Advanced Mitigating Measures for the Cell Internal Short Risk

by

Eric Darcy\textsuperscript{1} and Kandler Smith\textsuperscript{2}

\textsuperscript{1} NASA-JSC/NREL; \textsuperscript{2} NREL

for the

Electric Aircraft Symposium

23 April 2010

Rohnert Park, CA

NREL/PR-5400-48673
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?

*C. Mikolajczak, et. al., IEEE Portable 2007 Conference, Orlando, 2007
### CPSC Record of Relevant Field Failures

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

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

- Fire/Violent Rupture
  Due to cell internal short

- Separator Failure
- Insulator Failures
- Crimp Seal Failure
- Native or FOD Contamination

- Jellyroll top insulator
- Jellyroll bottom insulator
- Jellyroll outside wrap insulator
- Positive tab insulator

- Crimp seal
- JR top insulator
- JR bottom insulator

- JR wrap
- + tab insulator
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

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

Note the bank-to-bank separator/insulator

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 autocycle (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

9 rejects

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 Rejects 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 $1.2 \text{ mV (0.031\%)}$

$6\sigma$ range improves from $11.8 \text{ mV (0.31\%)}$ to $7 \text{ mV (0.18\% of mean)}$ after removing 9 outliers (not shown). No more outliers appear with this tighter $6\sigma$ 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.
COTS 18650 Initial Charge Capacity

Initial Charge Input of MoliJ cells
17 months after Apr 07 code date

Same 9 rejects as low OCVs

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)

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

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
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

- Circuit-board side
- Center-most cell
- LLB-wall side

- LLB wall
Model Validation – First 6000 seconds

Symbols: ABSL test data
Lines: NREL model prediction

Center cell
Edge cell
GRP
Al plate-c
Al plate-p
Corner cell
Box

Temperature (°C)

Time (s)
External Short Now Positioned Internal to Pack

e.g. bank 3 short caused by conductive debris between banks 3 and 4
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/seperator is omitted for clarity
Overview of Bank 3 Short Results

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

<table>
<thead>
<tr>
<th>$R_{\text{short}}$</th>
<th>Short Condition (SOC₀ = 100%)</th>
<th>Cell 42 $T_{\text{max}}$ (Bank 3)</th>
<th>Cell 56 $T_{\text{max}}$ (Bank 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mΩ</td>
<td>External-to-pack, earth</td>
<td>97°C @ 6000-s</td>
<td>75°C @ 6000-s</td>
</tr>
<tr>
<td></td>
<td>Internal-to-pack, earth</td>
<td>150°C @ 16-s</td>
<td>146°C @ 16-s</td>
</tr>
<tr>
<td></td>
<td>Internal-to-pack, space</td>
<td>153°C @ 16-s</td>
<td>147°C @ 16-s</td>
</tr>
<tr>
<td>20 mΩ</td>
<td>Internal-to-pack, space</td>
<td>525°C @ 110-s</td>
<td>522°C @ 110-s</td>
</tr>
<tr>
<td>30 mΩ</td>
<td>Internal-to-pack, space</td>
<td>595°C @ 240-s</td>
<td>591°C @ 240-s</td>
</tr>
</tbody>
</table>
Bank 3 short from 100% SOC: 10 mΩ vs. 20 mΩ

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

- **20 mΩ:**
  - Bank 3 PTCs trip slowly, at different times dependent upon bank 3 temperature distribution

Cell 42 PTC trips at 8-s

Remaining bank 3 PTCs trip at 16-s

Cell 42 PTC trips at 10-s

Remaining bank 3 PTCs trip between 60-s and 110-s
Bank 3 short from 100% SOC: 10 mΩ vs. 20 mΩ

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

- **20 mΩ:**
  - Bank 3 PTCs trip slowly, at different times dependent upon bank 3 temperature distribution

---

**Graphs:**

- **Left:**
  - All bank 3 PTCs trip by 16-sec
  - Cell 42
  - Rest of bank 3

- **Right:**
  - All bank 3 PTCs trip by 110-sec
  - Cell 42
  - Rest of bank 3
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 $R_{\text{short}}$
  - 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 $R_{\text{short}} \geq 20 \, \text{mΩ}$
- 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
Acknowledgements

• Gi-Heon Kim, Larry Chaney, and Ahmad Pesaran at NREL for their thermal analysis contributions
• ABSL, Exponent, and Mobile Power Solutions for providing key data for this study