Advanced Mitigating Measures for the Cell Internal Short Risk

by

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for the

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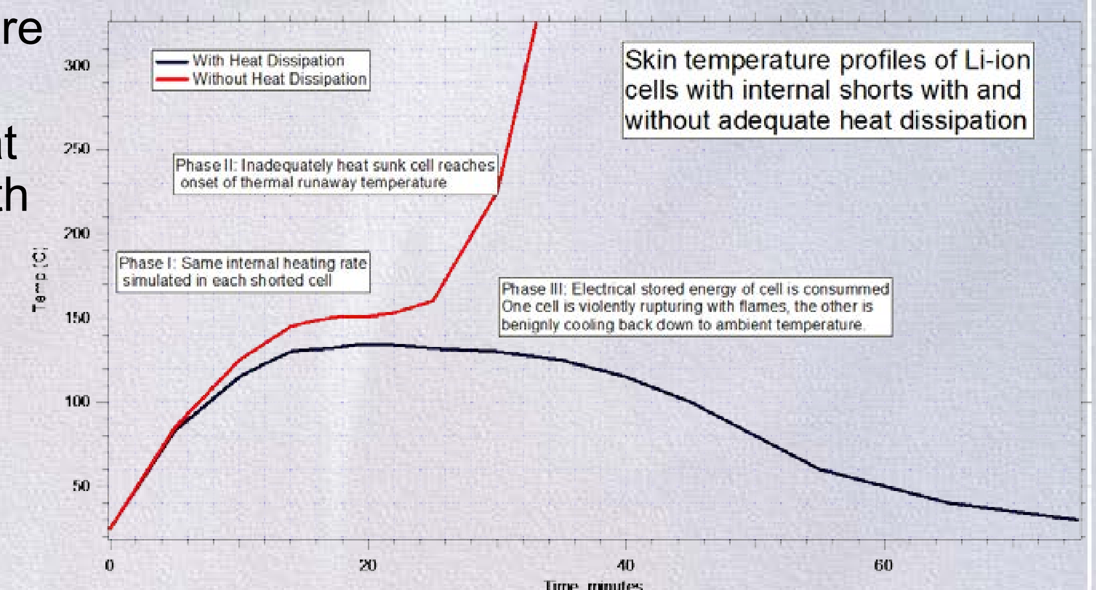
Outline Mitigating Measures For Cell Internal Shorts

- Why are internal cell shorts a concern?
- Fault tree example for cell internal shorts
- Measures to mitigate cell internal shorts
  - Design
  - Manufacturing
  - Operations
  - Testing
  - Analysis
- Conclusions

Why are Li-ion cell internal shorts a concern?

- Li-ion cells provide the highest specific energy (>180 Wh/kg) and energy density (> 350 Wh/L) rechargeable battery building block to date with the long life necessary for vehicles
- Electrode/electrolyte thermal instability and flammability of the electrolyte of Li-ion cells make them prone to catastrophic thermal runaway under some rare internal cell short conditions.
- These incidents are estimated at a 1 in 1-10 million probability with COTS cells in consumer applications*
  - Can we lower that probability?



•B. Barnett, et. al., Power Sources Conference, Philadelphia, July 2008
•C. Mikolajczak, et. al., IEEE Portable 2007 Conference, Orlando, 2007

CPSC Record of Relevant Field Failures

Date	Recall #	Description	Incidents qty	Injury qty	Recall qty
May-05	05-179	Apple iBook laptop batteries, LG Chem cells (Taiwan/China)	6	0	128,000
Jun-05	05-204	Hi-Capacity ® laptop batteries, China/Korea/Taiwan	6		10,000
Apr-06	06-145	HP Compaq laptop batteries, unknown cell	20	1	15,700
Aug-06	06-245	Apple Powerbook, Dell laptops, Sony cell (Japan)	9	0	1,800,000
Jul-07	07-267	Toshiba laptop batteries, Sony cell (Japan)	3	0	1,400
Oct-08	09-035	Dell, HP, Toshiba laptop batteries, Sony cell (Japan) made from 0ct 04 to Jun 05	19	2	100,000
		totals	63	3	2,055,100

All injuries were minor burns

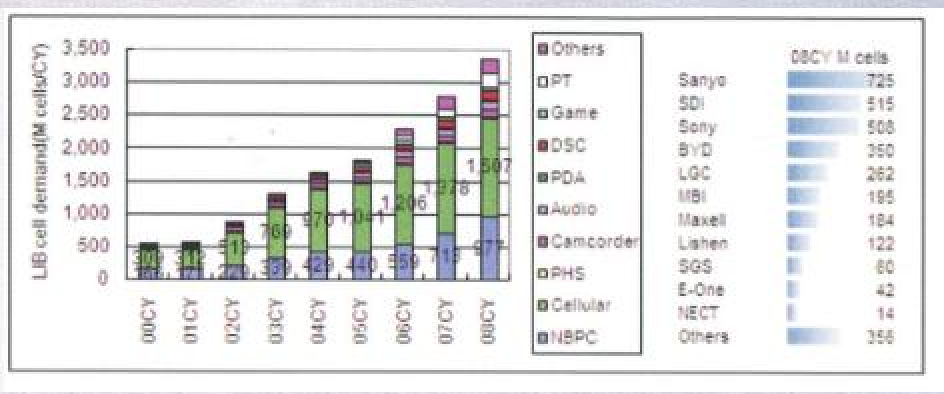
Above list contains only recalls since 2001 caused by cylindrical Li-ion cell issues

Total worldwide Li-ion cell demand from 2001 to 2008 was 14.5 billion cells*

Latest one (Oct 08) reported with cells made 4 years earlier and indicates a long latency.

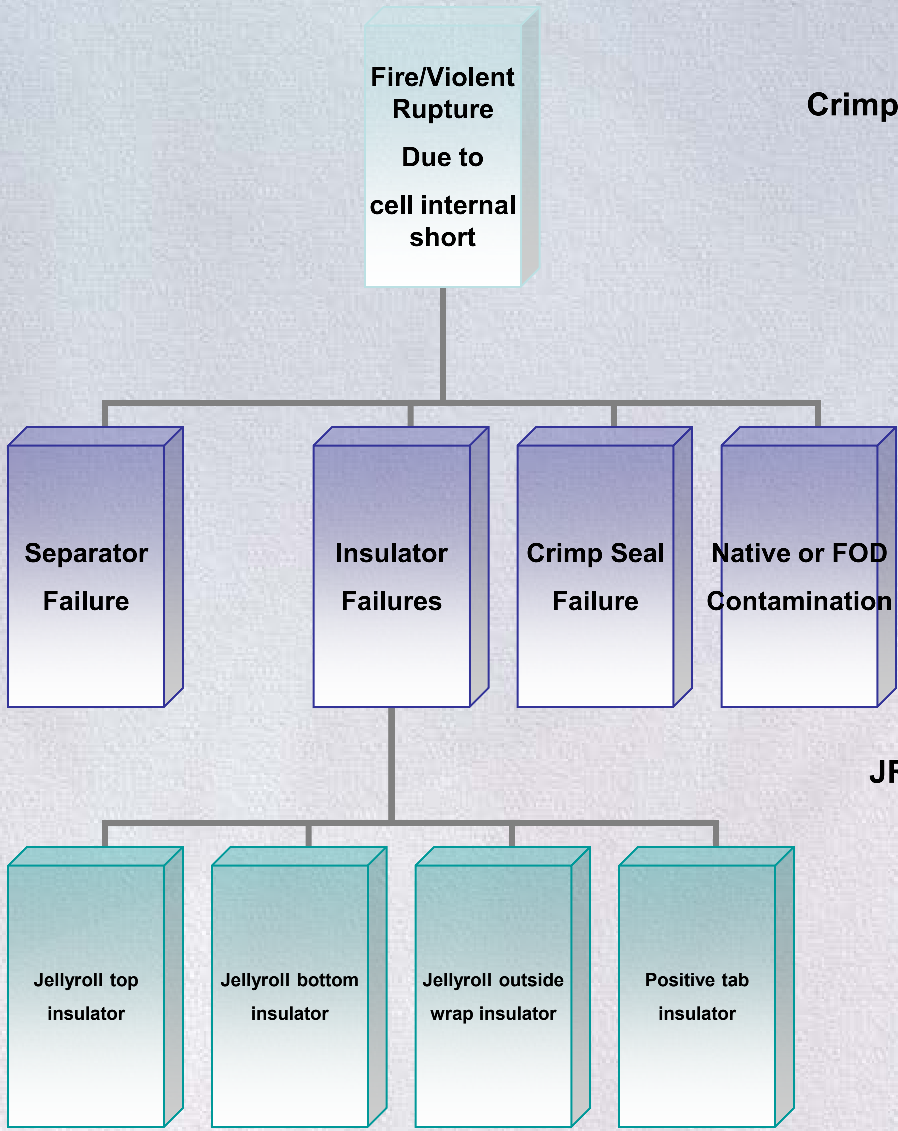
- ~100 incidents since 2001
- ~10 billion cells since 2001

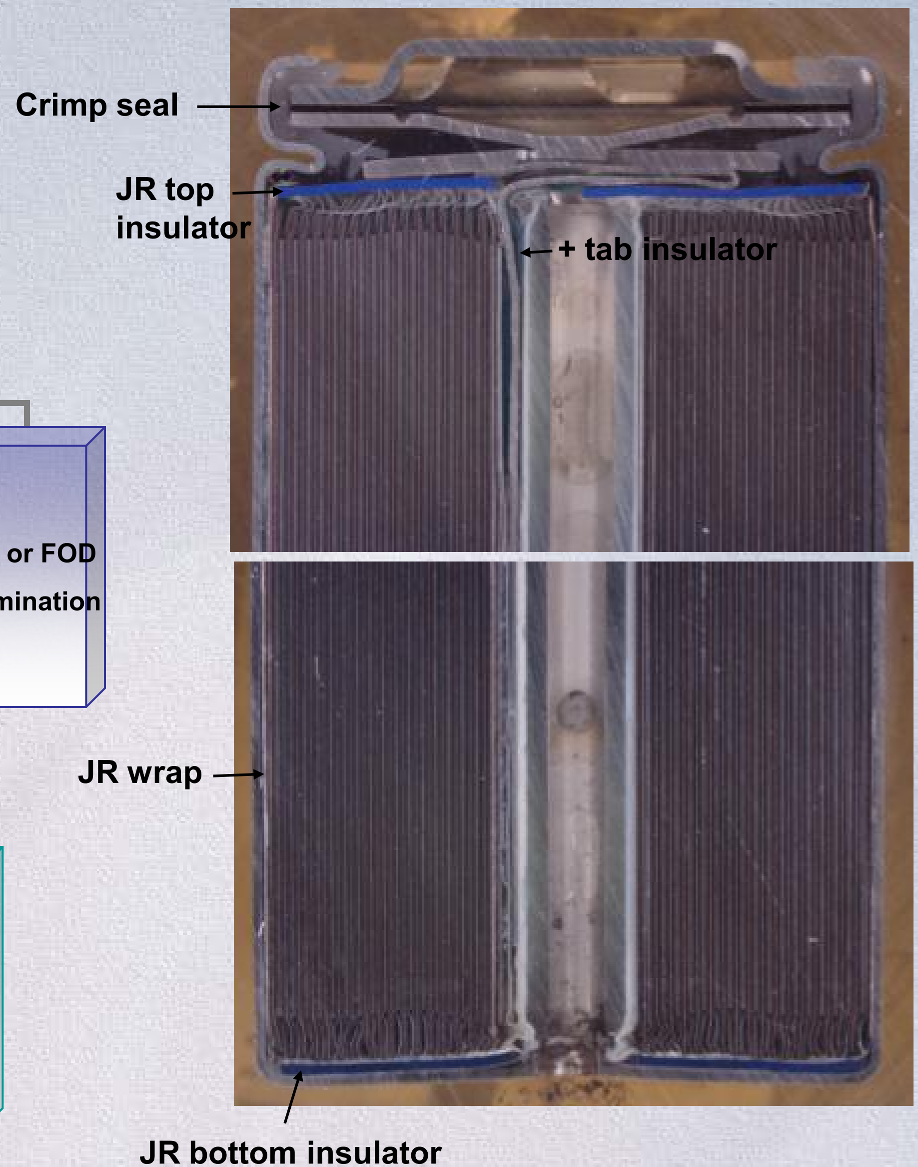
➡ 1 in 100 million probability



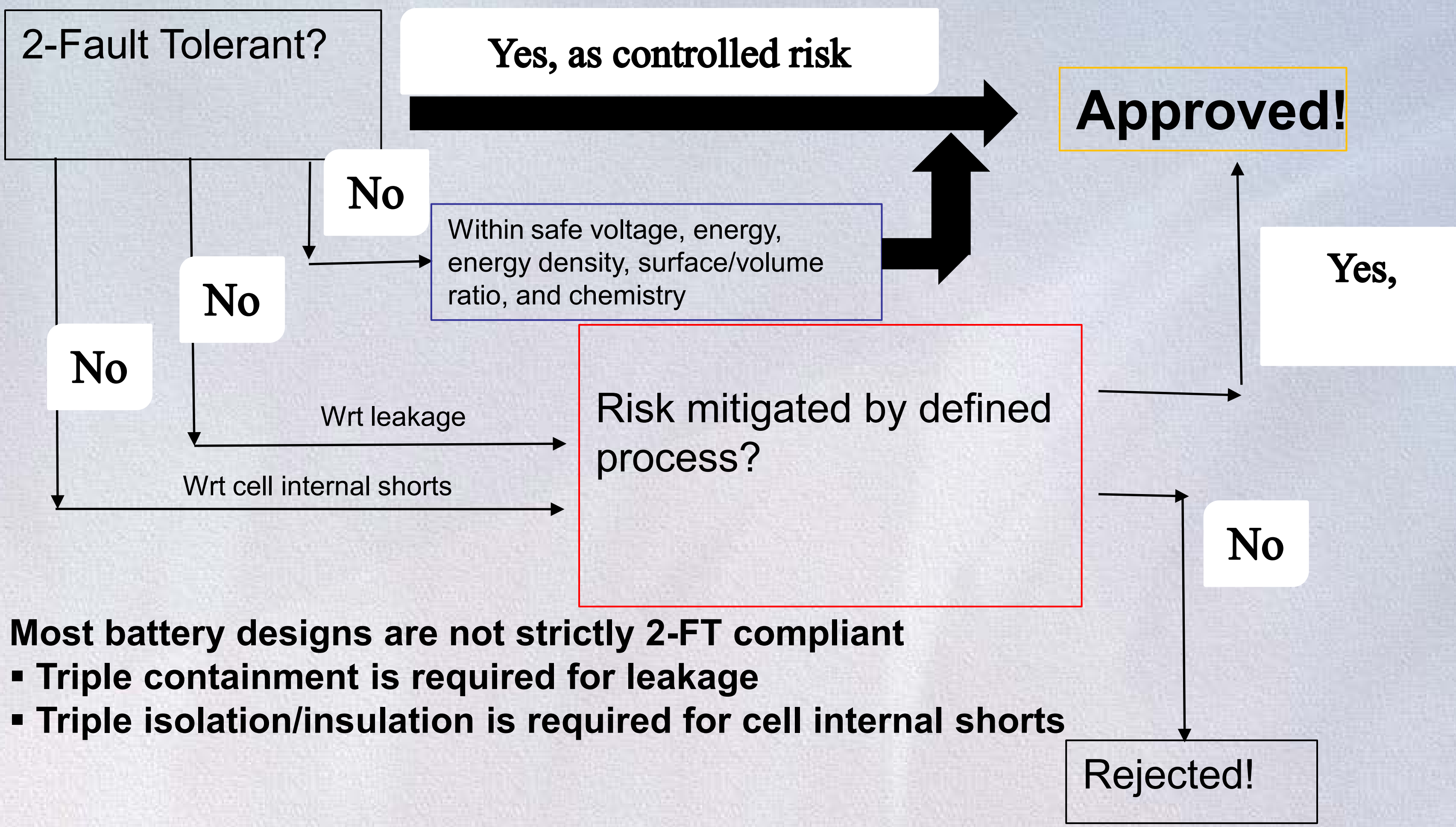
*Institute of Information Technology, Ltd

