Advanced Models and Controls for Prediction and Extension of Battery Lifetime

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**Multi-Scale Multi-Domain (MSMD) model**

- Inter-domain coupling of field variables, source terms
- Efficient, flexible framework for physics expansion
- Leading approach for large-cell computer-aided engineering models

Life-predictive model

- Physics-based surrogate models tuned to aging test data
- Implemented in system design studies & real-time control
- Regression to NCA, FeP, NMC chemistries

NCA = Nickel-Cobalt-Aluminum
FeP = Iron Phosphate
NMC = Nickel-Manganese-Cobalt

**Calendar fade**
- SEI growth
- Loss of cyclable lithium
- Coupled with cycling
  \[ a_1, b_1 = f(\Delta \text{DOD}, T, V_{0C}, \ldots) \]

**Cycling fade**
- Active material structure degradation and mechanical fracture
  \[ a_2, c_2 = f(\Delta \text{DOD}, T, V_{0C}, \ldots) \]

Relative Resistance
\[ R = a_1 t^z + a_2 N \]

Relative Capacity
\[ Q = \min \left( Q_{Li}, Q_{\text{sites}} \right) \]
\[ Q_{Li} = b_0 + b_1 t^z + \ldots \]
\[ Q_{\text{sites}} = c_0 + c_2 N + \ldots \]
Challenges and Needs for Life/Degradation Models

Challenges:

• No standard process for life certification
• Predictive models must consider some 5 to 10 coupled degradation mechanisms
  o Electrochemical/thermal/mechanical mechanisms not yet fully understood or modeled
• Lifetime uncertainty absorbed in excess design and warranty costs of xEV battery systems

Needs:

• Predict lifetime more accurately, with less test data
  o Critical to capture accelerating fade effects nearing end-of-life
• Provide engineering feedback for cell, pack and system control designs
Outline

• Models
  o Surrogate life models (cell level)
  o Physics life models (cell level)
  o System life (pack level)

• Lifetime extension
  o Thermal control
  o Charge control
  o Cell electrochemical-based control
  o Active cell balancing
  o Prognostic-based supervisory control
Models

• **Surrogate life models (cell)**
  - Present state of art for lifetime prediction
  - Ranking of importance of mechanical-coupled degradation mechanisms on electrode site-loss

• **Physics life models (cell)**
  - Coupling of solid mechanics with electrochemical/thermal physics

• **System life (pack)**
  - Vehicle & pack thermal models
  - Cell performance & aging process variation
NREL Life Predictive Model

### Calendar fade
- SEI growth
- Loss of cyclable lithium
- Coupled with cycling
- \( a_1, b_1 = f(\Delta \text{DOD}, T, V_{oc}, ...) \)

### Cycling fade
- Active material structure degradation and mechanical fracture
- \( a_2, c_2 = f(\Delta \text{DOD}, T, V_{oc}, ...) \)

### Relative Resistance
\[ R = a_1 t^z + a_2 N \]

### Relative Capacity
\[ Q = \min (Q_{\text{Li}}, Q_{\text{sites}}) \]
- \( Q_{\text{Li}} = b_0 + b_1 t^z + ... \)
- \( Q_{\text{sites}} = c_0 + c_2 N + ... \)

- Statistical regression to experimental data
- Correct separation of calendar vs. cycling mechanisms
- In rate form, extensible to untested scenarios

- \( r^2 = 0.942 \)

- Data: J.C. Hall, IECEC, 2006.

- Arrhenius-Tafel-Wohler model describing \( a_2(\Delta \text{DOD}, T, V) \)
NREL Life Model Framework

Data

A. Resistance growth during storage
   Broussely (Saft), 2007:
   - T = 20°C, 40°C, 60°C
   - SOC = 50%, 100%
B. Resistance growth during cycling
   Hall (Boeing), 2005-2006:
   - DoD = 20%, 40%, 60%, 80%
   - End-of-charge voltage = 3.9, 4.0, 4.1 V
   - Cycles/day = 1, 4
C. Capacity fade during storage
   Smart (NASA-JPL), 2009
   - T = 0°C, 10°C, 23°C, 40°C, 55°C
   - Broussely (Saft), 2001
   - V = 3.6V, 4.1V
D. Capacity fade during cycling
   Hall (Boeing), 2005-2006: (see above)

