Passively Thermal Runaway Propagation Resistant Battery Module that Achieves > 190 Wh/kg

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Author & Contents

• Eric Darcy, NASA-Johnson Space Center
  – Ph.D, ChE, University of Houston, 1998
  – 29 years with battery group at JSC, senior battery specialist
  – “Safe, high performance batteries for manned spacecraft” mandate
  – Specializing on reducing the severity of single cell thermal runaway (TR) hazards ever since the first 787 battery incidents, after many years focusing exclusively on prevention

• Contents
  – Background on the spacesuit battery
  – New high energy cell designs
  – 5 design rules for safe Li-ion battery designs
  – Redesign features of new spacesuit battery
  – Passive TR propagation resistance verification
  – Take away message
    • Being TR propagation resistant and achieving > 190 Wh/kg battery module is possible and suitable for manned aircraft
Current Li-ion Spacesuit Battery

Features
- 80 Moli (ICR18650J) 2.4Ah cells (16P-5S)
- 35Ah and 650 Wh at BOL (in 16-20.5V window)
- Cell design unlikely to side wall rupture
- 0.5mm cell spacing
- Adjacent cells insufficiently protected from TR ejecta
- Inadequate vent path for TR ejecta

Used on over 22 spacewalks for far
Project Top Level EMU Battery Requirements

- Capacity at End-of-Life (EOL)
  - 26.6 Ah with 9A, 5s start-up pulse, rest of discharge at 3.8A
  - Charge at 5A to 20.5V to a 1A taper
- Voltage (16 to 21V)
- Service life (5 yrs minimum)
  - 600 days at 100% SoC (4.1V/cell) with the rest at < 50% SoC, all at 20°C
- Cycle Life (>100 cycles)
  - No cell bank balancing
- Mass (<7.04 kg)
- Volume (Do not exceed current LLB envelope)
- Environmental Performance
  - Meet capacity and life with 100 EVAs performed at worst case hot (32ºC) or cold (10ºC) starting conditions
  - No cell bank balancing
- Existing Charger Compatibility (LIB Charger)
  - Charge at 5A to 20.5V to a 1A taper
  - Annual “Autocycle” performed on all units stored on the ground and any dormant (> 1 yr) unit on-orbit shall be “Autocycled prior to being declared “Go for EVA (Spacewalk)”
    - Discharge at 1.25A, charge at 5A to 20.5V, discharge at 1.25A, and recharge to 10Ah
## Specifications (INR18650 MJ1)

<table>
<thead>
<tr>
<th>Item</th>
<th>Condition / Note</th>
<th>Specification</th>
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<tbody>
<tr>
<td>2.1 Energy</td>
<td>Std. charge / discharge</td>
<td>Nominal 3500 mAh</td>
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<tr>
<td></td>
<td></td>
<td>Minimum 3400 mAh</td>
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<tr>
<td>2.2 Nominal Voltage</td>
<td>Average</td>
<td>3.635V</td>
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<td>2.3 Standard Charge</td>
<td>Constant current</td>
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<td>(Refer to 4.1.1)</td>
<td>Constant voltage</td>
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<td>End current(Cut off)</td>
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<td>2.4 Max. Charge Voltage</td>
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<td>4.2 ± 0.05V</td>
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<td>2.5 Max. Charge Current</td>
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<td>1.0 C (3400mA)</td>
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<td>2.6 Standard Discharge</td>
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<td></td>
<td>End voltage(Cut off)</td>
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<td>2.7 Max. Discharge Current</td>
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<td>10A</td>
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<td>2.8 Weight</td>
<td>Approx.</td>
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<td>2.9 Operating Temperature</td>
<td>Charge</td>
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<td>Discharge</td>
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<td>2.10 Storage Temperature</td>
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<td>(for shipping state)</td>
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<td>-20 ~ 45°C</td>
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<td>1 year</td>
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<td>-20 ~ 20°C</td>
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### Sample Weight Data