Example Fault Tree for Cell Internal Shorts





Manned Spacecraft Battery Approval Flow Chart

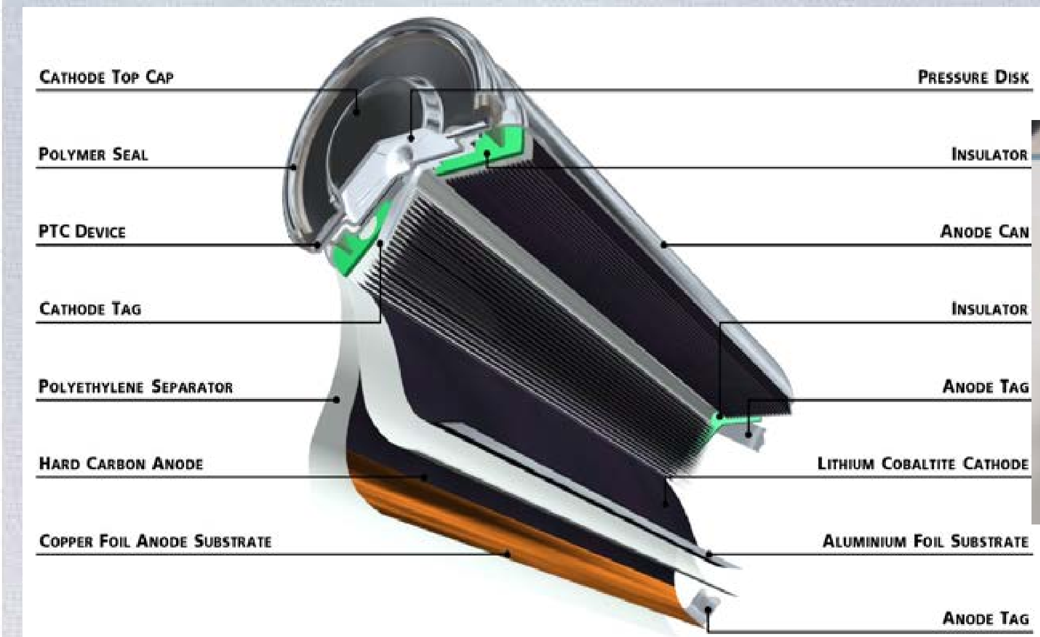


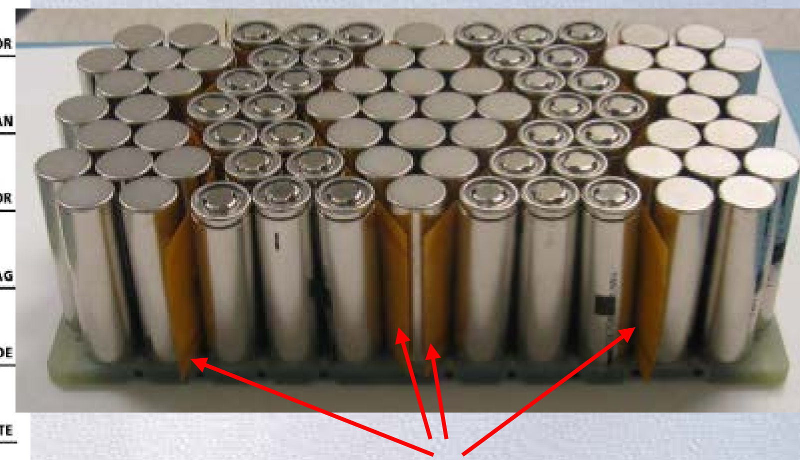
Most battery designs are not strictly 2-FT compliant

- **Triple containment is required for leakage**
- **Triple isolation/insulation is required for cell internal shorts**

Building Block Cell is 18650

Consumer Electronics Industry Standard COTS



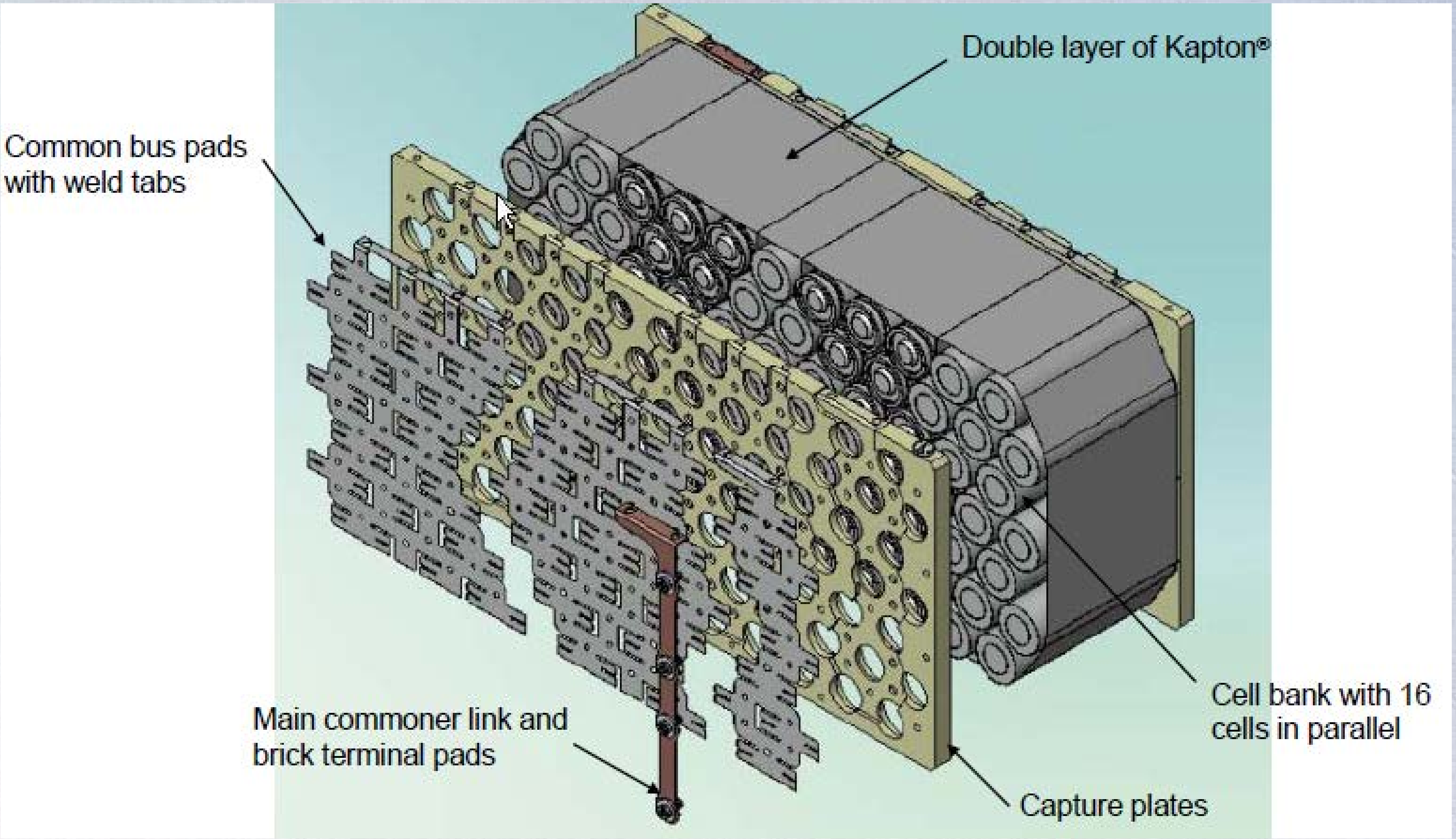


Note the bank-to-bank separator/insulator

- Eighty 18650 cells in 16p-5s topology are used in the new spacesuit battery

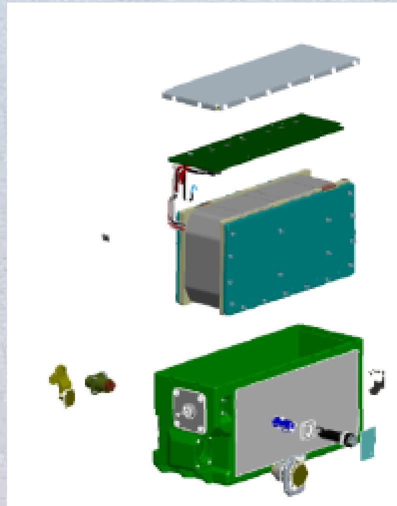
Graphic and photo courtesy of ABSL

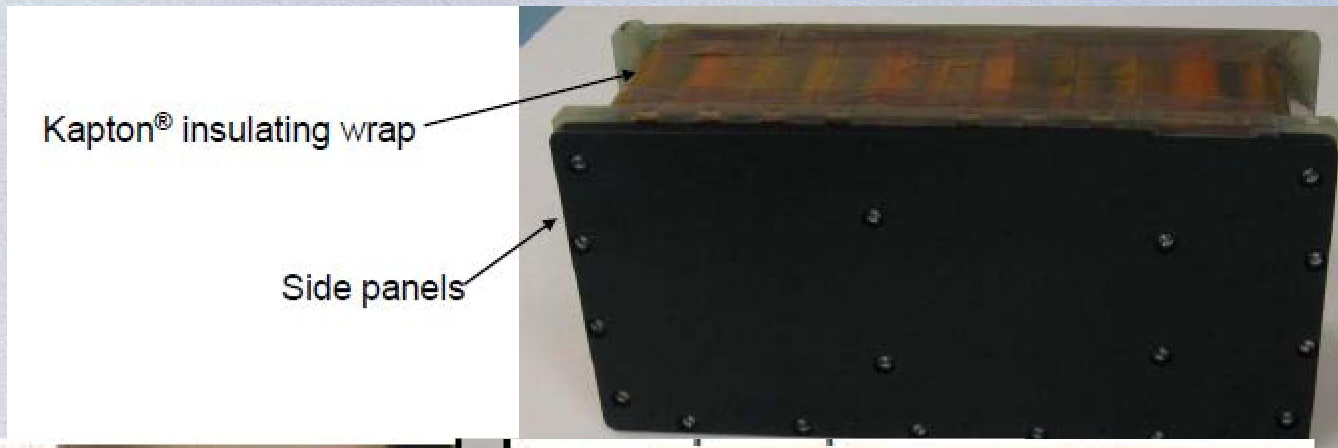
Spacesuit Battery “Brick”



Graphic courtesy of ABSL

Final Assembly Steps of Spacesuit Battery





Graphic and photos courtesy of ABSL

Mitigating Measures Applied to Spacesuit Battery – Design, Fab, & Ops

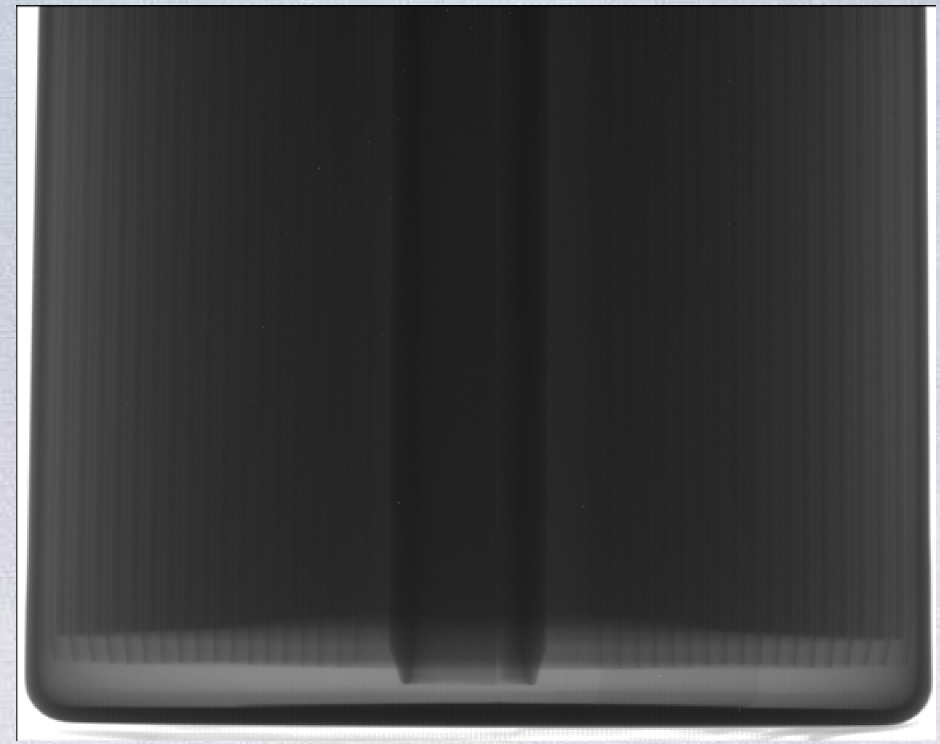
- Design
  - Selected mature cell designs in production since 2003 – not highest Wh/L models
  - Fully characterized for another program in 2004
  - Excellent calendar life proven with lots 3 and 4 years old
  - A p-s topology and charger design allows insight into cell bank balance every charge
- Manufacturing
  - Completely automated cell production line at both LLB cell vendors (Japan & Canada)
  - Fab rates > 1 million cells per month with very high performance uniformity
  - Date code of both cell lots is April 07
  - Selected cell designs are not subject to any CPSC recalls
- Operations
  - Tighter voltage window (3.2V to 4.12V/cell) than consumer applications (3.0V to 4.2V) puts less stress on the jellyroll as do C/8 charge/discharge rates
  - Low cycle life expected (~25) thru 2020, vs >500 for consumer electronic applications
  - Majority of calendar life at 30% vs 100% SoC for laptops
  - Much lower operating temp (10 to 41°C) vs (0 to 55°C for laptop batteries)

