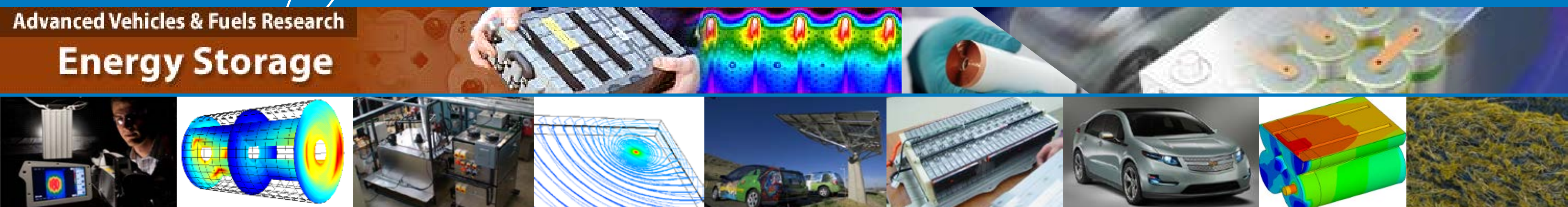
NATIONAL RENEWABLE ENERGY LABORATORY

Predictive Models of Li-ion Battery Lifetime



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Golden, Colorado

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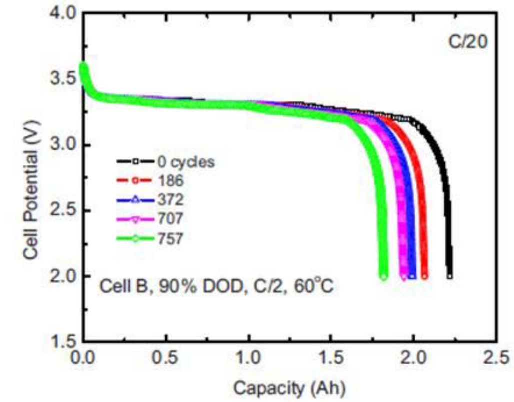
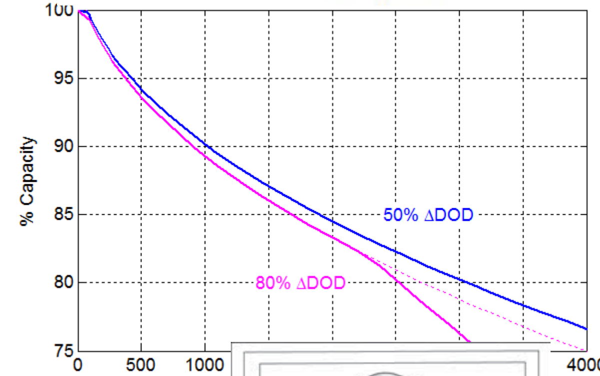
NREL/PR-5400-62813

Key Messages

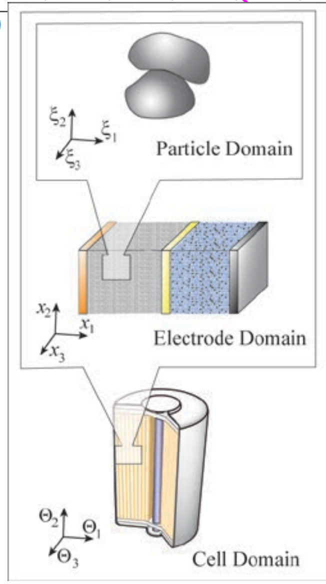
- **Semi-empirical battery lifetime models are generally suitable for system design & control**
  - Long-term validation still needed
  - Standardization would benefit industry
  - Characterization requires expensive cell aging experiments
- **Physics lifetime models are needed to reduce test time as well as guide future cell design**
  - Open questions remain how best to model electrochemo-thermo-mechanical processes across length- and time-scales

Liu et al., J. Echem Soc. (2010)





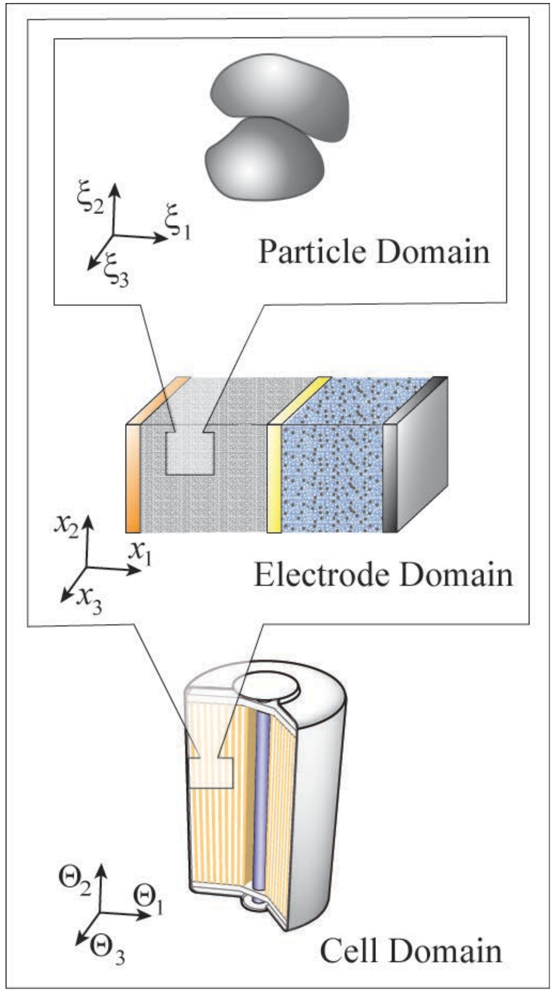
NREL Life & MSMD Models

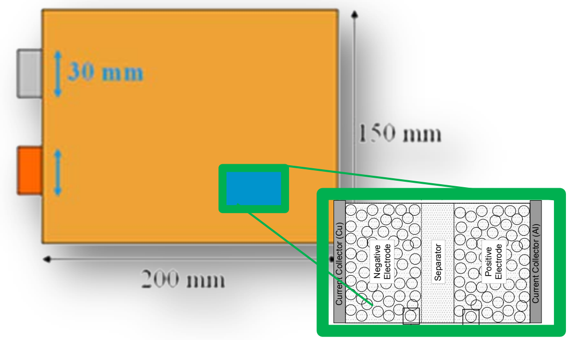


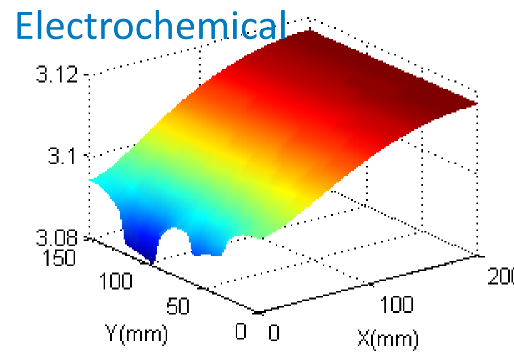
NREL Electrochemical/Thermal/Life Models

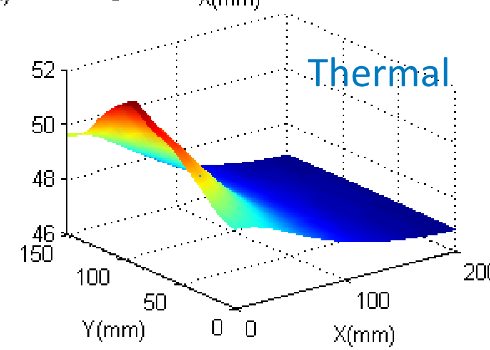
Multi-Scale Multi-Domain (MSMD) model

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









Kim et al. (2011) "Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales", J. of Electrochemistry, Vol. 158, No. 8, pp. A955–A969

NREL Electrochemical/Thermal/Life 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
- $a_1, b_1 = f(\Delta DOD, T, V_{oc}, \ldots)$

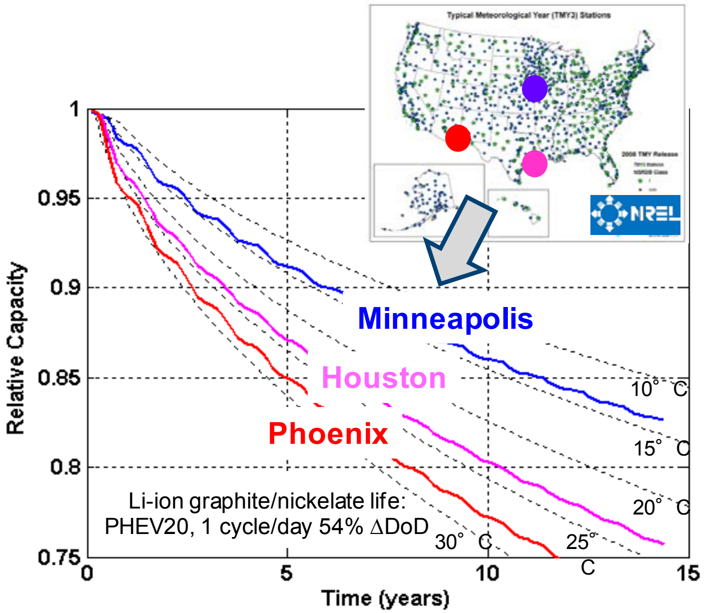
Cycling fade
- Active material structure degradation and mechanical fracture
- $a_2, c_2 = f(\Delta DOD, T, V_{oc}, \ldots)$

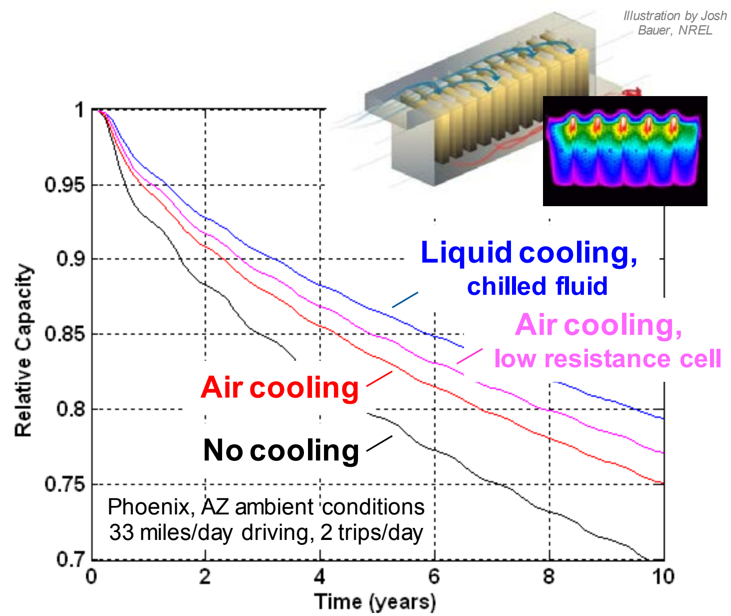
Relative Resistance $R = a_1 t^z + a_2 N$