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<tr>
<th>Sample</th>
<th>as rec'vd (g)</th>
<th>bare (g)</th>
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<td>%sdev</td>
<td>0.12%</td>
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Panasonic NCR18650B & GA vs LG INR18650 MJ1

Voltage vs Capacity at room temp
Charge at 850mA to 4.2V to 70mA taper
Discharge at 850mA to 2.5V with 4.8A, 1s Re pulse at ~50% SoC
Panasonic NCR18650B and NCR18650GA
LG Chem INR18650 MJ1
Re for B: 55.9 mohm
Re for GA: 41.0 mohm
Re for MJ1: 32.5 mohm

LG MJ1 achieves 265 Wh/kg
Ah, DC Re Comparison

Capacity, DC Re vs Cycle #
Panasonic NCR B vs LG MJ1
Charge at 800 mA to 4.2V, 70mA taper
Discharge at 800 mA to 2.5V
5A, 100ms pulse near 50% SoC
LG Chem’s New High Energy/Power Cell Design

• Advantages of the LG INR18650 MJ1 cell design
  – Slightly higher Wh/L, Wh/kg vs competing designs from Panasonic
  – Thicker cell can wall (0.0063” vs 0.0050”)
  – LG wants their cell design to be used in space applications
  – LG willing to implant our ISC device in special production runs of the MJ1 cell (enabling verification of battery PPR features)
  – No cell PTC current limiting switch
    • More compatible with high voltage missions because PTC is 30V device
    • Lower internal resistance helps with power margins and blowing fusible links
  – Slightly better cycle life
  – Slightly less temperature dependent performance
5 Design Driving Factors for Reducing Hazard Severity from a Single Cell TR

- Reduce risk of cell can side wall ruptures
  - Without structural support most high energy density (>600 Wh/L) designs are very likely to experience side wall ruptures during TR
- Provide adequate cell spacing & heat dissipation
  - Direct contact between cells without alternate heat dissipation paths nearly assures propagation
- Individually fuse parallel cells
  - TR cell becomes an external short to adjacent parallel cells and heats them up
- Protect the adjacent cells from the hot TR cell ejecta (solids, liquids, and gases)
  - TR ejecta is electrically conductive and can cause circulating currents
- Prevent flames and sparks from exiting the battery enclosure
  - Provide tortuous path for the TR ejecta before hitting battery vent ports equipped flame arresting screens
**LLB2 Design Features**

- Combined structural and heat dissipative features required into one part
  - Al 6061T6 interstitial heat spreader for each bank
  - 0.5mm spacing between cells within bank
  - 1.5mm spacing between cells of adjacent banks
  - Line cell bores with mica sleeves
  - Cells lined with their shrink sleeves as additional insulating layer
  - Snug fitting bores to support cell cans from side wall ruptures
  - Ceramic bushing protects G10 capture plate at cell vent opening
  - Tough 0.002” plasma Al₂O₃ dielectric coating on outer surfaces to isolate banks
    - Mica paper (100 micron) between heat sinks

- Mica paper (100 micron) between heat sinks

Middle bank heat sink with cells

2nd & 4th bank heat sinks

65-cell brick for LLB2 (no Ni)
LLB2 Heat Sinks

No corner cells - Every cell has at least 3 adjacent cells

0.5mm cell spacing, Al 6061T6
LLB2 Heat Sinks With Alumina Coating

- White Engineering aluminum oxide coating (A-100) process spray coats 0.002” thick Al₂O₃ layer on external surfaces
  - Cell bores and screw holes masked from coating process
- Heat sinks retain their proper fit with each other and with capture plates
Ni-201 Bus Plates (0.005” thk)

Bus plate 1

(+) Terminal

(19.5)

Fusible link
On negative
Cell terminal

(36.5)

Bus plate 2

(82.57)

Bus plate 3

(20)

Bus plate 4

(-) Terminal

(R9.97)

(R5)

(R1)

(R0.25)

