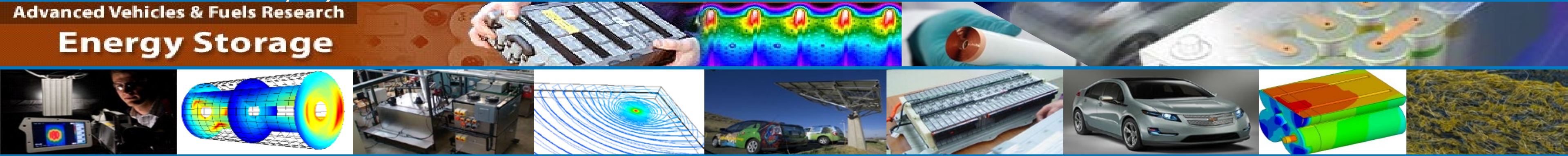

Predictive Models of Li-ion Battery Lifetime

Kandler Smith, Ph.D.
Eric Wood, Shriram Santhanagopalan, Gi-Heon Kim, Ying Shi, Ahmad Pesaran
National Renewable Energy Laboratory
Golden, Colorado

Advanced Automotive Battery Conference &
Large Li-ion Battery Technology & Application Symposium
Detroit, Michigan• June 15-19, 2015

NREL/PR-5400-64622

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Collaborators

- Texas A&M: Prof. Partha Mukherjee & team
- Utah State: Prof. Regan Zane & team
  - Ford: Dyche Anderson; UCCS: Plett & Trimboli; CU-Boulder Maksimovic
- Eaton Corporation: Dr. Chinmaya Patil & team

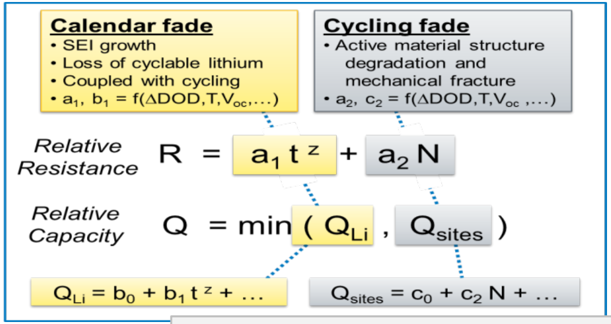
Outline

- Analysis of degradation mechanisms
- Modeling of particle fracture physics
- Cell-level prognostic control
- Pack-level prognostic control

NREL Battery Life Prognostic Model

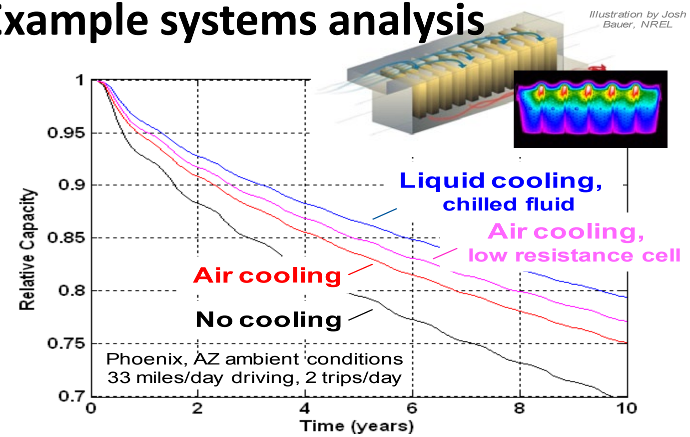
- Physics-based surrogate models regressed to aging test data
  - Li loss (SEI growth + cycling damage)
  - Site loss (initial damage + continuous fatigue)
  - Electrolyte decomposition
- Typical error across 20-50 test conditions
  - Capacity: 3-4%
  - Resistance: 6-12%
  - → Similar error for independent validation cases
- Next slides show examples for iron-phosphate (FeP) 2.3 Ah cell from A123

Example equations



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

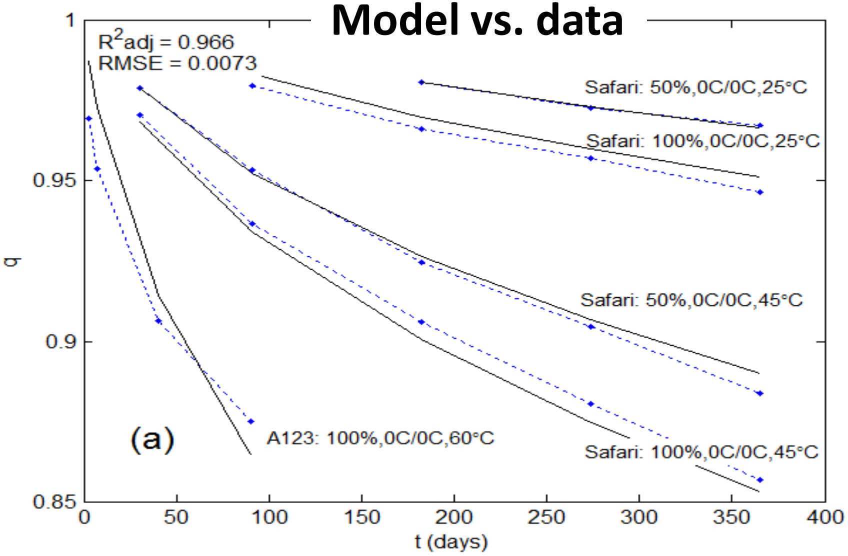
Example systems analysis



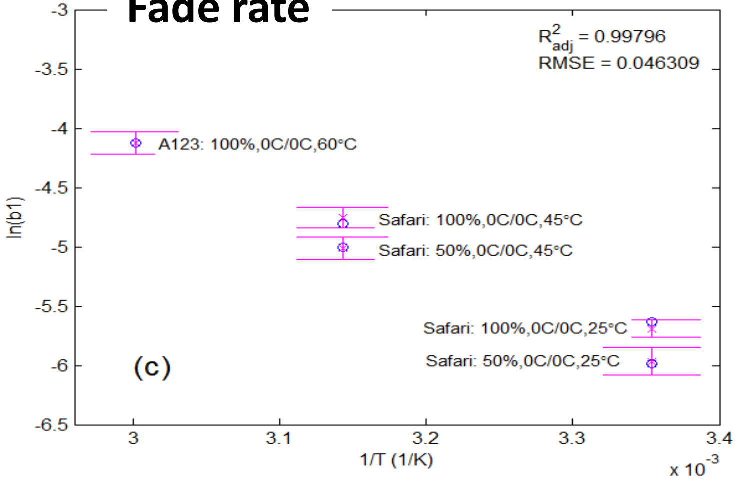
Calendar/storage fade

- **Li loss/SEI growth model[1] captures $t^{1/2}$ fade with rate dependent on**
  - Temperature
  - Negative electrode equilibrium potential