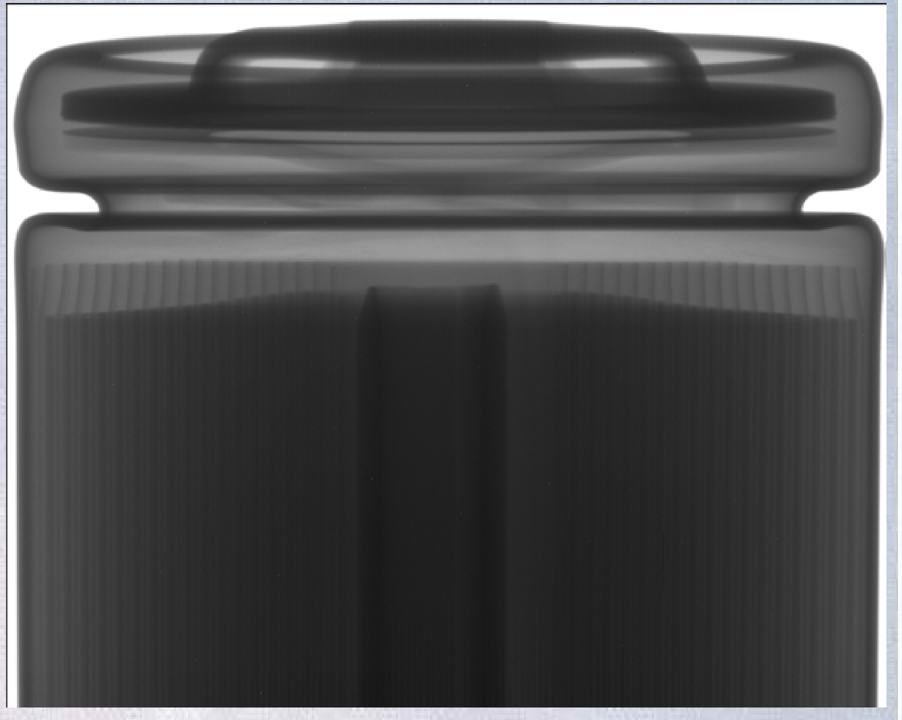
Cross sections of candidate Li-ion cell designs

Mitigating Measures Applied to Spacesuit Battery – 100% Testing

- Flight COTS cells are rigorously screened to detect manufacturing flaws
  - Mass, OCV (after > 24 months storage), AC impedance, visual examination
  - Thermal cycling, vacuum cycling with residual gas analysis (leak check)
  - Initial charge input (after long storage), capacity performance (2 cycles), DC resistance
  - Screen out all cells that outside ± 3 sigma and store
  - **100% X-ray examination for proper jellyroll alignment**
  - Repeat OCV, capacity cycling, AC impedance, DC resistance prior to selecting cells for brick assembly
- Flight 80-cell bricks are rigorously tested to detect assembly flaws
  - Visual, Mass, OCV, AC impedance, insulation resistance, fit check with housing
  - 15 depress/repress cycles with final one holding vacuum for 3 days (& at 35°C)
  - 5 thermal cycles with 3 hr dwells at the extremes (-14 to 45°C)
  - 2 Capacity cycles at room temperature
    - one at high rate (C/2 charge to 21V with 1A taper, C/2 discharge to 15V)
    - one at mission rate (5A charge to 21.5V with 1A taper, 3.8A discharge to 16V)
- Flight LLBs will be rigorously tested to detect assembly flaws
  - OCV, CCV, Thermistor Check, Insulation Resistance, Bonding, Mass, and Visual Inspection
  - Thermal cycling with 3 hr dwells at the extremes (-14 to 45°C)
  - Random vibration at 0.06 g^2/Hz for 1 minute/axis (0.03 is mission, 0.04 is standard workmanship level)
  - 1 hot and 1 cold mission simulation cycle (charge at ambient, discharge in vacuum)
  - 1 autocyle (discharge, charge, discharge, recharged to 30%) with the LIB Charger GSE

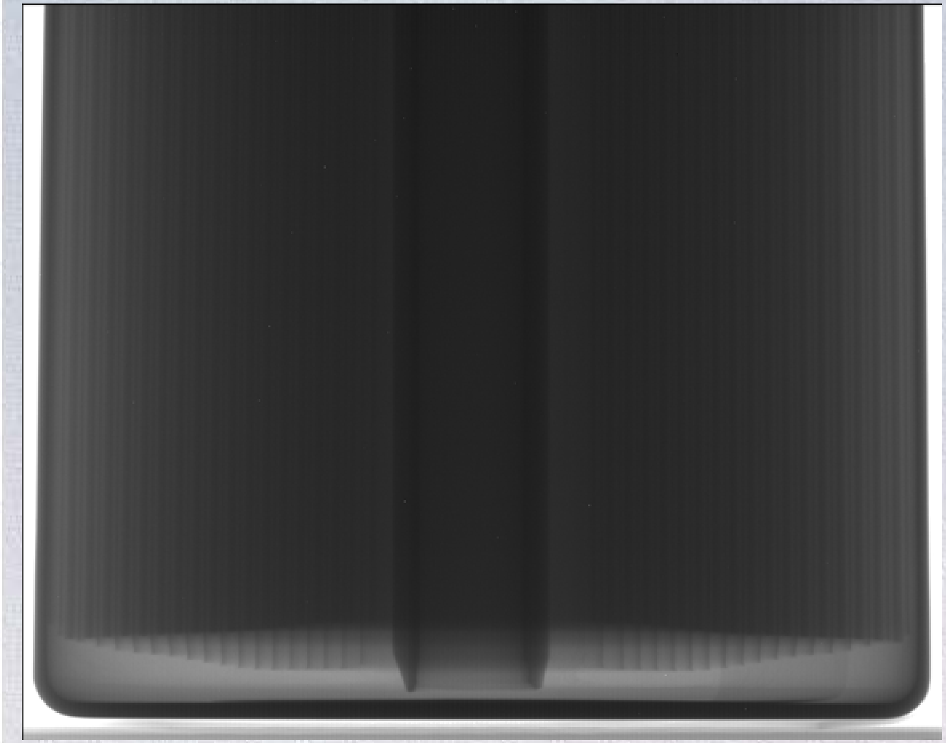
Typical X-ray – COTS 18650

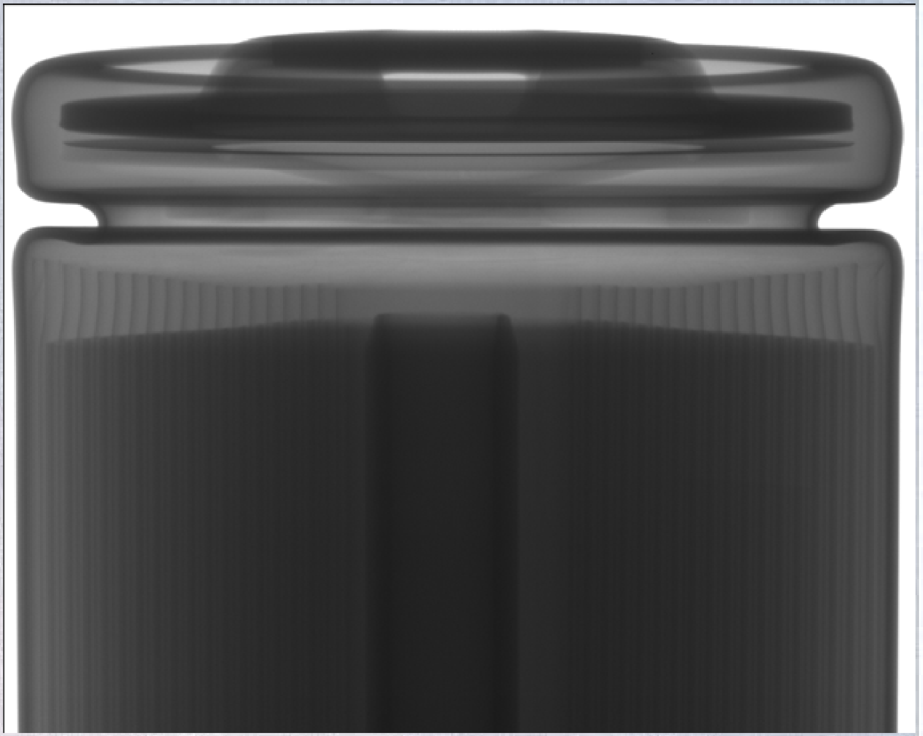




Note the proper jellyroll anode overlap alignment

Example of an X-ray Reject – COTS 18650

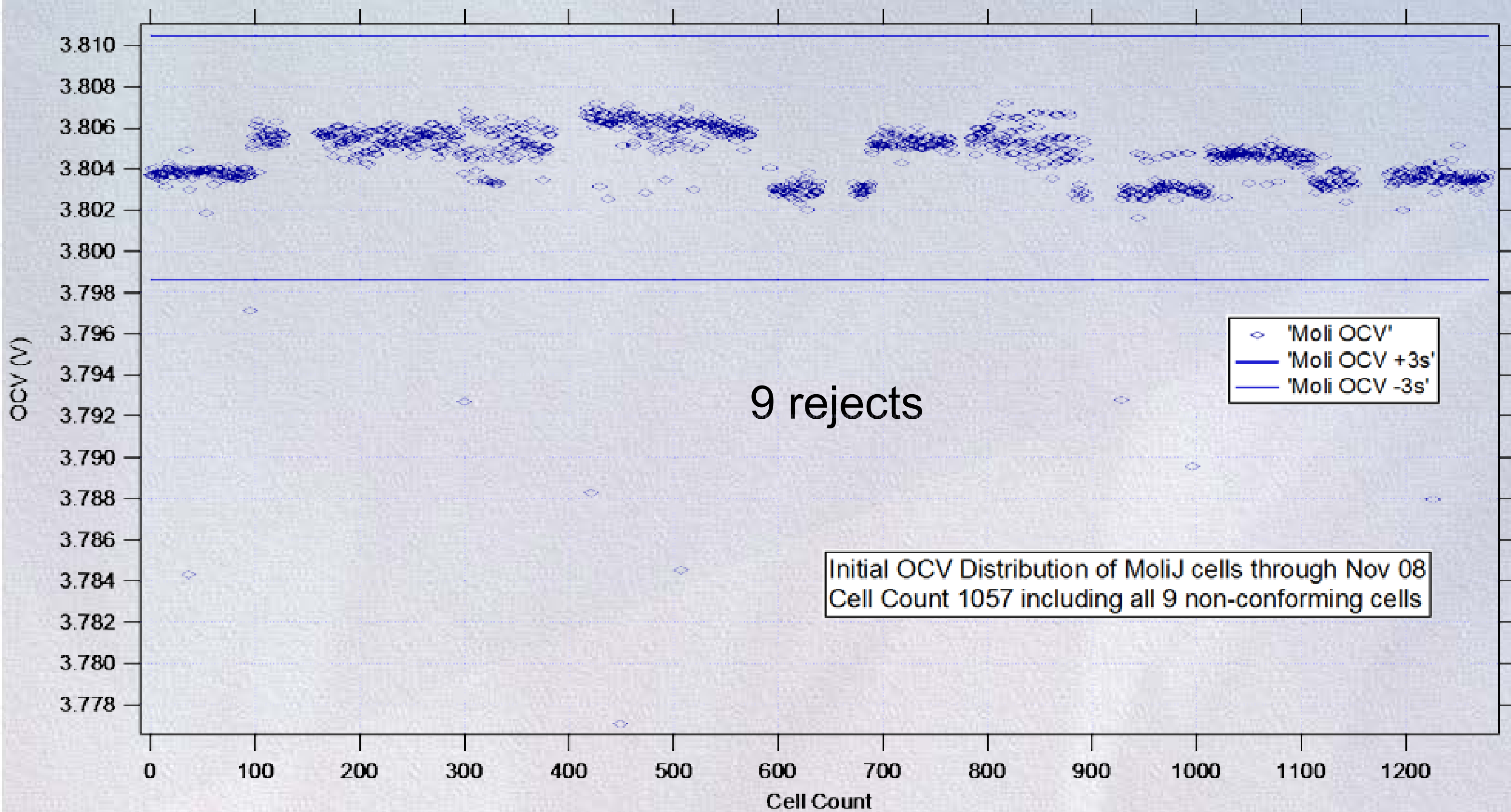




Note the telescoping jellyroll anode overlap misalignment

- Insufficient anode overlap can lead to Li plating
- This s/n cell had passed all other cell acceptance tests

