Cycle Life Prediction for NCM-Composite/Graphite Lithium Ion Battery Cells

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Life Modeling of NCM Composite/Graphite Cell: Mechanical & Chemical Degradation

Outline:

1. Overview of matrix testing

2. Develop of model
   1. Chemical degradation (temperature and time)
   2. Mechanical fatigue (rate and # of cycles)

3. Summary

18650 cylindrical Sanyo/Panasonic cell
Cathode (Positive) Chemistry: \( \text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3} \) (L333) + LiMn\(_2\)O\(_4\)
Anode (Negative) Chemistry: graphite
# Cycling Test Matrix

## 60 Test Conditions (120 cells)

- Two cells are tested at each condition
- Temperature: 10°C to 46°C
- Discharge rates: C/2 to 6.5C
- Depth of Discharge, DOD 10% to 90%
- For modeling work, only consider the 50% DOD results

### Table

<table>
<thead>
<tr>
<th>DoD</th>
<th>10°C</th>
<th>22°C</th>
<th>34°C</th>
<th>46°C</th>
<th>Rate</th>
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<td>90</td>
<td>90</td>
<td>90</td>
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<td>50</td>
<td>50</td>
<td>50</td>
<td>0.5C</td>
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<td>10</td>
<td>10</td>
<td>2C</td>
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<tr>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>2C</td>
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<tr>
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<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>2C</td>
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<td>50</td>
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<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>3.5C</td>
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<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>3.5C</td>
</tr>
<tr>
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<td>90</td>
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<td>90</td>
<td>90</td>
<td>5C</td>
</tr>
<tr>
<td>70</td>
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<td>70</td>
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<td>50</td>
<td>50</td>
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<td>30</td>
<td>30</td>
<td>6.5C</td>
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<td>10</td>
<td>10</td>
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<td>10</td>
<td>6.5C</td>
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<tr>
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<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>6.5C</td>
</tr>
</tbody>
</table>
**Testing and Characterization Protocols**

**Beginning of Life (BOL) full characterization**
- Capacity Test
- HPPC

**weekly C/2 capacity**

**Life test cycling at given test condition**
- Temperature
- Discharge C-rate
- Charge C-rate

**full characterization**
- Capacity Test
- HPPC

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weekly C/2 Capacity</td>
<td>Fully discharge cell to 2.5V at C/2 rate.</td>
</tr>
<tr>
<td>Full characterization</td>
<td>Charge the cell to 4.2V; hold until the current drops below C/20 (max 48 hrs). Charge &amp; discharge the cell twice at C/20, C/2, 3C. The cycle ends with a discharge.</td>
</tr>
</tbody>
</table>
Understanding Capacity Loss Mechanisms
Calendar Loss vs. Cycle Loss

Number indicates % loss/1000 cycles

<table>
<thead>
<tr>
<th>Rate</th>
<th>0.5C</th>
<th>2C</th>
<th>3.5C</th>
<th>5C</th>
<th>6.5C</th>
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</thead>
<tbody>
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<td>90</td>
<td>5.0</td>
<td>4.5</td>
<td>6.3</td>
<td>13</td>
<td></td>
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<tr>
<td>50</td>
<td></td>
<td></td>
<td>4.1</td>
<td>4.7</td>
<td>12.2</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>5.6</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>13.5</td>
<td>5.7</td>
<td>5.9</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>18.5</td>
<td>7.4</td>
<td>6.6</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>28.0</td>
<td>11.7</td>
<td>10.4</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>28.0</td>
<td>11.7</td>
<td>10.4</td>
<td>18.5</td>
<td></td>
</tr>
</tbody>
</table>

Temperature Effects:
Calendar Life Loss ↔ Chemical Degradation

Rate Effects:
Cycle Life Loss ↔ Mechanical Degradation

Loss increases with temp
High loss at high T
Dominated by chemical degradation
Dominated by mechanical degradation
Chemical Degradation – SEI Formation

Continuous SEI Growth

Assume diffusion through SEI is rate-determining process

Parabolic film growth (\( \sim \sqrt{t} \))

This is why very low rates of lithium-consuming reactions can lead to premature cell failure

Importance of Coulombic efficiency (\( \eta_i \))

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( Ah_0 \times \eta_i )</td>
</tr>
<tr>
<td>2</td>
<td>( (Ah_0 \times \eta_i) \times \eta_i )</td>
</tr>
<tr>
<td></td>
<td>( \downarrow )</td>
</tr>
<tr>
<td>( N )</td>
<td>( Ah_0 \times (\eta_i)^N )</td>
</tr>
</tbody>
</table>

For \( N=5000 \) cycles, and \( \eta_i=0.99994 \), capacity retention is \( \eta_i^{5000} = 0.75 \)
Mechanical Degradation in Li-ion Batteries

