Modeling of Nonuniform Degradation in Large-Format Li-ion Batteries

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Background

• Context: Trend towards larger cells
  – Higher capacity applications (HEV → PHEV → EV)
  – Reduced cell count reduces cost & complexity
  – Drawback: Greater internal nonuniformity
    • Elevated temperature,
    • Regions of localized cycling \rightarrow Degradation

• Objectives
  – Understand impact of large-format cell design features on battery useful life
  – Improve battery engineering models to include both realistic geometry and physics
  – Reduce make-and-break iterations, accelerate design cycle
Overview

• Previous work
• Multiscale approach
  – Multidimensional echem/thermal model
  – Coupled with empirical degradation model
• Empirical degradation model
  – NCA chemistry
  – Degradation factors: $t^{1/2}$, $t$, # cycles, $T$, $V$, $\Delta DOD$
  – Impedance growth, capacity loss
• Modeling investigation of nonuniform degradation
  – 20 Ah cell
  – Accelerated cycling for PHEV10-type application
Some previous work

- Multidimensional Li-ion cell modeling
  - Thermal only, w/ uniform heat generation (Chen 1994)
  - 2-D echem model of Li-plating (Tang 2009)
  - 2-D echem/thermal w/simplified geometry (Gu 1999)
  - 2-D & 3-D multiscale electrochemical/thermal models (Kim & Smith 2008-2009)

- Li-ion degradation modeling
  - Physical corrosion/SEI growth (Ramadass 2002; Christensen 2004)
  - Physical cycling stress/fracture (Christensen 2006; Sastry 2007)
  - Empirical corrosion & cycling stress model (Smith 2009)

Present work couples the underlined models above.
Multiscale approach for computational efficiency

- Length scales:
  1) Li-transport (1~100 μm)
  2) Heat & electron transport (<1~20 cm)
Multiscale approach for computational efficiency

- **Length scales:**
  1) Li-transport (1~100 μm)  
  2) Heat & electron transport (<1~20 cm)

- **Time scales:**
  1) Repeated cycling profile (minutes)  
  2) Degradation effects (months)*

* Neglects sudden degradation caused by misuse (Li plating, overdischarge/charge, etc.)
Empirical Degradation Model*

* Presented in full :

Model fit to Li-ion carbon/NCA cell data from the following :
Accurate life prediction must consider both storage and cycling degradation effects

Storage (Calendar) Fade
- Typical \( t^{1/2} \) time dependency
- Arrhenius relation describes \( T \) dependency

Cycling Fade
- Typical \( t \) or \( N \) dependency
- Often correlated \( \log(\# \text{ cycles}) \) with \( \Delta \text{DOD} \) or \( \log(\Delta \text{DOD}) \)

Source: V. Battaglia (LBNL), 2008

Source: John C. Hall (Boeing), IECEC, 2006.

Source: Christian Rosenkranz (JCS/Varta) EVS-20
Impedance growth mechanisms: Complex calendar and cycling dependency

NCA chemistry: Different types of electrode surface film layers can grow
(1) SEI film  (2) Solid surface film

SEM Images: John C. Hall, IECEC, 2006.

Cell stored at 0°C

- SEI film
  - grows during storage $\alpha t^{1/2}$
  - suppressed by cycling

Cell cycled 1 cycle/day at 80% DOD

- Solid surface film
  - grows only with cycling $\alpha t$ or $N$
Impedance (R): Cycling at various ΔDODs

*Fitting t^{1/2} and N components*

- Simple model fit to cycling test data: Boeing GEO satellite application, NCA chemistry
- Model includes $t^{1/2}$ (~storage) and N (~cycling) component

$$ R = a_1 t^{1/2} + a_2 N $$

(Note: For 1 cycle/day, N = t)

**Curve-fit at 51% ΔDOD:**
- $a_1 = 1.00001e-4$ Ω/day^{1/2}
- $a_2 = 5.70972e-7$ Ω/cyc
- $R^2 = 0.9684$

4.0 EoCV Data: John C. Hall, IECEC, 2006.
Impedance (R): Cycling at various ΔDODs

Fitting $t^{1/2}$ and $N$ components

- Simple model fit to cycling test data: Boeing GEO satellite application, NCA chemistry
- Model includes $t^{1/2}$ (~storage) and $N$ (~cycling) component

$$R = a_1 \ t^{1/2} + a_2 \ N$$

(Note: For 1 cycle/day, $N = t$)

