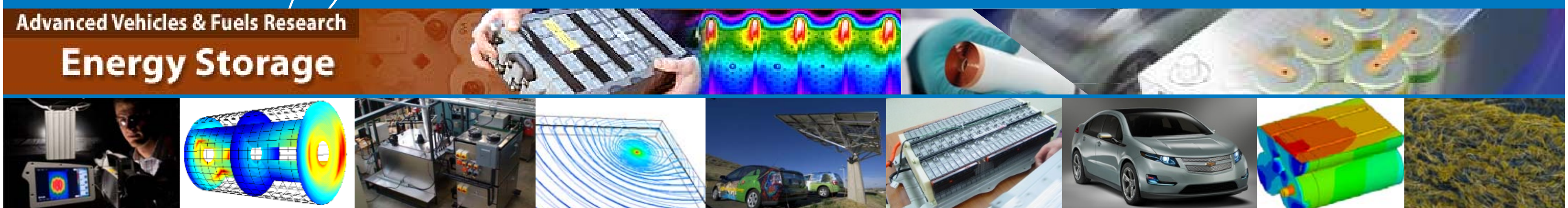
ECEN5017 Guest Lecture

Overview of NREL Battery Lifetime Models & Health Management R&D for Electric Drive Vehicles



Kandler Smith
kandler.smith@nrel.gov

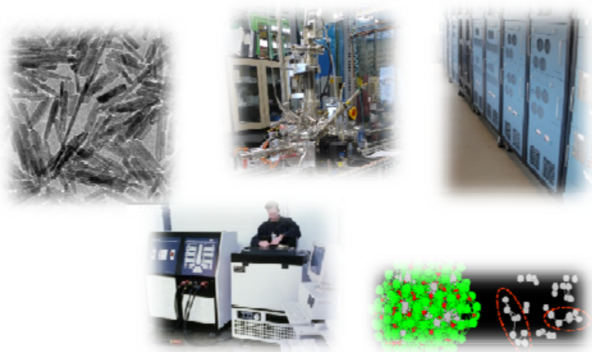
Ahmad A. Pesaran
ahmad.pesaran@nrel.gov

Center for Transportation Technologies and Systems
National Renewable Energy Laboratory

September 2012

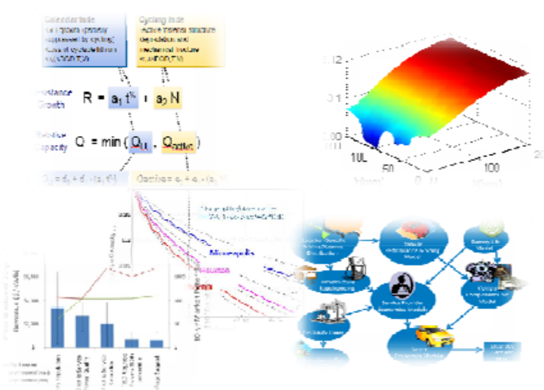
NREL EDV Energy Storage Projects

Supporting DOE and industry achieve energy storage targets for electrified vehicles



NREL

Energy Storage Task



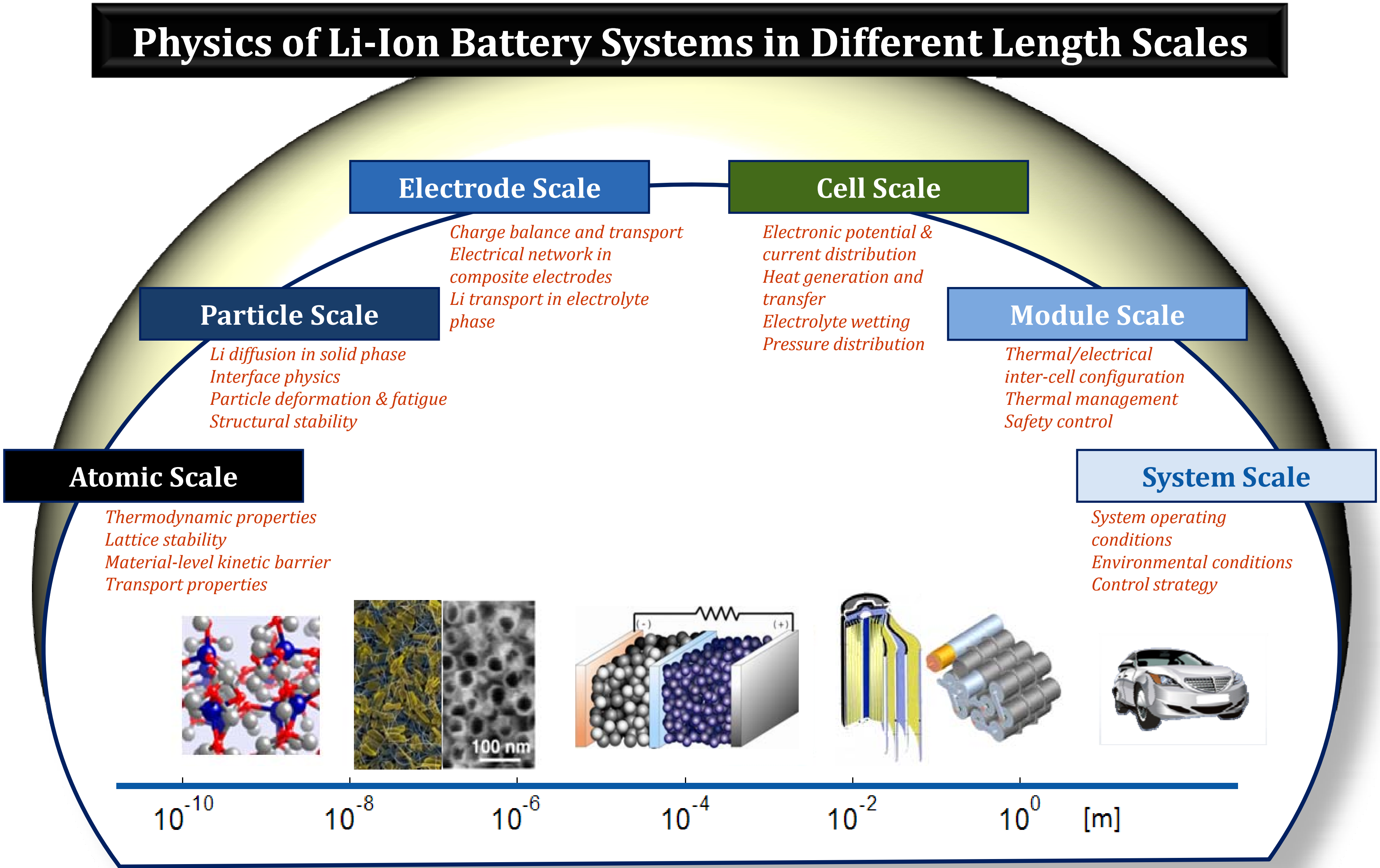
Battery Material Research and Development

Component Testing and Characterization (Including Safety)

Multi-physics Battery Modeling (including Safety)