18650 Initial OCVs after 17 months at as received SoC

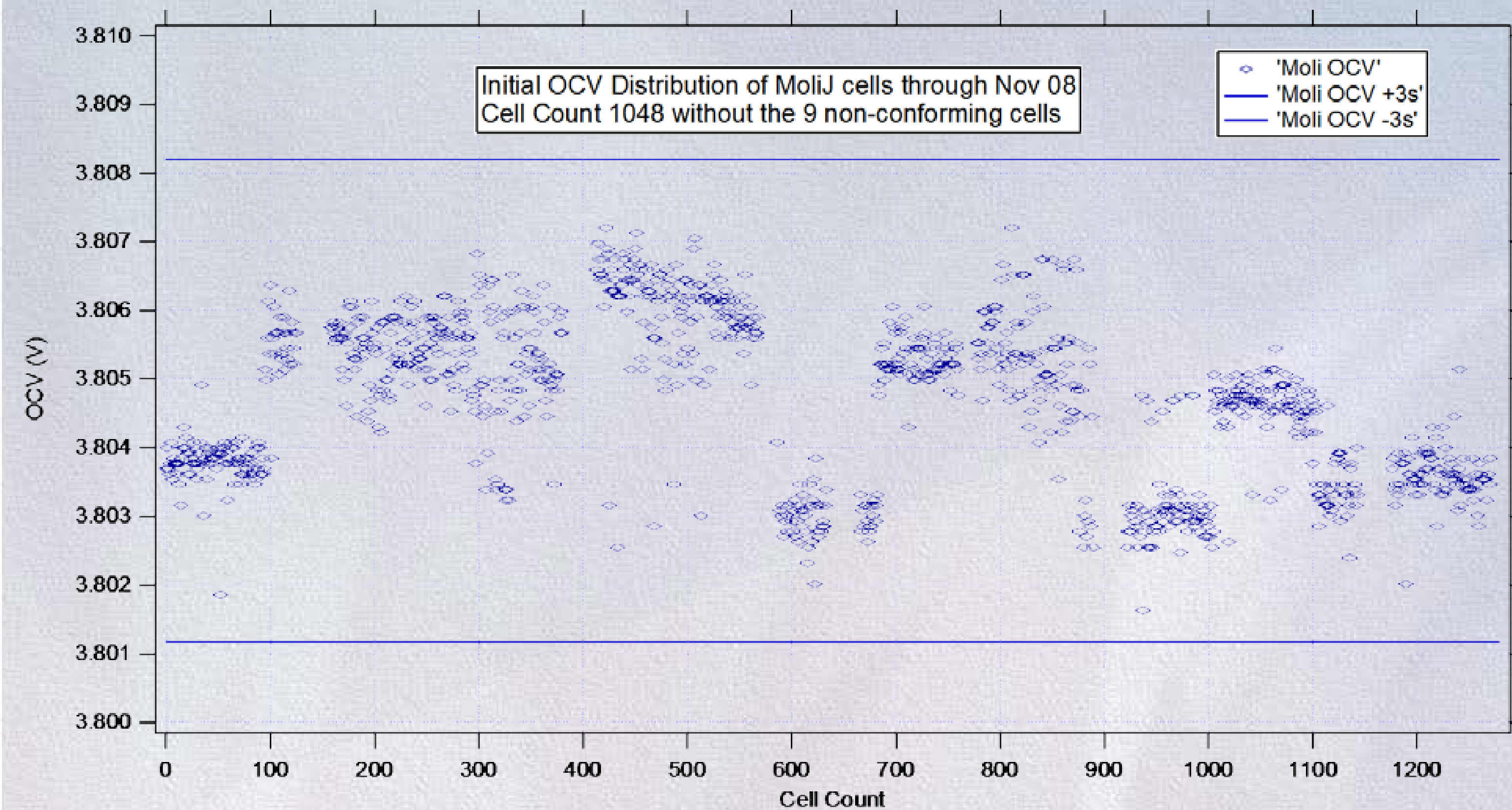


Average	3.8046
sdev	0.00197
sdev%	0.052%
Min	3.7771
Max	3.8072
Range	0.0301
Range%	0.792%
-3sigma	3.7986
+3sigma	3.8105
Range	0.0118
Range%	0.311%
Lo Rejects	9
Hi Rejects	0
Total Rejec	9
Count	1057
Reject%	0.85%

6σ range is 11.8 mV (0.311% of mean)
9 outliers out of 1057 cells tested

18650 Initial OCVs after 17 months at as received SoC

Standard dev is at ***1.2 mV (0.031%)***



Average	3.8047
sdev	0.00117
sdev%	0.031%
Min	3.8016
Max	3.8072
Range	0.0056
Range%	0.146%
-3sigma	3.8012
+3sigma	3.8082
Range	0.0070
Range%	0.184%
Lo Rejects	0
Hi Rejects	0
Total Rejects	0
Count	1048
Reject%	0.00%

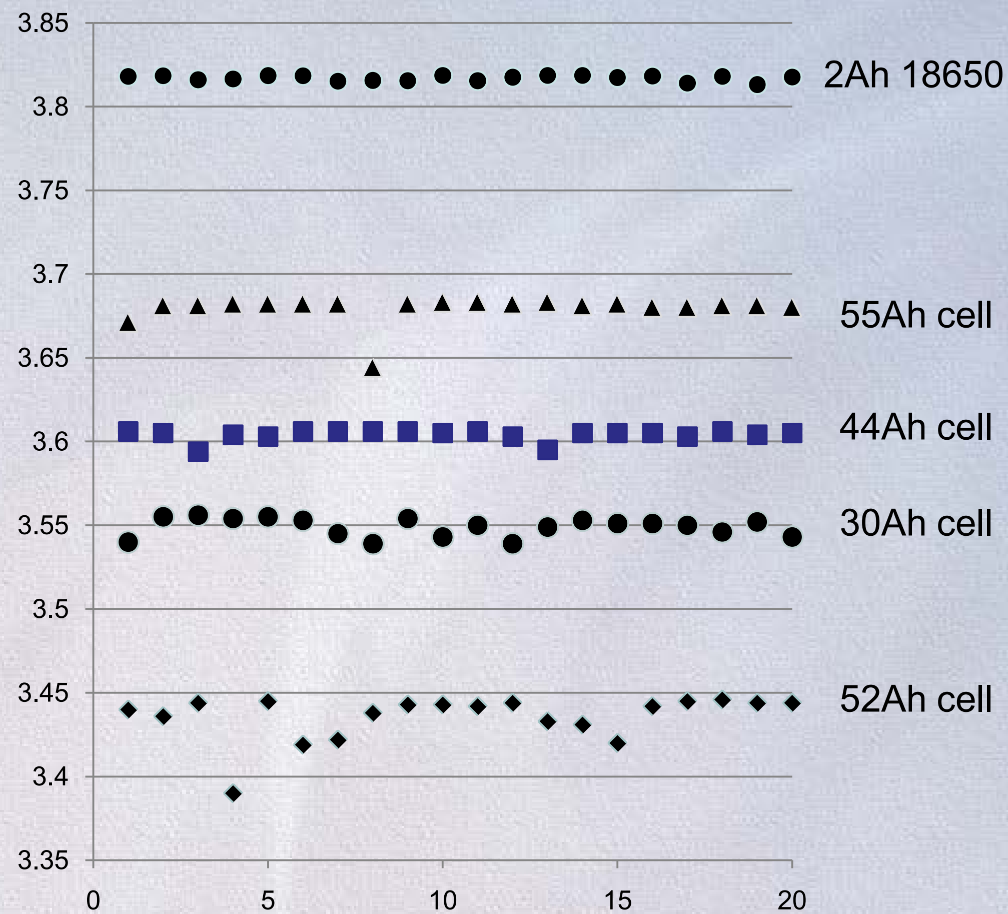
6σ range improves from 11.8 mV (0.31%) to ***7 mV (0.18% of mean)*** after removing 9 outliers (not shown). No more outliers appear with this tighter 6σ range

Excellent cell-to-cell OCV uniformity after 17 months at ~45% SoC

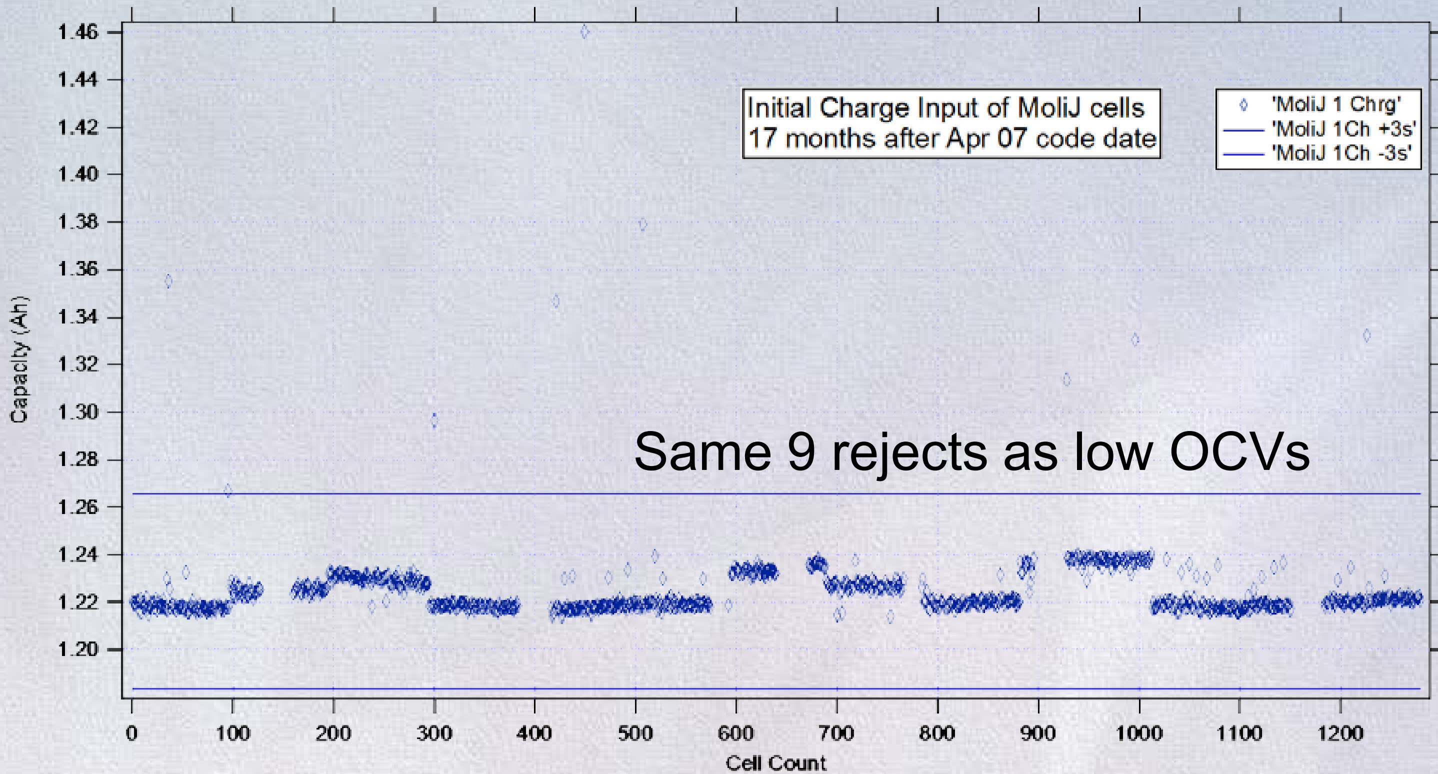
OCV Retention on Large Cell Designs

- OCVs measured after 2 years of storage on small 18650 cells vs < 3 months on large (15-55Ah) aerospace cell designs
- Large cell designs found more likely to have self-discharge outliers than small COTS cells

OCVs during receiving inspection



COTS 18650 Initial Charge Capacity

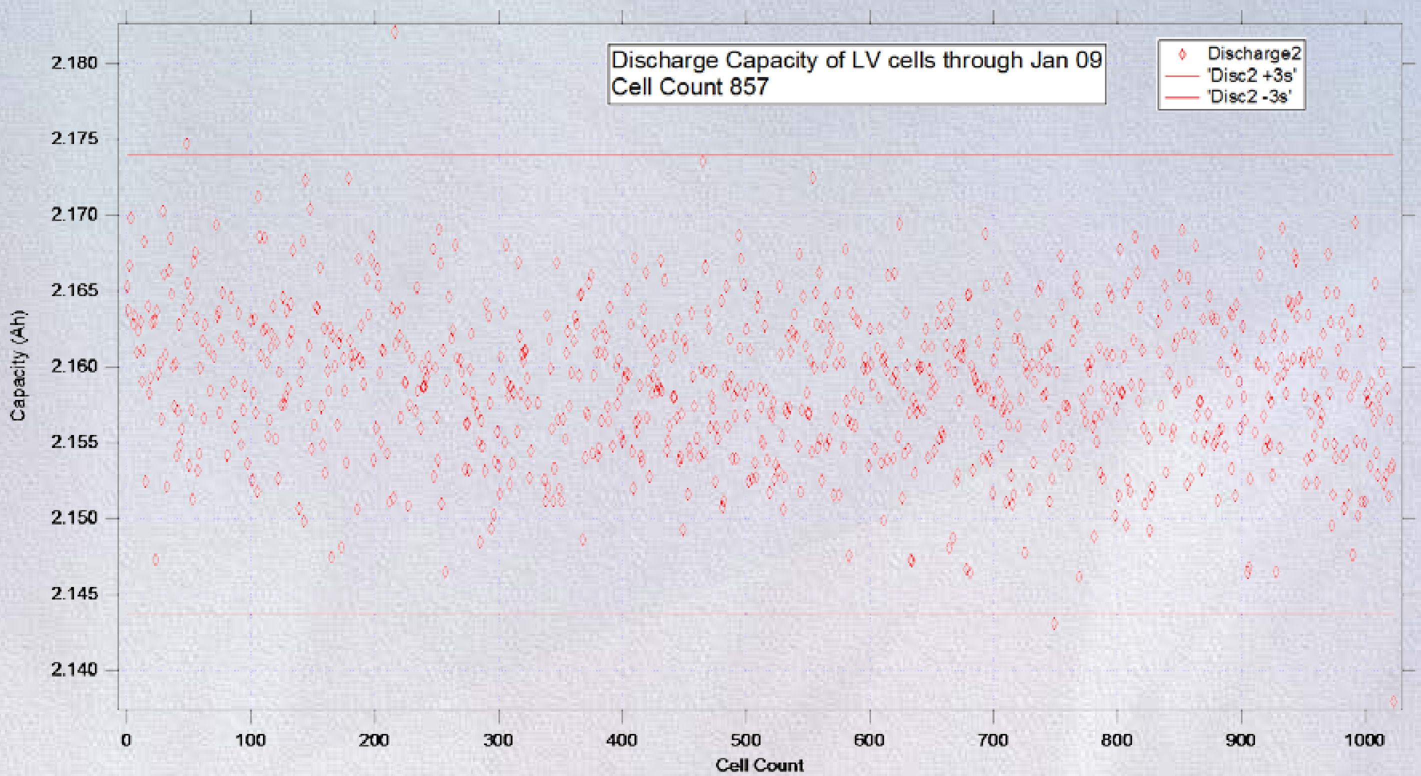


Average	1.2245
sdev	0.01368
sdev%	1.117%
Min	1.2138
Max	1.4602
Range	0.2464
Range%	20.123%
-3sigma	1.1835
+3sigma	1.2655
Range	0.0821
Range%	6.704%
Lo Rejects	0
Hi Rejects	9
Total Rejects	9
Count	1057
Reject%	0.85%

6σ range is 82 mAh (6.7% of mean)

