Li-ion Battery Chemistries under Grid Duty Cycles

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Standard grid service test procedures

Cell performance and degradation analyses
  • 6 months (180 days) of continuous test results
  • Cylindrical cell (18650 & 26650) from 4 different vendors
  • 3 different battery chemistries
    - LFP: LiFePO$_4$
    - NMC: LiNi$_x$Mn$_y$Co$_2$O$_2$
    - NCA: LiNi$_{0.85}$Co$_{0.1}$Al$_{0.05}$O$_2$

Post-mortem cell characterization (XPS)

Conclusion

Future work

Poster Session: Battery Reliability Laboratory at PNNL
Battery Test Method

- **Variables**
  - Time: 24h grid cycle (1day)
  - State-of-Charge (SOC): 20~80%
  - Depth of Discharge (DOD or ΔSOC): 20, 40, 60%
  - Power (C-rate): within cell specifications (voltage window)
  - Temperature: 25°C
  - Number of cells: 3 under same test condition (total: 156 cells)

- **Schedules (# of conditions)**
  - BS: Baseline (3) – holding (aging) at different SOC levels
  - FR: Frequency Regulation (4)
  - PS: Peak Shaving (3)
  - EV: Electric Vehicle (3)
Testing Methods

State of Charge (SOC)

BS 70
BS 50
BS 30

FR d20
FR d40
FR d60

PS d20
PS4 d20

EV d20
EV4 d20

Cell Temperature (°C)

NCA
LFP

Days

Testing Methods

BS 70
BS 50
BS 30

FR d20
FR d40
FR d60

PS d20
PS4 d20

EV d20
EV4 d20

Cell Temperature (°C)

NCA
LFP

Days
Degradation Trends

- Capacity degrades with higher SOC level aging
- LFP aging degradation is the lowest
- FR, PS and EV show similar degradation rate
- NMC (3.2 and 3.0Ah) cell show different degradation behavior

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<tr>
<th>Scenario</th>
<th>Capacity Loss</th>
<th>Change Resistance</th>
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<td>BS</td>
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<td>PS</td>
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**Change per Day**

- LFP (2.6Ah)
- NMC (3.2Ah)
- NCA (3.2Ah)
- NMC (3.0Ah)
FR service utilizes more energy per degradation rate
Capacity Loss Trends

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</tbody>
</table>

Scenario:
- BS SOC30 d20
- BS SOC50 d20
- BS SOC70 d20
- EV SOC80 d20
- EV SOC80 d60
- EV4 SOC80 d20
- FR LP SOC80 d20
- FR SOC80 d20
- FR SOC80 d40
- FR SOC80 d60
- PS SOC80 d20
- PS SOC80 d60
- PS4 SOC80 d20

Capacity Loss Trends over Days
- 180 days of continuous frequency regulation service cycles ΔSOC 60%.
- NMC & NCA: the cathode degrades faster than the graphite anode.
- LFP: Lithium loss.
Ref) A.J. Crawford et al., “Lifecycle comparison of selected Li-ion battery chemistries under grid and electric vehicle duty cycle combinations”, J. Power Sources 380 (2018) 185–193
LFP cells have better aging, capacity, and energy retention.

Frequency regulation degrades the least per energy utilized.

Even with a same battery chemistry, cycling stability varies with cell engineering.

dV/dQ analyses can be used for in-situ battery health monitoring.

Higher SOC level degrades the battery the most.

Cathode dissolution occurs for NCA and NMC cells.
Future Work

- Test methods developed here will be applied to larger energy storage modules and systems including Li-ion, lead acid, high temperature sodium and flow batteries.

- For better understanding the dV/dQ analyses, three-electrode setup for cylindrical cell will be implemented to separate cathode and anode voltage profiles and capacities using Li metal as a reference.

- Additional 192 test channels will be installed with temperature and impedance monitoring.

- Post-mortem cell characterization will be conducted using advanced techniques.
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