Battery Life Prediction and Trade-off

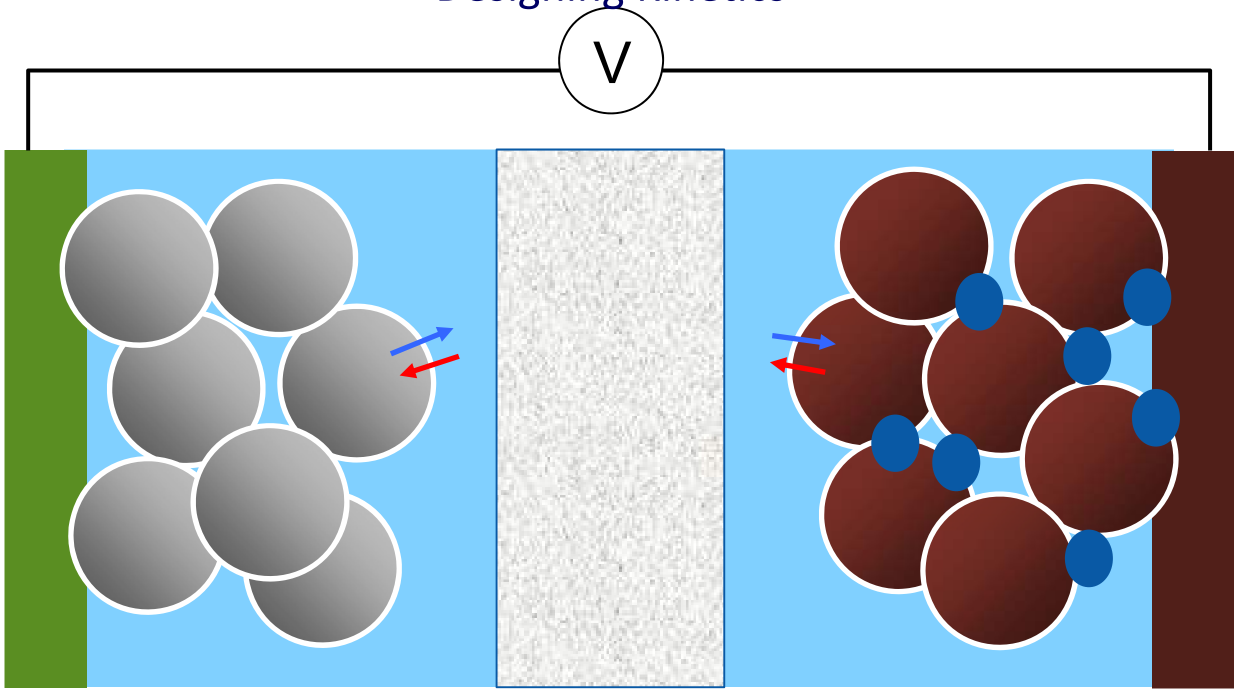
Battery System Evaluation



DOE/NREL Computer-Aided Engineering of Batteries (CAEBAT) Program Integrating Battery R&D Models

Typical Structure of Li-ion Batteries

Designing Thermodynamics
Designing Kinetics



Why Lithium Ion?

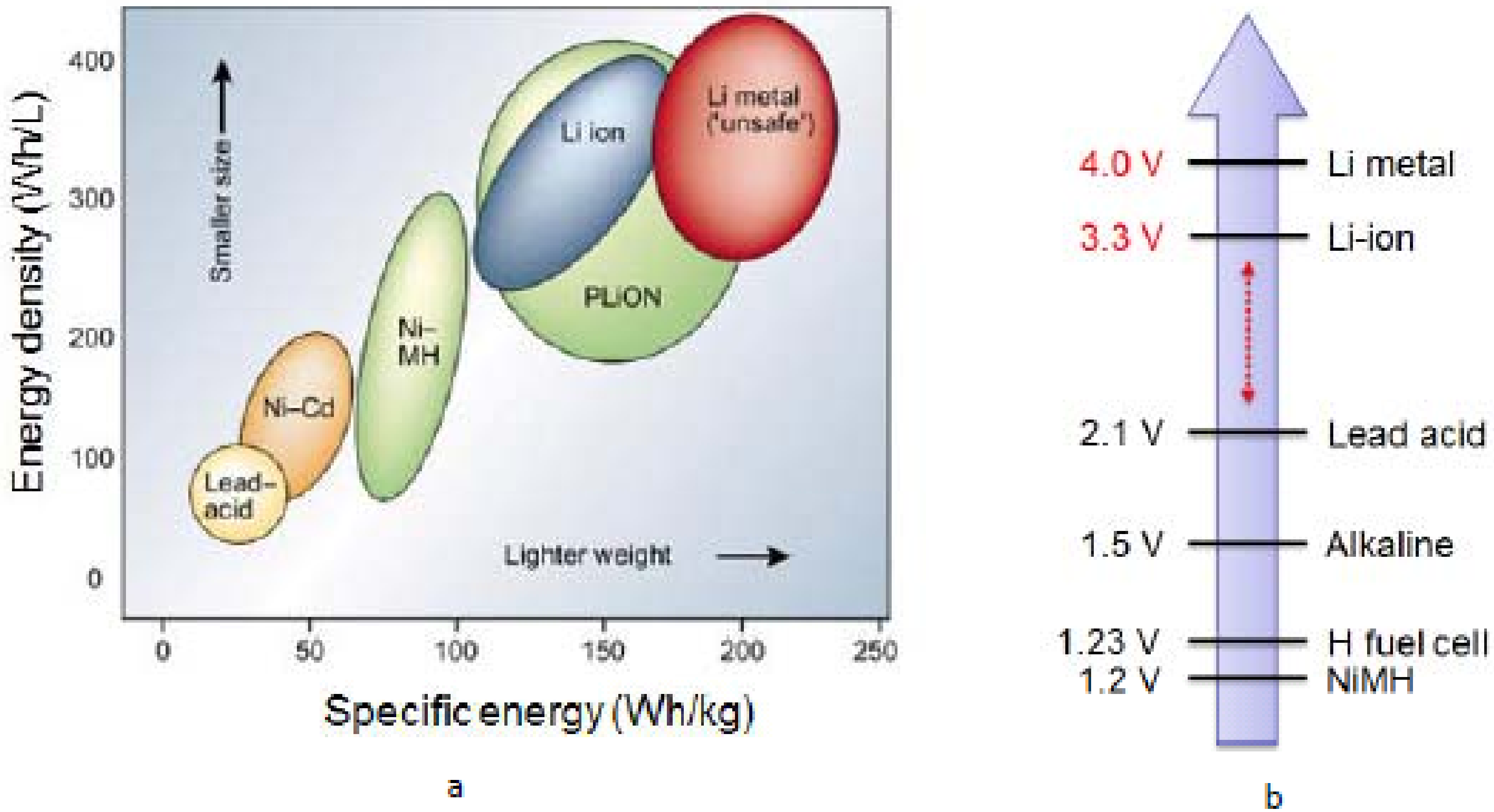


Figure 2 a) Energy density per unit mass and volume for common secondary cells[4]; b) Electrochemical cell voltages

Figures:
Cyril Truchot, MS Thesis

What determines working voltage?

Thermodynamic potential = Cathode potential – Anode potential

Anode:

Graphite, Li_xC6

Lithium metal

Silicon

Cathode:

Choice of transition metals

Choice of crystal structures

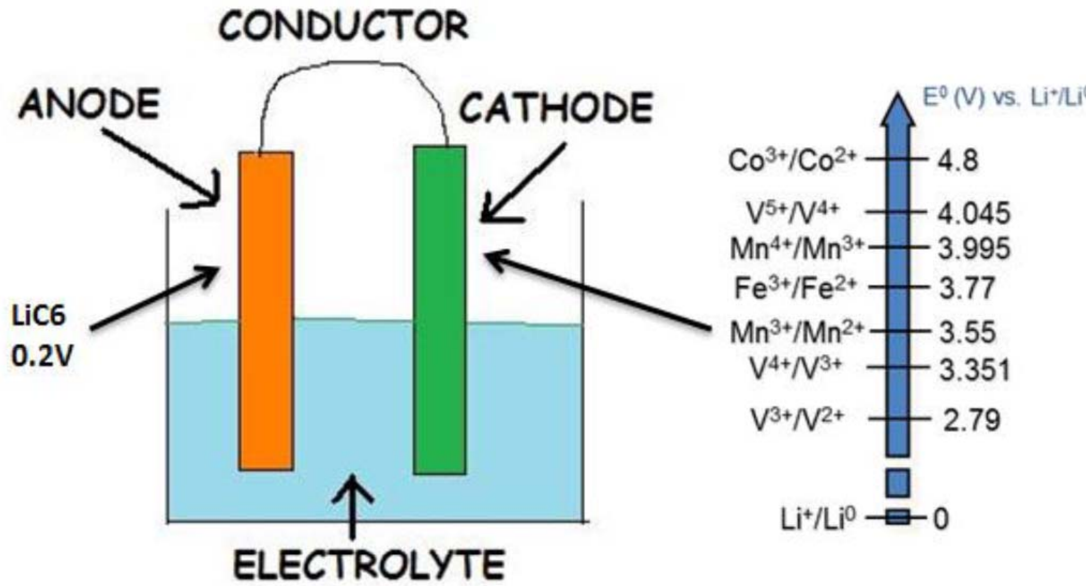
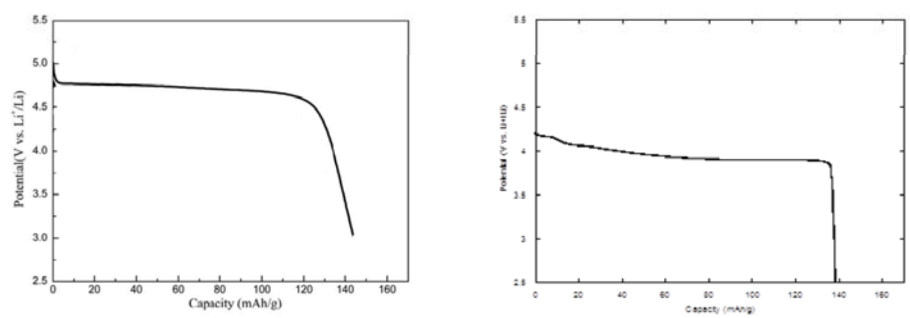


