Life Prediction Model for Grid-Connected Li-ion Battery Energy Storage System

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Applications of Energy Storage (ES) on the Grid

Focus of present ES system life study

Batteries can provide up to 13 services to three stakeholder groups.

Figure credit: Rocky Mountain Institute
Example Application: Behind-the-meter ES enables PV use in locations such as Hawaii (where power export is prohibited)

Figure: "Solar Plus: An Holistic Approach to Distributed Solar PV" Eric O'Shaughnessy, Kristen Ardani, Dylan Cutler, Robert Margolis (NREL Pub #68371)
Outline

• Degradation mechanisms
• Modeling approach
• Aging tests
• Model and parameter identification
• Example life prediction
Li-ion Working Principles

Neg. Electrode
Graphite
Hard carbon
Silicon
Titanate
Li metal

Pos. Electrode
LiXO$_2$,
$X =$ NiMnCo
  Co
  NiCoAl
LiMn$_2$O$_4$,
LiFePO$_4$

Figure credit: Gi-Heon Kim
Electrochemical Operating Window

Potential vs. Li (V)

SOC

U+

U−

Cobalt Oxide

Graphite

Potential measured at cell terminals

Figure credit:
Ilan Gur (ARPA-E) & Venkat Srinivasan (LBNL), 2007

(x in LiₓC₆ or y in Li₁-0.6yCoO₂)

Potential measured at cell terminals

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(x in LiₓC₆ or y in Li₁-0.6yCoO₂)
Electrochemical Window – Degradation

Figure: Ilan Gur (ARPA-E) & Venkat Srinivasan (LBNL) 2007

Cycling at
- High T & high DOD
- Low T, & high C-rate

Cycling at low T, & fast charging

Time at high SOC & T. Accelerated with DOD

Potential vs. Li (V)

SOC

(x in Li_xC_6 or y in Li_1-0.6yCoO_2)
Reduced-order models for physical fade mechanisms, e.g.

- SEI growth & damage
- Particle fracture
- Electrode isolation
- Electrolyte decomposition
- Gas generation, delamination
- Li plating

Semi-automated software aids model equation selection and parameter identification

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### Table: NREL Battery Life Predictive Model Framework

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Trajectory equation</th>
<th>State equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion-controlled reaction</td>
<td>$x(t) = k t^{3/2}$</td>
<td>$\dot{x}(t) = k \frac{2}{ \text{x}(t) }$</td>
<td>$k$ - rate (p=1/2)</td>
</tr>
<tr>
<td>Kinetic-controlled reaction</td>
<td>$x(t) = k t$</td>
<td>$\dot{x}(t) = k$</td>
<td>$k$ - rate (p=1)</td>
</tr>
<tr>
<td>Mixed diffusion/kinetic</td>
<td>$x(t) = k t^p$</td>
<td>$\dot{x}(t) = k p \frac{1}{2} \left( \frac{k}{ \text{x}(t) } \right)^{1/2}$</td>
<td>$k$ - rate p - order, $0.3 &lt; p &lt; 1$</td>
</tr>
<tr>
<td>Diffusion controlled reaction with mechanical damage</td>
<td>See Appendix A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclic fade - linear</td>
<td>$x(N) = k N$</td>
<td>$\dot{x}(N) = k$</td>
<td>$k$ - rate (p=0)</td>
</tr>
<tr>
<td>Cyclic fade - accelerating</td>
<td>$x(N) = \left[ x_0^{1-p} + k x_0^p (1+p) N \right]^{1-p}$</td>
<td>$\dot{x}(N) = k \left( \frac{x_0}{x(N)} \right)^p$</td>
<td>$k$ - rate p - order, $0 &gt; p &gt; 3$</td>
</tr>
<tr>
<td>Break-in process</td>
<td>$x(t) = M (1 - \exp(-k t))$ or $x(N) =$</td>
<td>$\dot{x}(t) = k (M - x(t))$</td>
<td>$M$ - maximum fade $k$ - rate</td>
</tr>
<tr>
<td>Sigmoidal reaction</td>
<td>$x(t) =$</td>
<td>$x(N) =$</td>
<td></td>
</tr>
</tbody>
</table>

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Model assumes measured capacity is minimum of:

1. Cycleable lithium, $Q_{Li}$
2. Negative electrode sites, $Q_{neg}$
3. Positive electrode sites, $Q_{pos}$
Aging tests – Kokam 75Ah Gr/NMC Li-ion cells

- **Tests design to include both benign and highly accelerated aging**
  - Some real-world, some reaching 30% capacity fade in 6-9 months
- **Pure storage (0%), partial cycling (50% DC*), & fully accelerated cycling (100% DC)**
  - Separate calendar from cycling fade
- **Capacity check run at test temperature**
  - Simplifies testing but makes model ID more difficult
- **Ideal test matrix would include more aging conditions**