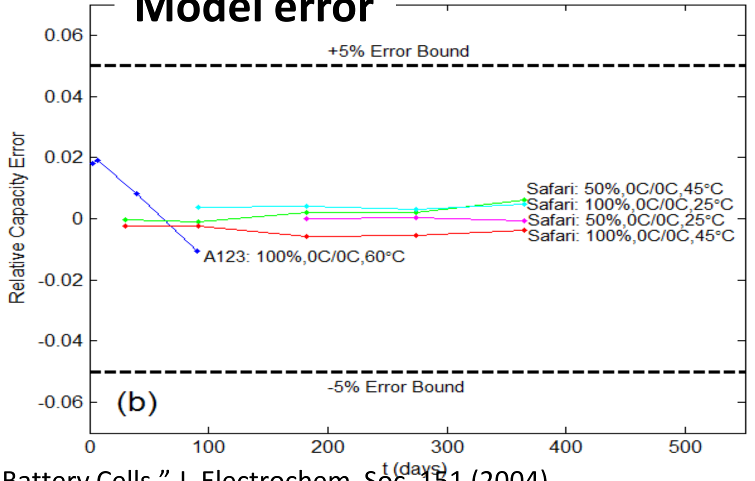
Model vs. data



Fade rate



Model error



1. H.J. Ploehn, P. Ramadass, R.E. White, "Solvent Diffusion Model for Aging of Lithium-Ion Battery Cells," J. Electrochem. Soc. 151 (2004).

Coupled calendar/cycle life-predictive models

1. Additive Model (Schmalstieg, 2014)

$$q = 1 \square \square\, t^{z} \; \square \square\, N^{p}$$

Schmalstieg: z=1/2, p=1/2 → no knee
Our experience: p=1.0 → extends calendar life model for mild cycling

2. Limiting mechanism model (NREL)

$$q_{Li} = b_0 \square b_1 t^{z} \qquad \frac{dq_{Sites}}{dN} = \square c_2 \left(\frac{1}{q_{Sites}} \right)$$

$$q = \min(q_{Li}, q_{sites})$$

Described in previous presentations

3. SEI micro-cracking model (Deshpande, 2012)

$$\frac{dq_{sei,0}}{dt} = \frac{1}{2} \times (b_1)^2 \times \frac{1}{q_{sei,0}}$$

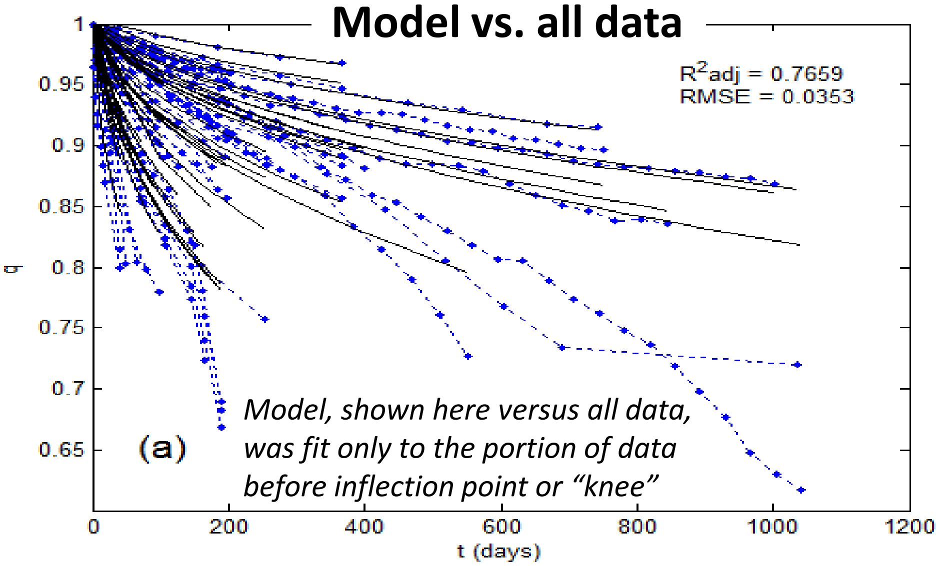
$$\frac{dD_{sei}}{dN} = k \times \left(\sqrt{D_{sei}}\right)^{m} \quad \rightarrow \quad \frac{dq_{sei,j}}{dt} = \frac{1}{2} \times (b_1)^2 \times D_{sei} \times \frac{1}{q_{sei,j}}$$

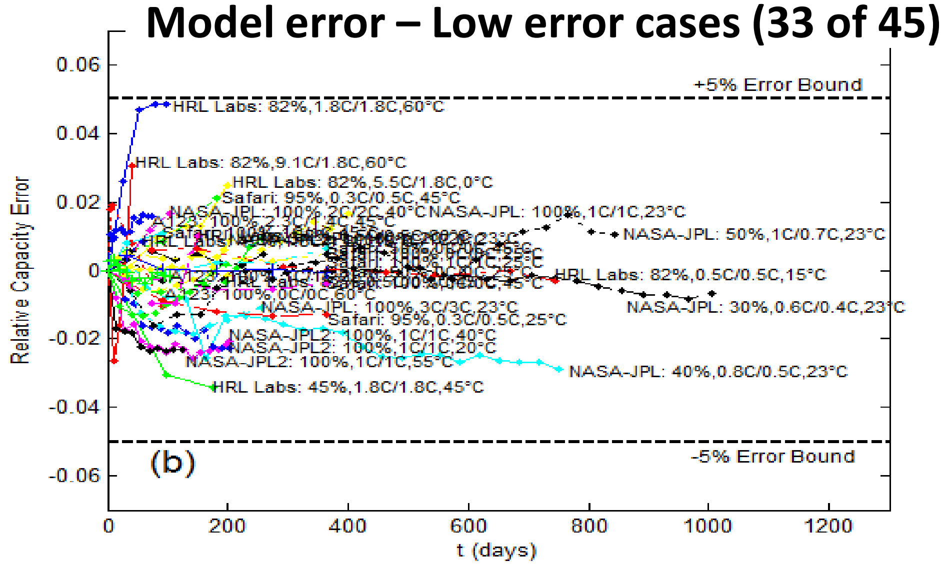
$$q_{Li}(t) = b_0 \square \square_{j=0}^{N} q_{sei,j}(t)$$

