Safety and Long-Term Performance of Lithium-ion Pouch Cells

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Background

• Commercial off-the-shelf (COTS) li-ion cells are frequently subjected to a standard set of tests to determine their performance and safety and add them to a database that allows users at NASA-JSC to choose cell designs for specific applications.
• In recent years, Li-ion pouch cell designs are used increasingly in portable equipment applications and are commonly being referred to as lithium polymer cells, although these cells are not of the true polymer types.
• Several Li-ion polymer or pouch cells have been tested at NASA-JSC in the past 15 years and the cells from developed from being low rate (Ultralife, 1998) to medium rates in the 2005 timeframe (Valence, Samsung, Kokam, etc.) to high energy and high rates during the present time.
• Testing of these li-ion polymer cells have shown that long term storage as well as vacuum exposures cause swelling of the pouch.
• Recent test programs at NASA-JSC have focused on testing the li-ion polymer cells for their safety as well as their performance under different rates and temperatures as well as under vacuum and reduced pressure conditions.
• The most recent tests included cells of the following types:
  SKC 15 Ah (high-rate capability)
  Tenergy 6 Ah (medium rate medium energy density)
  Altairnano 13 Ah (nanotitanate anode with high rate capability)
  Wanma 5 Ah (medium rate medium energy density)
SKC 15 Ah Li-ion Performance Tests
SKC 15 Ah Li-ion Cell Cycling Under Vacuum Environments

Unrestrained SKC Cell Data

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Pre OCV</th>
<th>Post OCV</th>
<th>Pre Capacity</th>
<th>Post Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>4.069 V</td>
<td>3.097 V</td>
<td>14.93 Ah</td>
<td>14.855 Ah</td>
</tr>
</tbody>
</table>

Restrained cells show change in performance under vacuum conditions

Unrestrained

Restrained
SKC Li-ion Cell Performance After Vacuum Exposure and Storage at Ambient

20 Day storage period

Restrainted

Voltage(V)

Discharge Capacity(Ah)

SKC JSC-S009 Pre Vac
SKC JSC-S009 Post Vac1
SKC JSC-S009 Post Vac2
SKC Li-ion Cell Performance After Vacuum Cycling and Storage at Ambient

20 Day storage period

Unrestrained

Voltage (V)

Discharge_Capacity (Ah)

SKC JSC-S011 Pre Vac
SKC JSC-S011 Post Vac1
SKC JSC-S011 Post Vac2

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Pouch Material Cross-Section

Outside: Nylon 6
Inside: Polypropylene
SKC 15 Ah Cell Safety Tests

Overcharge Test
(15 A; 12 V limit; max 6 hours)

Cell swelling
SKC 15 Ah External Short Test

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Pre OCV (V)</th>
<th>OCV at Peak Current (V)</th>
<th>Post OCV (V)</th>
<th>Load Value (mΩ)</th>
<th>Peak Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>4.165</td>
<td>≈2.03</td>
<td>1.353</td>
<td>3.60</td>
<td>482.00</td>
</tr>
<tr>
<td>301</td>
<td>4.148</td>
<td>≈2.49</td>
<td>4.083</td>
<td>1.76</td>
<td>1,410.10</td>
</tr>
<tr>
<td>302</td>
<td>4.151</td>
<td>≈2.37</td>
<td>1.733</td>
<td>1.76</td>
<td>1,393.30</td>
</tr>
<tr>
<td>309</td>
<td>4.137</td>
<td>≈2.77</td>
<td>0.658</td>
<td>1.60</td>
<td>1,395.80</td>
</tr>
<tr>
<td>313</td>
<td>4.161</td>
<td>≈2.96</td>
<td>2.853</td>
<td>1.60</td>
<td>1,404.10</td>
</tr>
</tbody>
</table>

Cell Swelling
SKC 15 Ah Li-ion - Simulated Internal Short Test

With Restraints

Without Restraints

Thermal runaway
SKC 15 Ah Li-ion - Heat to Vent Test

Venting and thermal runaway above 175 deg C
SKC 15 Ah Li-ion Cell Test Results Summary

- The cells provide significant performance at the rates studied:
  - less than 3% capacity loss after 500 cycles at 1 C rates
- The cells did not show any change in performance while being charged and discharged under vacuum conditions when they were restrained and displayed a loss in capacity if the cells were not restrained.
- The cells swell under overcharge and external short conditions but go into thermal runaway during simulated internal short and heat-to-vent test conditions.
Rate Capability Tests for Tenergy 6 Ah Li-ion Cell

1.7 % cap loss

the difference in discharge capacity between Cycle 127 and Cycle 2 is: 0.114 Ah

1.9 % cap loss

Difference between the discharge capacities of cycle 2 and 272: 5.9109-5.7554=0.117 Ah
Rate Capability Tests for Tenergy 6.0 Ah Li-ion Cells

3.1% cap loss

2% less initial cap between C/10 and C/2

2.2% cap loss
Tenergy Li-ion Cell Performance After Vacuum Cycling and Storage at Ambient

Discharge_Capacity(Ah)

Voltage(V)