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

$Q_{Li} = b_0 + b_1 t^z + \ldots$

$Q_{sites} = c_0 + c_2 N + \ldots$



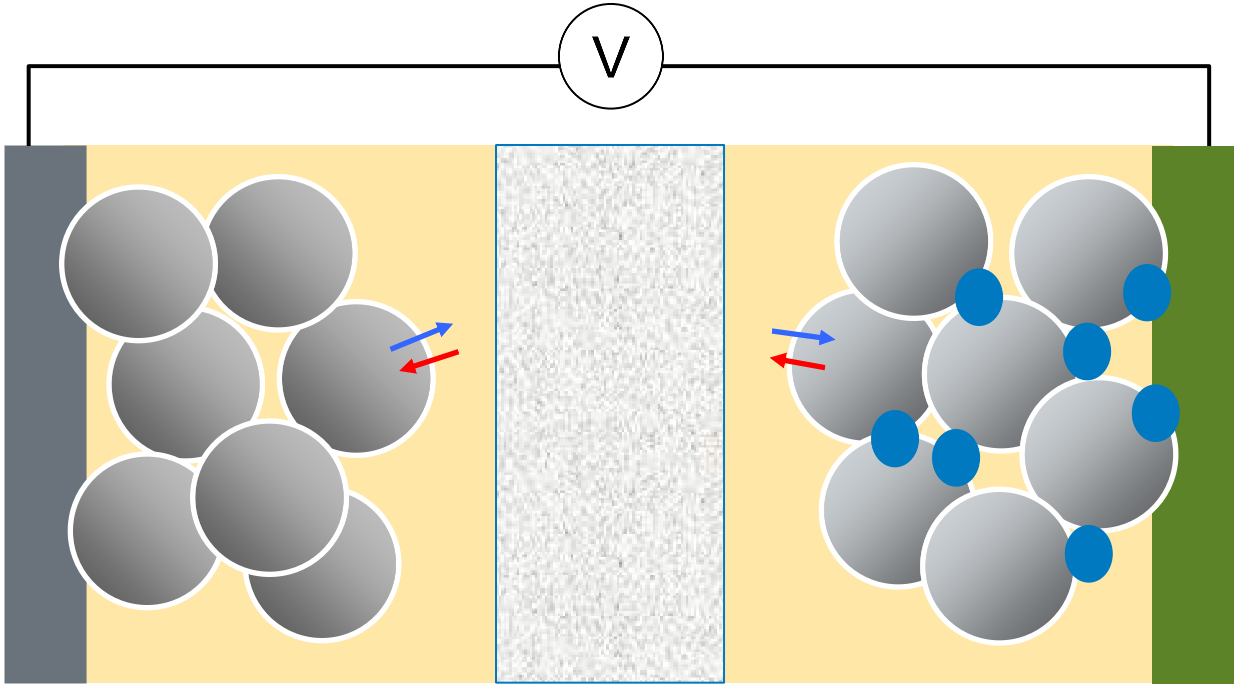


Outline

- **Background – Li-ion Batteries**
  - Working principles
  - Electrochemical window
  - Degradation mechanisms
- **Life Predictive Modeling**
- **Automotive Life Studies & Control**

Working Principles

Neg. Electrode
Graphite
Hard carbon
Silicon
Titanate
Li foil

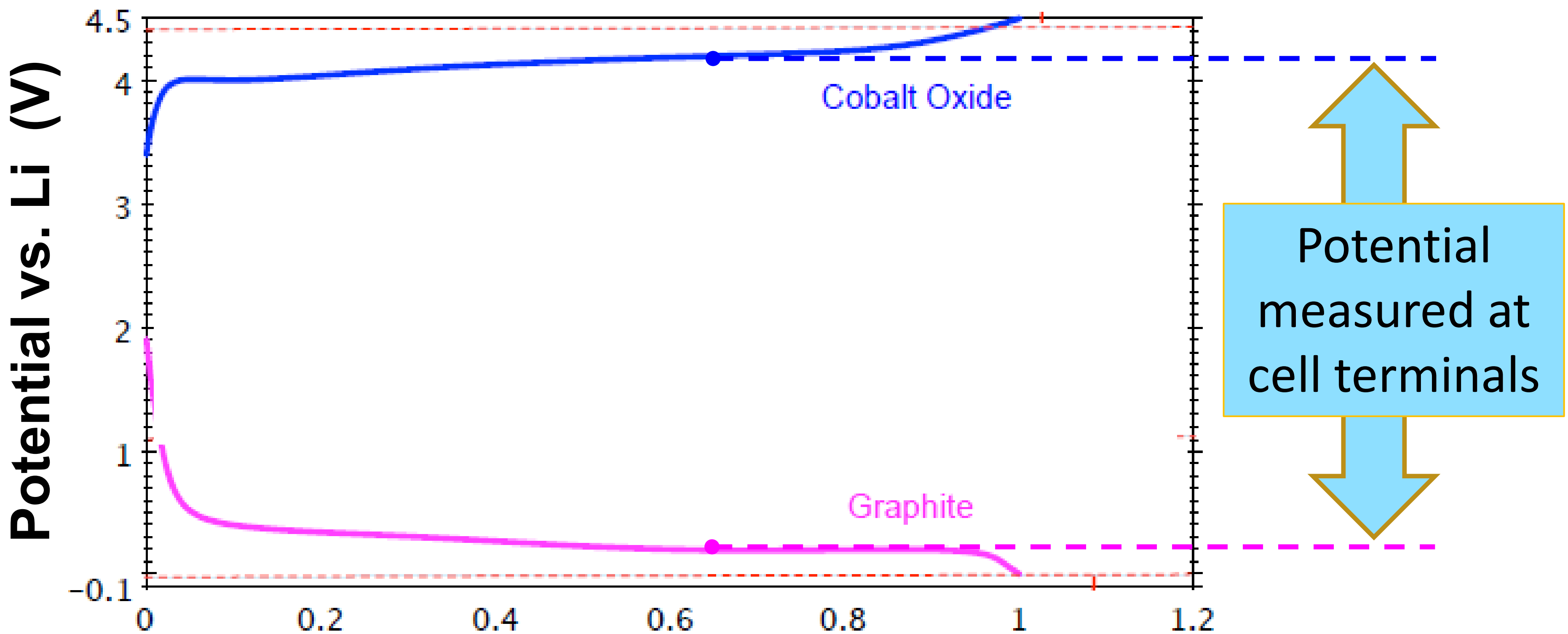


Pos. Electrode
$LiXO_2$,
X = NiMnCo
Co
NiCoAl
$LiMn_2O_4$,
$LiFePO_4$

Electrochemical Operating Window

0% SOC ⟶ charge ⟶ 100% SOC

0% SOC ⟵ discharge ⟵ 100% SOC



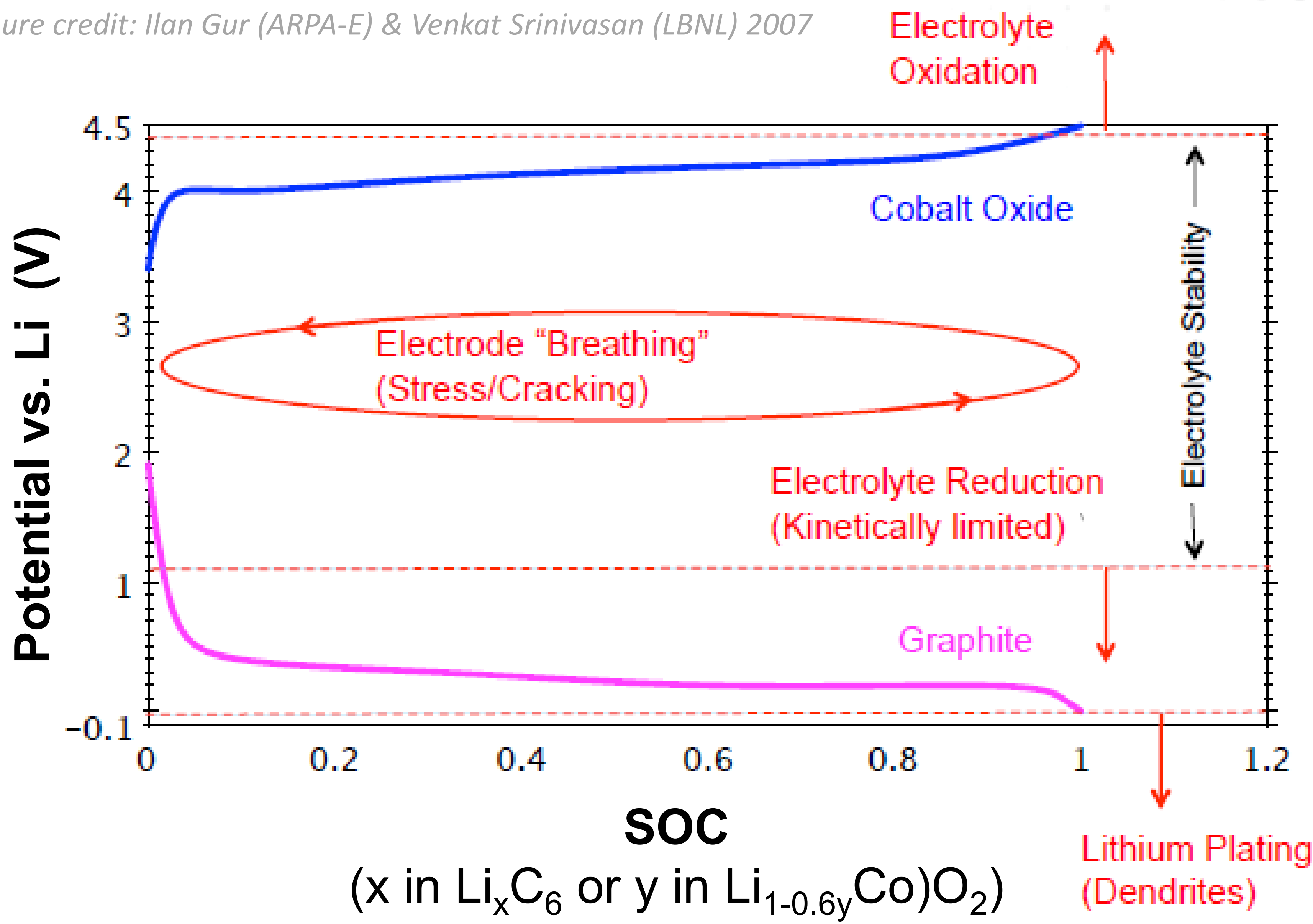
SOC

(x in Li_xC_6 or y in $Li_{1-0.6y}CoO_2$)