Figure 74 Diverse redox couples used in Li-ion batteries



a b

Figure 75 Potential vs. capacity of lithium insertion in a) LiCoPO4 and b) LiCoO2

Figures: Cyril Truchot, MS Thesis

Cathode selection

Chemical name	Material (short form)	Specific capacity (mAh/g)	Cell voltage (V)	Notes
Lithium Cobalt Oxide	$LiCoO_2$ (LCO)	170	3.7	High capacity, low rate capability
Lithium Manganese Oxide	$LiMn_2O_4$ (LMO)	120-140	3.9	Most safe, lower capability but high power
Lithium Nickel Manganese Cobalt Oxide	$LiNiMnCoO_2$ (NMC)	160-170	3.7	High capacity, low rate capability
Lithium Iron Phosphate	$LiFePO_4$ (LFP)	130	3.3	Low capacity, high rate capability

Table 1 Li-ion cell chemistry summary

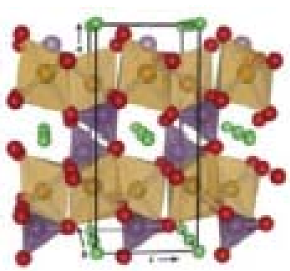
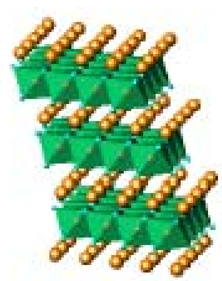
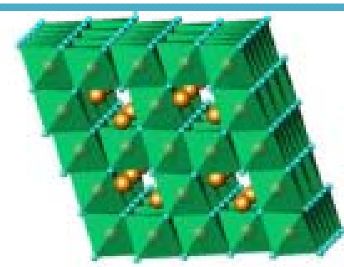
Electrode material	1-D tunnel structure of LFP	2-D layered structure of LCO or NMC	3-D structure of LMO
Crystal structure			

Table 9 Positive electrode crystal structures

Source:
Cyril Truchot,
MS Thesis

Battery Aging / Performance Fade

System-level observations

- Capacity loss
- Impedance rise/power fade
- Potential change

Calendar life goal: 10 to 15 years → Effects during storage

- Self discharge, impedance rise

Cycle life goal: 3,000 to 5,000 deep cycles → Effects during use

- Mechanical degradation, Li metal plating

Where do changes occur?

1. Electrode/electrolyte interface, affecting both electrode & electrolyte
2. Active materials
3. Composite electrode

Anode Aging

1. Solid/Electrolyte Interphase (SEI) Layer

Passive protective layer, product of organic electrolyte decomposition

SEI formation = f(a_s, formation conditions)

Mostly formed during first cycle of battery, but continues to grow at slow rate

May penetrate into electrode & separator pores, inhibiting Li transport in the electrolyte

High temperature effects

- Exothermic side reactions cause self heating
- Film breaks down and dissolves, later precipitates
- More-stable inorganic SEI formed, blocking Li insertion

Low temperature effects (during charging)

- Slow diffusion causes Li saturation at Li_xC_6 surface
- Slow kinetics causes increased overpotential

Anode Aging

2. Changes of Active Material

Volume changes during insertion/de-insertion (~10%)

Solvent intercalation, electrolyte reduction, gas evolution inside Li_xC_6

→ Stress → Cracks

3. Changes of Composite Electrode

SEI & volume changes cause:

- contact loss between Li_xC_6, conductive binder, and current collector
- reduced electrode porosity

Anode Aging

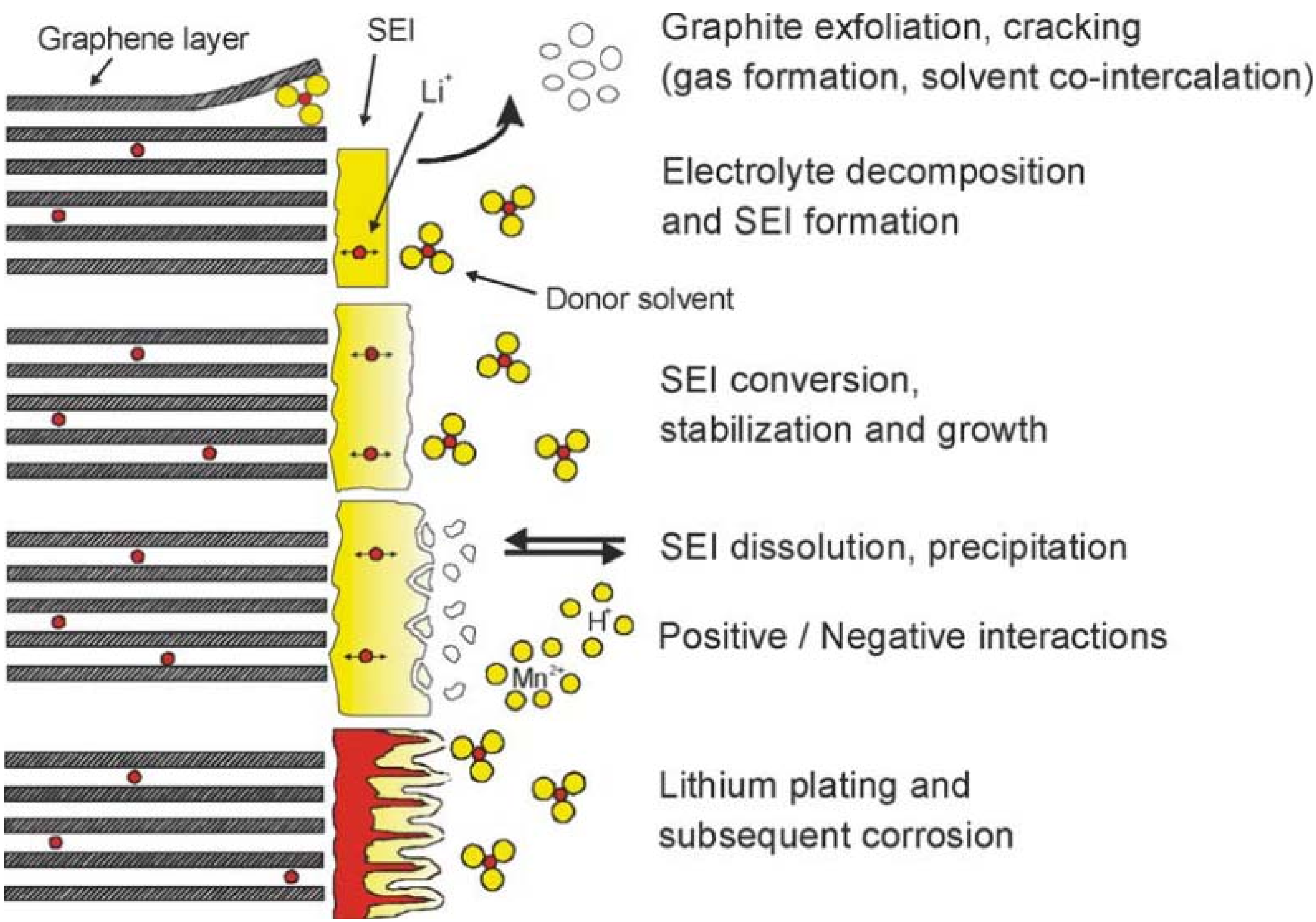


Image: Vetter et al., "Ageing mechanisms in lithium-ion batteries," J. Power Sources, 147 (2005) 269-281