Note: Test performed in Sep 08 and cell date code is Apr 07
(17 months at 50% SoC, RT and 0°C)

18650 Discharge Capacity (C/10 to 3.0V)

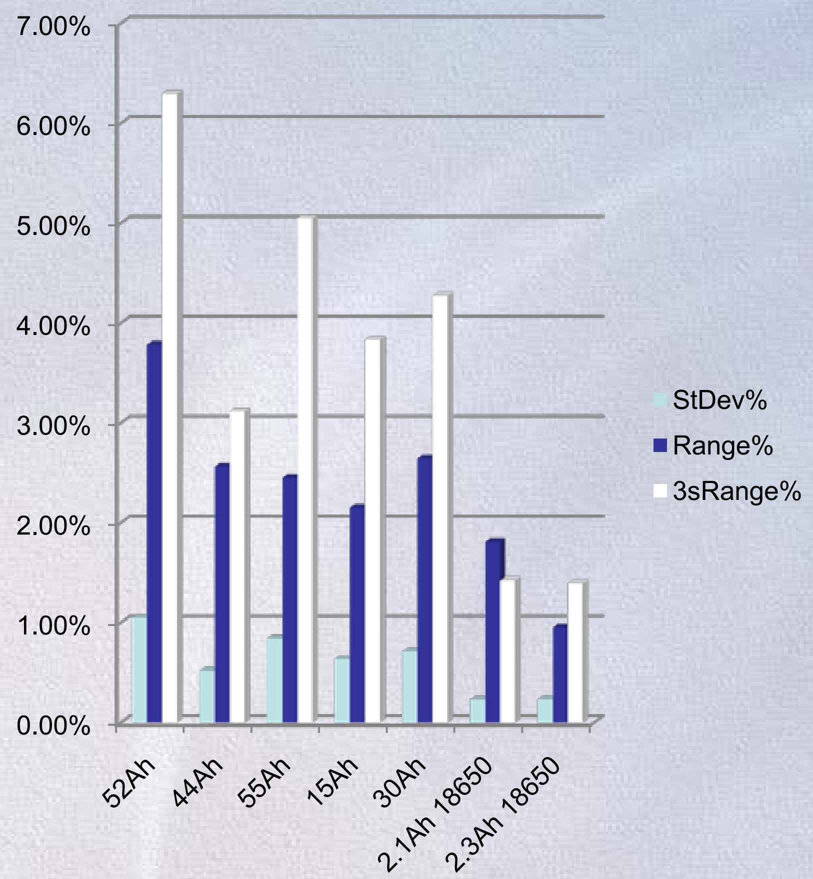


Average	2.1589
sdev	0.0050
sdev%	0.233%
Min	2.1380
Max	2.1821
Range	0.0441
Range%	2.044%
-3sigma	2.1437
+3sigma	2.1740
3sRange	0.0302
3sRange%	1.400%
Low Rejects	2
High Rejects	2
Total Rejects	4
Count	857
Reject%	0.23%

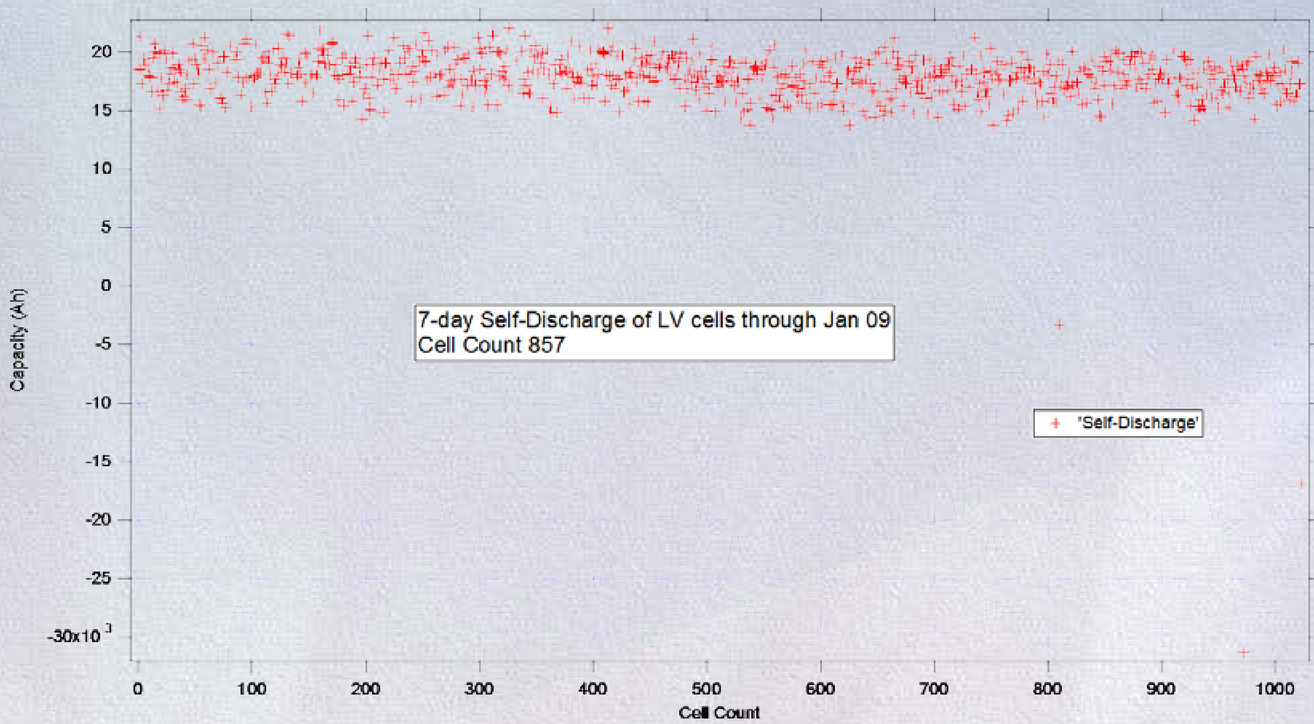
Standard deviation of 5 mAh (0.23%) is very tight

Comparing Large vs Small Cell

- Comparing C/10 discharge capacity variations at room temperature, all on BOL cells, n=20, except for 2.1Ah cell where n=857
- Large cell standard deviation ranges from 0.64% to 1.05% of mean (vs 0.23% for 18650 cells)
- Small cell designs are more uniform discharge capacity performers



18650 Self-Discharge



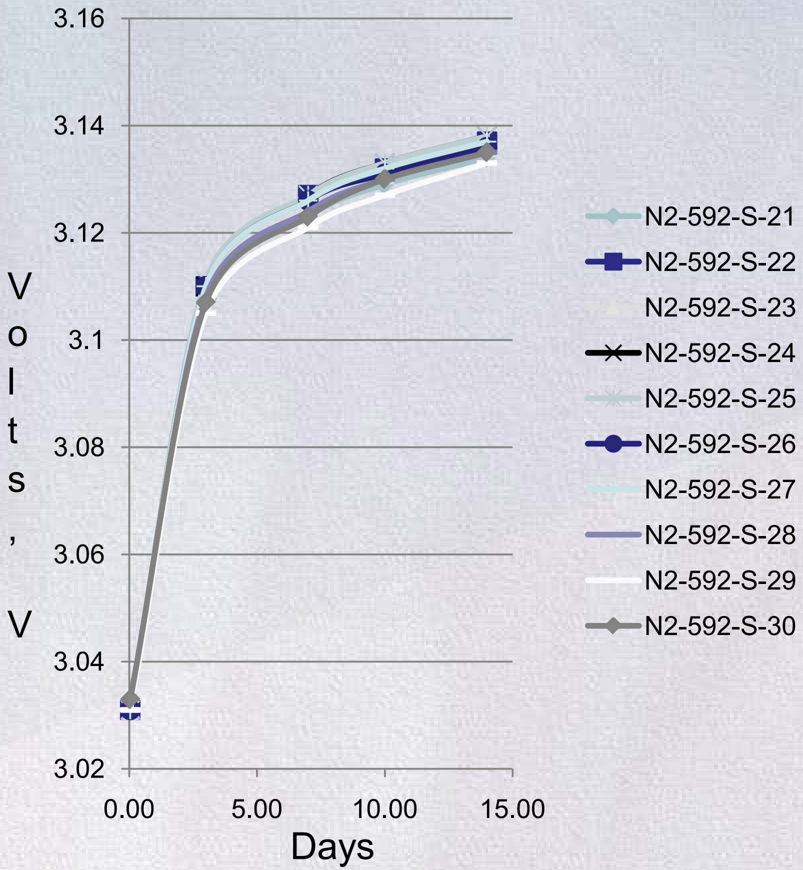
Average	0.0178
sdev	0.0027
sdev%	15.149%
Min	-0.0313
Max	0.0220
Range	0.0533
Range%	300.093%
-3sigma	0.0097
+3sigma	0.0258
3sRange	0.0162
3sRange%	90.895%
Low Rejects	3
High Rejects	0
Total Rejects	3
Count	857
Reject%	0.35%

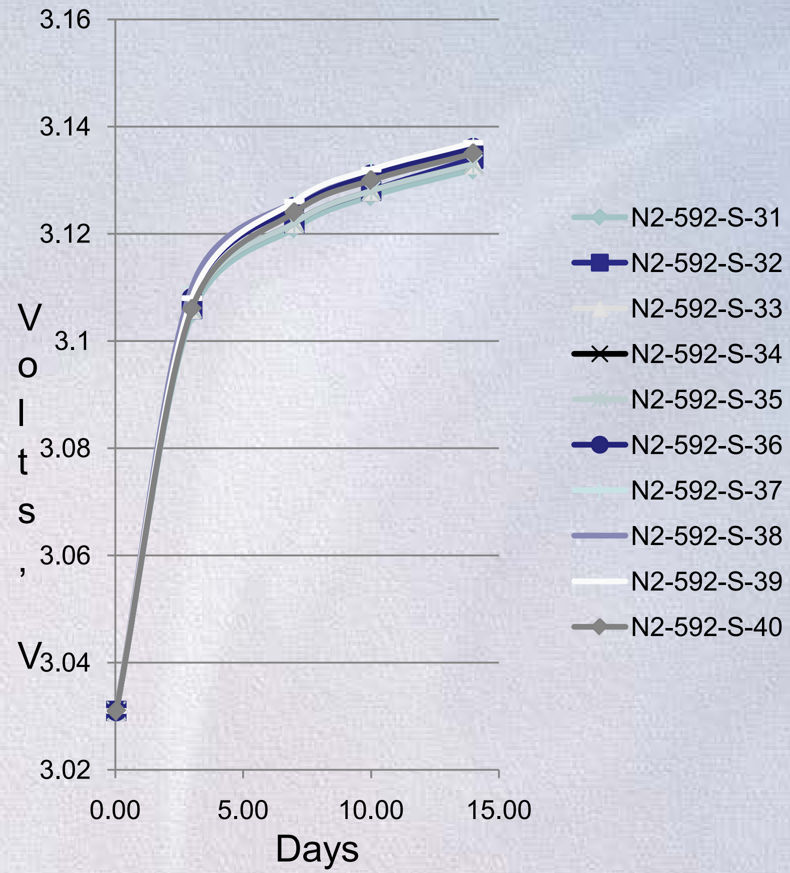
7-day at 4.2V self-discharge rate measured by difference in capacity delivered

Average capacity lost to self-discharge is 17.8 mAh w/ standard deviation = 2.7 mAh

Soft Short (Small COTS Cell)

14-day OCV bounce back after deep discharge (constant voltage to 3.0V)

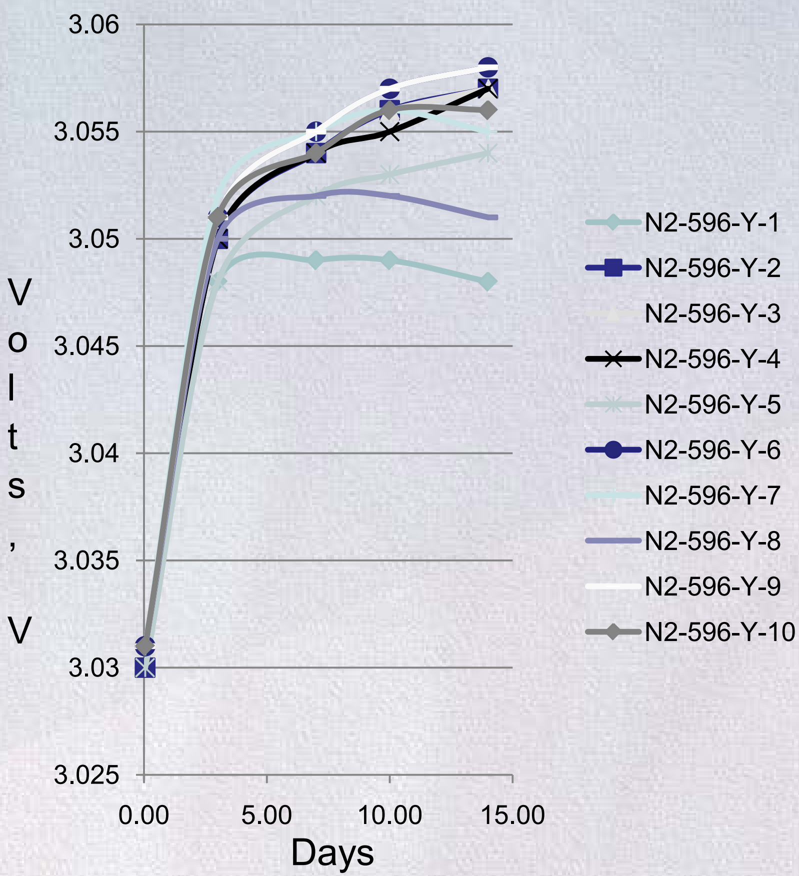


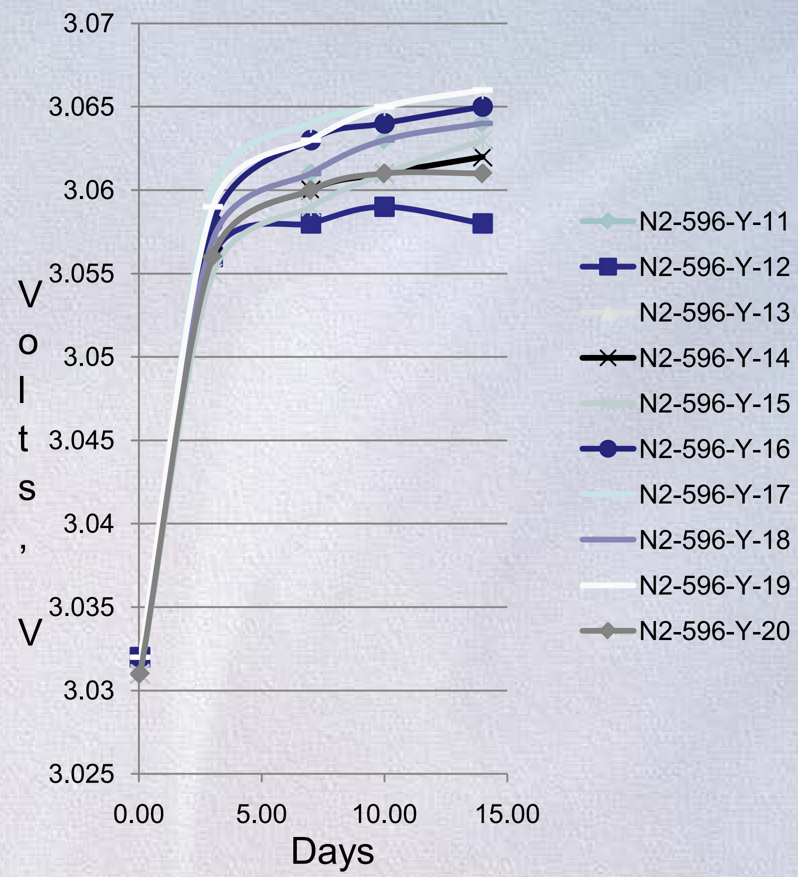


Very uniform OCV bounce back performance

Soft Short (Large Cell Design)