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

Electrochemical Window – Degradation

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

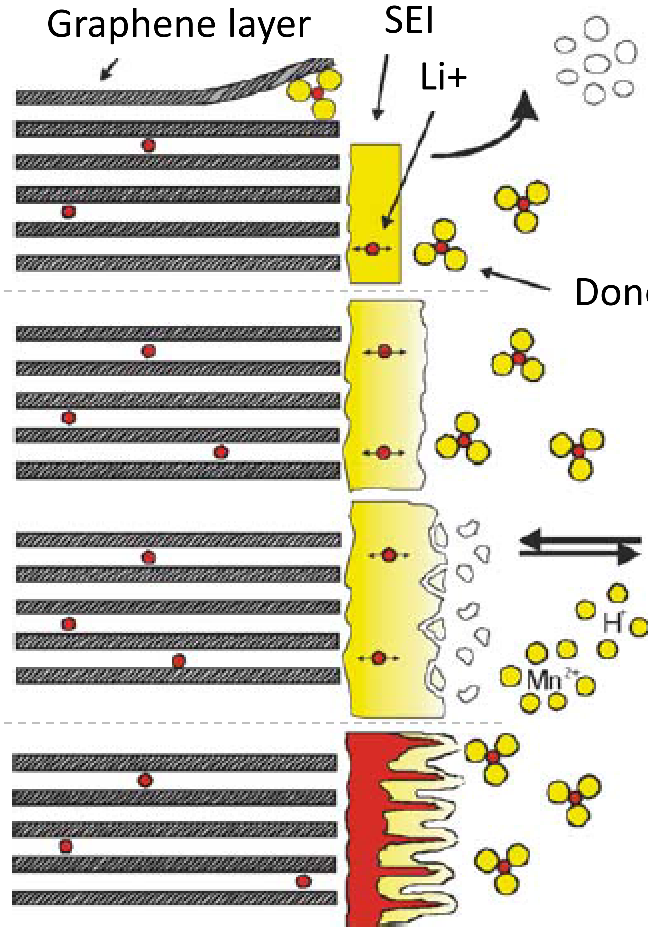


Negative Electrode Degradation (Graphite)

1) Manufacturing environment

2) Application environment
i) graceful fade
(time at high T,SOC)

ii) sudden fade/ damage
(cycling at low T)



Graphite exfoliation, cracking (gas formation, solvent co-intercalation)

Electrolyte decomposition and SEI formation

Negative/ electrolyte interactions

SEI conversion, stabilization and growth

SEI dissolution, precipitation

Positive/negative interactions

Lithium plating and subsequent corrosion

Figure credit: Vetter et al., Journal Power Sources, 2005

Positive Electrode Degradation (Metal Oxide)

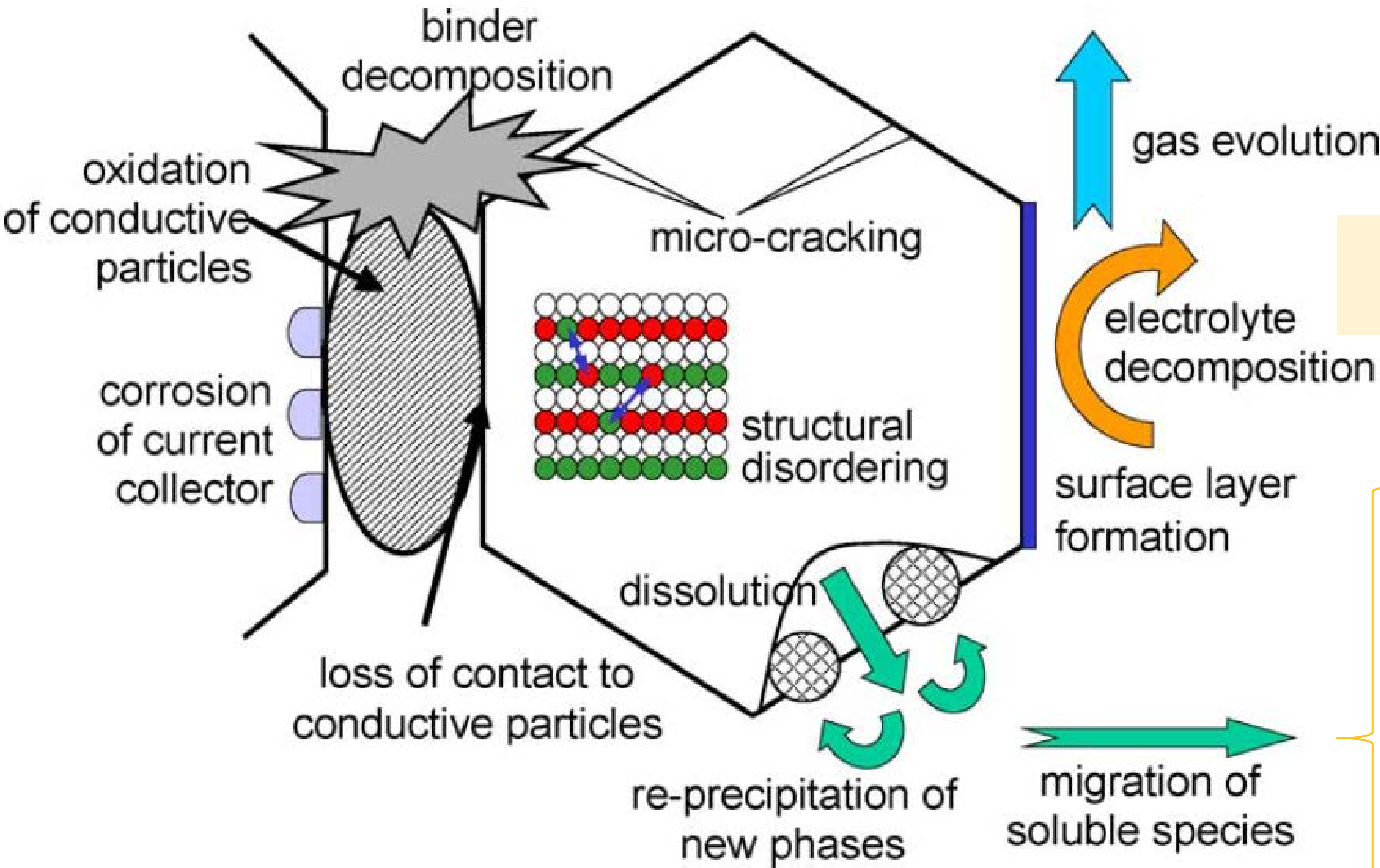
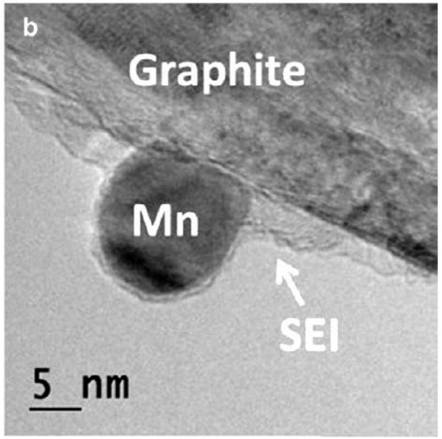


Figure credit: Vetter et al., Journal Power Sources, 2005

Positive/electrolyte interactions

Positive/negative interactions



X. Xiao et al., Echem Comm., 32 (2013) 31-34.

Mechanical Coupled Stress & Degradation

- Least understood amongst ECTM physics

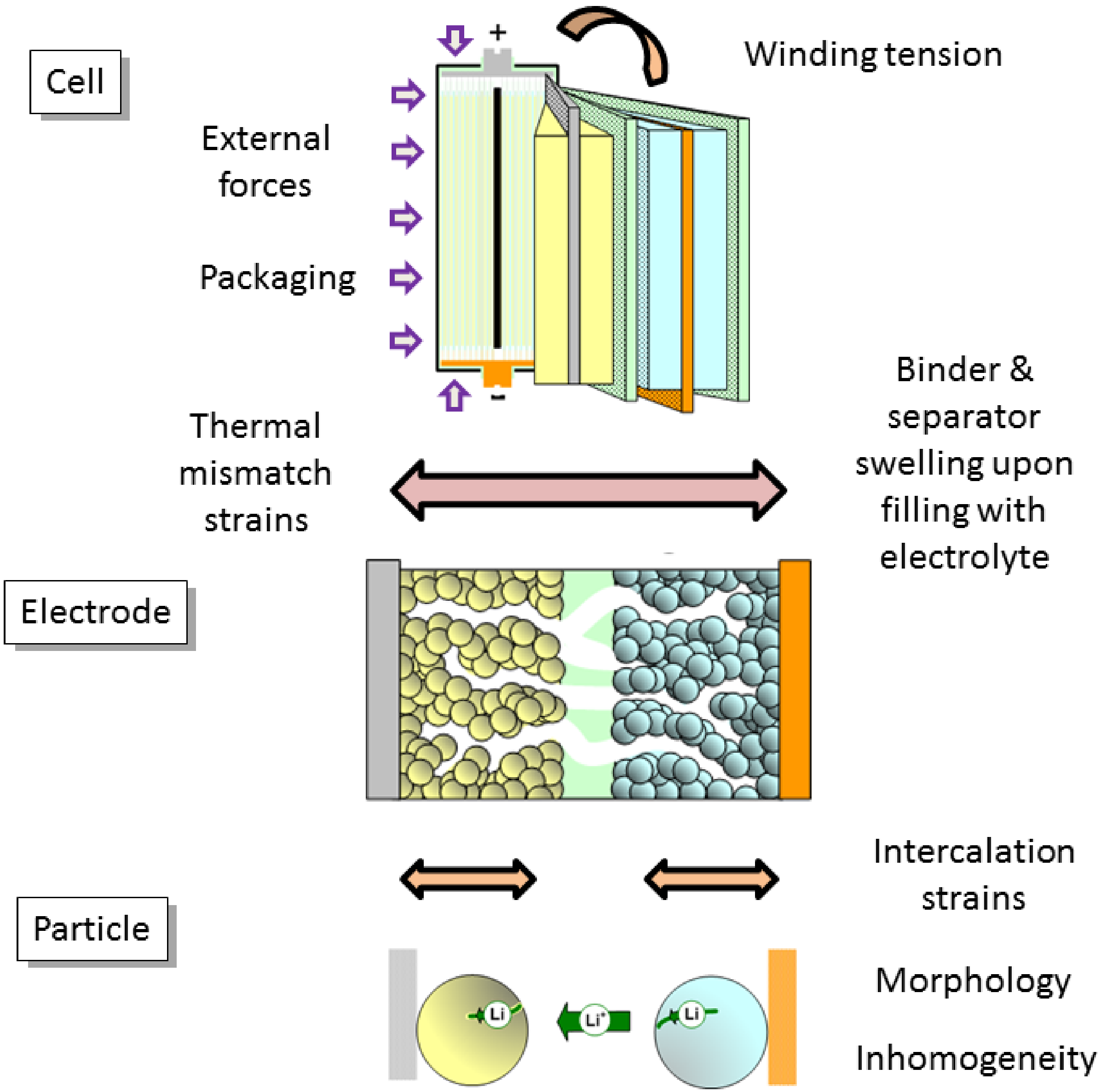
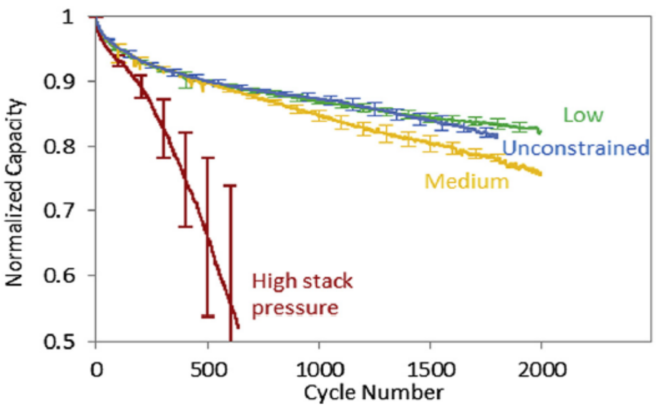