Regression of candidate models

1. Fit local model(s)
2. Visualize rate-dependence on operating condition
3. Hypothesize rate-law(s)
\[ \theta_r = \exp \left( - \frac{E_a}{RT} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right) \]
\[ \theta_r = \exp \left[ \frac{\alpha R}{T(t)} \left( \frac{V_\infty(t) - V_{ref}}{T_{ref}} \right) \right] \]
\[ \theta_{\Delta DoD} = \left( \frac{\Delta DoD}{\Delta DoD_{ref}} \right)^{\beta} \]
4. Fit rate-laws(s)
5. Fit global model(s)

Predictive model

Model selection based on statistics

<table>
<thead>
<tr>
<th>#</th>
<th>Storage Model</th>
<th>Parameters</th>
<th>RMSE (% capacity)</th>
<th>R2</th>
<th>Adjusted R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>( q = 1 + b_1 T^{0.5} )</td>
<td>b1(T,Voc)</td>
<td>2.06</td>
<td>0.925</td>
<td>0.923</td>
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<td>8</td>
<td>( q = 1 + b_1 T )</td>
<td>b1(T,Voc, z)</td>
<td>2.01</td>
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<td>0.926</td>
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<td>9</td>
<td>( q = 1 + b_1 T )</td>
<td>b1(T,Voc, z(T))</td>
<td>2.03</td>
<td>0.925</td>
<td>0.925</td>
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<td>( q = 1 + b_1 T^{0.5} + b_2 T )</td>
<td>b1(T,Voc), b2</td>
<td>1.99</td>
<td>0.930</td>
<td>0.927</td>
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<tr>
<td>11</td>
<td>( q = 1 + b_1 T^{0.5} + b_2 T )</td>
<td>b1(T,Voc), b2(T)</td>
<td>2.00</td>
<td>0.931</td>
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<td>( q = 1 + b_1 T^{0.5} + b_2 T )</td>
<td>b1(T,Voc), b2(T,Voc)</td>
<td>1.87</td>
<td>0.941</td>
<td>0.935</td>
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</tbody>
</table>
Knee in Fade Critical for Predicting End of Life

Example simulation: 1 cycle/day at 25°C

50% DOD: Graceful fade (controlled by lithium loss)

80% DOD: Graceful fade transitions to sudden fade ~2300 cycles

Life over-predicted by 25% without “knee”

Hypothesis based on analysis of aging data: Transition from Li loss (chemical w/ weak mech. coupling) to site loss (mechanical)
Sources of Mechanical Stress in Li-ion Cells

- Current Collector (Cu)
- Current Collector (Al)
- Negative Electrode
- Positive Electrode
- Li⁺
- e⁻
- Li⁰
- CoO₂
- Electrolyte
- Intercalation Strains
- Thermal Strain
- Binder/Separator Swelling
- Residual stresses of manufacturing
- Winding Tension
- External Loads, Cell Packaging
- Separator Visco-Elastic Creep
- Fracture
- Delamination

- cell
- electrode
- particle
# Open Areas in Mechanics Modeling

1) **At which length-scale do stresses most impact battery life, e.g.:**
   - Particle-level fracture
   - Active material bulk expansion/contraction
   - Thermal expansion/contraction
   - Polymer creep (binder, separator)

2) **Optimal packaging of jellyroll (esp. pouch cells)**
   - Performance
   - Lifetime

3) **Multi-scale linkage to 3D automotive cell level**
   - Grains $\rightarrow$ particles $\rightarrow$ particles + PVDF + carbon black $\rightarrow$ composite electrode $\rightarrow$ neg./sep./pos. electrode sandwich $\rightarrow$ jellyroll $\rightarrow$ cell
   - Accompanying property measurement

4) **Linkage of mechanical stress with life (capacity, resistance)**
Active Site Loss Visible in Cell Aging Data

- Iron-phosphate meta-dataset combines tests from multiple labs – 50+ tests
- In “knee-region” of capacity fade data below, graphite site loss (mechanical process) has exceeded Li loss (predominantly chemical process)
Mechanical Stress Effects Contributing to Active Site Loss

Dependence on operating parameters:

- C-rate (intercalation gradient strains)
- DOD (bulk intercalation strains)
- Low T (exacerbates Li intercalation gradients)
- High T (exacerbates polymer creep of binder, separator)
- ΔT (thermal strains)
Hypothesized Active Site Loss Model

\[ q = \min(q_{Li}, q_{sites}). \]

\[ q_{Li} = b_0 + b_1 t^z + b_2 N \]

\[ q_{sites} = c_0 + c_2 N \]

\[
c_2 = c_{2,ref} \exp\left(-\frac{E_a^{\text{binder}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)[m_1 \Delta \text{DOD} + m_2 \Delta T] + m_3 \exp\left(-\frac{E_a^{\text{intercal.}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)\left(\frac{C_{\text{rate}}}{C_{\text{rate,ref}}}\right)\left(\sqrt{\frac{t_{\text{pulse}}}{t_{\text{pulse,ref}}}}\right)\right].
\]