14-day OCV bounce back after deep discharge (constant voltage to 3.0V)





4 cells out of 20 had declining OCV between days 10 and 14

Mitigating Measures - Testing

- Perform rigorous cell acceptance screening
  - Serialization and visual
  - ***OCV after long storage period***
  - AC impedance
  - Insulation resistance
  - Mass
  - Dimensional (or use of go/no go gauges are acceptable)
  - Capacity cycling with DC internal resistance (for secondary only)
  - Thermal cycling with leak detection
  - Vibration (can be done at battery level)
  - Pressure cycling with leak detection
  - Self-discharge at 100% SoC (can be replaced with long OCV stand test
  - ***Soft short at <0% SoC (for secondary only and can be replaced with long OCV stand)***
  - X-ray inspection (optional)
  - Reject all ± 3 sigma outliers

- Perform rigorous cell qualification testing of each lot
  - Capacity performance
  - Environmental exposure
    - Thermal cycling
    - Shock & Vibration
    - Repress/Depress
  - Capacity performance
  - Mission simulation life
  - OCV vs SOC, temperature
  - Calendar life and self-discharge vs SOC and temperature
  - Abuse Tolerance
    - Electrical, mechanical, and thermal abuse
  - ***NDE (CT scan) and DPA***
  - ***Cell Production Line Audit (if possible prior to committing to cell buy)***
  - Archive a quantity of cells for each lot

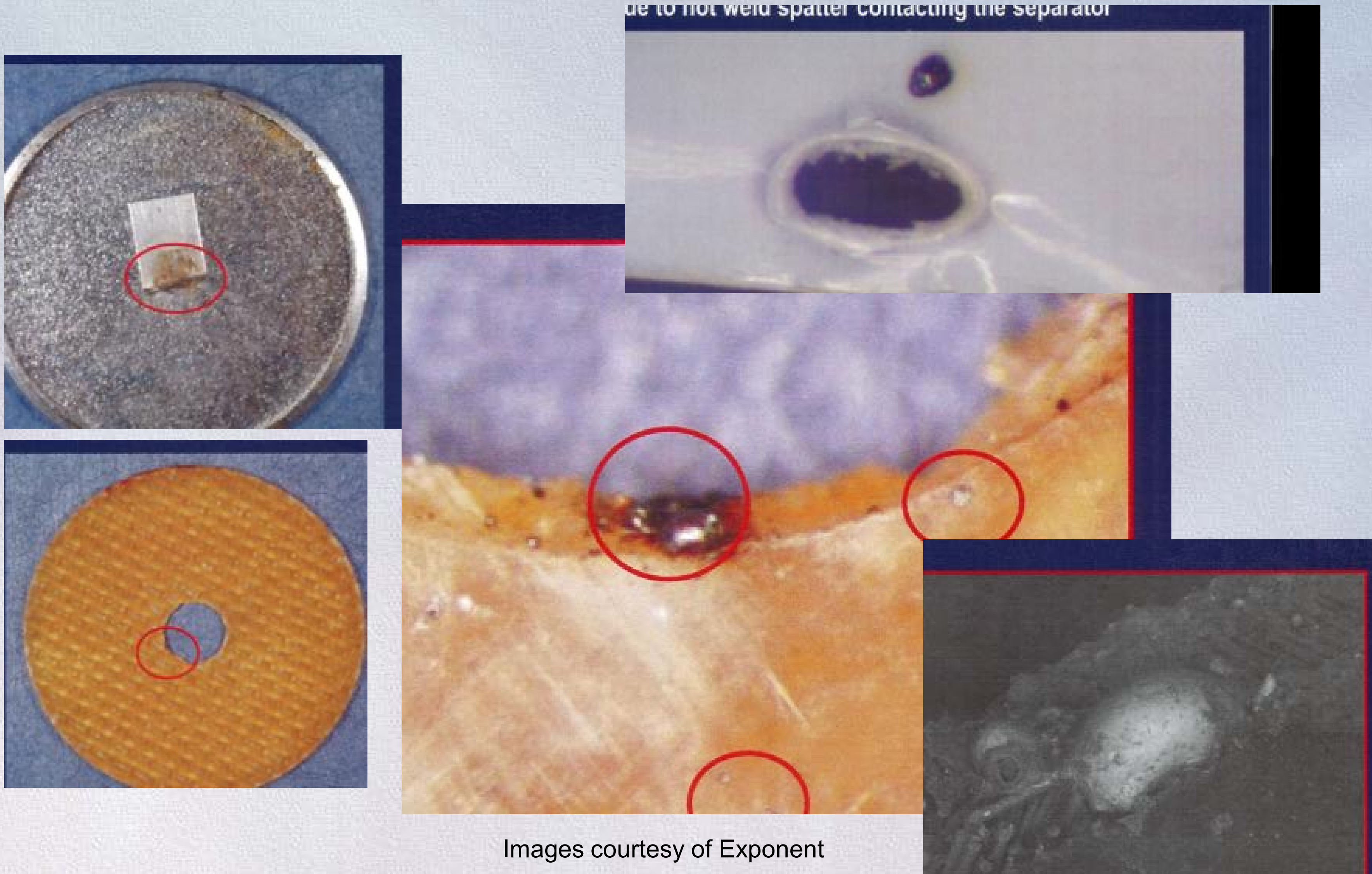
What to look for in CT scan?

- Proper alignment of jellyroll contents
- Consistent active material coatings
- Lack of contamination, high density particles show up as bright specs

Cross section of high density material on cell base insulator, possibly weld spatter from anode lead weld

Scan courtesy of Exponent

18650 Weld Splatter Finding



Images courtesy of Exponent

What to look for in DPAs?

- Consistent mechanical alignment
  - Anode overlapping cathode
  - absence burrs
  - No separator tears or wrinkles
- Lack of contamination
  - Heat effective zone halos
  - No foreign or native delamination debris
- No Li deposits or plating
- Consistent active material coating with smooth edges
- Solid weld connections without splatter

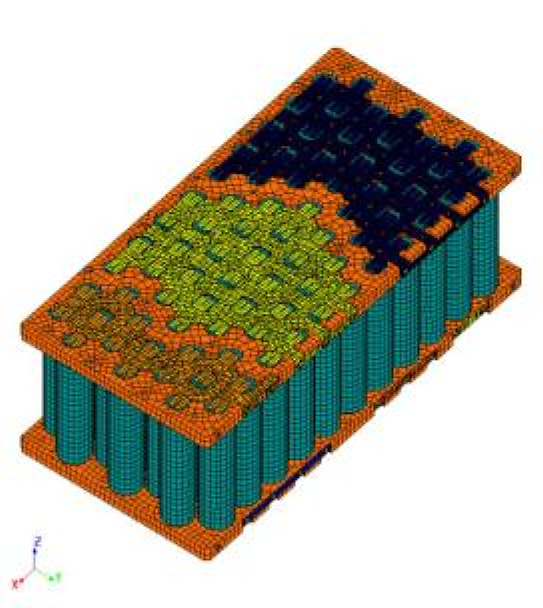
Photos courtesy of Exponent

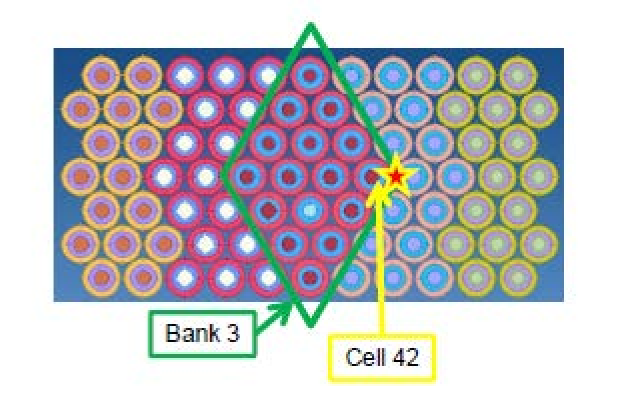
Cell Production Line Audits

- Audit cell manufacturers to identify processes that present high risk to generate latent cell defects and evaluate current measures taken to mitigate them
  - 2 day cell production line visits with technical battery experts
  - Metallic particle generation prevention and contamination control
  - Periodic particle contamination sampling of key processes
  - Humidity control of dry rooms and incoming materials
  - Real-time process monitoring and implementation of statistical process control
  - Defective part removal, isolation, and destruction
  - Inventory control
  - Product returns and failure investigation
- Deliverables
  - Presentation detailing findings
  - Action item list with recommendations

Analyses

- Thermal analysis by NREL
  - Complete model of spacesuit battery
  - Includes cell electrochemical and PTC device electrical and thermal characteristics
  - Validated by external short circuit testing
  - Demonstrating tolerance to short circuit external to battery
  - Projecting catastrophic thermal runaway for a small range of short circuits internal to battery but external to cells
- Probability Risk Assessment by SAIC
  - Considered manufacturing history and quality of the 18650 cell design along with its reject rate during our acceptance tests
  - Predicts that chances of cell failure in a battery at 1 in 160,000 over a 5-year service life