Analogy to fatigue in materials

- Rapid Li\(^+\) discharge generates tensile stress at surface
- Repeated charge/discharge cycles → fatigue stress
Mechanical Fatigue in Graphite Anode Particles

Conditions for fatigue
1. Maximum tensile stress is sufficiently large ($\sigma_{\text{max}}$)
2. Large fluctuation in applied stress ($\Delta \sigma$)
3. Large number of cycles ($N$)

Paris’ Law:
- Edge crack in large plate
- Uniaxial tensile stress

$$\frac{dL}{dN} = k \left( \sigma_{\text{max}} b \sqrt{\pi L} \right)^m$$

Estimating $\sigma_{\text{max}}$ in graphite particles by linear elastic theory\(^1\)
- Galvanostatic discharge conditions
- Isotropic, spherical graphite particle
- Long time limit ($t > R^2/D$)

$$\sigma_{\theta,\text{max}} = \frac{1}{15} \frac{E \Omega}{(1 - \nu)} \left( \frac{iR}{FD} \right)$$

Parameter | Value
--- | ---
$D$ | $1 \times 10^{-13}$ m$^2$/s
$R$ | 5 µm
$\nu$ | 0.27
$\Omega$ | 3.3 cm$^3$/g
$E$ | 15 GPa

Partial molar volume of Li solute in LiC$_6$

R$^2$/D = 250 sec (~4 min)

Lithium inventory model

• Slow SEI growth (~$\sqrt{t}$) on initial graphite surface area ($dQ/dN_{\text{chemical}}$)
• SEI formation on new graphite surface areas exposed by growth of surface cracks through mechanical fatigue
• Relies on an estimate of Li density of the SEI layer (take the average of LiF and Li$_2$CO$_3$, result = 79 mol$_{\text{Li}}$/L).
# Summary of Model

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Formula</th>
<th>Adjustable Parameters</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crack growth</td>
<td>( \frac{dL_{cr}}{dN} = k(\sigma_{\theta,\text{max}} b \sqrt{\pi L_{cr}})^m )</td>
<td>( k, m )</td>
<td>Edge crack in large plate ( b = 1.12 )</td>
</tr>
<tr>
<td>SEI growth</td>
<td>( L_{SEI} = K_{th} \sqrt{t} )</td>
<td>( K_{th} )</td>
<td>Consistent with both empirical and simulated results</td>
</tr>
</tbody>
</table>

Two parameters \((k, K_{th})\) are temperature-dependent, but rate-independent.

A single value of \( m = 2.2 \) works for all temperatures.

We only consider life testing data at a single depth of discharge (DOD=50%) when fitting the model.
Capacity Fade During Cycling at 10°C, 5C rate

T = 10°C

Cycle Conditions:
- Charge: 2C
- DischG: 5C

**Li losses:**

- **SEI deposited on new surfaces**
  - Surface area increases from 10 m²/g to 20 m²/g
  - Consumes Li

- **Thickness increase of original SEI layer**
  - SEI thickness increases from 1.4 nm to 2.5 nm
  - Consumes Li
Capacity Fade at 46°C and 3.5 C rate

- Thickness increase of original SEI layer
  - SEI increases from 1.4 nm to 4.3 nm

- SEI deposited on new surfaces
  - *Surface area* increases form 10 m²/g to 11.7 m²/g
Comparison of model to measured capacity fade

Model is consistent with extreme cycling conditions:
1. low temperature & high rate
2. high temperature & low rate
Large increase in $k$ at low temperature may indicate:
1. Ductile-to-brittle transition of polymeric component of (composite) SEI layer
2. Slower solid-state Li diffusion in graphite increases strain/stress
Rate Capability After Extended Cycling

(BOL) 0 Cycles

Discharge Rate:
- C/20
- C/3
- 3C

Capacity (Ah)

Voltage (V)

6415 cycles

Discharge rate:
- C/20
- C/3
- 3C

Capacity (Ah)

Voltage (V)

Rate Capability:
\[
\frac{Q_{C/20} - Q_{3C}}{Q_{C/20}} \times 100
\]

\(Q_{C/20} = C/20\) capacity

\(Q_{3C} = 3C\) capacity
Rate Capability After Cycling L333 Cells At Different Rates/Temperatures

When cells are cycled at 10°C, the C-rate has a large impact on the evolution of rate capability.
Summary

- Accelerated capacity fade is observed for cells cycled at low temperature (10°C) and fast discharge (5C, 6.5C).
- Apparently caused by mechanical degradation of electrode material, coupled with loss of usable Li.

- Model for Li loss (inventory)
  1) Original SEI layer slowly increases according to $\sqrt{t}$ parabolic film growth
  2) Cracks in graphite particle grow due to mechanical fatigue (repeated Li intercalation/de-intercalation)
  3) New surface area consumes usable Li

- With this approach, we predict capacity fade during cycling over wide operating ranges from 10°C/6.5C to 46°C/0.5C
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