Following slides

Cycling fade

- **Causes apparent acceleration of $t^{1/2}$ Li-loss/SEI growth rate**
  - Evidence for SEI damage (particle-to-particle displacement and/or surface cracking)
  - Rate correlates best by including multiplicative term, $(1+DOD^{\beta}) \times t^{1/2}$
    - – discharge C-rate next best correlation

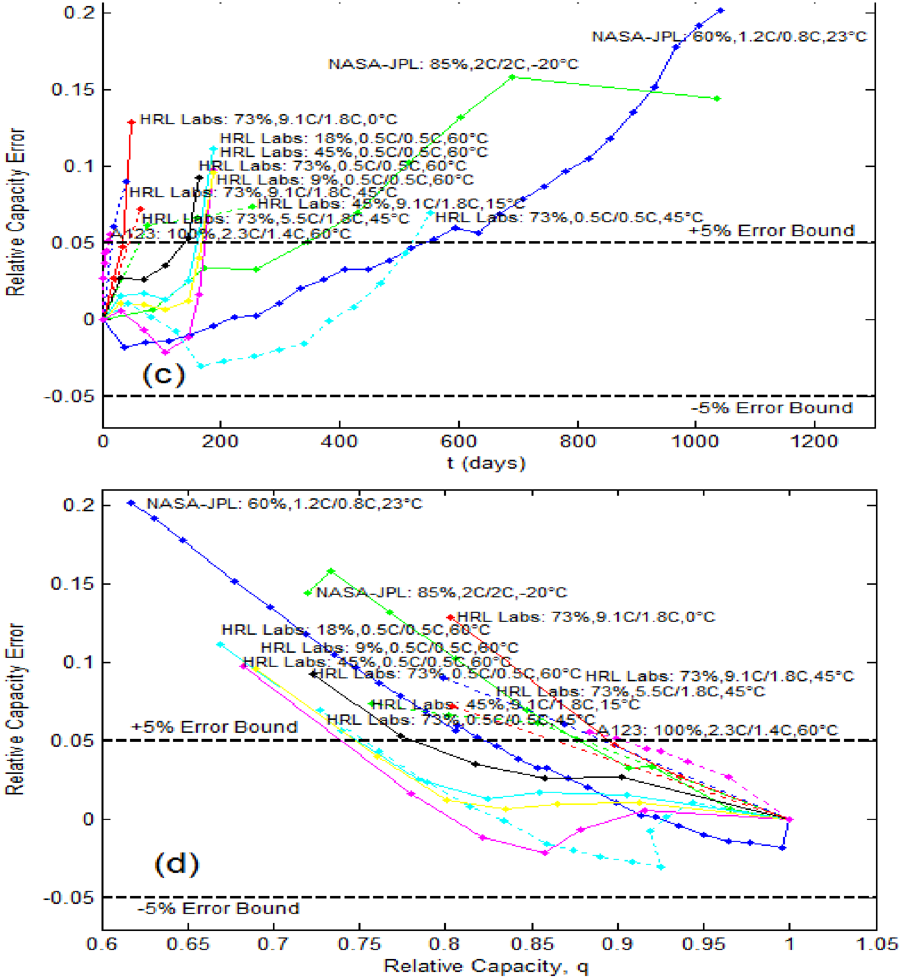




Cycling fade - knee

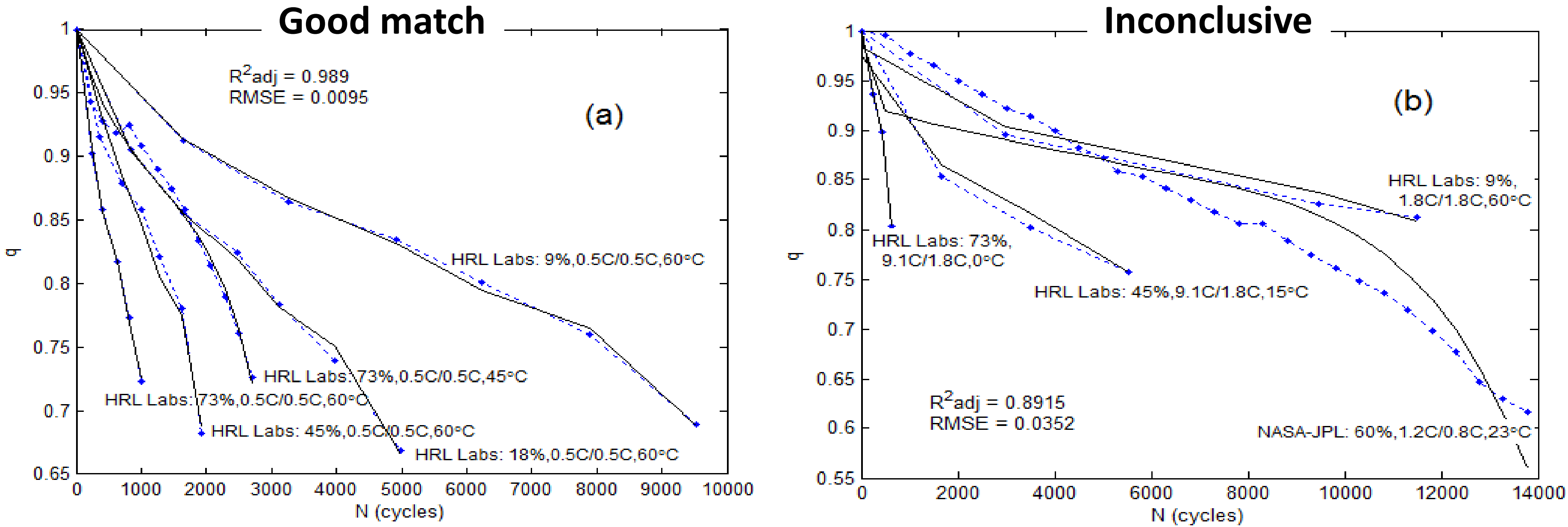
- **12 of 45 cases show apparent "knee" not captured by $t^{1/2}$ model**
- **Possible mechanisms**
  - Li-loss / SEI micro-cracking
  - Site-loss / cycling fatigue
- **Plotted vs. remaining capacity (bottom) seems to indicate similar mechanism across multiple cases**