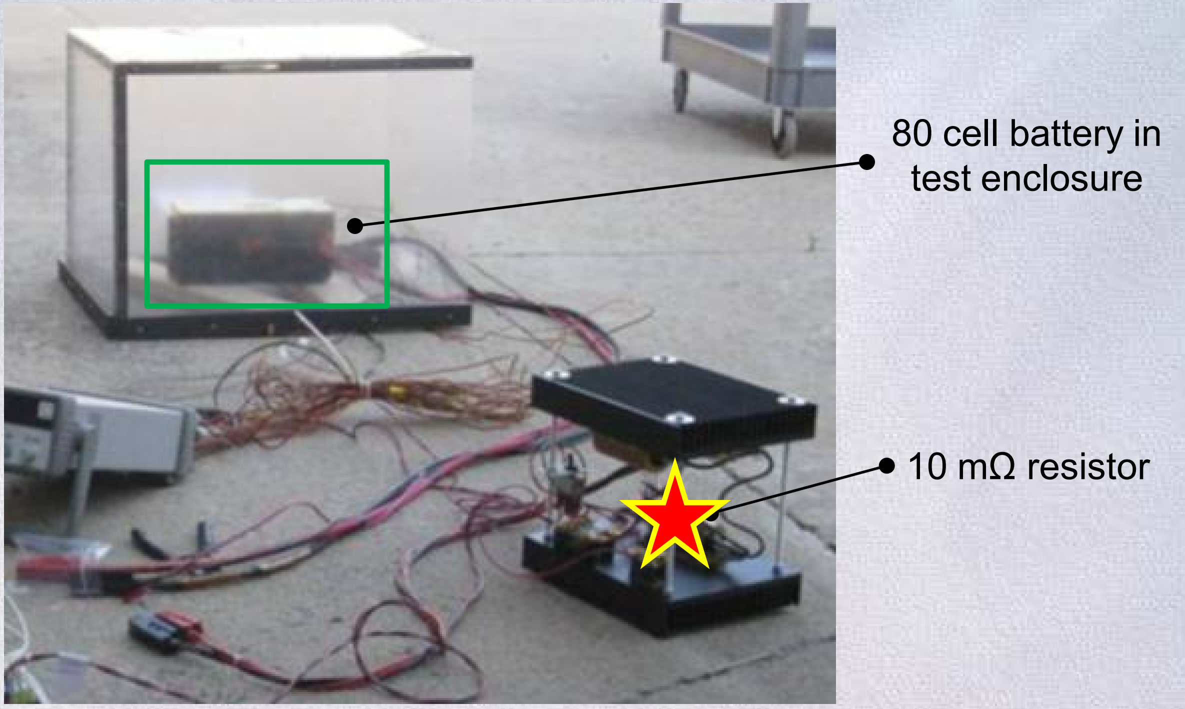




Graphics courtesy of NREL

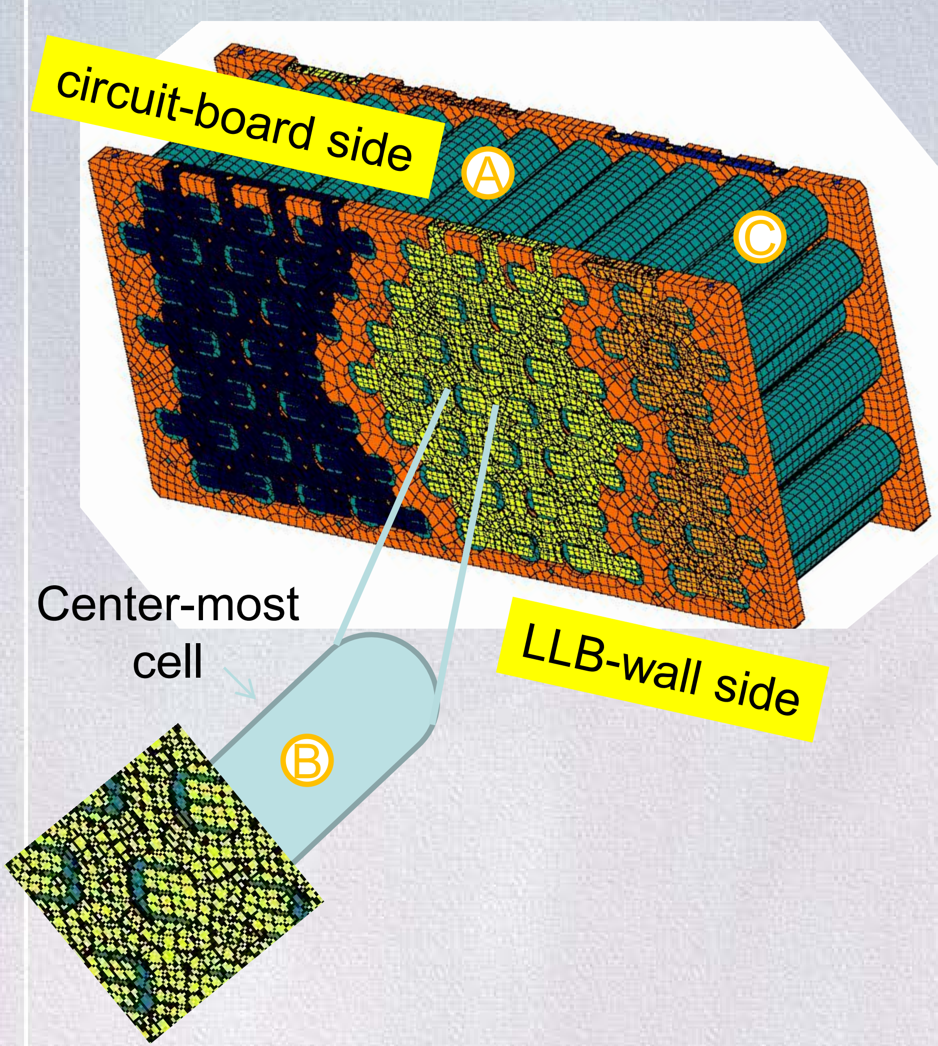
MODEL VALIDATION FOR PACK-EXTERNAL SHORT

ABSL experiment: Bank 3 short through external resistor

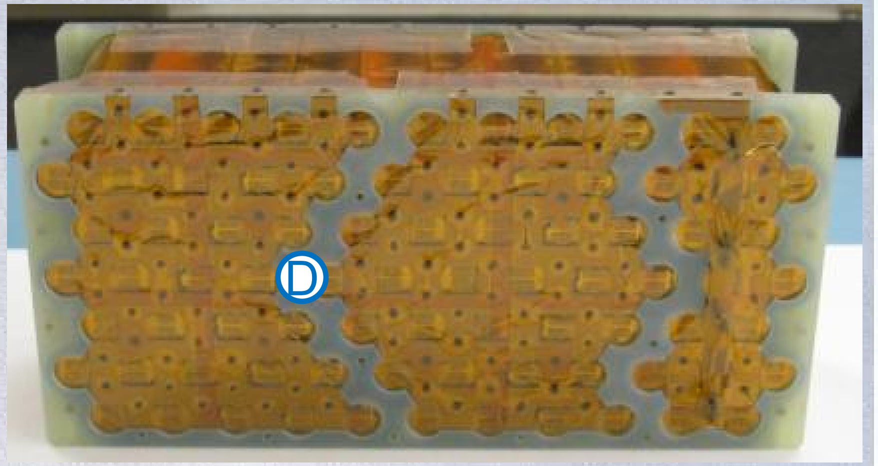


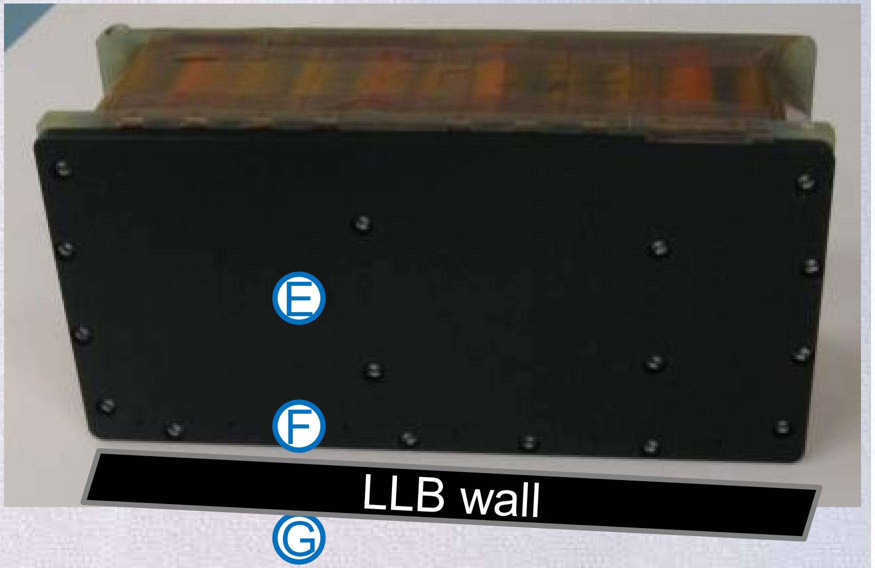
Model vs Test Article

Cell Temperature Sensor Locations

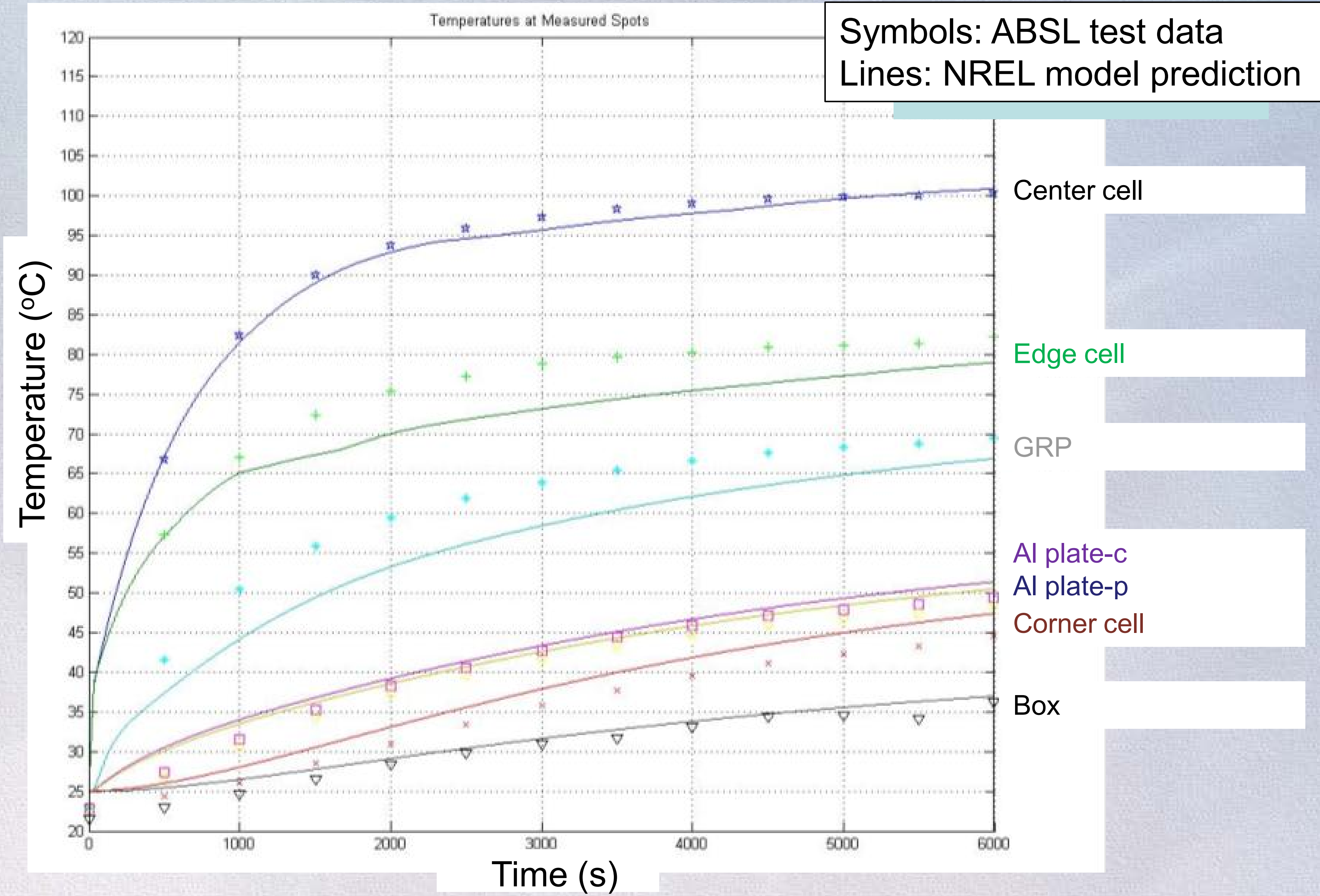


Brick Temperature Sensor Locations



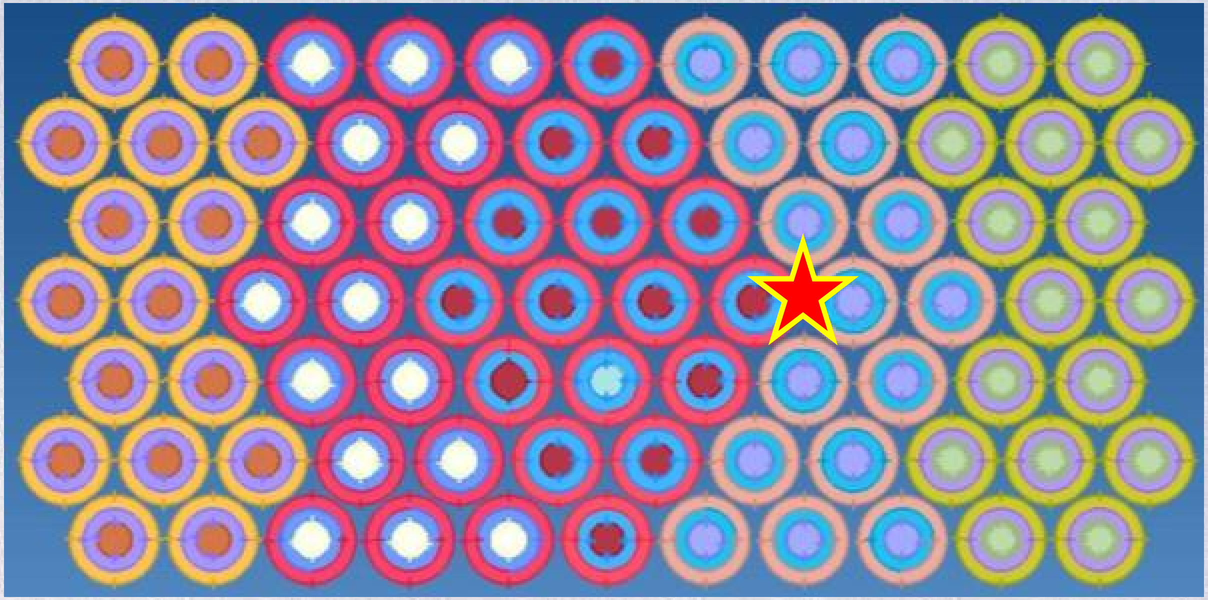


Model Validation – First 6000 seconds



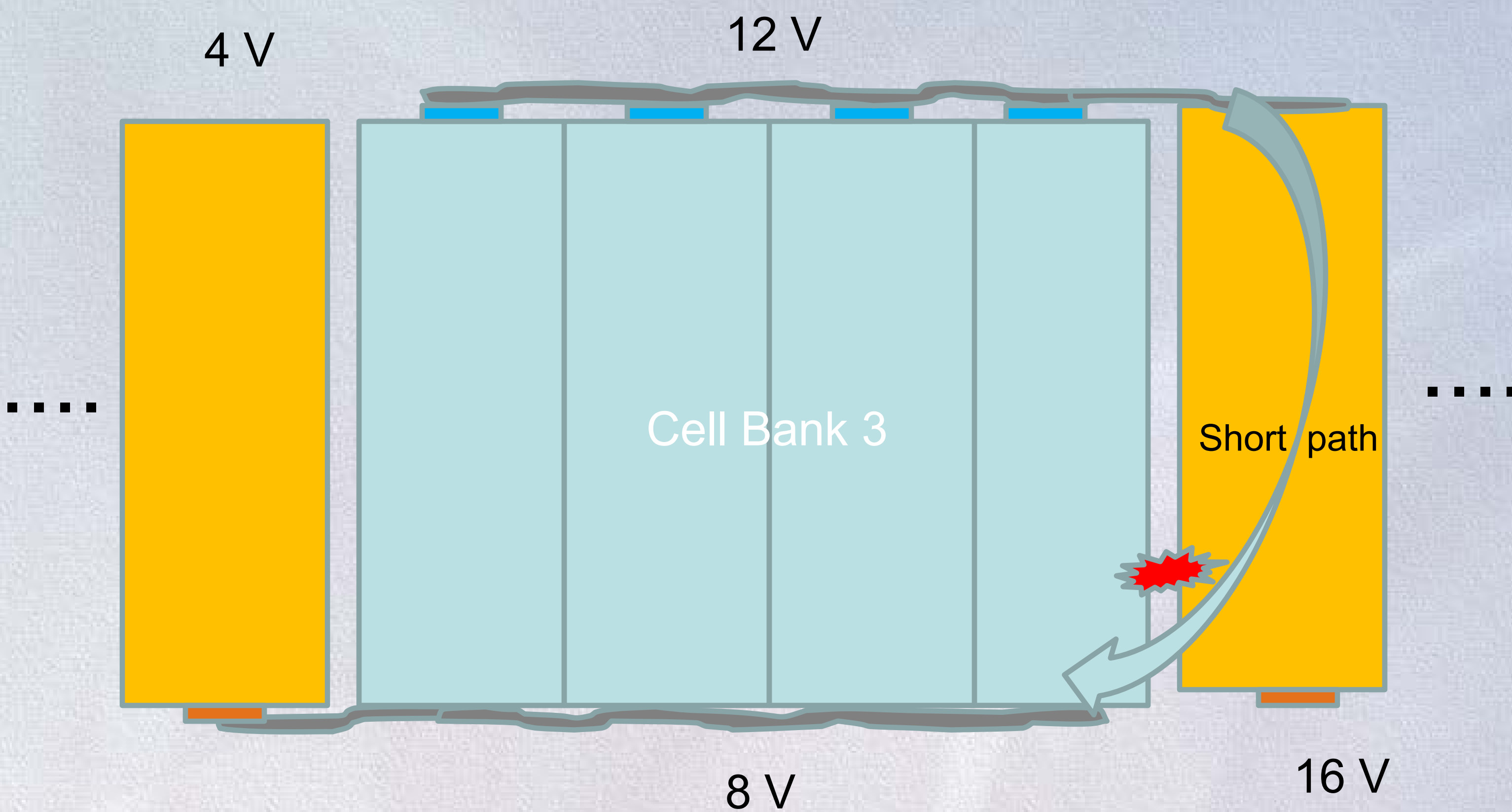
External Short Now Positioned Internal to Pack