Cathode Aging

$Li(Ni,Co,Al)O_2$ Materials

$LiCoO_2$ common cathode material

$LiNiO_2$ structure unstable unless doped with Co or Al

$Li(Ni,Co,Al)O_2$ volume changes are small → good cycle life

Discharged state stable at high temperatures

$LiCoO_2$ charged beyond 4.2 volts, Co dissolves and migrates to anode

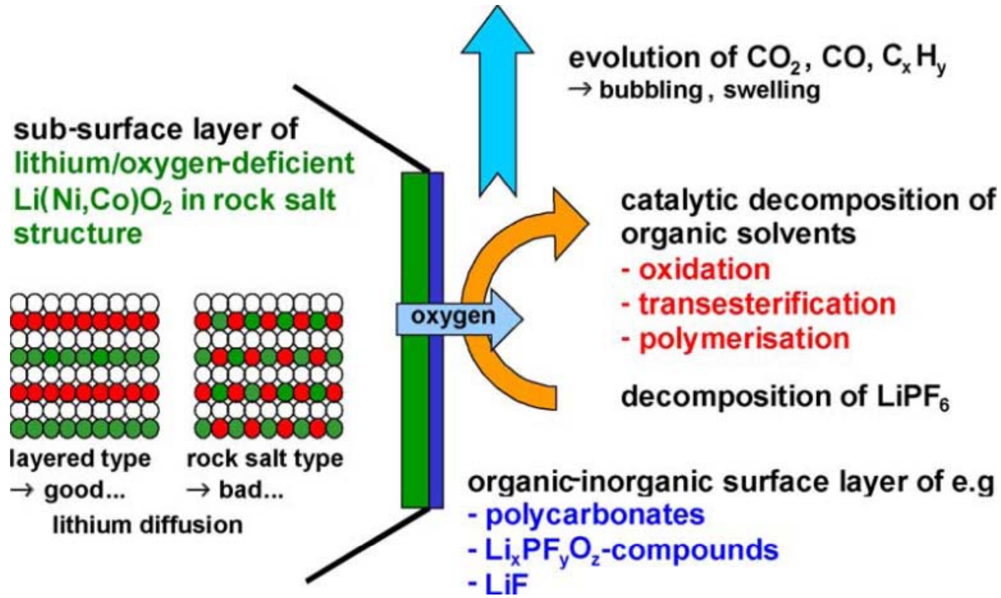
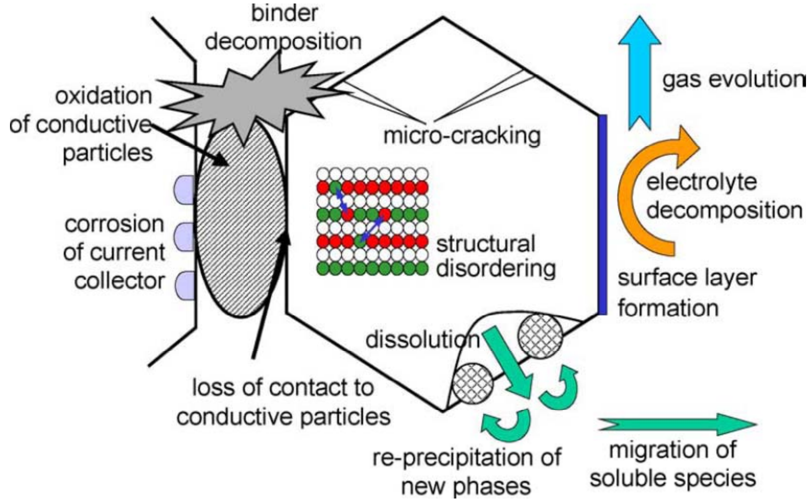


Image: Vetter et al., “Ageing mechanisms in lithium-ion batteries,” J. Power Sources, 147 (2005) 269-281

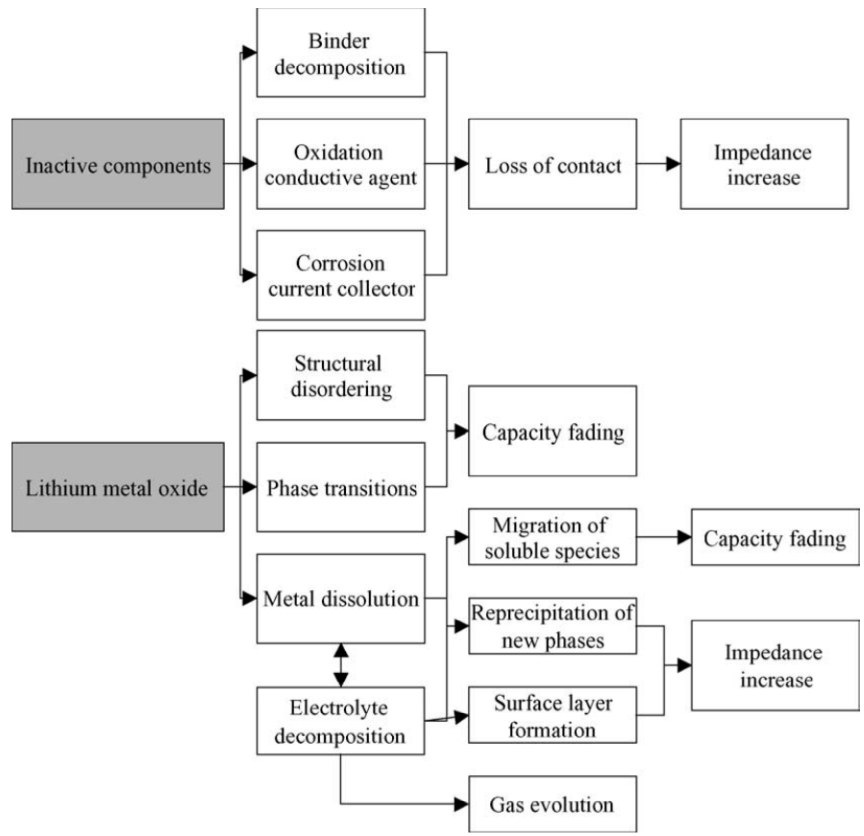
Surface effects

- SEI film formation accelerated when charged > 4.2 V, high temperatures
- Electrolyte oxidation and $LiPF_6$ decomposition
- $Li(Ni,Co,Al)O_2$ source O_2 → rock-salt structure with low electronic conductivity & Li diffusion
- Gas evolution

Cathode Aging



Source: Vetter et al., “Ageing mechanisms in lithium-ion batteries,” J. Power Sources, 147 (2005) 269-281



Source: Wohlfahrt-Mehrens et al., “Aging mechanisms of lithium cathode materials,” J. Power Sources, 127 (2004) 58-64

Summary of Aging

Aging influenced by:

Both high and low SOC

High temperatures

Low temperatures during charging

Surface chemistry (anode and cathode)

Phase transitions/structural changes (cathode)

Both calendar life (years) and cycle life (driving and charging patterns) are important

How Can We Predict Battery Life?