Model error – High error cases (12 of 45)



Cycling fade – SEI micro-cracking model[1]

- **Matches individual aging tests well, especially at 60°C**
- **Difficult to justify model at T < 45°C.**
  - 23°C, 60% DOD case not matched well

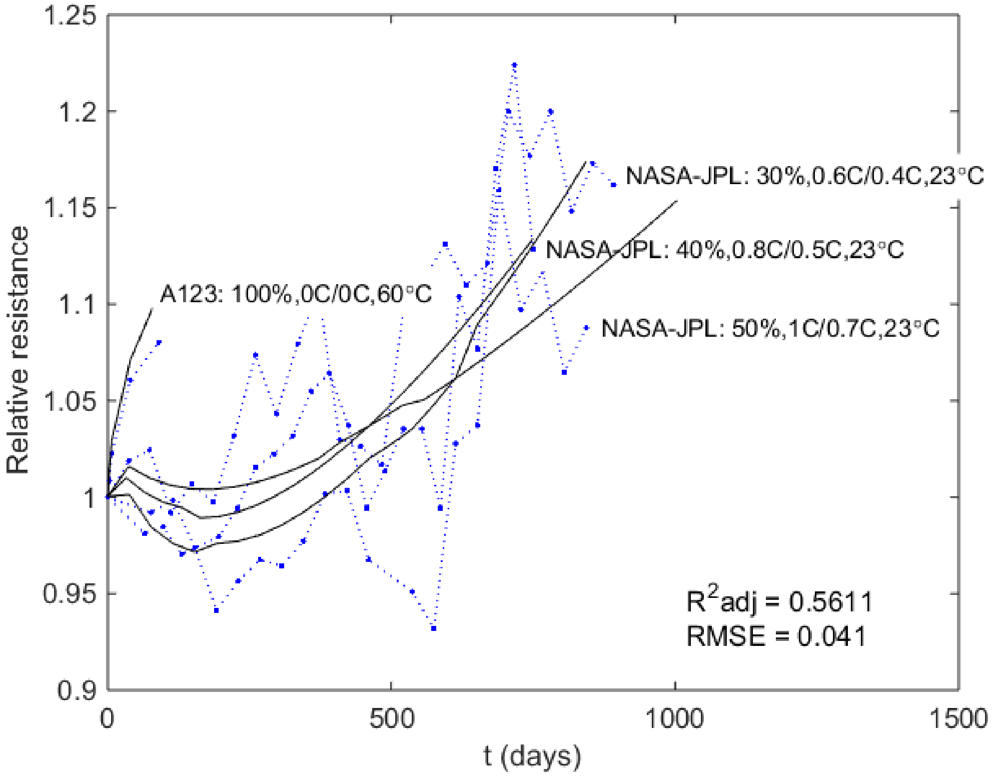


1. R. Deshpande, M. Verbrugge, Y.T. Cheng, J. Wang, P. Liu, "Battery cycle life prediction with coupled chemical degradation and fatigue mechanics," J. Electrochem. Soc. 159 (2012).

Resistance growth

Typical mechanisms

- SEI growth
- Particle fracture
- Site loss
- Electrolyte decomposition

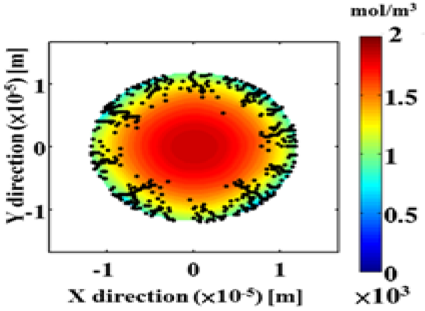


Outline

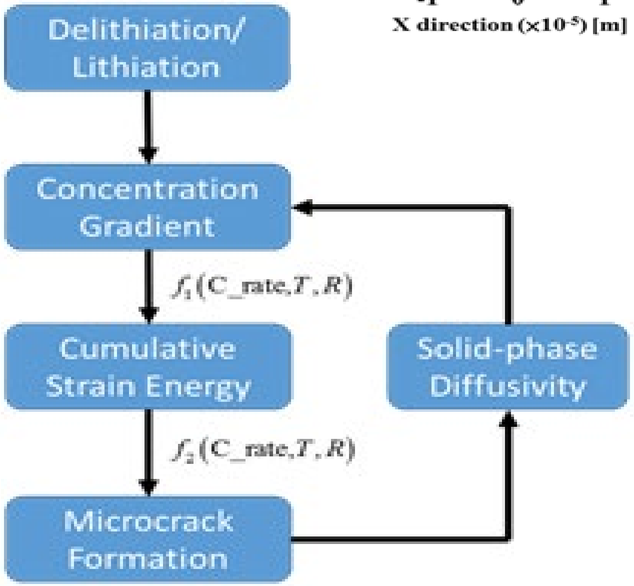
- Analysis of degradation mechanisms
- Modeling of particle fracture physics
- Cell-level prognostic control
- Pack-level prognostic control

Modeling of Particle Fracture Physics

with Texas A&M[1]



- Strain of electrochemical cycling causes stress and fracture in particles
  - Micro-cracks inhibit solid phase diffusivity
- Texas A&M has developed high-order mechanical-electrochemical models of micro-cracking + transport
- Goal: Develop reduced-order scaling laws that can be integrated with fatigue models & validated with aging data



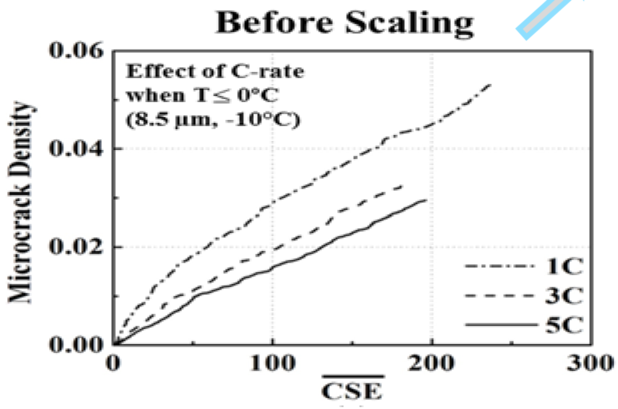
1. C.F. Chen, B. Vajipeyajula, P. Barai, K. Smith, P. Mukherjee, "Scaling of Intercalation Induced Damage in Electrodes," Phys. Chem. Chem. Phys., submitted.