### Cycling tests

<table>
<thead>
<tr>
<th>Temperature</th>
<th>DOD</th>
<th>Dis./charge rate</th>
<th>Duty-cycle*</th>
<th># of cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>80%</td>
<td>1C/1C</td>
<td>100%</td>
<td>2</td>
</tr>
<tr>
<td>30°C</td>
<td>100%</td>
<td>1C/1C</td>
<td>100%</td>
<td>1</td>
</tr>
<tr>
<td>30°C</td>
<td>80%</td>
<td>1C/1C</td>
<td>50%</td>
<td>1</td>
</tr>
<tr>
<td>0°C</td>
<td>80%</td>
<td>1C/0.3C</td>
<td>100%</td>
<td>2</td>
</tr>
<tr>
<td>45°C</td>
<td>80%</td>
<td>1C/1C</td>
<td>100%</td>
<td>1</td>
</tr>
</tbody>
</table>

### Storage tests

<table>
<thead>
<tr>
<th>Temperature</th>
<th>SOC</th>
<th># of cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>100%</td>
<td>1</td>
</tr>
<tr>
<td>45°C</td>
<td>65%</td>
<td>1</td>
</tr>
<tr>
<td>45°C</td>
<td>100%</td>
<td>1</td>
</tr>
<tr>
<td>55°C</td>
<td>100%</td>
<td>1</td>
</tr>
</tbody>
</table>

Gr = Graphite negative electrode  
NMC = Nickel-Manganese-Cobalt positive electrode
C/5 Capacity vs. Time

- Tight agreement for replicate cells 1&2 at 23°C
- Some divergence for replicate cells 6&7 at 0°C
- Unexplained temporary capacity increase for 55°C storage cell
C/5 Capacity vs. Cycles

- Storage data omitted
- Just 6% capacity loss after 3000 cycles at 23°C, 80% DOD
Capacity Evolution—Reversible and Irreversible

**State**

- $Q_{Li}$
- $Q_{Neg}$
- $Q_{Pos}$

**Mechanism**

0) Temperature (reversible)

1) SEI growth $\sim t^{1/2}$

2) Cycling fatigue $\sim N$

3) Break-in
   a) Damage $\sim 1 - \exp(-\lambda t)$
   b) Increase $\sim 1 - \exp(-\lambda \Delta t)$

**Dependence on operating condition**

- Temperature
  \[ \exp \left( -\frac{E_a}{R_{\text{eff}}(T(t))} \right) \]
- State of charge
  \[ \exp \left( \frac{a_{\text{ref}} F \eta(t)}{R_{\text{ref}} T(t)} \right) \quad \eta = U_\text{ref} - U_{\text{ref}} \]
- Depth-of-discharge
  \[ (1 + \theta DOD_{\text{max}}) \exp \left[ \eta (DOD_{\text{max}}) \right] \]
  \[ (DOD)^\beta \exp \left[ \eta (DOD_{\text{max}}) \right] \]
- C-rate
  \[ \frac{C_{\text{rate,2}}}{\sqrt{C_{\text{rate,1}}}} \]
- Electrochemical
  \[ \eta = U_\text{ref} - U_{\text{ref}} - C_\text{rate} R_{\text{film}} \]

Neglect due to insufficient data (present application $\leq 1C$)
**$Q_{pos}$ Capacity Break-in & Initial Temperature Dependence**

- Hypothesize initial cycles induce microcracks in NMC particles, increasing electrolyte wetting and surface area

\[
Q_{pos} = d_0 + d_3 \left(1 - \exp\left(-A h_{dis} / 228\right)\right)
\]

\[
d_0 = d_{0,ref} \left[\exp\left(-\frac{E_a d_{0,1}}{R_g T_{RPT}(t)} - \frac{1}{T_{ref}}\right) - \left(\frac{E_a d_{0,2}}{R_g T_{RPT}(t) - T_{ref}}\right)^2\right]
\]

*Image: Dean Miller & Daniel Abraham, Argonne National Laboratory*
QLi Local Models

- **Local models**: Separately fit $b_0$, $b_1$, $b_2$ for each data set, excluding
  - First 50 days of data (allows y-intercept to vary with break-in)
  - Knee at $0^\circ$C (to be captured later with $Q_{\text{neg}}$ model)

\[
Q_{Li} = d_0 \left[ b_0 - b_1 t^{1/2} - b_2 N \right]
\]

- Choice of mechanisms justified by $R^2=0.990$ and flat residuals
**Q_{Li}** Magnitude of break-in Li-loss

**Local model**

\[ Q_{Li} = d_L \left[ b_0 - b_1 t^{1/2} - b_2 N \right] \]

- Least degraded cells show ~3-4% excess Li capacity
- High temperature causes rapid loss in first 50 days
  - Open-circuit voltage and DOD also increase loss
  - Evidence of film layer formation at positive electrode?