<u>Accelerated storage tests</u>

Relatively well understood

Mechanism: SEI growth, Li loss

Model:

- $t^{1/2}$ time dependency
- Arrhenius T dependency

<u>Accelerated cycling tests</u>

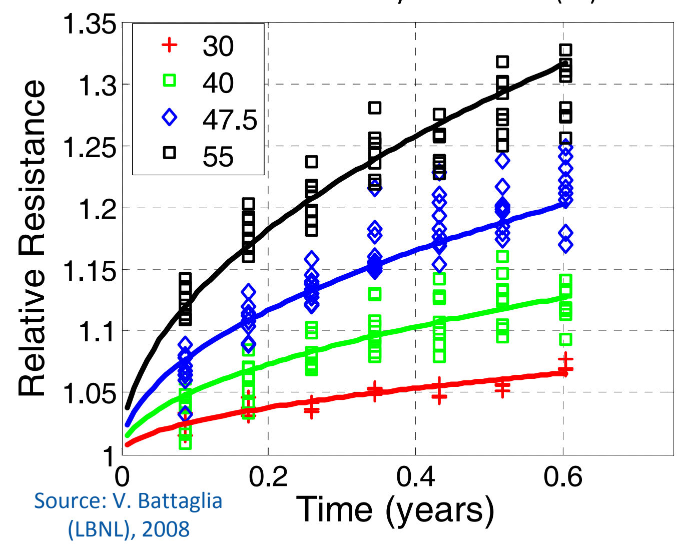
Poorly understood

Mechanism: Mechanical stress & fracture
(may be coupled with SEI fracture + regrowth)

Model:

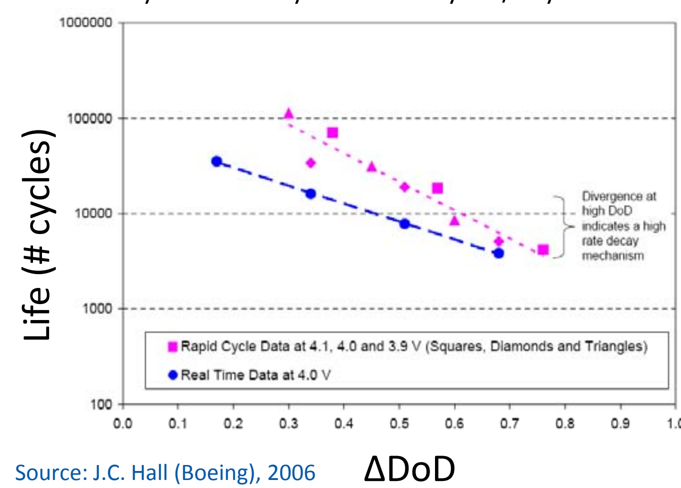
- Typical t or N dependency
- Often correlated log(# cycles) with ΔDOD

Calendar Life Study at Various T (°C)



Source: V. Battaglia (LBNL), 2008

Cycle Life Study at Various Cycles/Day & ΔDoD



Source: J.C. Hall (Boeing), 2006

<u>Real-world cycling & storage</u>

- **Poorly understood**
- NREL model extends previous work by enabling extrapolation beyond tested conditions

NREL's Battery Life-Prognostic Model

Battery aging datasets fit with empirical, yet physically justifiable formulas

Calendar fade
- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- a_1, d_1 = f(ΔDOD,C-rate,T,V)

Cycling fade
- active material structure degradation and mechanical fracture
- a_2, e_1 = f(ΔDOD,C-rate,T,V)

Relative Resistance

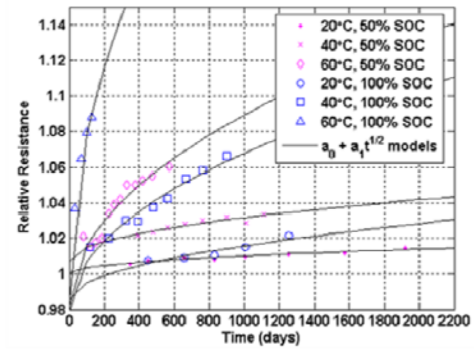
$$R = a_1 t^{1/2} + a_2 N$$

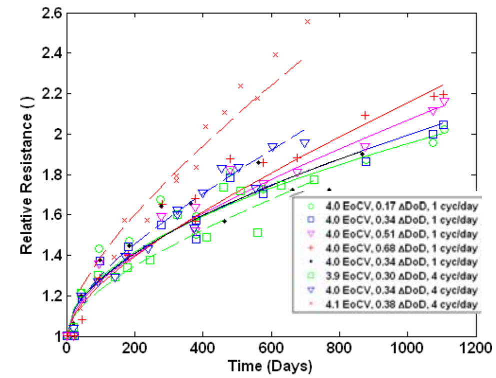
Relative Capacity

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

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

$$Q_{active} = e_0 + e_1 N$$





Enables life predictions for untested real-world scenarios

Fitting of NCA/Graphite Baseline Life Model to Lab Data

1. Resistance growth during storage
   - ♦ Broussely (Saft), 2007:
     - T = 20°C, 40°C, 60°C
     - SOC = 50%, 100%
2. 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
3. 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
4. Capacity fade during cycling
   - ♦ Hall/Boeing, 2005-2006: (same as # 2 above)

- **30 different tests**
- **>$1M in test equipment**
- **1-4 years duration**

→ <u>Expensive!!</u>

Acceleration Factors

Arrhenius Eqn.

$$\theta_T = \exp\left[\frac{-\boxed{E_a}}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right]$$

Tafel Eqn.

$$\theta_V = \exp\left[\frac{\boxed{\alpha}F}{R}\left(\frac{V_{oc}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}}\right)\right]$$

Wöhler Eqn.

$$\theta_{\Delta DoD} = \left(\frac{\Delta DoD}{\Delta DoD_{ref}}\right)^{\boxed{\beta}}$$

- Describe a_1, a_2, b_1, c_1 as f(T,V_{oc},ΔDoD)
- Combined effects assumed multiplicative

Acceleration Factors

Resistance growth during storage

Data: Broussely, 2007

Arrhenius Eqn.

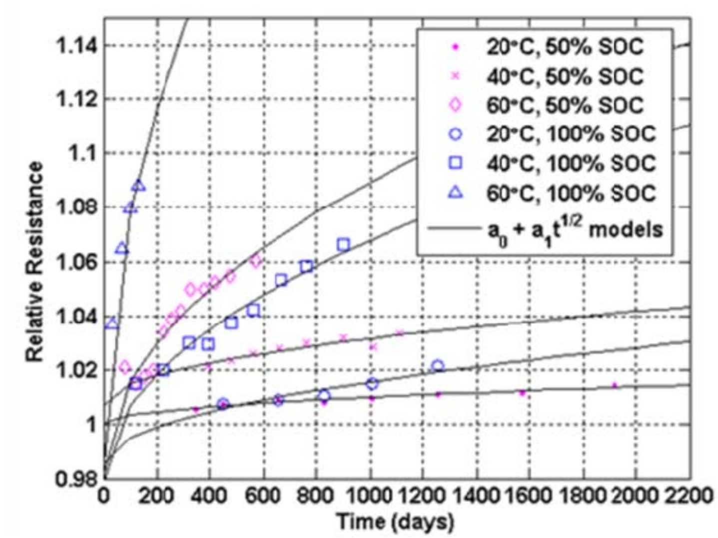
$$\theta_T = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right]$$

