits have observed with a major cell manufacturer – cells have undergone more than 15,000 LEO cycles and the lithium deposits look the same as with a fresh cell.
- Destructive analysis of the cells that showed the occurrence of an internal short with a voltage drops show that there is a crack in the separator; and at least two layers of separators in the internal winds in the same location show separator shutdown (transparent separator).
- In the case of soft shorts that result in the observations in bullet 3, no heat effect is seen on subsequent separator layers. Hence it can be concluded that a catastrophic internal short occurs only when the localized heat produced is spread to more than one layer of separator inside the cell. This sustained and localized heat is required to produce a catastrophic internal short.

Observations

- Even with the 1/8" rods, the radius of curvature of the tip was important. With the wider tips, the test was incomplete, no internal short occurred. With the thin tips, penetration of can occurred. The medium curvature tips were the best.
- NASA designed rods using a type of stainless steel.
- Rods had to be cleaned and polished periodically since the heat would affect the tips and the vent products would adhere to the tips causing uneven tip surfaces.
- Cells that underwent 1000 cycles showed a range of capacity losses. The cells that had capacity loss of 19 % or more for Sony cells, did not undergo thermal runaway during crush test. Cells did not show any variation for the Sanyo cells although the cells lost almost 50 % capacity at 1000 cycles.
- Sony cobaltate cells of indeterminate or < 50 % SOC did not undergo thermal runaway.
- Sony cells that were overcharged consistently went into violent thermal runaway a few seconds after the voltage drop occurred. BP cells and Sanyo cells did not show any thermal runaway.

Summary

- CT scans indicate that 1/8” blunt rod is better than the 1/4”.
- The lower speed for crush 0.01 mm/sec provided more consistent results.
- The loads and displacement at test completion are consistent within experimental error.
- There is no difference in test results based on location of crush.
- The voltage drop is too fast to be able to use it as a criteria for the standard but the 500 mV change seems to be a reasonable point to stop the crush. 100 mV is in the noise - level and the results with that value as a limit were not consistent.
- Cells at lower SOC (<50 %) exhibit benign results compared to those at full SOC. This result has been consistent and reproducible.
- Cycled Sony cells that had a loss of greater than 20 % capacity did not result in venting or thermal runaway. Cycled Boston Power cells behaved similar to fresh cells and this may be due to the fact that they lost less than 20 % capacity after 1000 cycles.
- So far, the results have been very consistent with the results obtained from NASA-JSC’s old crude test setup.

Future Work

- Carry out simulated internal short tests on li-ion pouch cell designs.

NASA's Approach

- NASA has used this crush test method for more than 14 years to determine a cell design's tolerance to internal shorts.
- Results dictated the type of screening method to be used for flight acceptance testing of batteries.
- 100 % of flight batteries undergo flight acceptance testing.
- Except for button cells and alkalines, all batteries undergo vibration testing
- Batteries that are tolerant to internal shorts (aqueous battery chemistries such as NiMH, NiCd and Ag-Zn) undergo workmanship vibration.
- Those intolerant to internal shorts (Li primary and Li-ion) undergo a higher level of vibration to screen for internal shorts. For LiBCX chemistries, X-rays of 100 % of cells was also conducted. (X-rays for Li-ion are not as informative due to the packing density of the cells).
- No battery chemistries are eliminated due to their lack of tolerance to internal shorts since on our hazard criticality and likelihood matrix, although this is a catastrophic hazard, the likelihood is very low to remote. Screening methods are used to mitigate such hazards (design for minimum risk approach).

Acknowledgment

Test Team Members

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