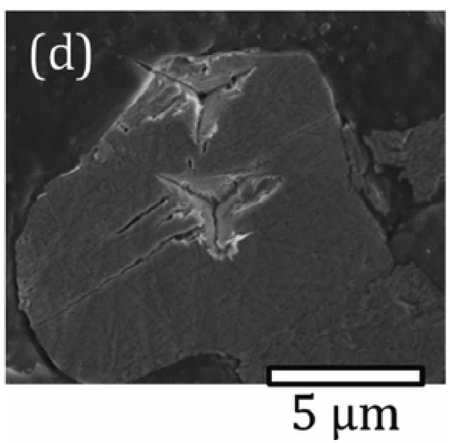
Figure credit: Santhanagopalan, Smith, et al., Artech House (in press)

Mechanical Coupled Stress & Degradation

- Examples



Cannarella, J. Power Sources (2014)



Diercks, Packard, Smith et al., J. Echem Soc (2014)

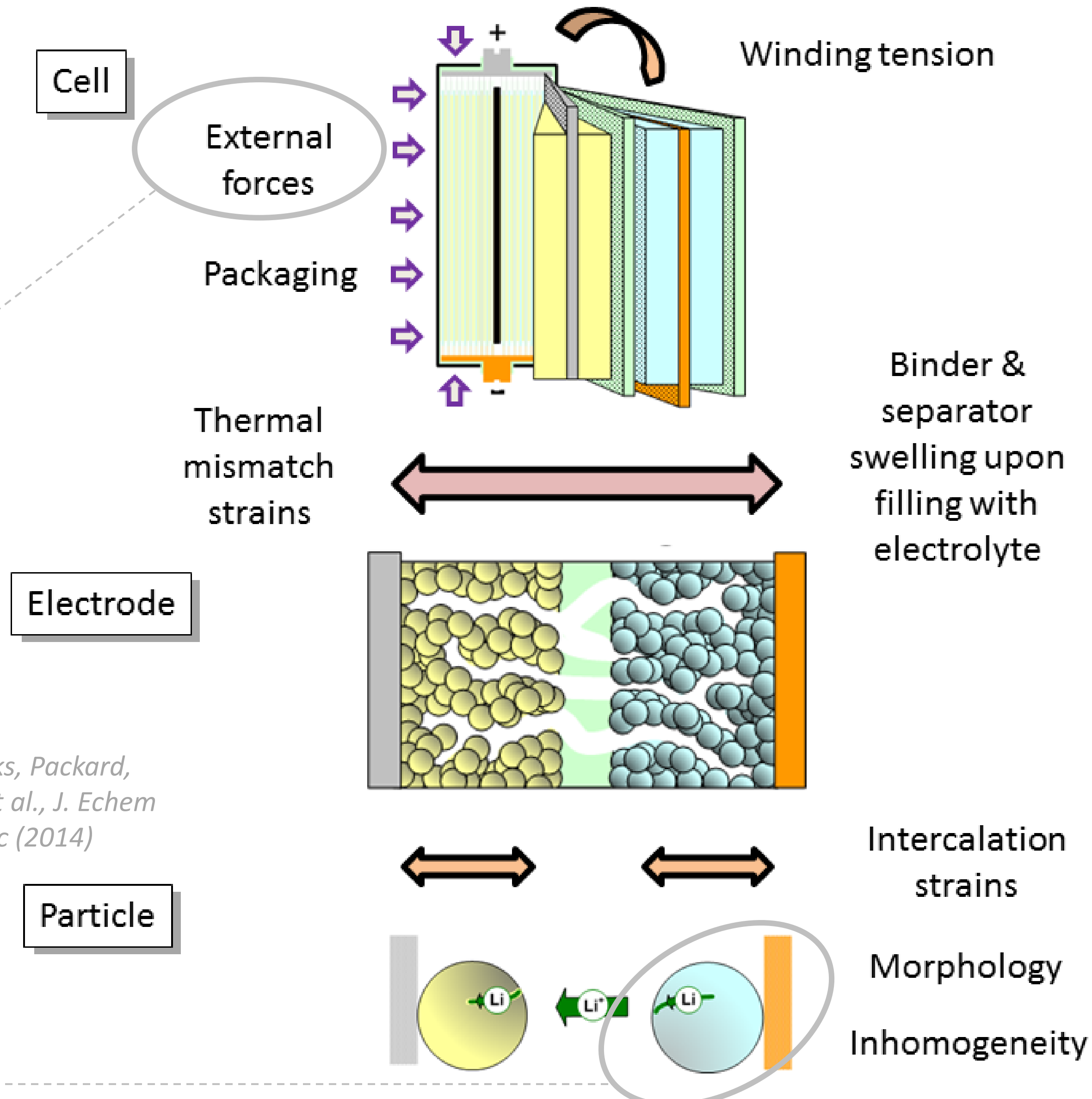


Figure credit: Santhanagopalan, Smith, et al., Artech House (in press)

Outline

- Background – Li-ion Batteries
- **Life Predictive Modeling**
  - Physics-based
  - Semi-empirical
- Automotive Life Studies & Control

Degradation Mechanism vs. Length Scale

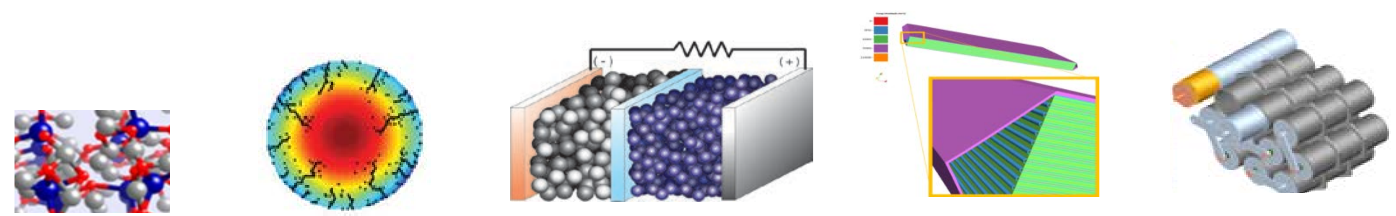
<u>Chemistry</u>
- SEI growth
- Li plating
- Electrolyte decomposition
- Gas generation

<u>Particle scale</u>
- SEI μ-cracking
- Fracture, damage of transport paths
- Phase evolution, voltage droop

<u>Electrode scale</u>
- Electrode creep, delamination, isolation
- Separator pore closure
- Pore clogging

<u>Cell scale</u>
- 3D elec, thermal, mech. inhomogeneities
- Tab effects
- Stack/wind

<u>Module scale</u>
- Thermal & mechanical boundary conditions

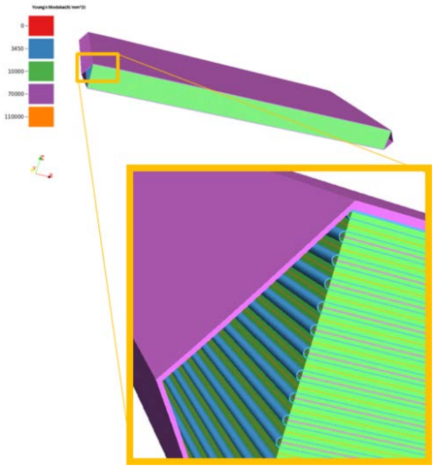


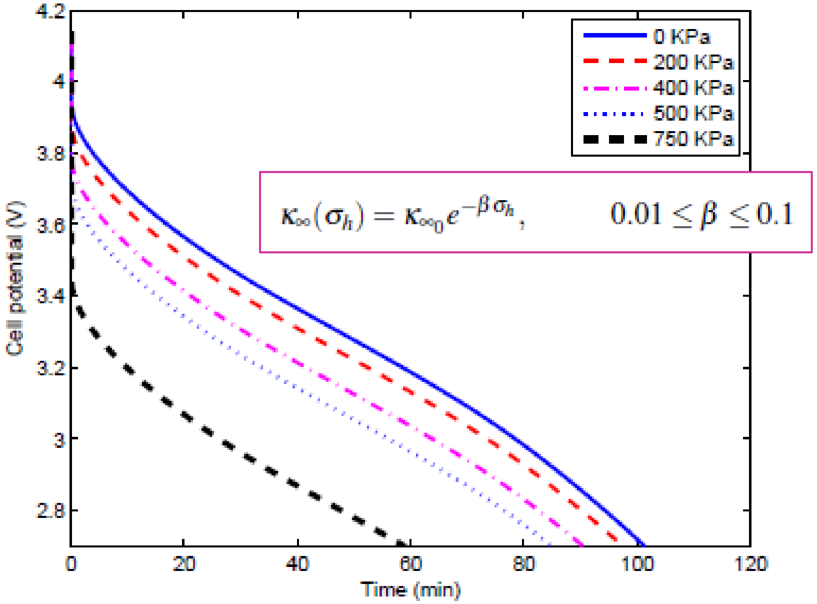
10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{-0}