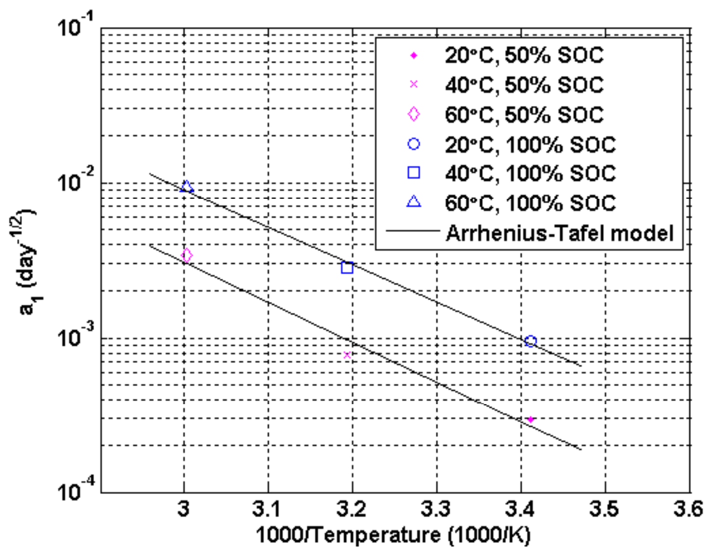
Tafel Eqn.

$$\theta_V = \exp\left[\frac{\alpha F}{R}\left(\frac{V_{oc}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}}\right)\right]$$

Wöhler Eqn.

$$\theta_{\Delta DoD} = \left(\frac{\Delta DoD}{\Delta DoD_{ref}}\right)^{\beta}$$





Acceleration Factors

Arrhenius Eqn.

$$\theta_T = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right]$$

Tafel Eqn.

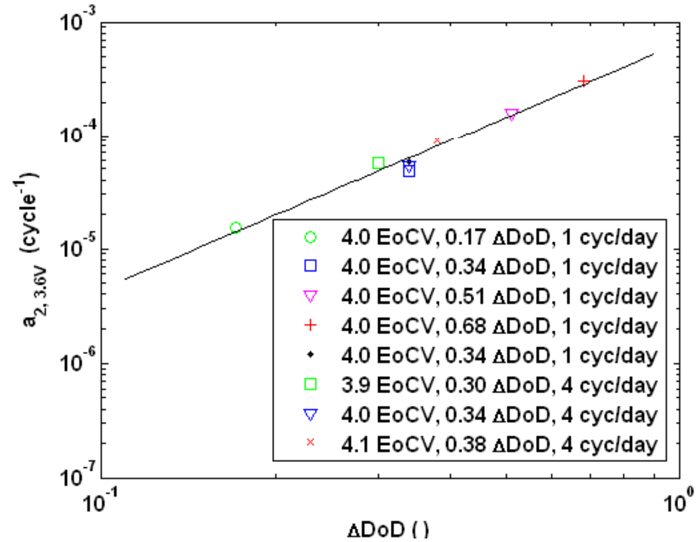
$$\theta_V = \exp\left[\frac{\alpha F}{R}\left(\frac{V_{oc}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}}\right)\right]$$

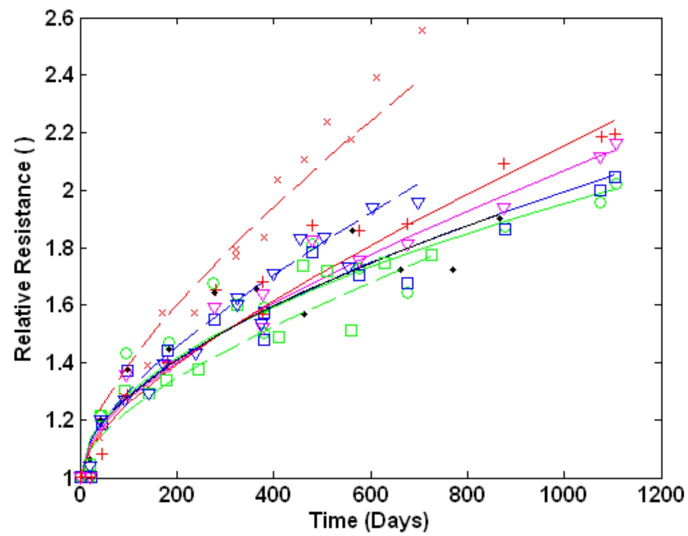
Wöhler Eqn.

$$\theta_{\Delta DoD} = \left(\frac{\Delta DoD}{\Delta DoD_{ref}}\right)^{\beta}$$

Resistance growth during cycling

Data: Hall, 2006





Acceleration Factors

Arrhenius Eqn.

$$\theta_T = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right]$$

Tafel Eqn.

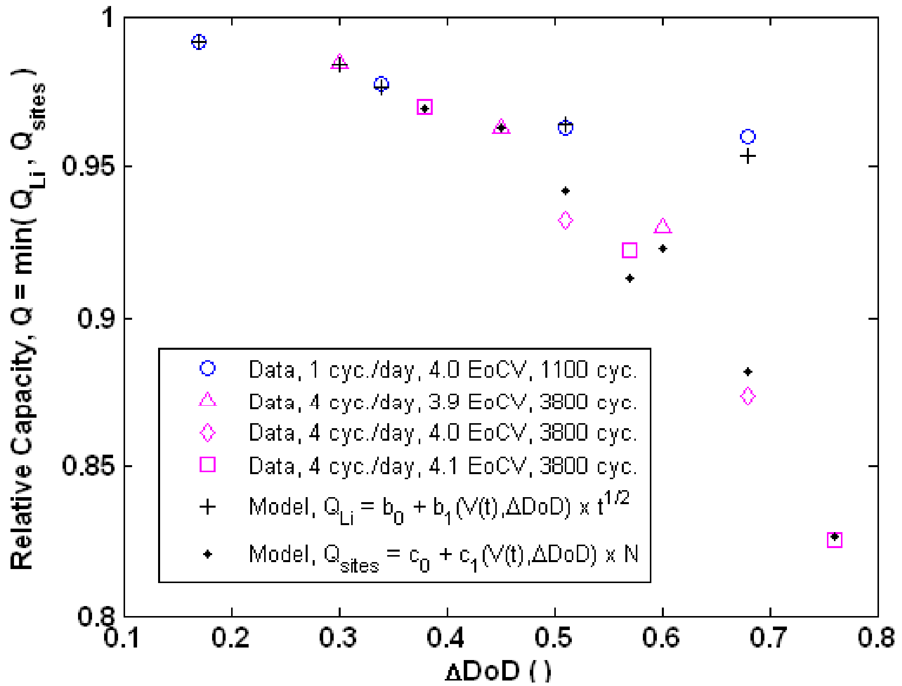
$$\theta_V = \exp\left[\frac{\alpha F}{R}\left(\frac{V_{oc}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}}\right)\right]$$

Wöhler Eqn.

$$\theta_{\Delta DoD} = \left(\frac{\Delta DoD}{\Delta DoD_{ref}}\right)^{\beta}$$

