Current Research – Safety, Design of Li-ion Cells and Modules

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Background

- Lithium ion batteries are being used in ground, aviation, space, sea, etc. applications in various sizes.
- Introduced in recent years into the utility/stationary energy storage industry.
- Tens of thousands to billions of cells manufactured for different types of applications from portable equipment to large ESS.
- Automotive batteries are being repurposed for utility/stationary storage applications.
- Questions arise on safety of used batteries.

- Challenge is to screen and match every individual cell.
  - Typical COTS and some custom battery manufacturing process does not include cell screening and matching.
  - Cells are assembled into batteries in the ‘as received” condition at lower SOC (typically 40%).
- Shipping/Transportation industry is facing major challenges in shipping lithium cells and batteries.

- Questions that arise:
  - Are cells or assembled batteries tested under relevant stringent conditions before they are transported or sent out into the field?
  - Does the safety change with cycle and calendar life (including storage)?
  - What parameters need to be characterized after first life and before installation in second life?
  - What parameters need to be studied closely during usage in second life?
  - Does safety change with state-of-charge? Can this factor be used for safe transportation?
  - Can one prevent cell to cell thermal runaway propagation?
  - Have fire suppressants been optimized for the various energy storage battery chemistries?
Li-ion Battery Designs and Challenges
Thermal Gradient and Safety are major Challenges

Low Voltage/ Low Capacity

High Voltage/High Capacity
Lithium-ion Cell Aging and Safety Research
Factors Affecting Aging and State of Health

Cycle Life

- Charge/Discharge Rate
- # of Cycles
- Usage Voltage Range
- Environmental Temperature
- Internal Temperature Gradient within a Battery
- Cell Uniformity within a Battery

Calendar Life

- Storage State of Charge
- Cell Uniformity within a Battery
- Storage and Usage Environmental Temperature
- Battery Management System

Safety

???
Aging Effects on Cell

• Lithiation and de-lithiation causes
  • Anode electrode morphology changes and volume changes – surface can form cracks leading to electrical isolation; delamination from current collector; changes in intercalation kinetics; loss of active lithium inside anode, etc.

• Decomposition
  • Binder and electrolyte; SEI decomposition; HF production, lithium side reaction with electrolyte; etc.

• Corrosion
  • Current collector, cell can materials, pouch cell swelling and shorting due to corrosion of pouch material, etc.

• Cathode changes
  • Structural disorder, metal dissolution, disproportionation, etc.
Cycle Life Aging and Simulated Internal Short Tolerance

- Cells were cycled at 1C rate of charge and discharge for 1000 cycles
  - Cells lost capacity between 12 to 25%
- Conducted Simulated Internal Short (SIS) tests (Crush test method) - Sample size – 10 cells
  - Tolerance to simulated internal shorts increased with higher loss in capacity – no fire or thermal runaway observed even with cells that lost greater than 19% capacity (SIS performed at 100% SOC); cells that lost between 12 to 16% capacity went into thermal runaway (SIS performed at 100 % SOC)
  - Note: All fresh cells at 100 % SOC when subjected to simulated internal short went into thermal runaway

Jeevarajan, et.al, The 2011 NASA Battery Workshop
Jeevarajan, et.al, Battery Safety 2012
Cycle Life Testing on Single 18650 Li-ion Cells - Capacity Trend

**Ba: 4.2 V to 2.7 V**

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Number of Cycles</th>
<th>Capacity Fade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba Cell 2</td>
<td>319</td>
<td>26.70 %</td>
</tr>
<tr>
<td>Ba Cell 1</td>
<td>300</td>
<td>24.23 %</td>
</tr>
<tr>
<td>Ba Cell 6</td>
<td>221</td>
<td>23.79 %</td>
</tr>
<tr>
<td>Ba Cell 5</td>
<td>222</td>
<td>22.97 %</td>
</tr>
<tr>
<td>Ba Cell 4</td>
<td>234</td>
<td>18.74 %</td>
</tr>
<tr>
<td>Ba Cell 8</td>
<td>201</td>
<td>16.21 %</td>
</tr>
<tr>
<td>Ba Cell 10</td>
<td>269</td>
<td>15.49 %</td>
</tr>
<tr>
<td>Ba Cell 3</td>
<td>201</td>
<td>15.41 %</td>
</tr>
<tr>
<td>Ba Cell 9</td>
<td>204</td>
<td>15.17 %</td>
</tr>
<tr>
<td>Ba Cell 7</td>
<td>174</td>
<td>10.59 %</td>
</tr>
</tbody>
</table>

**Bb: 4.0 V to 2.9 V**

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Number of Cycles</th>
<th>Capacity Fade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bb Cell 1</td>
<td>787</td>
<td>25.30 %</td>
</tr>
<tr>
<td>Bb Cell 2</td>
<td>785</td>
<td>25.29 %</td>
</tr>
<tr>
<td>Bb Cell 7</td>
<td>800</td>
<td>23.87 %</td>
</tr>
<tr>
<td>Bb Cell 8</td>
<td>640</td>
<td>20.11 %</td>
</tr>
<tr>
<td>Bb Cell 9</td>
<td>648</td>
<td>20.09 %</td>
</tr>
<tr>
<td>Bb Cell 10</td>
<td>616</td>
<td>15.65 %</td>
</tr>
<tr>
<td>Bb Cell 4</td>
<td>647</td>
<td>15.50 %</td>
</tr>
<tr>
<td>Bb Cell 6</td>
<td>324</td>
<td>15.44 %</td>
</tr>
<tr>
<td>Bb Cell 3</td>
<td>651</td>
<td>15.26 %</td>
</tr>
<tr>
<td>Bb Cell 5</td>
<td>267</td>
<td>14.94 %</td>
</tr>
<tr>
<td>Bb Cell 11</td>
<td>454</td>
<td>12.05 %</td>
</tr>
</tbody>
</table>
Cycle Life Testing on Single 18650 Li-ion Cells - Internal Resistance Trend

Ba: 4.2 V to 2.7 V
Bb: 4.0 V to 2.9 V

18% increase
14% increase

24% increase
30% increase

30% increase
20% increase

Ba9 CF = 10.64%
Bb6 CF = 10.26%

Ba10 CF = 15.49%
Bb10 CF = 15.65%
Faces 6 and 3 of the separator that faces the cathode have ceramic coating.