e.g. bank 3 short caused by conductive debris between banks 3 and 4



Bank 1	Bank 2	Bank 3	Bank 4	Bank 5
+	-	+	-	+

Cartoon of Shorted Middle Cell Bank

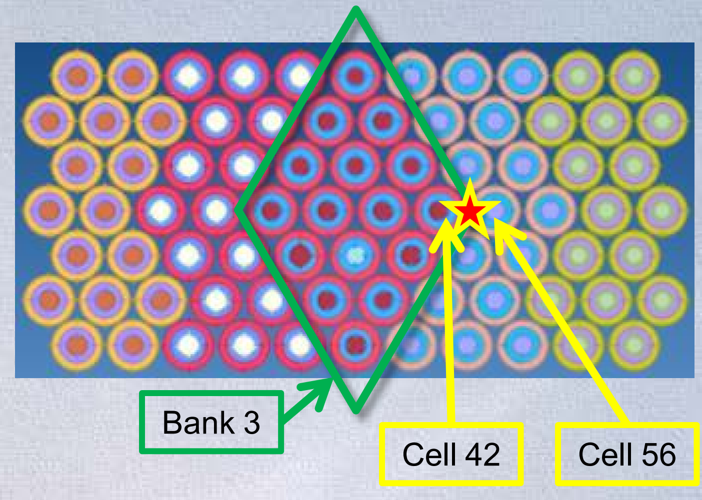


Short runs through cell can of cell from adjacent bank 4

Note that 3-layer (Kapton-Nomex-Kapton) bank-to-bank insulator/separator is omitted for clarity

Overview of Bank 3 Short Results

- Catastrophic thermal runaway is predicted at 20 mΩ
- Maybe also at 10m Ω



R_{short}	**Short Condition** (SOC_0 = 100%)	**Cell 42 T_{max}** (Bank 3)	**Cell 56 T_{max}** (Bank 4)
10 mΩ	External-to-pack, earth	97°C @ 6000-s	75°C @ 6000-s
	Internal-to-pack, earth	150°C @ 16-s	146°C @ 16-s
	Internal-to-pack, space	153°C @ 16-s	147°C @ 16-s
20 mΩ	Internal-to-pack, space	525°C @ 110-s	522°C @ 110-s
30 mΩ	Internal-to-pack, space	595°C @ 240-s	591°C @ 240-s

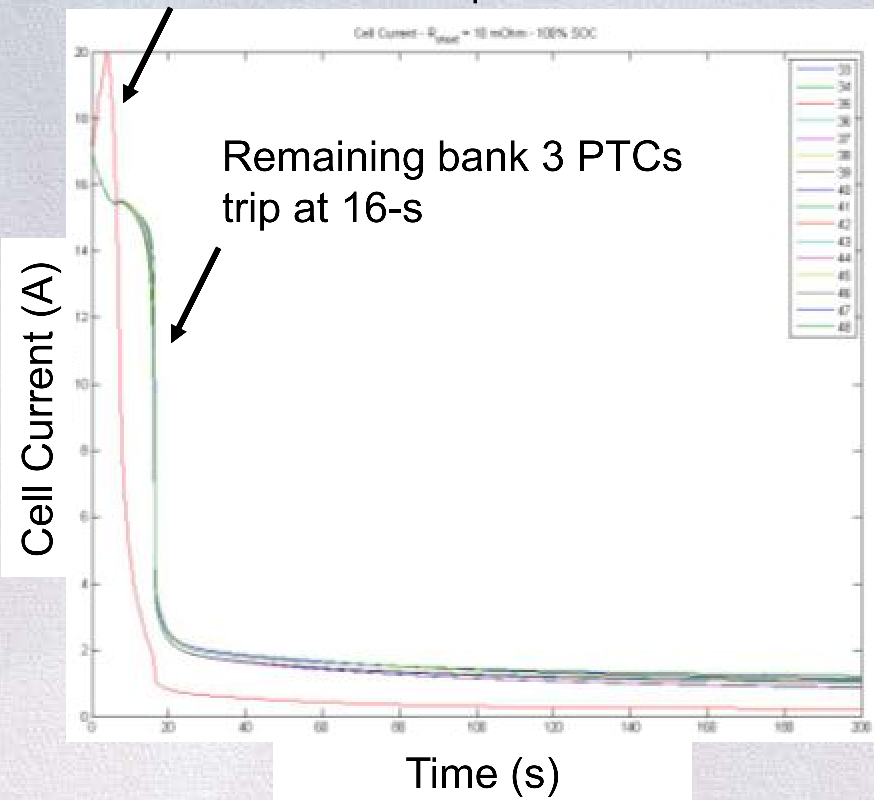
Bank 3 short from 100% SOC: 10 mΩ vs. 20 mΩ

- <u>10 mΩ:</u>
  - Bank 3 PTCs trip quickly and uniformly due to high in-rush current causing PTC self-heating

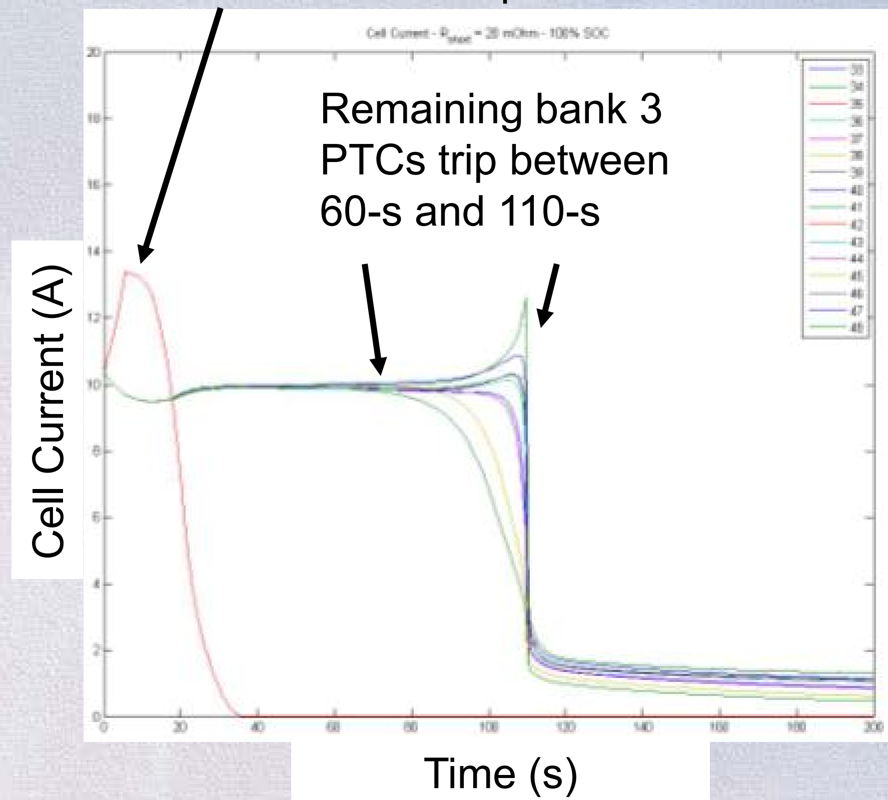
<u>20 mΩ:</u>

Bank 3 PTCs trip slowly, at different times dependent upon bank 3 temperature distribution

Cell 42 PTC trips at 8-s



Cell 42 PTC trips at10-s

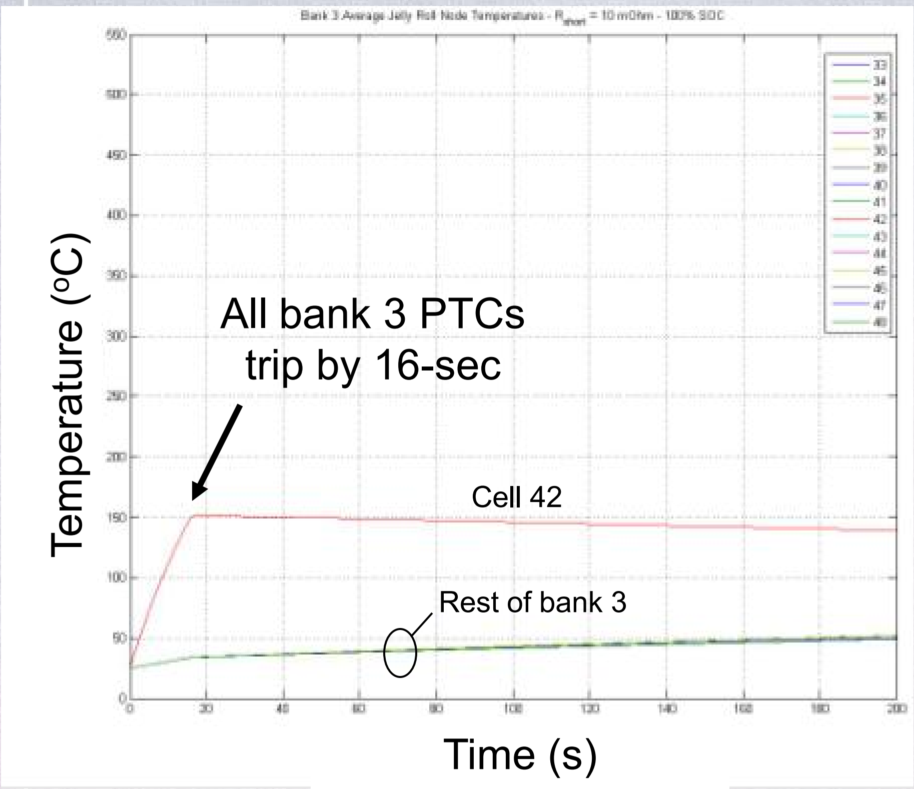


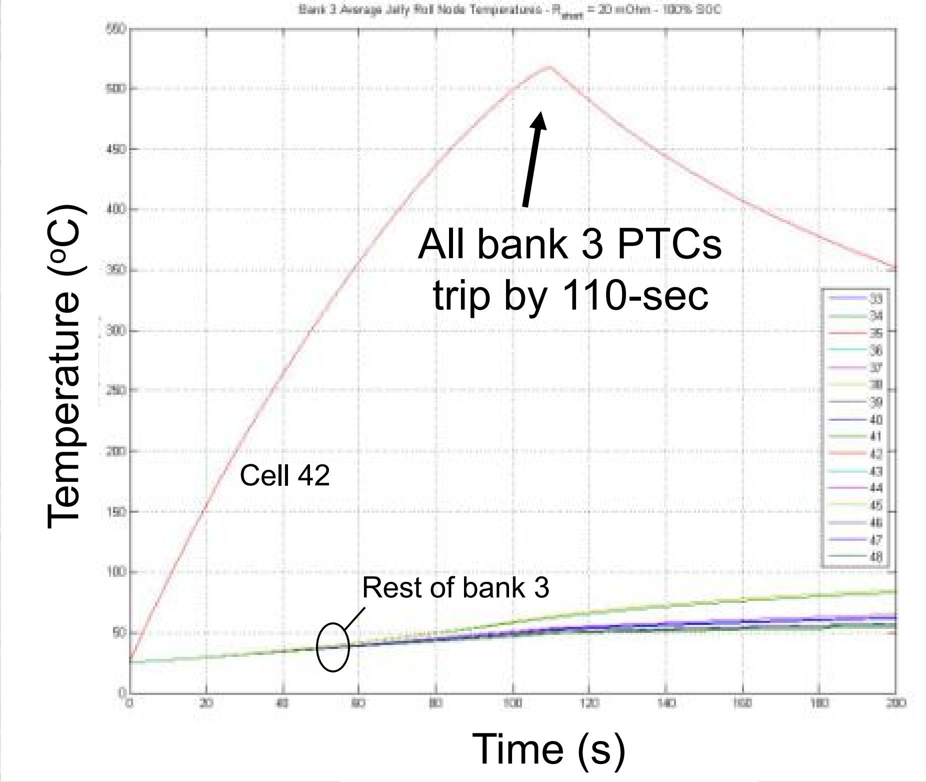
Bank 3 short from 100% SOC: 10 mΩ vs. 20 mΩ

- <u>10 mΩ:</u>
  - Bank 3 PTCs trip quickly and uniformly due to high in-rush current causing PTC self-heating

<u>20 mΩ:</u>

Bank 3 PTCs trip slowly, at different times dependent upon bank 3 temperature distribution





Analysis Findings

- Model agrees fairly well with external short test data
- Relocating short from pack-external to pack-internal will cause substantial additional heating of cells that can lead to cell thermal runaway
  - Large sensitivity to R_{short}
  - Negligible sensitivity to earth/space BCs on transient response (thermal mass dominates)
  - Additional heat sinking external to battery box won't help
- Thermal runaway predicted for $R_{short} \geq 20\ m\Omega$
- Cleanliness during battery assembly is critical
- Use of high temperature tolerant, electrically insulative materials will also prevent collateral propagation of short circuits inside battery packs

Conclusions

- A portfolio of mitigating measures are necessary to ensure safety
  - Selecting a mature cell design produced in large volumes with an absence of CPSC recalls is a very prudent measure
    - Commercial competition for runtime pushes every higher energy density (Wh/L) into same volume (i.e, 18650 standard)
    - All inert cell components are targeted for diets or elimination, such as thinner can and separator thickness, weakening design robustness
  - Small COTS cell designs made using highly automated processes typically yield unsurpassed performance uniformity, which indicates tight process tolerances
    - OCV retention after long rest periods and OCV bounce back after deep discharge are excellent discriminators of defective cells
  - NDE and DPA sampling and cell production line audits, targeted on defect and contamination control, are critical for assessing cell production quality
  - Operating cells within positive margins of voltage, current, temperature is also very important for life and safety
  - Detailed thermal models can predict short circuit vulnerabilities of a battery design
    - Example; certain external cell shorts that are internal to battery assembly are predicted to lead to cell thermal runaway in spacesuit battery
    - Implies similar vulnerability to cell internal shorts, but verification needed

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