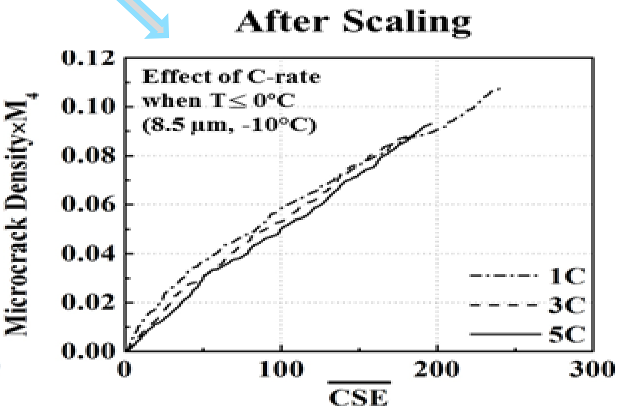
Reduced-order particle fracture model

- **Developed from numerical experiments run with full order model for various**
  - C-rates (constant)
  - Particle sizes
  - Temperatures

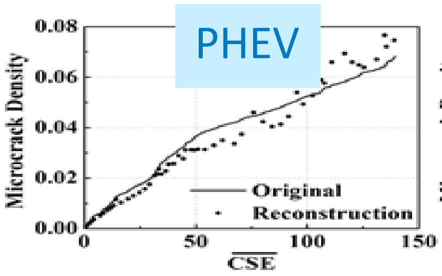
Table 2. Scaling Factor and Fitting Parameter in Eq. (12)

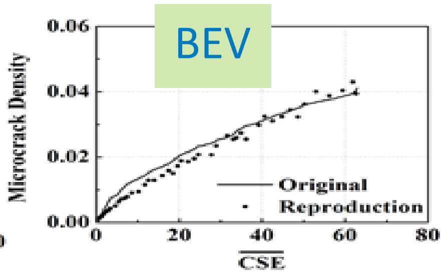
Relation	*a*	b	*M*
$\overline{CSE}$ and $\overline{C}$ (T > 0°C)	0.01942	0.35	$M_1 = \left[\frac{C-Rate \times \overline{R}}{\overline{T}^2}\right]^{0.14}$
$\overline{CSE}$ and $\overline{C}$ (T < 0°C)	0.01942	0.35	$M_2 = \left[\frac{C-Rate^2 \times \overline{R}}{\overline{T}}\right]^{0.14}$
$\overline{CSE}$ and *Microcrack Density* (T >0°C)	0.0015	0.657	$M_3 = \left[\frac{C-Rate \times \overline{R}}{\overline{T}^2}\right]^{-0.28}$
$\overline{CSE}$ and *Microcrack Density* (T < 0°C)	0.0016	0.8443	$M_4 = \left[\frac{C-Rate \times \overline{R}}{\overline{T}}\right]^{-0.28}$

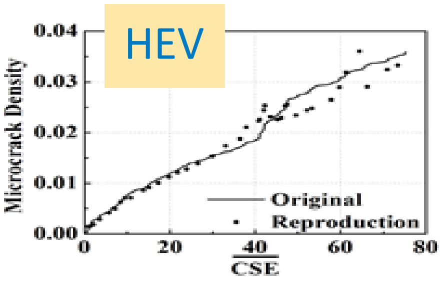




- **Validated for drive-cycle simulations**







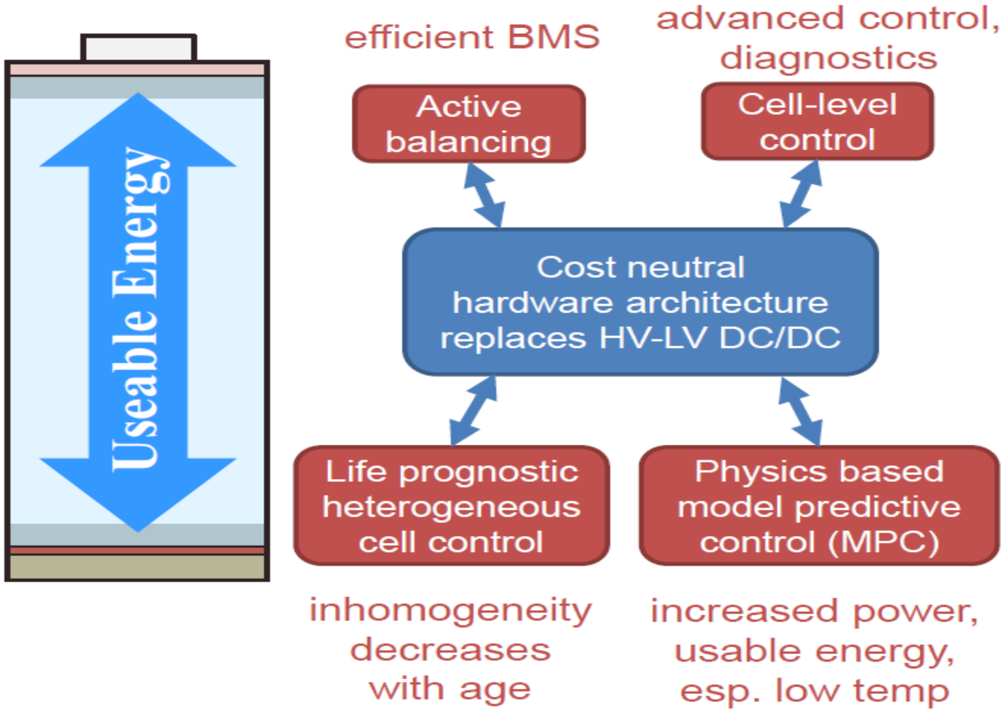
Outline

- Analysis of degradation mechanisms
- Modeling of particle fracture physics
- Cell-level prognostic control
- Pack-level prognostic control

Utah State ARPA-E AMPED Project

Team: USU (Zane), Ford (Anderson), NREL (K. Smith), UCCS (Plett & Trimboli), UC-Boulder (Maksimovic)