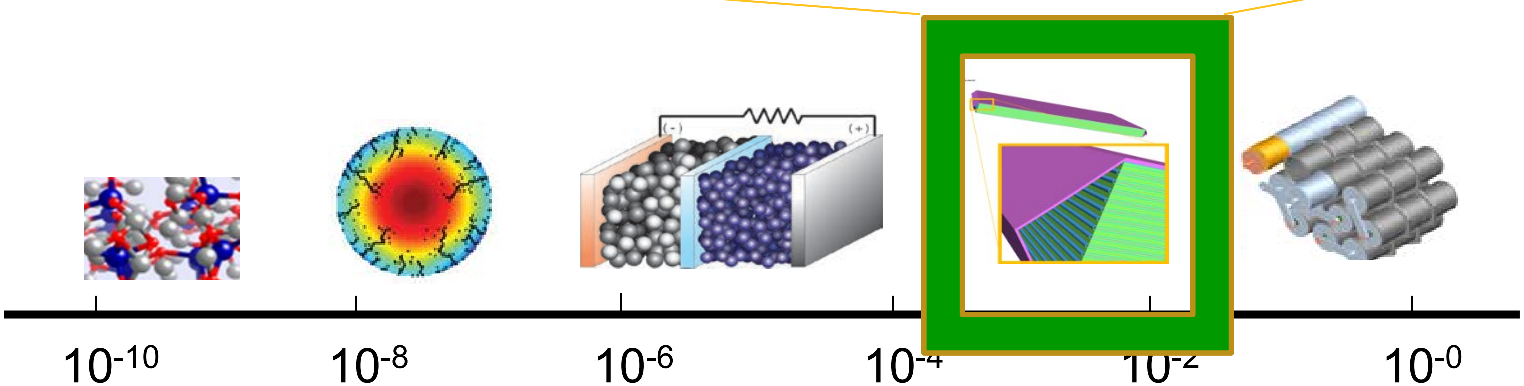
Macro-scale Stress Model

- Stress/strain due to thermal and electrode bulk concentration changes
- Coupled echem & thermal

Behrou, Maute, Smith, ECS Mtg. (2014)



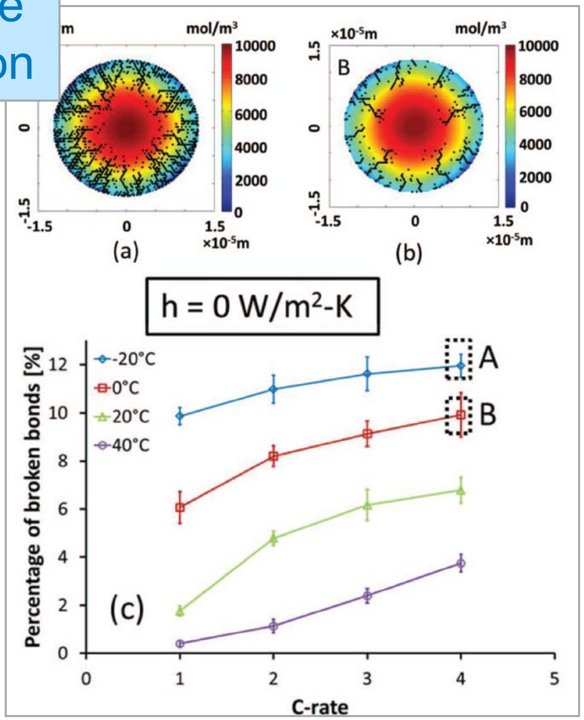




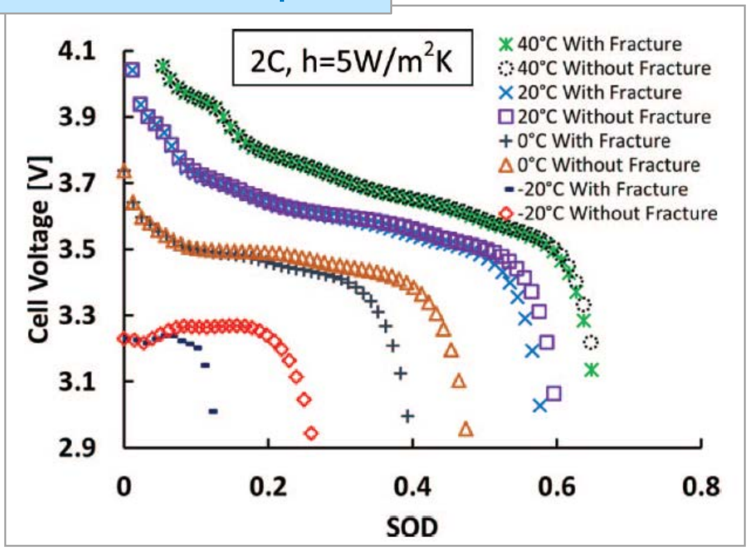
Micro-scale Stress/Degradation Model

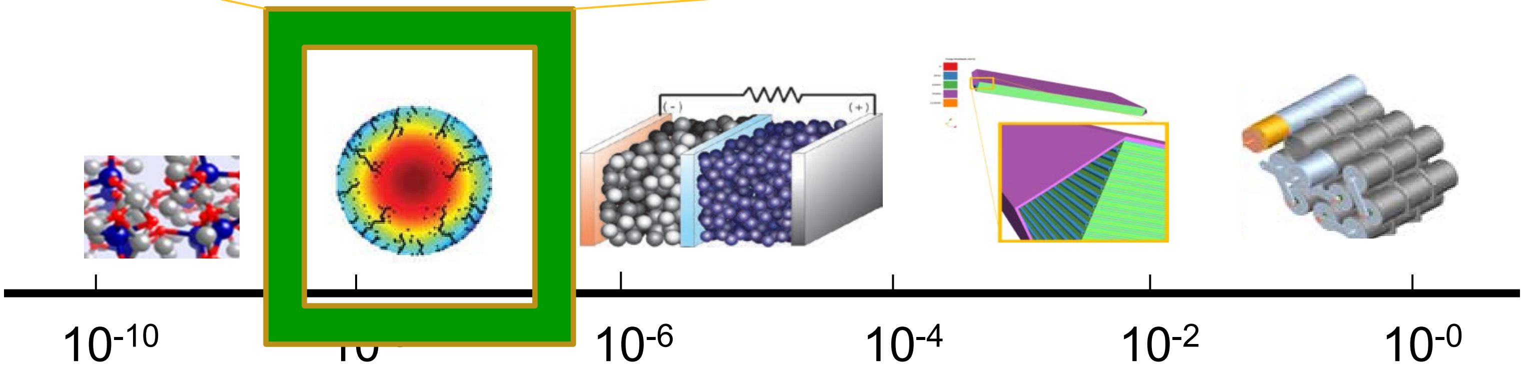
An, Barai, Smith, Mukherjee, JES 2014

Damage evolution



Performance impact





NREL Life Predictive Model

NCA

Calendar fade
- SEI growth
- Loss of cyclable lithium
- Coupled with cycling
- a_1, b_1 = f(ΔDOD,T,V_{oc},…)

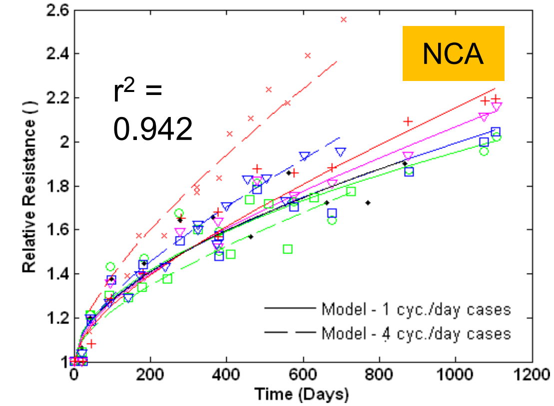
Cycling fade
- Active material structure degradation and mechanical fracture
- a_2, c_2 = f(ΔDOD,T,V_{oc} ,…)

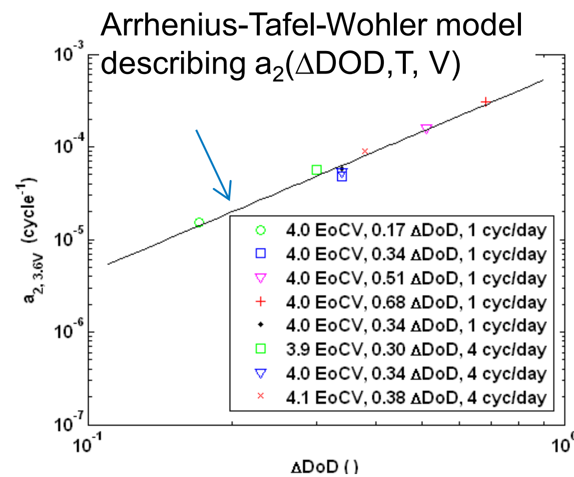
Relative Resistance $$R = a_1 t^z + a_2 N$$

