LEO life tests of ABSL batteries using SONY 18650HC cells

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Test Objectives

• Status in 1999:

  – Ground tests show promising lithium ion battery performance for GEO and short-duration LEO applications but is cycle life sufficient for long-duration LEO?

  – Can batteries using SONY 18650 HC cells remain balanced in state of charge without need for balancing electronics even for long-duration LEO applications?

  – Will ‘graceful’ degradation predicted for such batteries happen in practice?
Overview

- **Part 1: Test Details**
  - Set-up and hardware
  - Profiles

- **Part 2: Test Results**
  - Battery level
  - Cell level
  - String capacities

- **Part 3: Result Investigation**
  - Follow-on investigations

- **Conclusions**
Test battery:
- 18Ah test module (6s12p) made up of two 6s6p physical modules
- Individual string current monitoring via 20 mohm shunts
- Individual cell voltage monitoring of every string. However, only one string can be measured at any single moment in time
- Early version of cell screening and matching. Criteria subsequently tightened up, and number of criteria expanded
• Cell layout and attachment similar to Proba-1 flight battery
• Board with shunts underneath each module
• Battery in environmental chamber at 20 deg. C with air flow from front module to back module.
• Thermistor attached to the top of a central cell in each module and to the side wall of the back module
• Temperature difference between modules representative of typical spacecraft situation
• Test profile to represent a typical LEO communications or earth-observation spacecraft
• 10 constant power discharge cycles with different depths of discharge in a ‘sequence’
• Sequence repeated but one hour rest introduced after every 30 sequences (300 cycles)
• Test accelerated – 900 minute LEO cycles compressed into 540 minute sequence
  – Constant charge current of C/4 to 25.2 V with 0.2 A taper steps
  – Shorter taper charge periods
• Relative to nameplate energy:
  – Maximum depth of discharge: 27.75 % (at BoL)
  – Average depth of discharge: 12.4 % (at BoL)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Battery Discharge power (Watt)</th>
<th>discharge duration [min]</th>
<th>Charge duration [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>136.8</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>136.8</td>
<td>19</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>136.8</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>208.8</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>208.8</td>
<td>19</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>208.8</td>
<td>31</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>136.8</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>136.8</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>136.8</td>
<td>14</td>
<td>46</td>
</tr>
<tr>
<td>10</td>
<td>136.8</td>
<td>10</td>
<td>36</td>
</tr>
</tbody>
</table>

1 hour rest every 30 sequences after deepest discharge
Non-ideal start of test

- Cell matching not as comprehensive as currently used
- Three capacity cycles at performed with end of discharge voltage at 12V instead of 15V. (0.6 C discharge rate.)
- String 1 only monitored - lowest cell voltage 1V
- No evidence of performance impact
  - Cell voltage spread at end of charge: <6 mV
  - At end of deepest discharge: <12 mV
- So cycling started as planned
• Eight years and 75,000 cycles later……

  – No string or cell failures yet
  – Cell voltage dispersion similar to other long-life tests in most strings
  – Three strings each containing one ‘anomalous’ cell which has dispersed from the others
  – Despite this, battery performance is much better than predicted by ABSL ‘LIFE’ model
  – Test on-going …
• In terms of Ah / BOL nameplate capacity maximum DoD increases with time from 28% to 31% as average discharge voltage drops.

• Temperature difference between modules max. 1deg.C (eod)

• In plots which follow note that cycle number = 10x sequence number
Significant life left in battery - EODV > 15V
Temperature jumps due to change of test chamber following breakdowns
Battery voltage prediction at 75,000 cycles

<table>
<thead>
<tr>
<th></th>
<th>LIFE</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>47% fade</td>
<td>37% fade*</td>
</tr>
<tr>
<td>Resistance</td>
<td>157% increase</td>
<td>38% increase</td>
</tr>
</tbody>
</table>

* Estimate based on measured strings
Battery-level observations

- Battery behaving better than predicted by ABSL LIFE model
  - Significant over-discharge before test started appears not to have impacted performance at battery level
- Previous LIFE predictions show excellent correlation with in-orbit data
  - e.g. on PROBA and Mars Express (refs 1 & 2)
- Reason for over-performance not yet properly understood
  - Extrapolation of model fade data to longer life
  - Result of battery not being fully recharged after every cycle?
  - LIFE assumes battery returns to full SOC after every discharge
  - Benefits of reduced EOCV described yesterday (ref. 3)
- Long-term variable DOD LEO predictions are shown to be conservative
Cell - level results

- Cell voltages can only be monitored one string at a time (to reduce the number of measurement channels required).