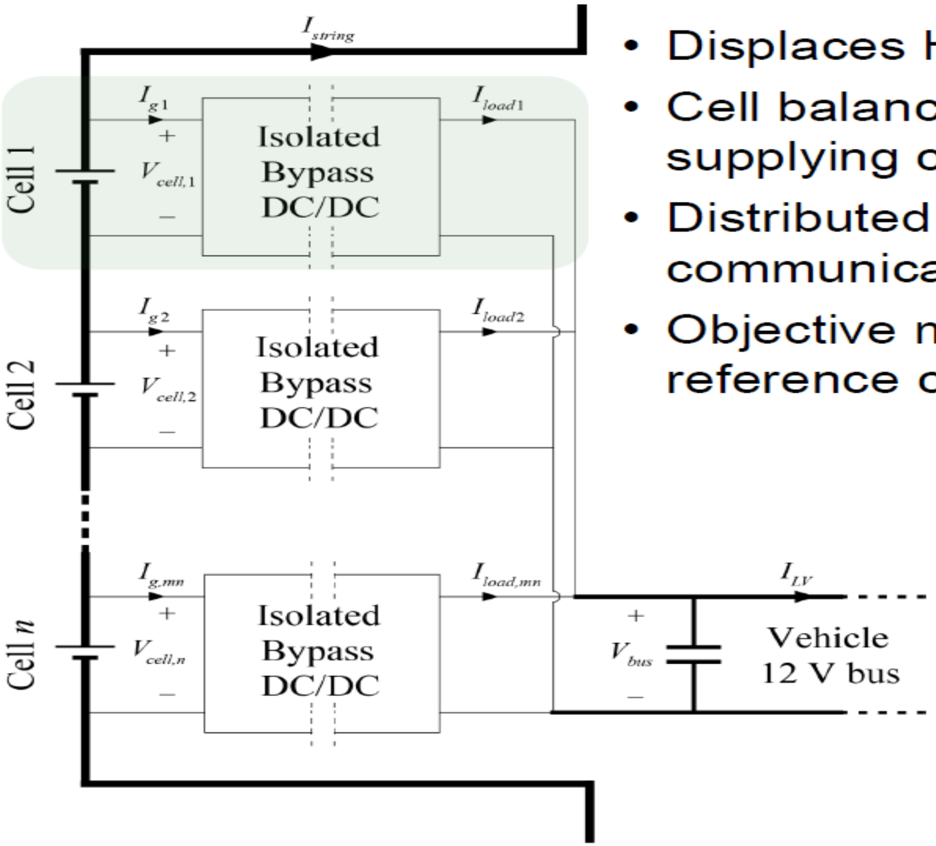
Approach



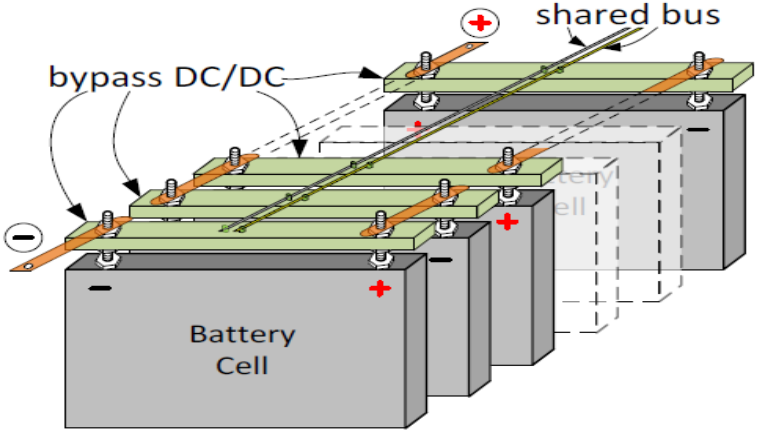
Benefits

- 20% greater usable energy at year 10
- 20% longer lifetime
- Improved power
- Simplified thermal design
- Reduced volume
- Improved 2nd use value

Hardware Architecture



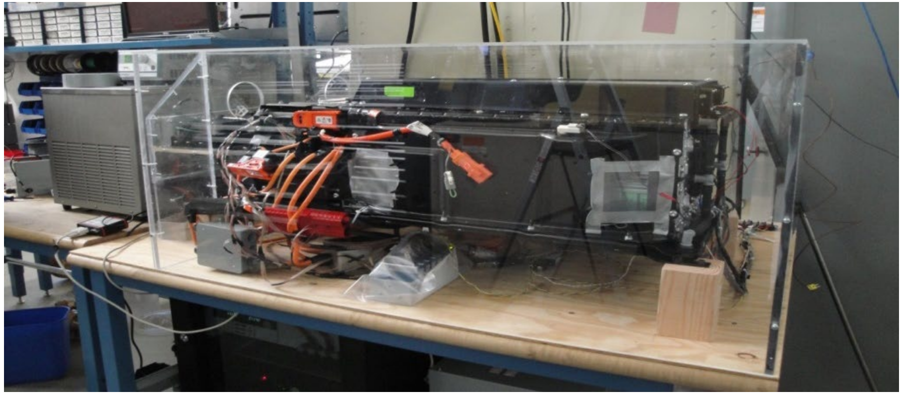
- Displaces HV-to-12V DC/DC converter
- Cell balancing achieved by differentially supplying current to the 12V bus
- Distributed control uses 12V bus voltage to communicate shared reference
- Objective map relates bus voltage to reference cell state



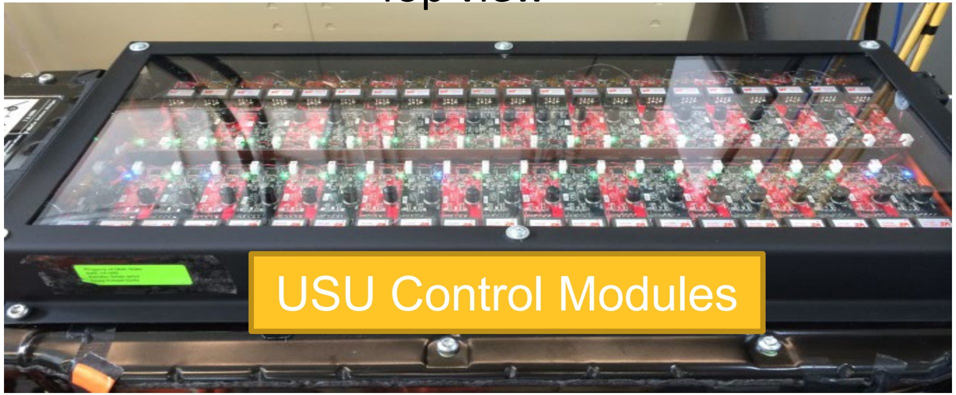
Pack Validation Test Setup

- **1 year aging test underway at NREL (4 US06 cyc/day, 35°C)**
  - Lower Half Pack: Cell#1-42, passive balancing
  - Upper Half Pack: Cell# 43-84, heterogeneous/life active balancing
  - Each half-pack purposely imbalanced with 50% new cells and 50% pre-aged cells