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

$$Q_{Li} = b_0 + b_1 t^z + \ldots$$

$$Q_{sites} = c_0 + c_2 N + \ldots$$

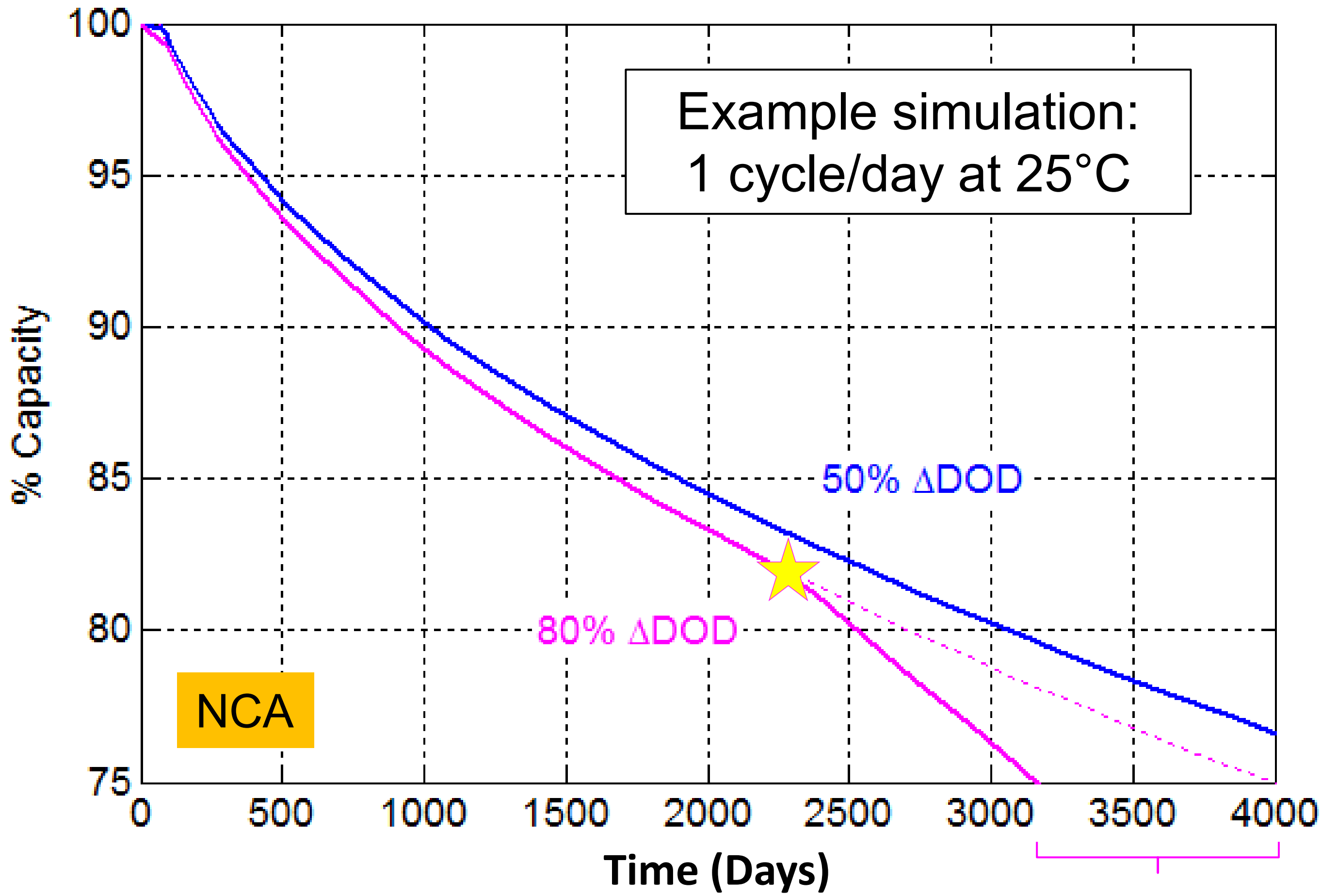




•Data: J.C. Hall, IECEC, 2006.

- **Correct separation of calendar vs. cycling degradation for extrapolation of ½ year testing to 10+ year life**
- **Extensible to untested drive cycles, environments (state form)**

Knee in Fade Critical for Predicting End of Life



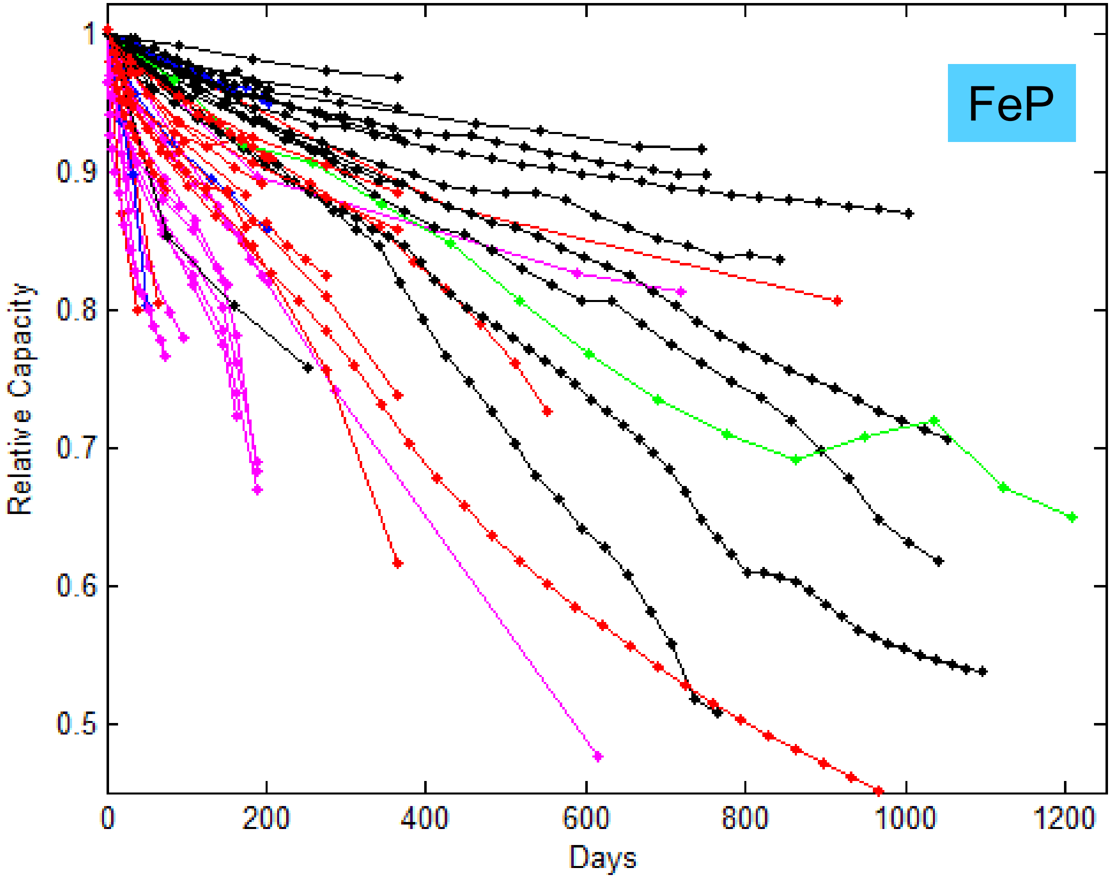
50% DOD:
Graceful fade controlled by Li loss ~ $t^{1/2}$

80% DOD:
Transitions to electrode site loss, N ~ 2300 cycles

Life over-predicted by 25% without accounting for transition from Li loss (~chemical) to site loss (~mechanical)

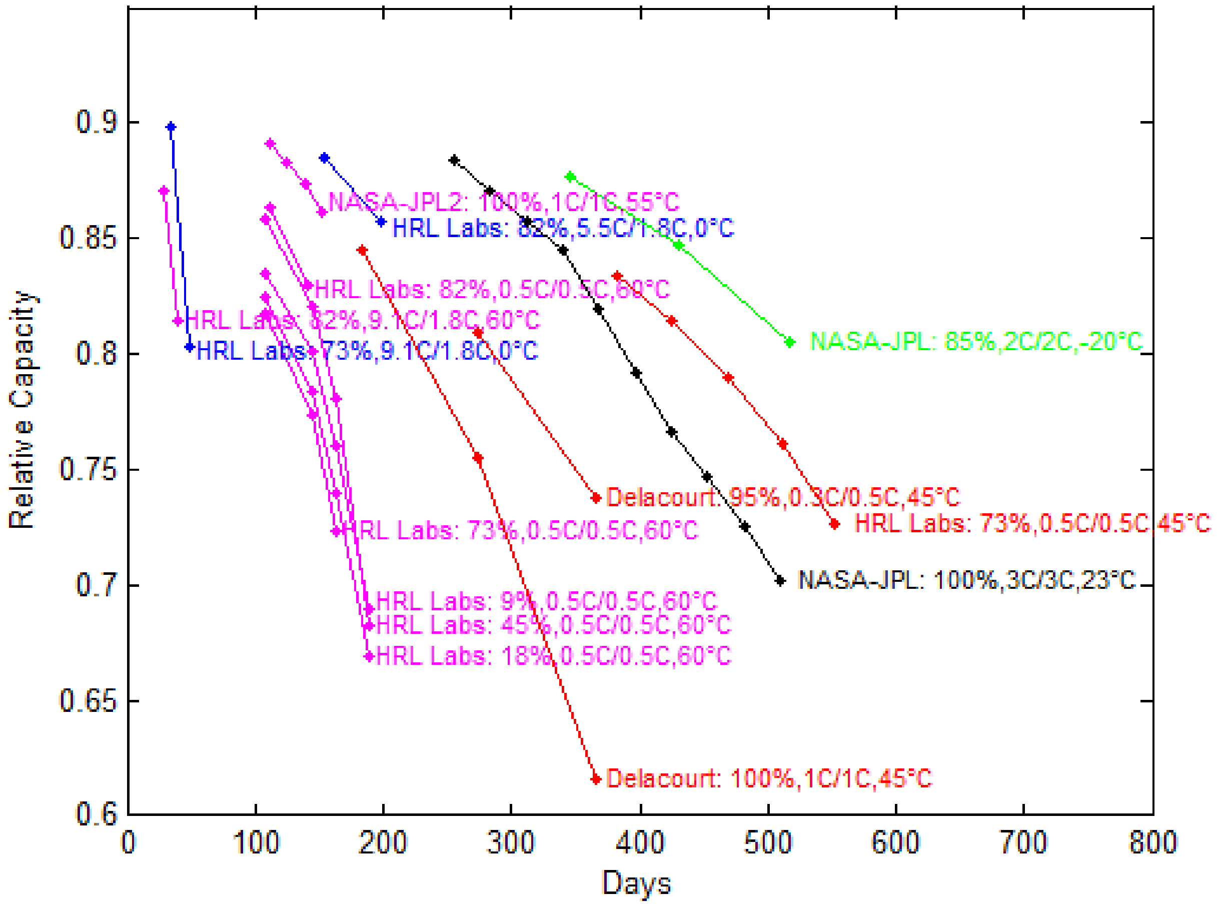
Electrode Site Loss – Cell Aging Data

- Graphite/iron-phosphate meta-dataset from multiple labs



Electrode Site Loss – Cell Aging Data

- Graphite/iron-phosphate meta-dataset from multiple labs
- 13 of 50+ test conditions show apparent “knee” in capacity fade curve