- Every few months the monitored string is changed every three days until all twelve strings have been monitored.

- During each 3 day period 100 mS current -interrupt resistance measurements are made on each cell during six successive sequences.

- Between these periods one string only is monitored.
• EOCVs remain very closely matched, as expected
  – Spread increased from 2 mV to 11 mV

• EODVs diverge slowly, as expected
  – Spread at (deepest) discharge from 9 mV to 157 mV
String 8 at 250 and 71110 cycles

Sequence 25 [Cycle 250]

Sequence 7111 [cycle 71110]
Anomalous strings (7, 9, 10)

- But …. three strings each have a single cell with anomalous behavior
- EOCV in a single cell drops – remaining cells overcharged to maximum 4.248V
- EODV of affected cell also drops

End of charge

End of (deepest) discharge

Weakest string (10) is still contributing 95% of the string average Ah
Average cell resistance during cycle versus cycle number

- Resistances increase very uniformly for most cells.
- Three cells show anomalous increases (not due to lower SoC).
- These are the same cells which show low end of charge voltages.

Resistances measured in discharge & charge during the deepest cycle in sequence and averaged over cycle.
String capacity measurements

- Battery capacity measured before start of cycling
- No further capacity measurements (representative of real missions)
- At cycle 73,335 strings isolated after deepest discharge (0.461 Ah/string)
- Capacity measurements performed on some separate strings
  - Typical strings 1,2,3,8
  - Strings with low-voltage cells 7,9,10
  - Other strings untested (as a ‘control’ for when test continues)
- Capacity measured by:
  - Continuing discharge until first cell in string reaches 2.5 V
  - In some cases continuing discharge was at 0.6C and others at constant power 11.4W (insignificant difference on result)
  - Continued discharge Ah added to 0.461 Ah
  - Capacity compared to average string BOL value
- Strings taper charged to 25.2 V (no cell SoC rebalancing), reconnected in parallel and cycling resumed
String capacity measurements

<table>
<thead>
<tr>
<th>String number</th>
<th>String Type</th>
<th>String Capacity (Ah)</th>
<th>% of average BOL capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Typical string</td>
<td>0.884</td>
<td>60.1%</td>
</tr>
<tr>
<td>2</td>
<td>Typical string</td>
<td>1.044</td>
<td>71.0%</td>
</tr>
<tr>
<td>3</td>
<td>Typical string</td>
<td>0.961</td>
<td>65.4%</td>
</tr>
<tr>
<td>7</td>
<td>String with low-voltage cell</td>
<td>0.794</td>
<td>54.0%</td>
</tr>
<tr>
<td>8</td>
<td>Typical string (lowest resistance string)</td>
<td>1.014</td>
<td>69.0%</td>
</tr>
<tr>
<td>9</td>
<td>String with low-voltage cell</td>
<td>0.870</td>
<td>59.2%</td>
</tr>
<tr>
<td>10</td>
<td>String with low-voltage cell</td>
<td>0.763</td>
<td>51.9%</td>
</tr>
</tbody>
</table>

- Of the strings tested:
  - Typical strings have capacities of 60 to 70% of BOL capacity
  - Strings with low-voltage cells have capacities of 50 to 60% of BOL
  - String 10 has the lowest capacity at 52% of starting capacity
String 10 cell voltages before and after capacity check

Sequence 7138 (Cycle 71,380)

Sequence 7356 (Cycle 73,560)

• Capacity measurement has not impacted voltages – test continuing
Investigation into low-voltage cells

- **Not linked to single event**
  - Cell voltage drops start at different times

- ** CAUSED by lack of self-discharge screening in 1999?**
  - Unlikely cause as 3 out of 72 cells represents a drop-out rate which is an order of magnitude higher than normal

- **Caused by poorer matching criteria tightened in 1999?**
  - Possible, but unlikely given good performance of typical strings