0.5%
3.8%
3.0%
2.5%
2.0%
1.5%
1.0%
0.5%
0
1
2
3
4
5
6
7

Tenergy JSC-T018 Pre Vac
Tenergy JSC-T018 Post Vac1
Tenergy JSC-T018 Post Vac2
Tenergy Li-ion Cell Performance After Vacuum Cycling and Storage at Ambient

Unrestrained

Voltage(V)

Discharge_Capacity(Ah)

21.5%

3.4%

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Pouch Material Cross-Section

Outside: Nylon 6

Inside: Polypropylene
Tenergy 6.0 Ah Li-ion Prismatic Pouch Cell Overcharge Test

1 C current/ fresh cell

Both cells vented violently

1 C current/ Cell had undergone 300 cycles
Overcharge Test on Tenergy 6.0 Ah Li-ion Prismatic Pouch Cell

0.5 C current/ fresh cell
Overcharge Test of Tenergy 6.0 Ah Li-ion Cell

0.2 C current/ fresh cell

No thermal runaway was observed in both cases.

0.2C current/ Cell had undergone 300 cycles
External Short Test on Tenergy Li-ion 6.0 Ah Prismatic Pouch Cell

<table>
<thead>
<tr>
<th>Test Temp (°C)</th>
<th>Sample Condition</th>
<th>Sample #</th>
<th>Sample ID</th>
<th>Resistance (mOhm)</th>
<th>Initial OCV (V)</th>
<th>Initial ACR (mOhm)</th>
<th>Maximum Temp (°C)</th>
<th>Maximum Current (A)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>1</td>
<td>11</td>
<td>30</td>
<td>4.1284</td>
<td>20.4</td>
<td>28.9</td>
<td>62.0</td>
<td>Cathode tab burned off</td>
</tr>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>2</td>
<td>8</td>
<td>30</td>
<td>4.1327</td>
<td>20.4</td>
<td>27.2</td>
<td>63.0</td>
<td>Cathode tab burned off</td>
</tr>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>3</td>
<td>9</td>
<td>30</td>
<td>4.1325</td>
<td>20.3</td>
<td>29.7</td>
<td>65.0</td>
<td>Cathode tab burned off</td>
</tr>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>3-Cell</td>
<td>25,26,27</td>
<td>27</td>
<td>12.431</td>
<td>63.2</td>
<td>27.2</td>
<td>113.0</td>
<td>Cathode tab burned off</td>
</tr>
</tbody>
</table>

Sample #1 - Voltage, Temperature, and Time Summary Table

Time (MM:SS)

Voltage | Cell Temperature | Chamber Temperature

Current (A) vs Time (MM:SS)

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External Short Test on 3S String of Tenergy Li-ion 6.0 Ah Prismatic Pouch Cell

113 A max; 27 deg C max

Cathode Tabs from all three cells burned off and became disconnected
Simulated Internal Short Test on Tenergy Li-ion 6.0 Ah Prismatic Pouch Cell

<table>
<thead>
<tr>
<th>Test Temp (°C)</th>
<th>Sample Condition</th>
<th>Sample #</th>
<th>Sample ID</th>
<th>Initial OCV (V)</th>
<th>Initial ACR (mOhm)</th>
<th>Maximum Temp (°C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>1</td>
<td>18</td>
<td>4.140</td>
<td>20.5</td>
<td>172.6</td>
<td>Fire</td>
</tr>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>2</td>
<td>20</td>
<td>4.137</td>
<td>20.6</td>
<td>309.8</td>
<td>Fire</td>
</tr>
</tbody>
</table>

Table 1: Li-Ion Test Summary Table
Burst Pressure Test for Tenergy Li-ion 6.0 Ah Prismatic Pouch Cell

<table>
<thead>
<tr>
<th>Test Temp (°C)</th>
<th>Sample Condition</th>
<th>Sample #</th>
<th>Sample ID</th>
<th>Max Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>1</td>
<td>40</td>
<td>662</td>
</tr>
<tr>
<td>20</td>
<td>Fresh Chg</td>
<td>2</td>
<td>5</td>
<td>617</td>
</tr>
</tbody>
</table>

89/96 psi

Heat-to-Vent Test for Tenergy Li-ion 6.0 Ah Prismatic Pouch Cell

<table>
<thead>
<tr>
<th>Test Temp (°C)</th>
<th>Sample Condition</th>
<th>Sample #</th>
<th>Sample ID</th>
<th>Initial OCV (V)</th>
<th>Initial ACR (mOhm)</th>
<th>Maximum Temp (°C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Fresh</td>
<td>1</td>
<td>15</td>
<td>4.1438</td>
<td>20.3</td>
<td>189.8</td>
<td>Fire</td>
</tr>
<tr>
<td>20</td>
<td>Fresh</td>
<td>2</td>
<td>14</td>
<td>4.1397</td>
<td>20.5</td>
<td>192.0</td>
<td>Fire</td>
</tr>
</tbody>
</table>
Altairnano 13 Ah Li-ion Cell Tests