- Accelerated polymer failure at high T
- Bulk intercalation strain
- Bulk thermal strain
- Intercalation gradient strain, accelerated by low temperature

Model successfully describes 13 aging conditions from 0°C to 60°C
Bulk Strains Show Strongest Correlation with Capacity Fade in Knee Region

Contribution to active site loss
(23°C, 1C, 100% DOD reference condition)

Important factors to capture in 3D CAE models to optimize cell lifetime, mechanical constraint

MSU/Xiao (2011)

Princeton/Peabody (2014)
**Objective:** Create cell design tool to predict lifetime, optimize mechanical packaging of large format cells

Multi-layer Li-ion battery discretized with solid shell elements

**Approach:**
- NREL MSMD Electrochemical/Thermal
- CU–Boulder Solid Mechanics
• $\Delta$SOC & $\Delta$T dependent stress (cell level) more significant contributor to capacity loss than diffusion-induced gradients (particle level)

• CU-Boulder and NREL developed multi-physics 3D model of commercial pouch cell

• Calibrated model versus electrical/thermal performance and measured changes in cell thickness with SOC, T, age

• Largest stresses at edge of electrode stack with separator wind

• Non-negligible in-plane displacements

• More significant stress/strain effects induced by electrochemical/thermal bulk changes rather than 3D gradients across the cell

• Temperature rise from electrochemical/thermal model important for capturing magnitude of mechanical strain
Capturing Vehicle & Ambient Impacts on Life

Vehicle thermal model fit to 3 days of Gen II Prius data recorded in Golden, CO in winter

Same model predicts Prius battery temperature fluctuation in Phoenix, AZ

- Winter: within $\frac{1}{2}$ °C
- Summer: within 1°C
  (Passenger cabin fluctuations within 6°C)
• Ambient conditions dominate
• Thermal connection with passenger cabin, parking in shaded structures strongly influence battery life

• Battery temperature and lifetime weakly coupled to ambient conditions
PHEV Life Variability – Phoenix, Arizona

Simulation of 782 drive cycles. Error bars show 5\textsuperscript{th} to 95\textsuperscript{th} percentile drive cycles

**Lifetime Variation**

- Drive cycle/annual mileage: $\pm 25$
- Value of chilled liquid vs. forced air battery thermal management:
  - PHEV10: +34\%
  - PHEV40: +42\%
  (equates to $500-600$ savings in reduced pack total energy at $300$/kWh)
- Frequent charging:
  - PHEV10: -8\% (more cycles)
  - PHEV40: +4\% (shallower cycles)
Sub-Ambient Standby Cooling Topologies

- Options: Chilled liquid, air, refrigerant evaporative plate or thermoelectrics (TE)
- Shown here: TE device on busbars
Optimized Charging Strategies

- Reduce time spent at high SOC (delay charging)
- Avoid high C-rates to lower peak temperatures

CU-Boulder/Hoke (2014)
Optimized Charging Strategies

A) Constant energy cost

- Delayed charging best
- No V2G energy exported until electricity price $0.50/kWh

B) Variable energy cost

- Response to price signals

Begin charge  End charge  Begin charge  End charge
ARPA-E AMPED: Battery Management

Advanced Management and Protection of Energy Storage Devices

• Develop advanced sensing and control technologies to provide new innovations in safety, performance, and lifetime for grid-scale and vehicle batteries.

Eaton Corporation

**Project:** Downsized HEV pack by 50% through enabling battery prognostic & supervisory control while maintaining same HEV performance & life

**NREL:** Life testing/modeling of Eaton cells; controls validation on Eaton HEV packs

Utah State/Ford

**Project:** 20% reduction in PHEV pack energy content via power shuttling system and control of disparate cells to homogenous end-of-life

**NREL:** Requirements analysis; life model of Ford/Panasonic cell; controls validation of Ford PHEV packs

Washington Univ.

**Project:** Improve available energy at the cell level by 20% based on real-time predictive modeling & adaptive techniques

**NREL:** Physics-based cell-level models for MPC; implement WU reformulated models on BMS; validate at cell & module level
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