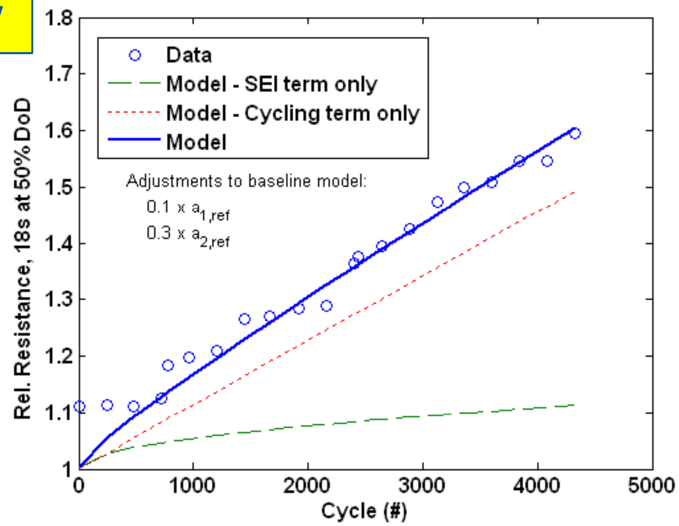
Capacity fade during cycling

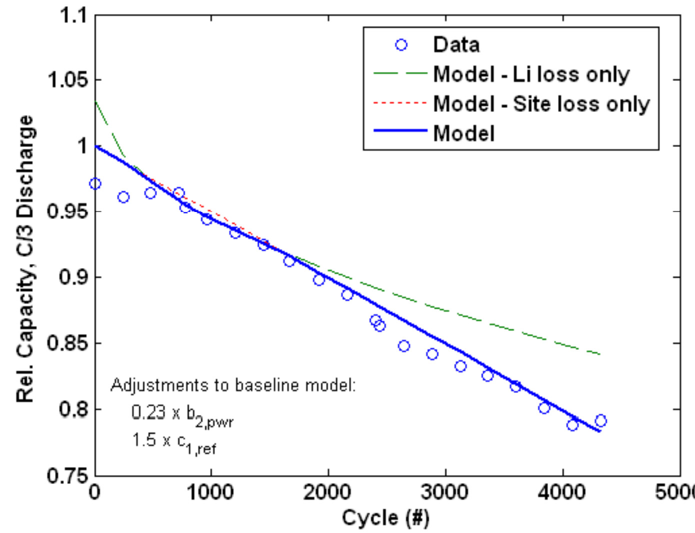
Data: Hall, 2006



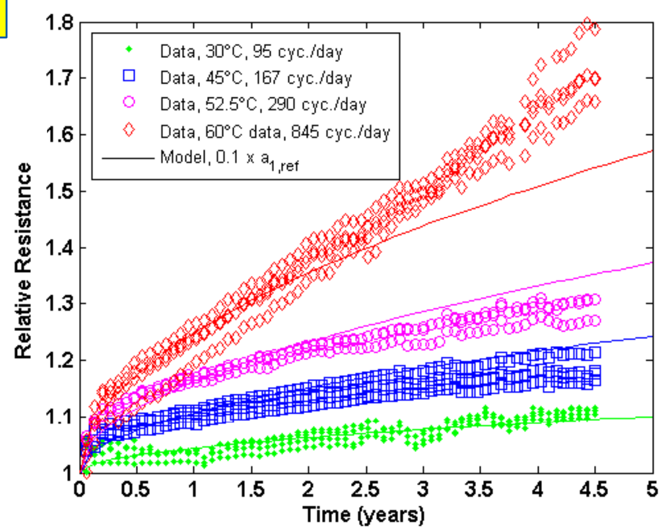
Model Comparison with Laboratory Data

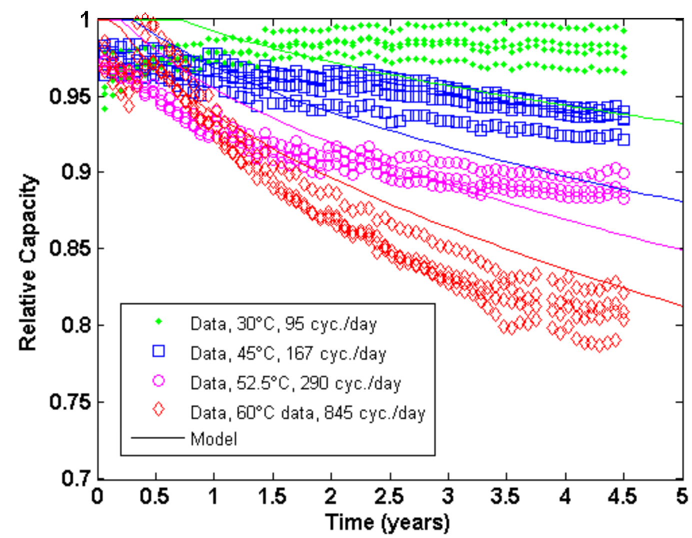
PHEV





HEV





Factors in Vehicle Battery Aging

Cell Design	Environment	Duty Cycle

• **Chemical**
• **Electrochemical**
• **Electrical**
• **Manuf. uniformity**
  o defects
	• **Thermal**
	  o geography
	  o thermal management system ($)
	  o heat generation
	• **Humidity**
	• **Vibration**
		• **System design**
		  o vehicle
		  o excess power & energy @ BOL ($)
		  o system controls
		• **Driver**
		  o annual mileage
		  o trips/day
		  o aggressiveness
		  o charging behavior
		    – charges/day
		    – fast charge

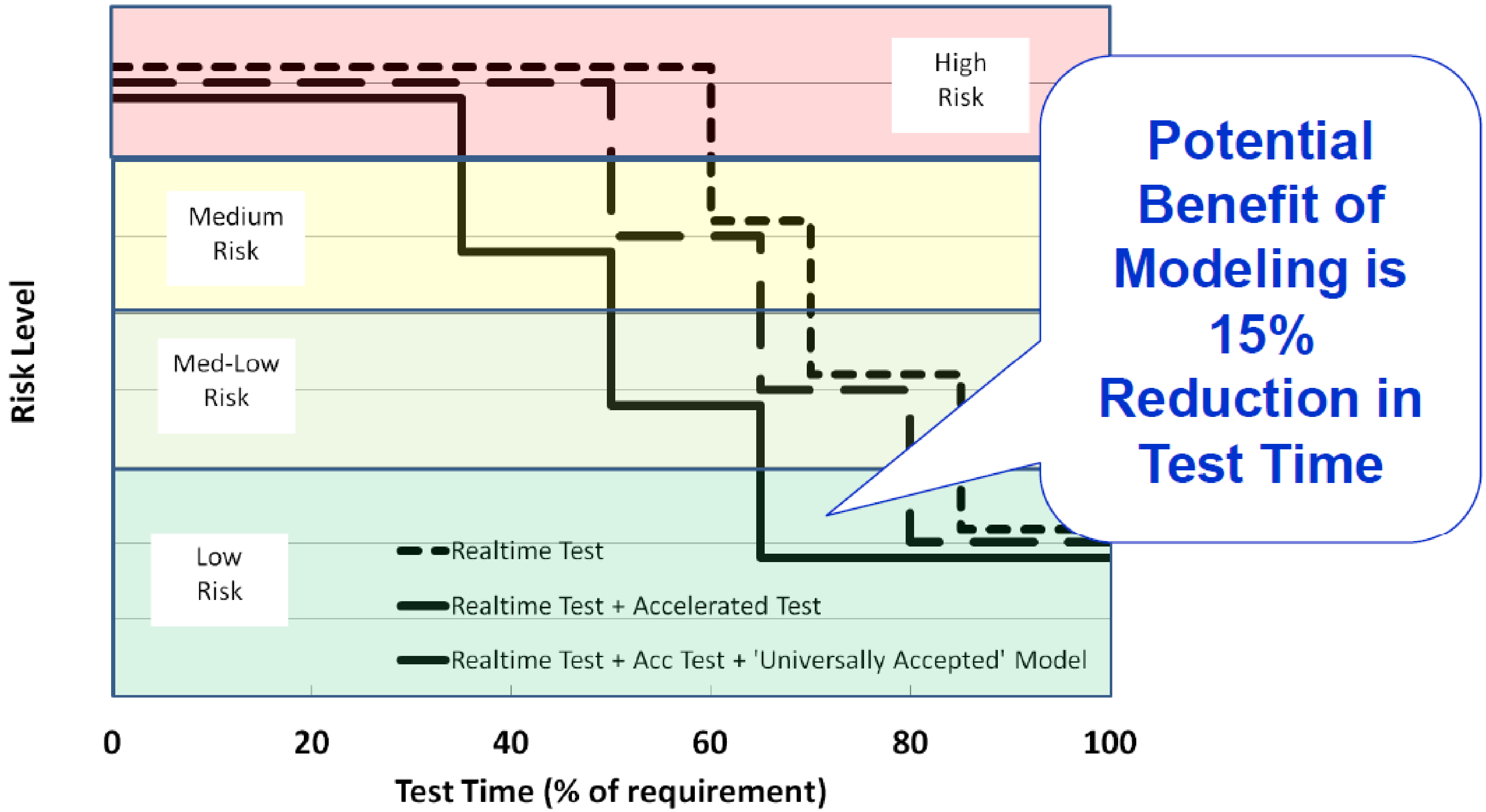
Factors in Vehicle Battery Aging

Cell Design	Environment	Duty Cycle
• **Chemical** • **Electrochemical** • **Electrical** • ~~**Manuf. uniformity**~~ o ~~defects~~	• **Thermal** o geography o thermal management system ($) o heat generation • ~~**Humidity**~~ • ~~**Vibration**~~	• **System design** o vehicle o excess power & energy @ BOL ($) o system controls • **Driver** o annual mileage o trips/day o aggressiveness o charging behavior – charges/day – ~~fast charge~~