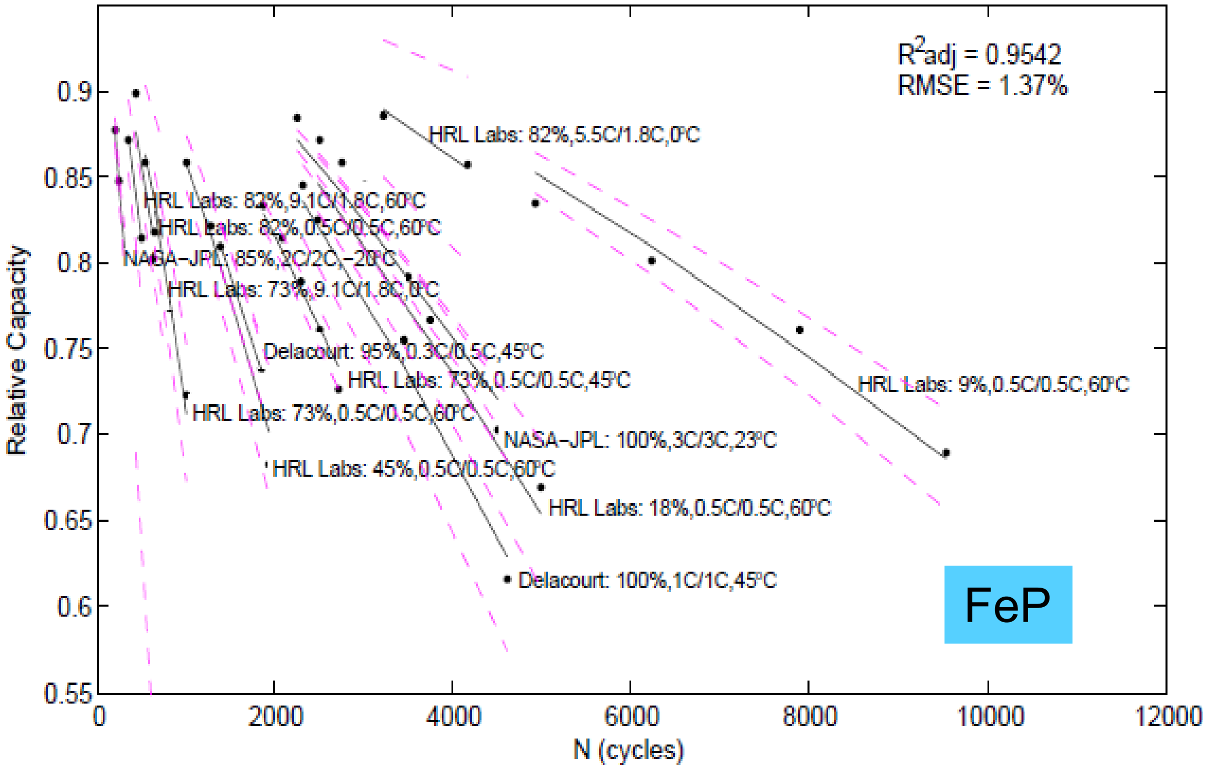
Electrode Site Loss Model (graphite/iron phosphate)

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

$$\boxed{q_{Li} = b_0 + b_1 t^z + b_2 N}$$

$$\boxed{q_{sites} = c_0 + c_2 N}$$

$$c_2 = c_{2,ref}\left\{ \underbrace{\exp\left(\frac{-E_a^{\text{binder}}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)}_{\text{accelerated polymer failure at high T}}\left[\underbrace{m_1\, DOD}_{\text{bulk intercalation strain}} + \underbrace{m_2\,\Delta T}_{\text{bulk thermal strain}}\right] + \underbrace{m_3 \exp\left(\frac{-E_a^{\text{intercal.}}}{\text{R}}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)\left(\frac{C_{rate}}{C_{rate,ref}}\right)\left(\sqrt{\frac{t_{pulse}}{t_{pulse,ref}}}\right)}_{\text{intercalation gradient strain, accelerated by low temperature}} \right\}.$$

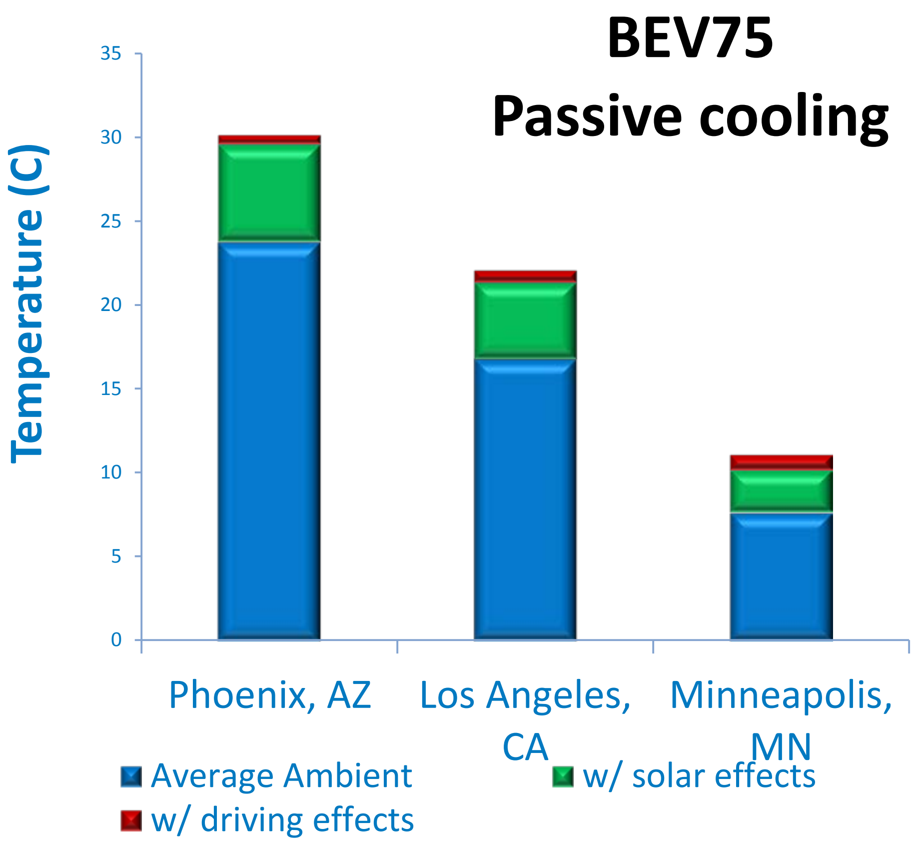


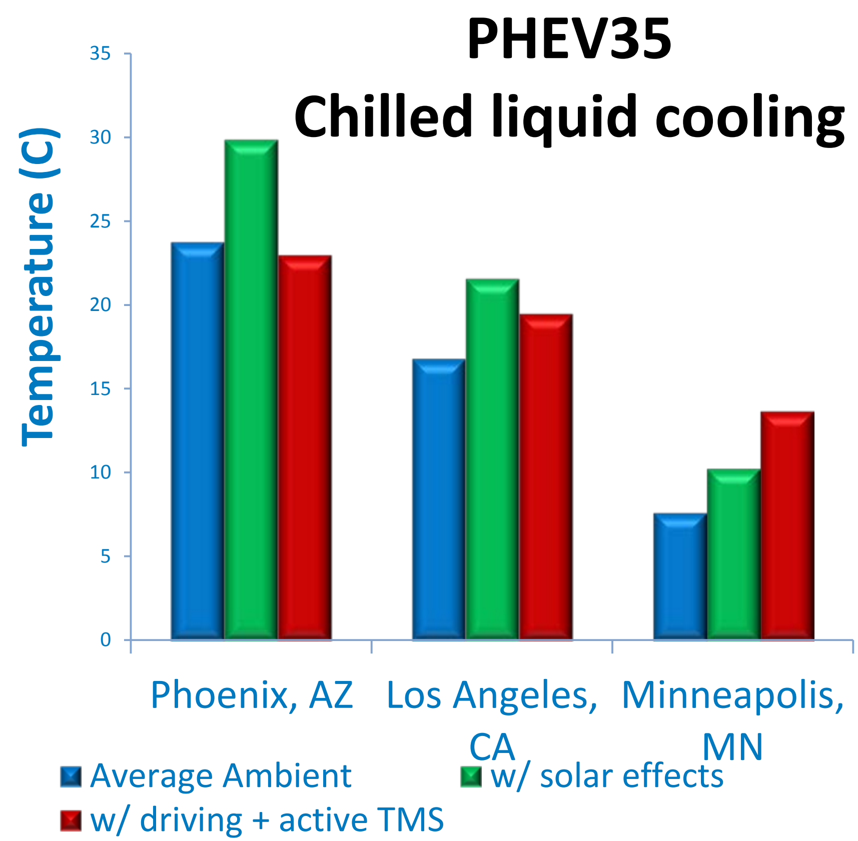
Model successfully describes 13 aging conditions from 0°C to 60°C

Outline

- Background – Li-ion Batteries
- Life Predictive Modeling
- **Automotive Life Studies & Control**
    - Temperature (xEV)
    - Charge control (xEV / grid)
    - Prognostic/duty-cycle control (xEV)

Ambient Effects on Battery Average Temperature





- **Ambient conditions dominate**
- **Thermal connection with passenger cabin, parking in shaded structures strongly influence battery life**

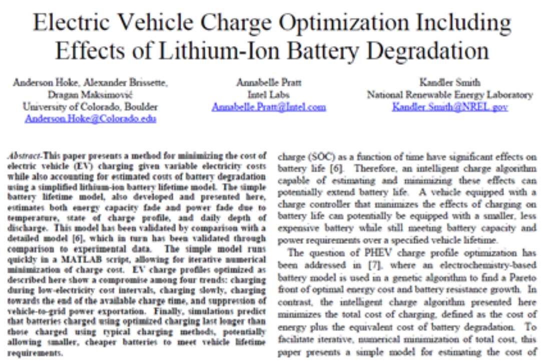
- **Battery temperature and lifetime weakly coupled to ambient conditions**

Optimized Charging Strategies

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

Cost function

$$c_{x,T} = c_{bat} \cdot \left(\underbrace{\int_{t_{ch}} \frac{1}{8760 \cdot L_x\left(T_{amb} + R_{th} \cdot \left|P(t)\right|\right)} dt}_{\Delta L/L \text{ due to charging}} + \underbrace{\frac{t_{max} - t_{ch}}{8760 \cdot L_x\left(T_{amb}\right)}}_{\Delta L/L \text{ while plugged in but not charging}} - \underbrace{\frac{t_{max}}{8760 \cdot L_x\left(P_{min} \cdot R_{th} + T_{amb}\right)}}_{\text{Baseline } \Delta L/L \text{ that would be expended by slow charging}} \right)$$


Electric Vehicle Charge Optimization Including Effects of Lithium-Ion Battery Degradation

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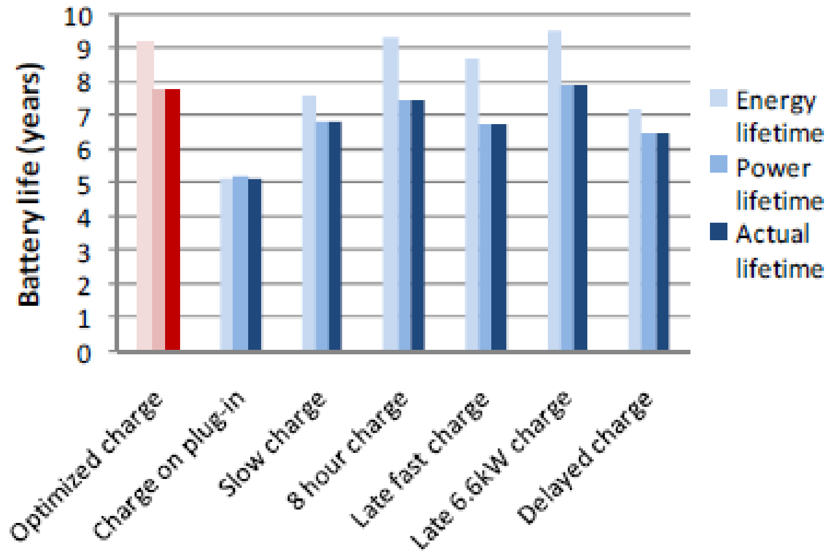
Abstract-This paper presents a method for minimizing the cost of electric vehicle (EV) charging given variable electricity costs while also accounting for estimated costs of battery degradation using a simplified lithium-ion battery lifetime model. The simple battery lifetime model, also developed and presented here, estimates both energy capacity fade and power fade due to temperature, state of charge profile, and daily depth of discharge. This model has been validated by comparison with a detailed model [6], which in turn has been validated through comparison to experimental data. The simple model runs quickly in a MATLAB script, allowing for iterative numerical minimization of charge cost. EV charge profiles optimized as described here show a compromise among four trends: charging during low-electricity cost intervals, charging slowly, charging towards the end of the available charge time, and suppression of vehicle-to-grid power exportation. Finally, simulations predict that batteries charged using optimized charging last longer than those charged using typical charging methods, potentially allowing smaller, cheaper batteries to meet vehicle lifetime requirements.

charge (SOC) as a function of time have significant effects on battery life [6]. Therefore, an intelligent charge algorithm capable of estimating and minimizing these effects can potentially extend battery life. A vehicle equipped with a charge controller that minimizes the effects of charging on battery life can potentially be equipped with a smaller, less expensive battery while still meeting battery capacity and power requirements over a specified vehicle lifetime.