<table>
<thead>
<tr>
<th>ΔDOD</th>
<th>$a_1$ ($\Omega/day^{1/2}$)</th>
<th>$a_2$ ($\Omega/cyc$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>68%</td>
<td>9.54812e-7</td>
<td>5.70972e-7</td>
<td>0.9667</td>
</tr>
<tr>
<td>51%</td>
<td>1.00001e-4</td>
<td>1.00001e-4</td>
<td>0.9684</td>
</tr>
<tr>
<td>34%</td>
<td>9.54812e-7</td>
<td>9.54812e-7</td>
<td>0.94928</td>
</tr>
<tr>
<td>17%</td>
<td>7.53354e-7</td>
<td>7.53354e-7</td>
<td>0.9174</td>
</tr>
</tbody>
</table>

4.0 EoCV Data: John C. Hall, IECEC, 2006.
Impedance (R): Cycling at various ΔDODs
Capturing parameter dependencies on ΔDOD

\[ R = a_1 t^{1/2} + a_2 N \]

**Additional models are fit to describe** \( a_1 \) **and** \( a_2 \) **dependence on ΔDOD.**

High \( t^{1/2} \) resistance growth on storage is suppressed by cycling

**High-DOD cycling grows resistance** \( \alpha N \)

**Low-DOD cycling reduces resistance** \( \alpha N \)

\[ a_1 = b_0 + b_1 (1 - \Delta \text{DOD})^{b_2} \]
\[ R^2 = 0.9943 \]

\[ a_2 / a_1 = c_0 + c_1 (\Delta \text{DOD}) \]
\[ R^2 = 0.9836 \]

\( a_2 < 0 \) not physically realistic. An equally statistically significant fit can be obtained enforcing constraint \( a_2 > 0. \)
Impedance: Cycling at various $\Delta$DODs

Example model projections

\[ R = a_1 t^{1/2} + a_2 N \]
\[ a_1 = b_0 + b_1 (1 - \Delta\text{DOD})^{b_2} \]
\[ a_2 / a_1 = \max[0, c_0 + c_1 (\Delta\text{DOD})] \]

4.0 EoCV Data: John C. Hall, IECEC, 2006.

Distinctly different trajectories result from storage, severe cycling and mild cycling.
Impedance: Voltage and temperature acceleration

• Increased impedance growth due to elevated voltage & temperature fit using Tafel & Arrhenius-type equations

• Dedicated lab experiments required to fully decouple voltage-$\Delta$DOD relationship

Data: John C. Hall, IECEC, 2006.

\[
a_1 = a_{1,\text{ref}} k_1 \exp(\alpha_1 F/RT \times V)
\]
\[
a_2 = a_{2,\text{ref}} k_2 \exp(\alpha_2 F/RT \times V)
\]

\[
k_1 = k_{1,\text{ref}} \exp(-E_{a1} \times (T^{-1} - T_{\text{ref}}^{-1}) / R)
\]
\[
k_2 = k_{2,\text{ref}} \exp(-E_{a2} \times (T^{-1} - T_{\text{ref}}^{-1}) / R)
\]

• This work assumes values for $k_1$ & $\alpha_1$.
• Activation energies, $E_{a1}$ and $E_{a2}$, are taken from similar chemistry.
Li-ion (C/NCA) degradation model summary

Impedance Growth Model

- Temperature
- Voltage
- ΔDOD
- Calendar Storage ($t^{1/2}$ term)
- Cycling ($t$ & $N$ terms)

Capacity Fade Model

- Temperature
- Voltage
- ΔDOD
- Calendar Storage (Li loss)
- Cycling (Site loss)