- **Initiated by initial over-discharge?**
  - Several plausible physical mechanisms
  - However, in String 1 (a ‘typical’ string) the most over discharged cells are not the worst performing – see next slide

- **Another hypothesis under investigation is that with ageing, negative electrodes become unable to support charge rates, causing weakest cells to plate lithium and drop in voltage**
String 1 results

- Only string 1 was monitored during initial capacity tests
- Cells 5 & 6 not overdischarged
- Other cells overdischarged to varying extents (but for < 3 minutes)
- Subsequent performance of string 1 has no relation to amount of overdischarge
- On the contrary, the least stressed cell (5) now has the worst performance!
- More severe overdischarge of some cells in other strings cannot be excluded
Application of cell model

- **ESA SONY 18650 cell model** (see refs. 4 & 5) has been verified for BoL cells and shown (ref. 6) to be capable of describing the behavior of aged cells with the following assumptions:
  - Electrode capacities decrease
  - Electrode EMF versus SoC doesn’t change
  - Ohmic and diffusion resistances increase

- **It was applied to the results of this test at two levels:**
  - Battery level (i.e applied to average cell behavior)
  - Individual cells in selected string

- **Each electrode divided into 8 slices**
  - Model gives state of charge of each slice of each electrode (in Ah relative to SoC at 4.2V taken as reference):
• During charge, SoC of negative electrode slice facing the separator can be greater than for fully charged cell in equilibrium (i.e. $A_{\text{hn}[1]} > 0$)
Polarization of negative electrode during charge

• This is possible because the slope of negative EMF versus SoC near full charge is much less than for the positive and the lithium diffusion rate in an electrode is proportional to this slope.

• As cells age the electrode capacity decreases and the diffusion resistance increases amplifying this effect for the same charge current.

• However, model fit to sequence 6000 (60,000 cycles) data shows that at full charge the negative electrode has lost 0.2 Ah of charge relative to the positive compared to a BoL cell.

• In following curves only the states of charge of the electrode elements facing the separator are shown.
Model of sequence 6000 (cycle 60,000)

- Model fit.

- What happens if we set negative SoC at 4.2 V to 0 instead of -0.2? …

- State of charge similar to sequence 30

Battery voltage: measured: red  model: blue

SoC of first negative electrode slice

SoC of first positive electrode slice

Negative slice overcharge!

NASA Aerospace Battery Workshop 27-29 Nov. 2007
On-going investigation

- With the reduction in electrode capacity and increase diffusion resistance with ageing, the negative electrode eventually may no longer support the charge current used in this test at all times during a sequence.

- This would result in lithium plating on the negative electrode.

- Some of this metallic lithium would disrupt the SEI and react irreversibly with the electrolyte and form an extra resistive layer, increasing the overall cell resistance.

- This ‘lost’ lithium must reduce the state of charge of the negative electrode relative to the positive.

- This analysis is still in progress ..... Update planned at the ESPC in September 2008!
Conclusions - this test

- Equivalent of more than 12 years LEO cycling demonstrated with a maximum depth of discharge around 30%.
- Battery performance better than predicted by ABSL “LIFE” model, despite initial overcharge.
- Three cells have fallen in end of charge voltage compared to the others in the string (but no strings have failed).
- This behaviour, which is absent in other comparable life tests may be the result of old cell matching procedures or the initial over-discharge though no direct evidence can be found for this.
- ESA battery model suggests that with ageing, negatives loose Li because of high state of charge of surface layer during charging.
- This could explain the observed ageing and also the low-voltage cells but more work including cell DPA is required to confirm the tentative conclusions as to the ageing mechanisms.
- The affected strings continue to contribute to the overall performance of the battery in a robust manner.
Conclusions - general

• Results show the very high level of robustness of these batteries despite:
  – Over-discharge of the battery during initial capacity measurements
  – The imbalance in three strings resulting from unusual behaviour of three cells

• Weakest cells drop in state of charge, reducing the stress level in the affected cell and transferring it to the other cells in the same string - an example of beneficial negative feedback!

• It is not obvious that any performance advantage would have been gained had cell SoC balancing been implemented in the battery

• We can already be confident that the ABSL SONY hard carbon cell batteries can support long-duration LEO missions without cell balancing and with graceful degradation
The ESBTC lab team is thanked for the careful running of this test over the past 8 years

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