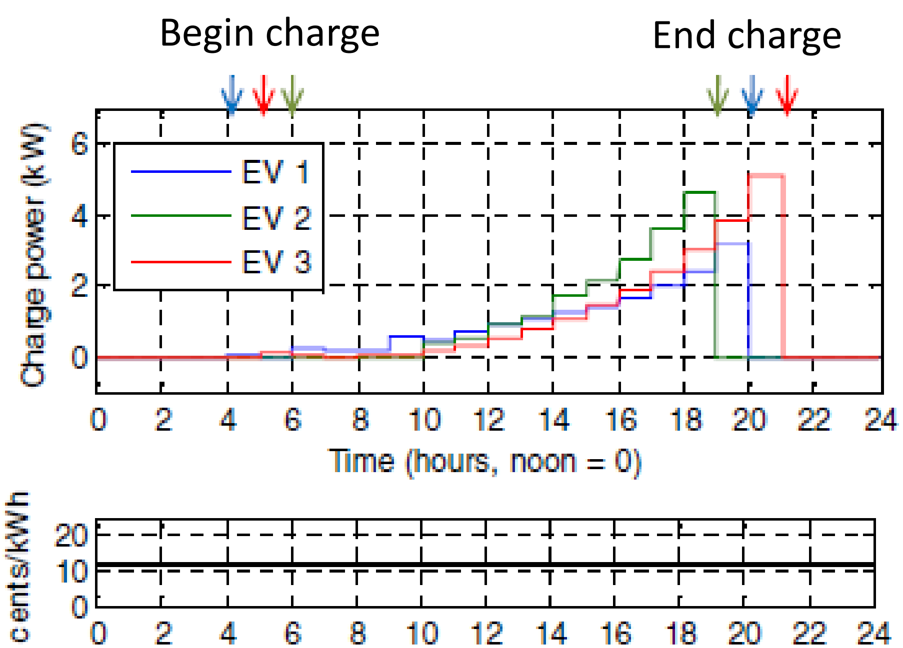
The question of PHEV charge profile optimization has been addressed in [7], where an electrochemistry-based battery model is used in a genetic algorithm to find a Pareto front of optimal energy cost and battery resistance growth. In contrast, the intelligent charge algorithm presented here minimizes the total cost of charging, defined as the cost of energy plus the equivalent cost of battery degradation. To facilitate iterative, numerical minimization of total cost, this paper presents a simple model for estimating the cost of

CU-Boulder/Hoke (2014)



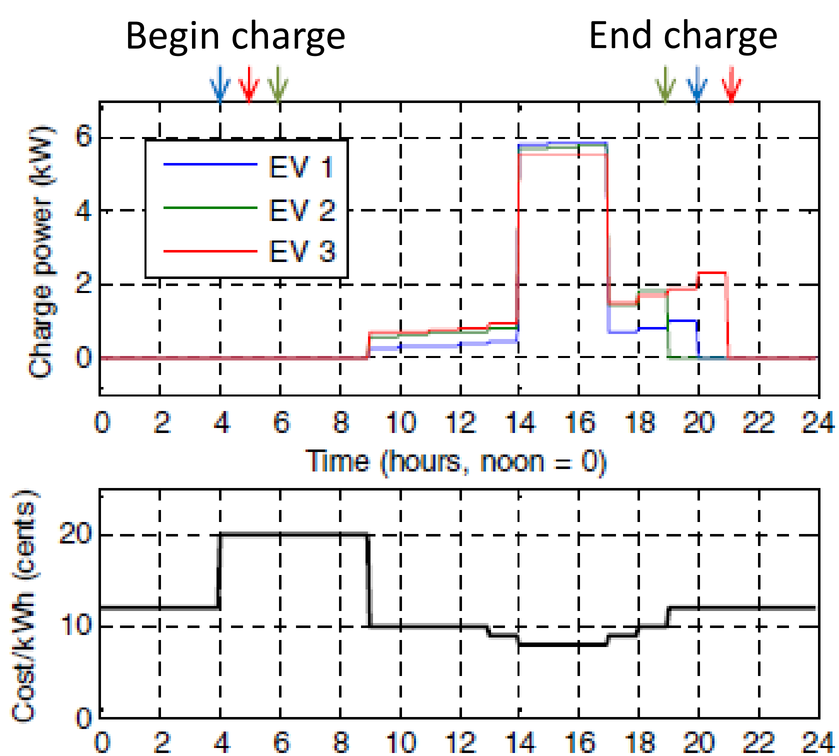
Optimized Charging Strategies

A) Constant energy cost



- Delayed charging best

B) Variable energy cost



- Response to price signals

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

NREL ARPA-E AMPED Projects in Battery Control

AMPED = Advanced Management and Protection of Energy Storage Devices

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

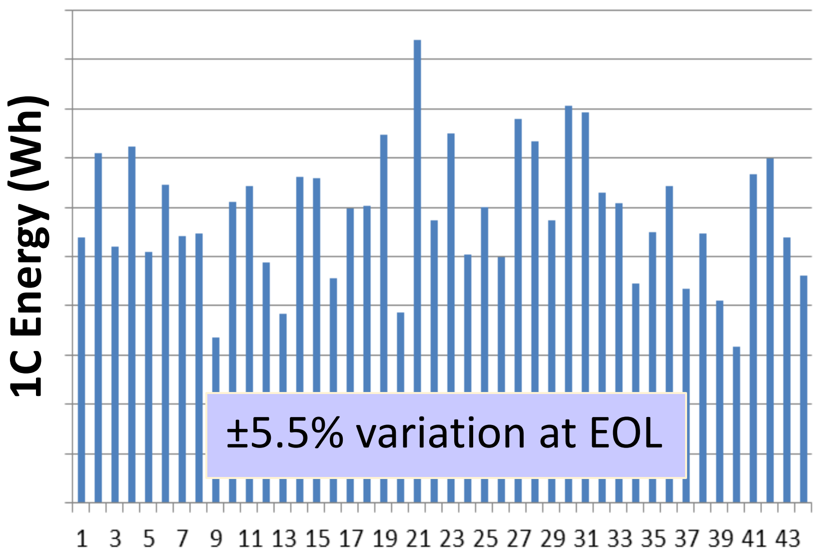
NREL: Physics-based cell-level models for MPC; implement WU reformulated models on BMS; validate at cell & module level

NREL ARPA-E AMPED Projects in Battery Control

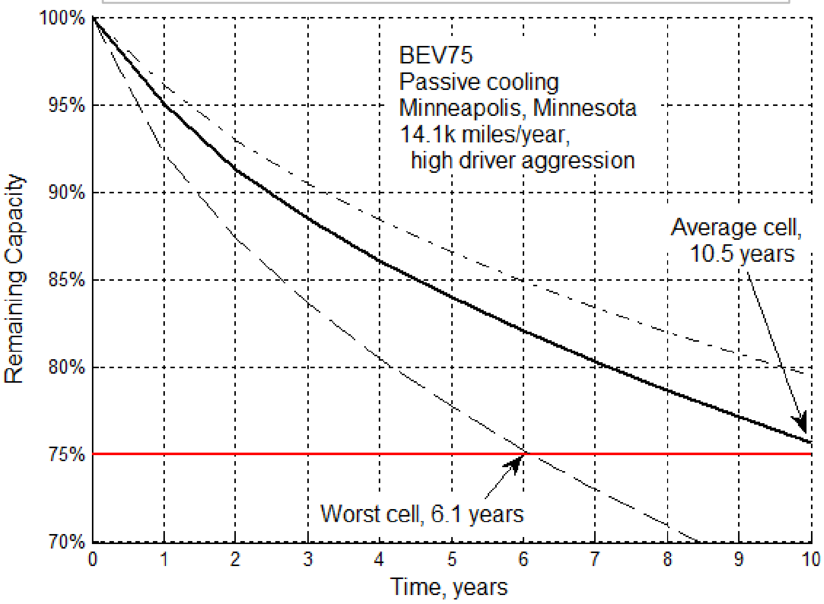
Eaton Corporation | **Utah State/Ford** | Washington Univ.

- Active balancing most benefits energy applications with large cell-to-cell disparity
- Key question: How much does cell-to-cell disparity grow with age?

Teardown analysis of automotive pack aged to 70% remaining energy shows ±5.5% variation at EOL



Extreme driving conditions, large pack ΔT cause abnormally large cell capacity imbalance growth



Summary

- **Main factors controlling battery lifetime**
  - Time at high T & SOC (weak coupling with DOD & C-rate)
  - Cycling at high DOD & C-rate; Low/high T & SOC
- **Semi-empirical battery lifetime models are generally suitable for system design & control**
  - NREL models describe various commercial chemistries
  - Life extensions of 20% to 50% may be possible
- **Physics lifetime models to provide design feedback**
  - Electrochemical/thermal processes well understood
  - Mechanics coupling underway at various length scales

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Collaborators

- Texas A&M University: Partha Mukherjee, Pallab Barai, Kai An
- University of Colorado at Boulder: Kurt Maute, Reza Behrou, Dragan Maksimovic, Andrew Hoke
- Colorado School of Mines: Corinne Packard, David Diercks, Brian Gorman
- Eaton Corporation: Chinmaya Patil
- Utah State: Regan Zane
- Ford Motor Company: Dyche Anderson

Thank you