**b_0 magnitude model**

\[
y_0 - b_3 \left( 1 - \exp\left( -t / \tau_{b_3} \right) \right) = b_{3,\text{ref}} \exp \left[ -\frac{E_a b_b}{R_{\text{opt}}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right) \right] \exp \left[ \frac{\alpha_{b_b} F (V_{\text{OC}}(t) - V_{\text{ref}})}{R_{\text{opt}} \left( T(t) - T_{\text{ref}} \right)} \right] (1 + \theta \text{ DOD}_{\text{max}})
\]
**Local model**

\[ Q_{Li} = d_0 \left[ b_0 - b_1 t^{1/2} - b_2 N \right] \]

\[ Q_{Li} \text{ Calendar fade rate} \]

**Visualization of rates suggests rate model equations**

**Fitted rate model parameters provide initial guess for global model parameters**
QLi Global Model

- With equations known, parameters fit to all data simultaneously
- \( R^2 = 0.985, \text{ RMSE } = 1\% \text{ of capacity, flat residuals} \)

\[
Q_{Li} = d_0 \left[ b_0 - b_1 t^{1/2} - b_2 N - b_3 \left(1 - \exp(-t/\tau_{b3})\right)\right]
\]

\[
b_1 = b_{1,\text{ref}} \exp\left[ -\frac{E_{a,b}}{R_{ag}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right) \right] \exp\left[ \frac{\alpha_b F (U_{\text{OC}}(t) - U_{\text{ref}})}{T(t)} \right] \exp\left[ \gamma_b (DOD_{\text{max}})^{\beta_b} \right]
\]

\[
b_2 = b_{2,\text{ref}} \exp\left[ -\frac{E_{a,b}}{R_{ag}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right) \right]
\]

\[
b_3 = b_{3,\text{ref}} \exp\left[ -\frac{E_{a,b}}{R_{ag}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right) \right] \exp\left[ \frac{\alpha_b F (V_{\text{OC}}(t) - V_{\text{ref}})}{T(t)} \right] (1 + \theta DOD_{\text{max}})
\]
**Q\textsubscript{Neg} Model**

- Captures **knee** with cold temperature cycling
- Minor importance in most real-world scenarios

\[ \frac{dQ_{\text{neg}}}{dN} = \left( \frac{c_2}{Q_{\text{neg}}} \right) \]

\[ Q_{\text{neg}} = \left[ c_0^2 - 2c_2c_0N \right]^{\frac{1}{2}} \]

\[ c_0 = c_{0,\text{ref}} \exp \left[ \frac{E_{a,c0}}{R_{\text{eg}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right)} \right] \]

\[ c_2 = c_{2,\text{ref}} \exp \left[ \frac{E_{a,c2}}{R_{\text{eg}} \left( \frac{1}{T(t)} - \frac{1}{T_{\text{ref}}} \right)} (\text{DOD})^{\beta_2} \right] \]
Life-time analysis – PV self consumption

- Model reformulated in rate-based form
- SOC(t) discretized into microcycles, DOD\textsubscript{i}, using Rainflow algorithm
- Application data
  - Multi-year, 4-season simulation
  - Same cycle each
- Impact of DOD and thermal management

\textbf{Graphs:}

- Cell current (A)
- SOC
- T (°C)
- Voltage

\textbf{Graphs:}

- Time (years)
- Depth of discharge (%)
- Years to 70% of nameplate, winter season

\textbf{Thermal management:}

- 20°C < T\textsubscript{cell} < 30°C
- 5°C < T\textsubscript{cell} < 35°C
Conclusions

• Battery energy storage can enable increased integration of renewable power generation on the grid

• Battery life modeling methodology formalized, aiding systems design process
  o Capacity error: \( L_2 = 1\%, \ L_\infty = 5\% \)
  o For studied Gr/NMC Li-ion ES technology, best to restrict daily cycles < 55% DOD with occasional larger excursions
  o Thermal management extends life from 7 to 10 years

• Battery aging experiments are time consuming & expensive

• Additional model validation needed
  o Longer duration
  o Variable cycling & temperature

• Life model accuracy may be enhanced in the future by coupling with electrochemical modeling & diagnostics
Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Program
- SunPower Corporation
Extra Slides
Previous Validation of Life Model

Cell-level aging tests
Prognostic model characterization

Eaton Corp. ARPA-E AMPED project resulting in 35% smaller HEV battery (PI: Dr. Chinmaya Patil/Eaton)

Pack-level HIL tests
HEV prognostic control algorithm validation

Model tuned to 6 months simple cell aging data matches 33 months 4-season cycling with same accuracy