(R4.375)

(R3.64)

(100.437)

(19.5)

(1)

(2)

(5)

(1)

(5)

(R2)

(R5)

Cell terminal

On negative
Cell Brick (with Ni bussing)

- Features
  - Ni-201 (0.005” thk)
  - 1mm wide fusible link on cell negative
    - Rated for ~19A
  - Terminating bus (0V, and 20V) plates not yet enhanced with Cu bus to handle peak currents
    - Not needed for TR test
Cell Brick Assembly > 180 Wh/kg

- With 12.41 Wh/cell, cell brick assembly achieves 191 Wh/kg
  - Assuming 12.41 Wh per cell
- Design has 1.4 parasitic mass factor
  - Cell mass x 1.4 = Brick mass

<table>
<thead>
<tr>
<th>Mass Categories</th>
<th>g</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>LG MJ1 Cells</td>
<td>3012.75</td>
<td>71.3%</td>
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<tr>
<td>Heat sinks</td>
<td>824.95</td>
<td>19.5%</td>
</tr>
<tr>
<td>Mica sleeves</td>
<td>182.31</td>
<td>4.3%</td>
</tr>
<tr>
<td>Capture plates</td>
<td>115.81</td>
<td>2.7%</td>
</tr>
<tr>
<td>Ceramic bushings</td>
<td>60.15</td>
<td>1.4%</td>
</tr>
<tr>
<td>Ni-201 bussing</td>
<td>29.71</td>
<td>0.7%</td>
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<tr>
<td><strong>Total</strong></td>
<td>4225.7</td>
<td></td>
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</table>

Current spacesuit LLB brick weighs ~5000g
180 Wh/kg Battery Module – Heater Test

- Reduce cell spacing and increase heat conduction from trigger to adjacent cells and heat sink and structurally support cell can walls

- Bottom heater was used instead of circumferential due to geometry of compact, lightweight heat sink covering length of can

- Bottom surface heater limited to 35W

- Adjacent cells were removed to test heater without risking damage to heat sink

- TR was not achieved after 30 minutes at 32W applied to cell bottom and test was aborted.

- This heat sink just dissipates away too much heat from small bottom heaters
Attempt to Drive TR with Bottom Heater While in Al HS

Can’t get trigger cell > 100°C after > 1hr and 3 attempts

Heater fails at 48W
Wax formulation used melts ~57°C

Top to Bottom:
1. Copper Pad
2. Battery Separator with Copper Puck
3. Wax – Phase Change Material
4. Aluminum Pad

2010 Inventors:
• Matthew Keyser, Dirk Long, and Ahmad Pesaran at NREL
• Eric Darcy at NASA

US Patent # 9,142,829

Thin (10-20 μm) wax layer is spin coated on Al foil pad

Graphic credits: NREL
Anode Active Material to Cathode Current Collector Short

Type 2 – “Anode Active to Collector”

Cathode Active layer < 76 microns

Aluminum ISC Pad 76 microns

Separator 20 microns

Copper ISC Pad 25 microns

Anode Active Layer X microns

Cathode Current Collector

Wax layer ~20 microns

Cu Puck 50 microns

NMP used to remove active material

Note: Trials with 25 micron Cu puck produces frequent activation duds
2.4Ah 18650 Cell

- NREL fabricated the ISC devices
- Partnered with E-one Moli Energy (Maple Ridge, BC) for the implantation into their 2.4Ah cells
- Moli performed cycling and activation tests
- NASA-JSC performed activation tests
Open air test with cell charged to 4.2V and with TCs welded to cell side wall (2) and bottom (1)
Cell vents with flames about 20 seconds before onset of TR. Bottom TC doesn't record the lowest peak.
Run 3 – MoliJ ISC Device TR in open air
Response is very similar inside \( \text{N}_2 \) chamber…..bottom TC tracks hotter side TC at peak.
Mid range TC selected for each run. N2 run has coolest peak, but cool down rates are similar. Overall, MoliJ with ISC device produces skin temperatures > 600°C
Heat Sink Prevents Side Wall Ruptures

