Reliability and Degradation Analysis of Energy Storage

Presented by
Summer Ferreira – Sandia National Laboratories
Goals

- Understand degradation of DC components and AC modules under laboratory and grid duty cycles
- In parallel with field deployed system, enable testing under controlled and accelerated conditions - develop State of Health Model
- Develop in-situ “state-of-health” sensors and feedback to controls to prolong lifetime.
- Develop standardized testing protocols for industry specific to reliability.
PNNL and Sandia Capabilities

Sandia Battery Test Facility

- New 7000 Sq Ft facility for analysis within spec
  - 350+ test channels
  - R&D 100 awarded high precision testers
  - 70+ thermal chambers - -72°C - 95°C
- Center for Integrated Nanotechnology for spectroscopy
- Abuse facilities for failure analysis Explosive Test Complex

PNNL Energy Storage Reliability Laboratory

- 7.6 kW Inverter
- Li-ion 9.8 kWh
- 9.6 kWh Na-NiCl₂
- 10 kWh Flow
  - Paired with 12 kW inverter
  - Cycled using battery cycler
System Selection Has Much to Consider

Problem:
Performance and safety data
  - Primarily manufacturer-provided data

Chemistry Selection for an ESS installation must consider

- Cost
- Size
- Safety
- Application
- Reliability
- Oversizing
- Manufacturer reputation
- Performance
- Pack management

Approach:
Quantify performance with uniform methodology
Evaluate fundamentals of material stability
Determine battery failure scenarios and mechanisms
Validate battery fire suppression techniques
Historical testing at cell and module level

**Cell Level Testing**
- East Penn Advanced Battery Cells
- Altairnano Lithium-titanate oxide cells
- International Battery Li-FePO₄ Cells

**Module Level Testing**
- East Penn Ultrabattery Modules
- RedFlow 10kWh Zn-Br flow battery module
- Furukawa Ultrabattery Modules
We Test a Variety of Technologies

Altairnano Lithium-titanate Gen 1 11 Ah Gen II 13 Ah and 60 Ah

A123 14 Ah cells

LiFe Battery Lithium-Fe 20 AH

International Battery 160 Ah Li-FePO₄ Cells

RedFlow 10kWh Zn-Br flow battery module and system

Encell Ni-Alkaline Battery

East Penn Ultrabattery
## Current Work on Commercial Lithium Ion Chemistries

<table>
<thead>
<tr>
<th>Cathode Chemistry</th>
<th>AKA</th>
<th>Specific Capacity (Ah)</th>
<th>Average Potential (V vs Li⁰/Li⁺)</th>
<th>Max Discharge Current</th>
<th>Acceptable Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>LCO</td>
<td>2.5</td>
<td>3.6</td>
<td>20</td>
<td>0 to 50</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>LFP</td>
<td>1.1</td>
<td>3.3</td>
<td>30</td>
<td>-30 to 60</td>
</tr>
<tr>
<td>LiNiₓCoᵧAl₁₋ₓ₋ᵧO₂</td>
<td>NCA</td>
<td>2.9</td>
<td>3.6</td>
<td>6</td>
<td>0 to 45</td>
</tr>
<tr>
<td>LiNi₀.₈₀Mn₀.₁₅Co₀.₀₅O₂</td>
<td>NMC</td>
<td>3.0</td>
<td>3.6</td>
<td>20</td>
<td>-5 to 50</td>
</tr>
</tbody>
</table>

**Diagram:**

- **LCO**
- **LFP**
- **NCA**
- **NMC**

**Graph:**

- **Discharge Current (A)**
  - Operating Temperature (°C)
  - Range: -40 to 70
  - Discharge Current Range: -10 to 40 A
Lithium ion batteries store energy

Charging

Fragment of the nanostructured cathode material LiFePO₄
LiPF₆ based electrolyte
Carbon anode material

Discharging
Aging Behavior and Abuse Response of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions

**Aging Study Design**

<table>
<thead>
<tr>
<th>Variable</th>
<th>LFP (LiFePO₄)</th>
<th>NCA (LiₓCoₓAlₓ−ₓO₂)</th>
<th>NMC (LiₓNiₓMnₓCoₓ−ₓO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge Rate*</td>
<td>C/2</td>
<td>1C</td>
<td>2C</td>
</tr>
<tr>
<td>State of Charge Range</td>
<td>40-60%</td>
<td>20-80%</td>
<td>0-100%</td>
</tr>
<tr>
<td>Environment Temperature</td>
<td>15°C</td>
<td>25°C</td>
<td>35°C</td>
</tr>
</tbody>
</table>