**Dependencies from impedance growth model**

$$R = a_1 t^{1/2} + a_{2,t} t + a_{2,N} N$$

$$Q_{Li} = d_0 + d_1 (a_1 t^{1/2})$$

$$Q_{sites} = e_0 + e_1 (a_{2,t} t + a_{2,N} N)$$

$$Q = \min(Q_{Li}, Q_{sites})$$

$$a_1 = a_{1,ref} k_1 \exp\left(\frac{\alpha_1 F}{RT} \times V\right)$$

$$a_2 = a_{2,ref} k_2 \exp\left(\frac{\alpha_2 F}{RT} \times V\right)$$

$$k_1 = k_{1,ref} \exp\left(-\frac{E_{a1} (T^{-1} - T_{ref}^{-1})}{R}\right)$$

$$k_2 = k_{2,ref} \exp\left(-\frac{E_{a2} (T^{-1} - T_{ref}^{-1})}{R}\right)$$

$$a_{2,t} = a_2 (1 - \alpha_N)$$

$$a_{2,N} = a_2 \alpha_N$$

Reasonably fits available data

Actual interactions of degradation mechanisms may be more complex.
Modeling Investigation of Nonuniform Degradation
Modeling investigation: Accelerated cycling of 20 Ah PHEV-type cylindrical cell

- **Cell Dimensions**: 48 mm diameter, 120 mm height
  - Well designed for thermal & cycling uniformity, low capacity fade rate
- **Thermal**: 30°C ambient, $h = 20 \text{ W/m}^2\text{K}$
- **ΔDOD**: 90% $\text{SOC}_{\text{max}}$ to 30% $\text{SOC}_{\text{min}}$
- **Accel. Cycling**: Various discharge (shown below), 10 min rest, 1C charge, 60 min rest, repeat.

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**Constant Current Discharge**

- Voltage (V) vs. Time (minutes)
- SOC (%) vs. Time (minutes)

**US06 Power Profile Discharge**

- Power (W) vs. Time (minutes)
- SOC (%) vs. Time (minutes)
Capacity fade & resistance growth for various repeated discharge profiles (1C, 5C, 10C, US06)
Capacity fade & resistance growth for various repeated discharge profiles (1C, 5C, 10C, US06)

- No accelerating trend observed for low-rate 1C discharge cycles
- Clear accelerating trend observed for high-rate US06 and 10C cases
Temperature rise due to resistance growth accelerates degradation for high-rate US06 & 10C cycling cases

- Significant growth in internal temperature during US06 and 10C discharge cycling
- Internal temperature remains ~constant for 1C discharge cycling
US06 – Nonuniform capacity loss

- Regions near terminals suffer most significant capacity loss
  Large overpotential → Excessive cycling
- Inner core loses capacity faster than outer cylinder wall
  High temperature → Material degradation

0 months:
(No degradation)

8 months:

16 months:
**US06 – Ah imbalance (nonuniform cycling)**

*Preferentially cycled regions shift early in life*

*Imbalance continually grows throughout life*

0 months: 0.7% Ah Imbalance

8 months: 1.7% Ah Imbalance

16 months: 4.8% Ah Imbalance

- Early in life, inner core and terminal areas are cycled the most

- Later in life, those same areas are most degraded and are cycled least
US06 Ah imbalance: Effect of uniform temperature

Multidimensional model rerun with temperature fixed to a spatially averaged value taken from nonuniform temperature simulations (previous slide)

0 months:
0.4% Ah Imbalance
(vs. 0.7% for nonuniform T)

8 months:
0.4% Ah Imbalance
(vs. 1.7% for nonuniform T)

16 months:
1.7% Ah Imbalance
(vs. 4.8% for nonuniform T)

• More clearly shows how degradation proceeds from terminals inward
• Compared with nonuniform temperature simulations …
  • Significantly reduces Ah imbalance (this slide)
  • But measured cell-level impedance and capacity will fade faster (next slide)
Nonuniform degradation effects important for predicting cell performance fade

- Lumped temperature model overpredicts cell level fade
  (1-D echem/thermal model also overpredicts fade)

- Illustrates strong coupling between multidimensional degradation and cell performance
Conclusions

For 20 Ah cylindrical cell with good thermal & cycling uniformity at beginning of life...

• **Imbalance grows throughout life** (T, Ah throughput, capacity loss)
• **Acceleration mechanism** apparent for high-rate cycling cases:
  • Higher impedance $\rightarrow$ Higher temperature $\rightarrow$ Faster degradation
• **Major factors leading to nonuniform degradation**
  • Nonuniform temperature (degrades inner core)
  • Nonuniform potential (degrades terminal regions)
• **Regions heavily used at beginning of life** (inner core, terminal regions) are used less and less as life proceeds
• **1-D echem/lumped thermal model not suited** to predict performance degradation for large cells
  • For a given electrode-level degradation mechanism, overpredicts cell-level capacity fade and impedance growth