Side view



Top view



- **Goal: Reduce cell capacity imbalance over 1 year test using heterogeneous cell control, optimized for life**
  - Simultaneously supply 1.5 kW auxiliary load

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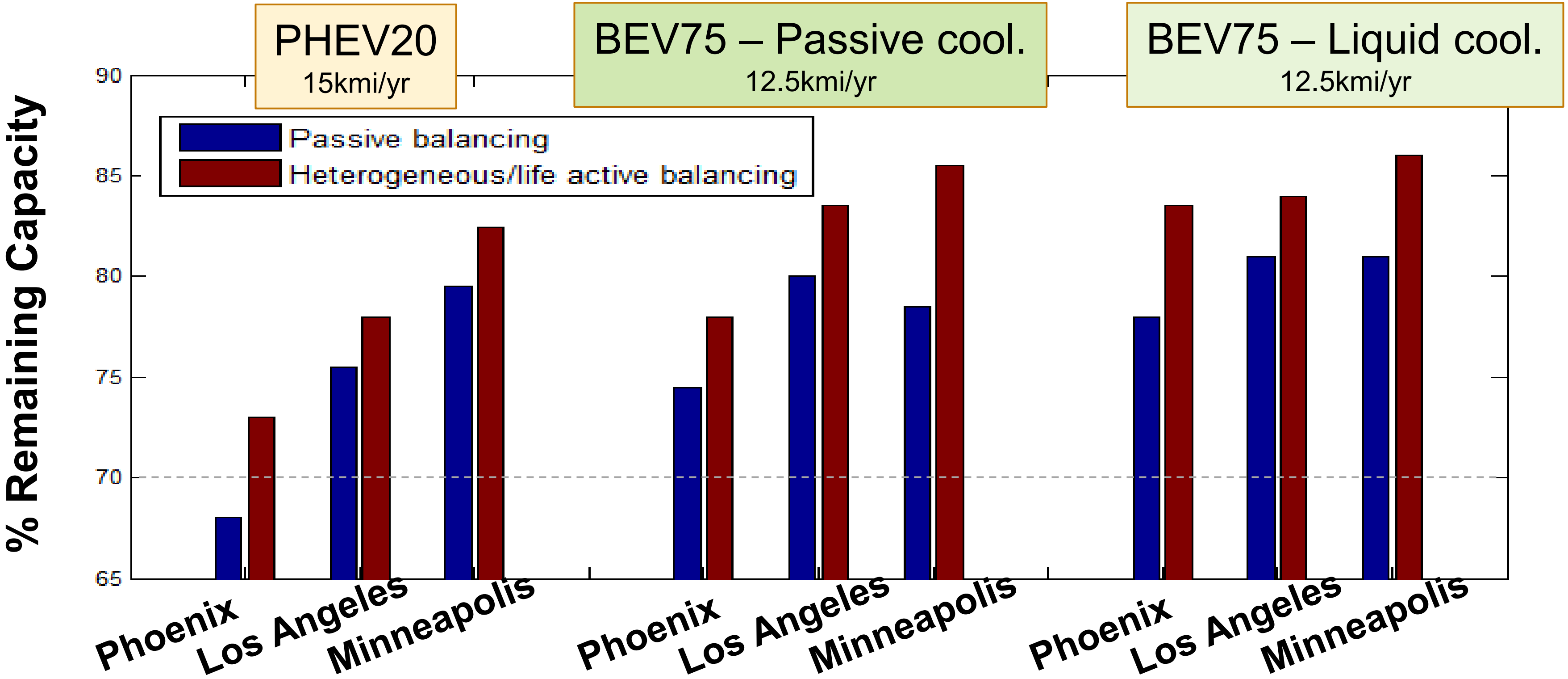
Life Benefit: Capacity at Year 10 (PHEV) / 8 (BEV)

- **PHEV20: +2% to 5% additional capacity (up to 20% life extension)**
- **BEV75: +3% to 7% additional capacity (up to 40% life extension)**
  - Active balancing provides benefit greater than liquid cooling

NREL BLAST-V Model Predictions



Outline

- Analysis of degradation mechanisms
- Modeling of particle fracture physics
- Cell-level prognostic control
- Pack-level prognostic control

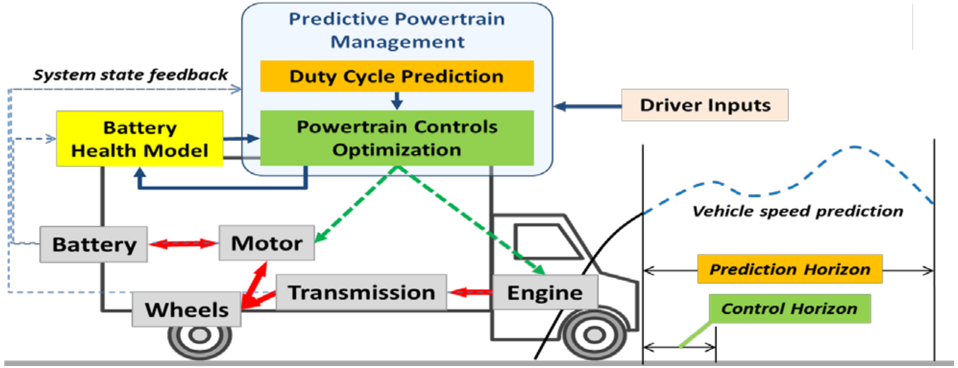
Eaton/NREL ARPA-E AMPED Project

Team: Eaton Corporation (Chinmaya Patil), NREL (K. Smith)

Medium-duty Commercial HEV

Photo credit: Eaton

- **Goal: 50% downsized HEV battery**



…meet the driver demand using least amount of fuel, without violating system constraints…