Test Procedure
- 0.5mm cell spacing Al 6061T6 heat sink
- 5 fully charged LG 3.5Ah cells
- 9 fully discharged Samsung 2.6Ah cells
- No fully charged cells adjacent to each other
- G10/FR4 capture plates on both ends
- Macor® bushings on the positives of the fully charged LG cells
- Slow heat to vent oven test

Results
- **No side wall ruptures along the can lengths supported by the heat sink** (2 tests = 10 LG cells)
- Very little damage to the heat sink
This sink should have 12 fully charged LG Cells (green)

Grey circles = as-is Samsung cells (pink)

Trigger Cells = Moli ISC (purple)
LLB2 Brick: Thermal Runaway Run 1
Average $\Delta T$ on adj cells = 34°C from onset to max. Adj cell OCVs unchanged pre and post.
LLB2 Brick: Thermal Runaway Run 2
LLB2: Thermal Runaway Test 2 – Interior Trigger

Average ΔT on adj cells = 19°C from onset to max. Adj cell OCVs unchanged pre and post.
LLB2: Thermal Runaway Run 3

Did campfire cause temperature spike?
LLB2 Brick: Thermal Runaway Run 3

Average $\Delta T$ on adj. cells = 52.4°C from onset to max (excluding flame peak). Adj. cell OCVs unchanged pre and post.
LLB2 Brick TR Test Findings

- No TR propagation and no OCV changes to adjacent cells
- Interior cell trigger are less vulnerable than edge cells based on temperature rise (max-onset T) on adjacent cells
  - Interior cell trigger $\Delta T \sim 19^\circ C$ (one run)
  - Edge cell trigger $\Delta T \sim 42^\circ C$ (two runs)
- 3 Caveats
  - MoliJ 2.4Ah trigger cell doesn’t provide the same thermal output as the 3.5Ah LG cell design
  - All cell TCs were welded to cell bottoms and not the side walls
  - No Ni bussing to interconnect the cells
LLB2 Battery Brick with Ni bus plates (13P5S) Test Series

Bank1 (-) terminal

Bank5 (+) terminal

Pre-test Photos
Erratic Heater. No propagation, but TCs on adjacent cells 1, 2, and 3 recorded maximums of 238 °C, 427 °C, and 1014 °C.
Run 1 Video Snapshots

- Cells go incandescent immediately
- Bead of molten Al exits header 2s after OTR
- Campfire in rear starts 1s after OTR and lasts for 91s
  - Could explain anomalous max temps
No propagation - Max adjacent cell temps (TC16: 70.9°C, TC17: 59.5°C, TC18: 56.3°C). TC19 on HS near trigger cell reached 153°C.

Max temperatures on HS are reached about 1 minute earlier than those on adjacent cells. Adjacent temps at OTR < 23.8°C, for a max $\Delta T = 47^\circ$C. Bank 5 OCV dips to 3.798V and recovers to 4.192V.
OCV dips to 4.111V then recovers to pre test level of 4.182V. Triggered in <3 min. TC10 & TC11 experienced early peaks (82 & 66°C). Then >2min after OTR, adj cell average $\Delta T_{\text{max}} = 29.5^\circ\text{C}$. Early peaks on the 2 TCs could be due to campfire.
3 non-adjacent cells with low OCVs were shorted most likely during assembly/disassembly. All adjacent cells indicate healthy unchanged OCVs.
Findings So Far

• Al Heat Sink Tests
  – 4 attempts to drive > 250Wh/kg cell into TR – All failures
    • 2 with Panasonics, 2 with LGs, all with home made bottom heaters
  – 5 attempts with MoliJ ISC device cells – No propagation of TR
    • 1 dud and 4 success with the MoliJ ISC cell driven into TR
  – 2 heat to vent tests with 5 fully charged LG cells each
    • No side wall ruptures in areas supported by the sink