**Overall Outcomes**

**Influence of Different Variables**

**Safety of Aged Cells**

- Pair of cells at < 80% capacity
- Disassembly at 50% SoC
- Accelerated rate calorimetry (ARC) at 50% SoC
- XRD, TGA-DSC, SEM
Cycling data for each chemistry is coalesced on one plot.

Discharge current

Corresponds to red LCO

@ 25 °C

Segmented discharging began at 45 °C
Degree of capacity loss varies with temperature, current, and chemistry

- No temperature effects at currents $\leq 10$ A
- Higher temperature = less capacity loss

Although manufacturer specifications allow battery operation at certain conditions, the battery may not perform well.
NCA experiences lasting capacity losses after cycling

**Diagram a:**
- **LCO**
- Fraction of initial capacity vs. temperature and current density

**Diagram b:**
- **LFP**
- Profound reversible losses

**Diagram c:**
- **NCA**
- Some irreversible loss
- Capacity loss at 5°C

**Diagram d:**
- **NMC**
- 

Some irreversibl e loss
Capacity loss at 5 °C
Significant self-heating can occur if cells are unmonitored.

- LCO: ~80 °C
- LFP: ~90 °C
- NCA: ~80 °C
- NMC: ~90 °C
Determining tradeoffs is clearer with a comprehensive performance evaluation.
Stacked Waveform Testing – approaching realistic uses

2.2 Multi-Application Control for Distributed CES Units

Figure 2-4 Load Leveling

Figure 2-5 Frequency Regulation Cycle Profile

Figure 2-6 Test Cycle - SOC

Figure 2-6 Multi-application Load Profile
Table 2-2 shows the power and energy allocations for a 25kW / 3-hour CES unit. The graph illustrates the DCH Capacity (normalized) across different months, with lines representing Peak Shaving, Frequency Regulation, Unused Operation Margin, and Margin. The graph shows the decrease in DCH Capacity over time, with a noticeable reduction in capacity for Peak Shaving compared to Frequency Regulation and Unused Operation Margin. The margin remains consistent throughout the months.
Cells are highly application-specific

- Technology selection should include more than cost
  - Performance under ambient conditions
  - Cycle life
  - Reliability
  - Efficiency
  - Safety

- This work can extend to include other relevant chemistries and cell formats
  - Need to confirm lab results with scale up and system performance
  - Build more complex profiles, and also employ modeling
  - Check results with demonstration data
$dQ/dV$ elucidates key reactions/changes

- graphite
- stage I: LiC$_6$
- stage II: LiC$_{12}$
- stage III: LiC$_{18}$

Fully charged:

- carbon layer
- lithium layer

New peak shape

Charge

Discharge

Potential (V)
Insights into Source of Variation

## Application-Specific Recommendations

<table>
<thead>
<tr>
<th>Cell</th>
<th>Capacity (Ah)</th>
<th>Voltage (V)</th>
<th>Max Dsch Current (A)</th>
<th>Max Temp (°C)</th>
<th>Recommended Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO</td>
<td>2.5</td>
<td>3.6</td>
<td>20</td>
<td>50</td>
<td>Over entire discharge current range while maintained in a 15 °C environment</td>
</tr>
<tr>
<td>LFP</td>
<td>1.1</td>
<td>3.3</td>
<td>30</td>
<td>60</td>
<td>Under a flexible temperature range at discharge currents of 10A or below.</td>
</tr>
<tr>
<td>NCA</td>
<td>2.9</td>
<td>3.6</td>
<td>6</td>
<td>45</td>
<td>Over entire discharge current range while maintained in a 15 °C environment</td>
</tr>
<tr>
<td>NMC</td>
<td>3.0</td>
<td>3.6</td>
<td>20</td>
<td>50</td>
<td>Over entire discharge current range while maintained in a 15 °C (&lt; 10A) or 35 °C (&gt; 10A) environment</td>
</tr>
</tbody>
</table>