**Cycled Cells**

- **Cathodes**: 20%
- **Anodes**: 20%
- **External Short**: 20%
- **Overcharge**: 20%
Challenges with Cell Safety Features – Safety tests on fresh cells

Overcharged cell (fresh cell) with CID activation showing charring of electrodes

Cell header (underside) showing charring in overcharged fresh cell with CID activation (CID activation is fail-safe mode)

Anode of Fresh cell

Anode surface of fresh (not cycled) externally shorted and overcharged cells

Cells exhibited PTC and CID activation under external short and overcharge conditions respectively
State-of-Charge versus Thermal Runaway Research
State-of-Charge versus Thermal Runaway for Commercial Li-ion Cells

Accelerating Rate Calorimetry (ARC) Test

Heating Tape Test
Prevention of Thermal Runaway Propagation Research
Cell Spacing

Lopez, Jeevarajan, Mukherjee, manuscript submitted to Journal of the Electrochemical Society (2015)
Radiant Barrier Between Cells in a Module

Lopez, Jeevarajan, Mukherjee, manuscript submitted to Journal of the Electrochemical Society (2015)
Intumescent Materials for Prevention of Thermal Runaway Propagation

Lopez, Jeevarajan, Mukherjee, manuscript submitted to Journal of the Electrochemical Society (2015)
Fire Suppressant Research
Fire Extinguisher for Li-ion Fires

J. Jeevarajan (NASA Research)
Li-Ion Module Fire Suppression Experiments

### Experiment

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>(1 mm and 0 mm spacing)</td>
</tr>
<tr>
<td>N₂ Early release</td>
<td></td>
</tr>
<tr>
<td>N₂ Late release</td>
<td></td>
</tr>
<tr>
<td>Water Mist Early</td>
<td>(side) release</td>
</tr>
<tr>
<td>Water Mist Late</td>
<td>(side) release</td>
</tr>
<tr>
<td>Water Mist Early</td>
<td>(overhead)</td>
</tr>
<tr>
<td>Water Mist Late</td>
<td>(overhead)</td>
</tr>
<tr>
<td>Stat-X Early</td>
<td>release</td>
</tr>
<tr>
<td>Stat-X Late</td>
<td>release</td>
</tr>
</tbody>
</table>

**Venting and Thermal Runaway Detection Cues**

- Cell temperature
- Light attenuation (smoke)
- Pressure
- Module voltage
- Visual (initial rupture and thermal runaway)
Baseline Test
Late Release Water Mist

64x Real Time
Late Release Water Mist

- Late water mist: Suspect that thermal runaway may have affected two other cells.
- Flames inside box
## Summary of Test Results

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$T_{\text{rupture}}$</th>
<th>$T_{\text{thermal runaway}}$</th>
<th>Propagation beyond cell 1</th>
<th>Flame outside box?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>~133°C</td>
<td>~210 °C</td>
<td>Yes (all)</td>
<td>Yes; sustained fire</td>
</tr>
<tr>
<td>Water Mist Early (side)</td>
<td>~136°C</td>
<td>~200 °C</td>
<td>Yes (all)</td>
<td>Yes</td>
</tr>
<tr>
<td>Water Mist Late (side)</td>
<td>~137°C</td>
<td>~197 °C</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Water Mist Early (Overhead)</td>
<td>127</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Water Mist Late (Overhead)</td>
<td>134 °C</td>
<td>~194 °C</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>N$_2$ Early</td>
<td>~129°C</td>
<td>~190 °C</td>
<td>No</td>
<td>Small or no sparks</td>
</tr>
<tr>
<td>N$_2$ Late</td>
<td>~133°C</td>
<td>~200 °C</td>
<td>No</td>
<td>Small or no sparks</td>
</tr>
<tr>
<td>Stat-X Early</td>
<td>~127°C</td>
<td>~215 °C</td>
<td>Yes (all)</td>
<td>Yes – at beginning and end</td>
</tr>
<tr>
<td>Stat-X Late</td>
<td>~137°C</td>
<td>~210 °C</td>
<td>Yes (2)</td>
<td>Small sparks</td>
</tr>
</tbody>
</table>
Summary

• Research shows that safety and reliability of cells and batteries can change with aging – cycling and calendar life
  – Stringent characterization of cells and modules can predict signs of deviations from normal patterns and provide warning signs
• Study on state of charge versus thermal runaway failures indicates that lower states of charge does reduce the risks of thermal runaway.
• Study on prevention of thermal runaway propagation can be as simple as providing adequate space between cells in a module; in some cell designs as with cells with side vents, physical barriers will be required to prevent cell to cell thermal runaway propagation.
• Fire suppressant research study indicates that the nature of the fire suppressant and when the release of suppressant occurs are critical; in addition, the suppressant must be present in the vicinity of the trigger cell to prevent a re-ignition of fire from the trigger cell.
THANK YOU.