• LLB2 brick tests (All 6 MoliJ ISC cells successfully driven to TR)
  – 3 no-Ni bussing brick tests
    • No TR propagation and no OCV changes to adjacent cells with excellent temp margins
      – Interior cell trigger ΔT ~ 19°C (one run)
      – Edge cell trigger ΔT ~ 42°C (two runs)
    • Interior cell trigger are less vulnerable than edge cells based on temperature rise (max-onset T) on adjacent cells
  – 3 Ni bussing (13P5S)
    • No propagation of TR, no impact on adjacent cell OCVs
    • Very good temperature margins (vs onset of TR temperature)
      – Interior cell trigger: ΔT ~ 30°C (one run)
      – Edge cell trigger ΔT ~ 48°C (one valid run)
LLB2 Redesign: Design vs Rules

Compliance with the 5 rules

• Minimize side wall ruptures ✓
  • Al interstitial heat sink
• No direct cell-cell contact ✓
  • 0.5mm cell spacing
• Individually fusing cell in parallel ✓
  • 19A fusible link
• Protecting adjacent cells from TR ejecta ✓
  • Ceramic bushing lining cell vent opening in G10 capture plate
• Include flame arresting vent ports ✓
  • Tortuous path with flame arresting screens
  • Battery vent ports lined with steel screens

Features

• 65 LG (INR18650 MJ1) 3.5Ah cells (13P-5S)
• 37Ah and 686 Wh at BOL (in 16-20.5V window)
• Cell design likely to side wall rupture, but supported
• 0.5mm cell spacing
• Adjacent cells sufficiently protected from TR ejecta
• Adequate vent path for TR ejecta
LLB2 Prototype Box Design Features

• Adjacent cell protection features
  – Thinner G10 capture plates with Macor bushings on positive vent holes
    • More can length support by the interstitial heat sink
  – Individually fuse cells within Ni bus strips at cell negative terminals
    • Cleaner end of the cell
  – Line the inside of the housing wall with porous ceramic or carbon fiber layer to absorb most of the ejecta slag
  – Internal lid placed on top of bank heat sinks to thermally link them to the housing and other banks
    • Include screen vents to allow hot gases
  – Screen vent ports in cavity above inside lid facing the label side of the battery (TMG side)
Protocase Enclosure (prior to anodization)

Prototype box for TR test only
Not the flight design

Features:
- Al 5052 H32, more bendable than 6061
- Thickness 0.81 mm (1/32”)
- We will seal the matting edges with a bit of caulk
Adjacent Cell Protection and Flame Arresting Features

- Ceramic bushings lining capture vent port
- 0.25” vent gap between capture plate and inside of box
- Inside lid with vent perforation lined with 40 mesh screen
- Box vent ports lined with steel screens
LLB2 Redesign: Box level mass breakdown

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<td>Ni-201 Bussing</td>
<td>29.71</td>
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<td>Box and Lid</td>
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Still maintains 162 Wh/kg with box!
Current battery only achieves 100 Wh/kg.

1.65 parasitic mass factor
LLB2 Future Work

• LLB2 full scale prototype test series
  – 3 MoliJ ISC trigger cells
  – Protocase enclosure with flame arresting features

• LLB2 full scale confirmation test series
  – Same as above but with 3 LG MJ1 ISC trigger cells
Take Home Message & Conclusions

- Achieving passive TR propagation resistance while > 190 Wh/kg in a building block battery module is possible and suitable for manned aircraft
- Newer higher energy cell designs require structural support to prevent side wall rupture
- Highly conductive interstitial heat sink between cells is most effective in protecting adjacent cells
- Corner and edge cells are more vulnerable than interior cells towards TR propagation
Acknowledgements

• TR Severity Reduction Team
  – Chris Iannello, NESC Technical Fellow for Electrical Power, and Deputy, Rob Button
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  – Paul Coman, PhD candidate Univ of South Denmark