Nameplate Capacity: 13 Ah
Average Capacity at C/2: 14.3 Ah

Ch/Disch: 13 A/60 A

Ch/Disch: 13 A

Ch/Disch: 13 A/60 A

Ch/Disch: 13 A

Ch/Disch: 13 A
Tenergy Li-ion Cell Test Summary

- The Tenergy Li-ion Pouch cells performed well under different rate protocols with a maximum of 3% capacity loss for the 300 cycles studied.
- The cells lose capacity when tested under vacuum conditions in an unrestrained mode.
- The cells go into thermal runaway when overcharged at 1 C and 0.5 C rates but show tolerance to overcharge at 0.2 C rates.
Altairnano 13 Ah Li-ion-

Ch: 60 A
Disch: 13 A

Ch: 60 A
Disch: 60 A

Ch: 120 A
Disch: 13 A

Ch: 60 A
Disch: 120 A
Altairnano 13 Ah Li-ion Tests

Lower capacity is obtained at lower temperatures but does not show degradation for the cycles tested.
Altairnano 13 Ah Li-ion Cell Internal Resistance

Burst Pressure Test

<table>
<thead>
<tr>
<th>MPS ID</th>
<th>Burst pressure (psi)</th>
<th>Burst location</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-825-E-15</td>
<td>25</td>
<td>side seal</td>
</tr>
<tr>
<td>N2-825-F-16</td>
<td>31</td>
<td>seal over tab</td>
</tr>
<tr>
<td>N2-825-F-18</td>
<td>23</td>
<td>seal over and near tab</td>
</tr>
</tbody>
</table>
Higher capacities observed with restrained than with unrestrained cells
Altairnano Safety Tests

Single Cell

Altair B1c, 11 A Overcharge, Cell 4

8SString

Cell Voltage vs. Time for Single Cell

Cell Voltage vs. Time for 8SString

Altair B1c Overcharge at 11 A

8SString

Cell Voltage vs. Time for 8SString

Altairnano Li-ion Cell Test Summary

• The Altairnano Li-ion cells performed well at the different rate protocols and did not display any change in capacity for all the discharge rates from 1C to 10C and for the number of cycles studied.

• The cells provide less than half the room temperature capacity at -30 deg C but the capacity does not show any degradation for the 50 cycles studied.

• The cells showed good performance under vacuum conditions and show a slight drop in capacity under vacuum conditions compared to that at ambient.

• Although the cells showed good tolerance to abuse as single cells, a string of 8 cells goes into thermal runaway during an overcharge test.
Wanma Performance Tests

Ch:C/2
D: 1C

4.8 Ah Cycle 1
4.1 Ah Cycle 250
Wanma Li-ion Pouch Cell Vacuum Exposure With Storage under Ambient

Voltage(V) vs. Discharge_Capacity(Ah)

- 15.9%
- 1%

Lines:
- Blue: Wanma JSC-W009 Pre Vac
- Pink: Wanma JSC-W009 Post Vac1
- Green: Wanma JSC-W009 Post Vac2
Wanma Li-ion Pouch Cell Vacuum Exposure With Storage under Ambient Unrestrained

- 33.5%
- 1.4%

Discharge_Capacity(Ah)

Voltage(V)

Wanma JSC-W011 Pre Vac
Wanma JSC-W011 Post Vac1
Wanma JSC-W011 Post Vac2
Pouch Material Cross-Section

Outside: Nylon 6 & with a possible Acrylic adhesive

Inside: Polypropylene

Wanma
Overcharge Test on Wanma Li-ion Pouch Cell

1C Overcharge
Limit: 12 V

All 3 samples vented violently with fire and thermal runaway
Wanma Li-ion Cell Test Summary

- Although all the tests for the Wanma cells have not been completed, the tests to date show that the cells lose about 16% capacity after 250 cycles at 1 C rate of discharge.
- The Wanma li-ion cells go into a thermal runaway at 1 C and 0.5 C rates of overcharge.
- The cells lose almost 50% capacity when cycled in an unrestrained mode under vacuum conditions.
Analysis of Pouch Materials from Different Manufacturers

Wanma
- Outside: Nylon 6 & with a possible acrylic adhesive
- Inside: Polypropylene

Tenergy
- Outside: Nylon 6
- Inside: Polypropylene

SKC 15 Ah
- Outside: Nylon 6
- Inside: Polypropylene

Altair nano 11 Ah
- Outside: Polyethylene terephthalate & Nylon 6
- Inside: Polypropylene
Summary

- Lithium-ion Pouch design cells are not true polymer cells.
- The li-ion pouch design cells exhibit similar behavior under off-nominal conditions as those in metal cans (that do not have the internal safety devices).
- The li-ion pouch cell designs react most violently to overcharge conditions.
- Some pouch cell designs have higher tolerance to vacuum exposures than some others.
- A comparison of the pouch material itself does not show a correlation between this tolerance and the number of layers or composition of the pouch indicating that this is a property of the electrode stack inside the pouch.
- Reduced vacuum (8 to 10 psi) test environments are currently being carried out and the results will be reported in the near future to determine if there is a higher tolerance to that environment.
Acknowledgment

Test Team Members:

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