…while meeting target battery life

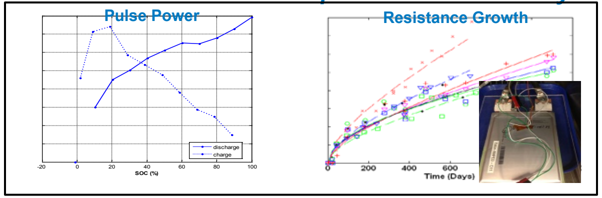
Objective function:

$$J(X,U) = \sum_{t=k}^{k+N_P} w_1 \cdot fuel + w_2 \cdot drivability + w_3 \cdot battery$$

Online Life Prognostic Model Development

1) Cell life test data

- Constant temperature & duty cycle



2) Regress life model parameters

Calendar fade
- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1, b_1 = f(\Delta DOD, C_{rate}, T, \ldots)$

Cycling fade
- active material structure degradation and mechanical fracture
- $a_2, c_2 = (\Delta DOD, C_{rate}, T, \ldots)$

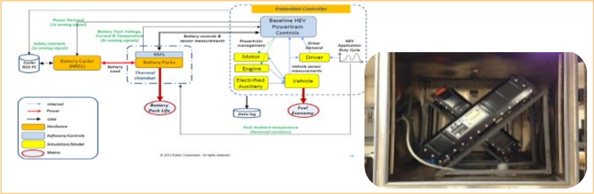
Relative Resistance $R = a_1 t^{1/2} + a_2 N$

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

$Q_{Li} = b_0 + b_1 t^{1/2} + b_2 N$ $Q_{sites} = c_0 + c_2 N$

3) Pack life test data

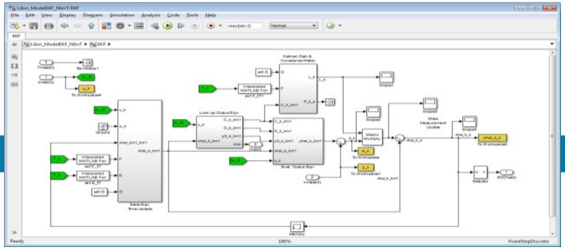
- Variable temperature & duty cycle



4) Validated pack life model

- Forward looking prognosis based on observed I,V,T,SOC,…

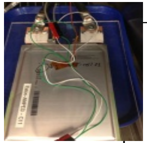
5) Control strategy prototyping

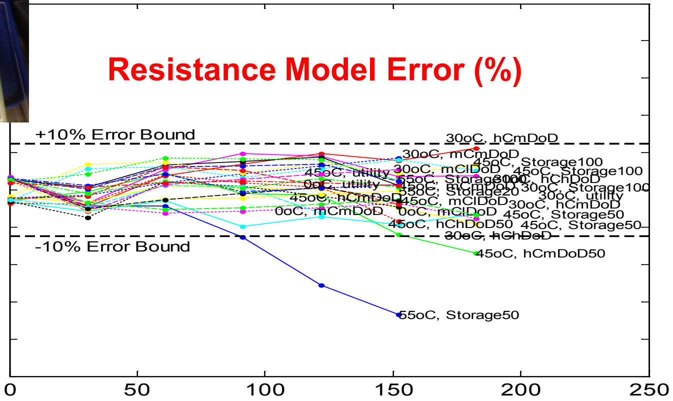


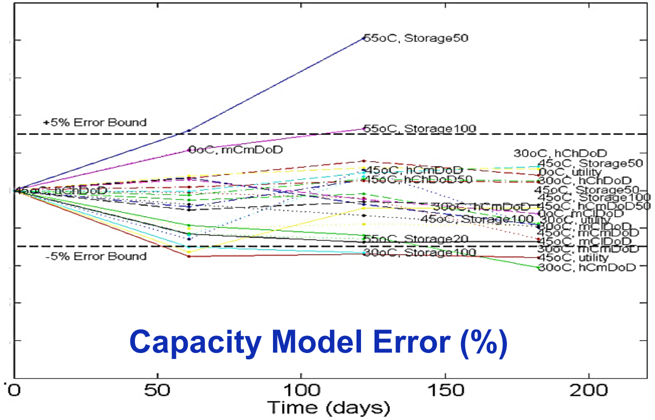
6) Closed-loop HIL testing

Life Prognostic Model Accuracy

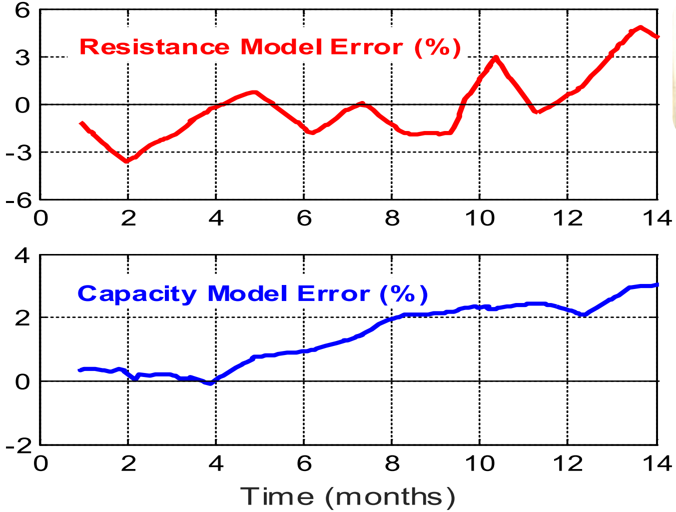
Cell Aging Model Error (Model Identification)







Pack Aging Model Error (Validation)



Current Status

- Secondary verification (EOL tests) underway
- Verification of iEPM algorithm based on battery health model

Next Steps

- Complete HIL validation testing of closed-loop performance for HEV application
- Application to ES with smart grid & renewables

Conclusions & Next Steps

- Applications show promise for
  - 50% downsized HEV battery
  - Up to 20% PHEV life extension
  - Up to 40% BEV life extension, relaxing need for liquid cooling
- For mature cell designs, modeling of 3-5 physics-based mechanisms predicts aging within
  - 3-4% capacity error
  - 6-12% resistance error

  → Long-term validation still needed
- Major degradation mechanisms are now reasonably well understood, ready for
  - Standardization of battery testing/modeling for determining warranty
  - Integration into computer-aided engineering design tools

Thank you