~~(Not considered)~~

Benefit of Life-Predictive Modeling

Source: Mark Isaacson, Lockheed Martin (satellite application)

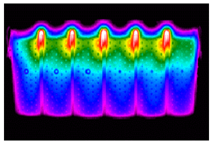


Simulation Approach

Vehicle drive cycles

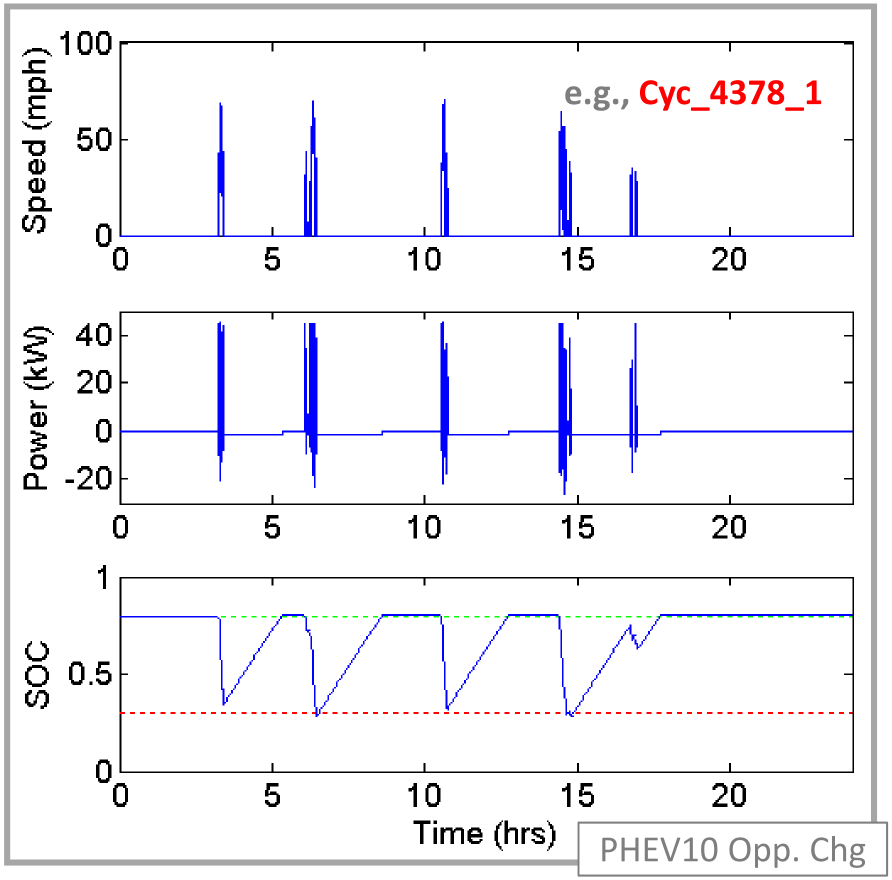
782 speed vs. time traces
Charging assumptions

Vehicle Model



Battery power profile

- **SOC(t), Heat gen(t), etc.**



Simulation Approach

Vehicle drive cycles
782 speed vs. time traces
Charging assumptions

Vehicle Model

Climate

- U.S. national distribution

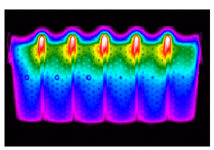
Battery power profile

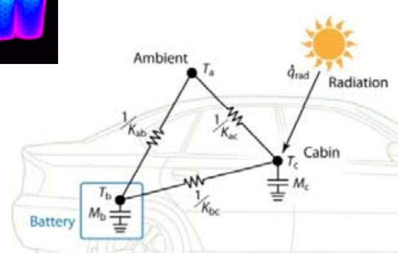
- SOC(t), Heat gen(t), etc.
- Thermal management assumptions

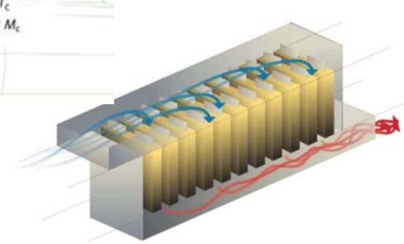
Battery Thermal Model

Battery stress statistics

- T(t), Voc(t), ΔDODi, Ni, …







Simulation Approach

Vehicle drive cycles
782 speed vs. time traces
Charging assumptions

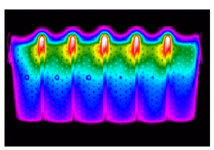
Climate

- U.S. national distribution

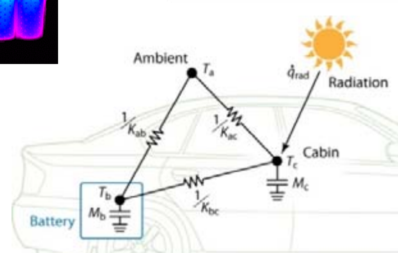
Battery power profile

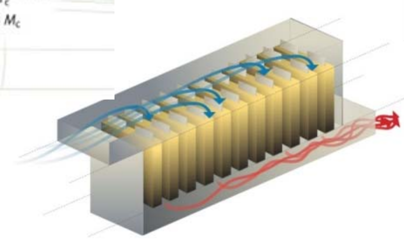
- SOC(t), Heat gen(t), etc.
- Thermal management assumptions

Vehicle Model



Battery Thermal Model



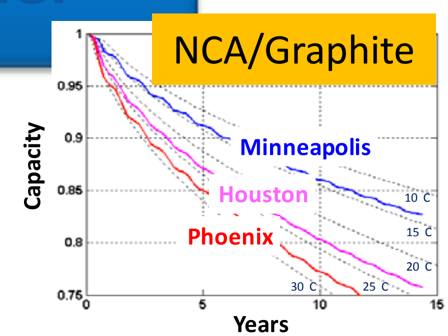


Battery stress statistics

- T(t), Voc(t), ΔDODi, Ni, …

Battery Life Model

Life



Vehicle & Battery Assumptions

		PHEV10	PHEV40
Vehicle	All-electric range, km	16.7	67
	Total vehicle mass, kg	1714	1830
	Electric motor power, kW	40	43
	IC engine power, kW	77	80
Battery Electrical[1]	Useable power, kW	44	48
	Useable energy, kWh	2.67	11.48
	Maximum SOC	80%	90%
	Minimum SOC at BOL	30%	30%
	Minimum SOC at EOL	13%	10%
	Excess energy at BOL	100%	67%
	Excess power at BOL, 10% SOC	43%	43%
Battery Thermal[2]	Heat transfer area - cells-to-coolant, m^2	1	3
	Heat transfer area - pack-to-ambient, m^2	1.2	2.9
	Heat transfer coeff. - pack-to-ambient, W/m^2K	2	2

PHEV10:
50% ΔDOD at BOL
80% SOC_{max}

PHEV40:
60% ΔDOD at BOL
90% SOC_{max}

1. EOL condition = 75% remaining capacity
2. Heat generation rate at 2/3 of EOL resistance growth

Real-World Life Variability with Duty Cycle

Matrix of analytic scenarios

Vehicles

- PHEV10 sedan
- PHEV40 sedan

Duty Cycles

- 782 Real-World drive cycles from Texas Dept. of Transportation

Thermal Management

- Fixed 28°C battery temperature*
- Limited cooling (forced ambient air)
- Aggressive cooling (20°C chilled liquid)

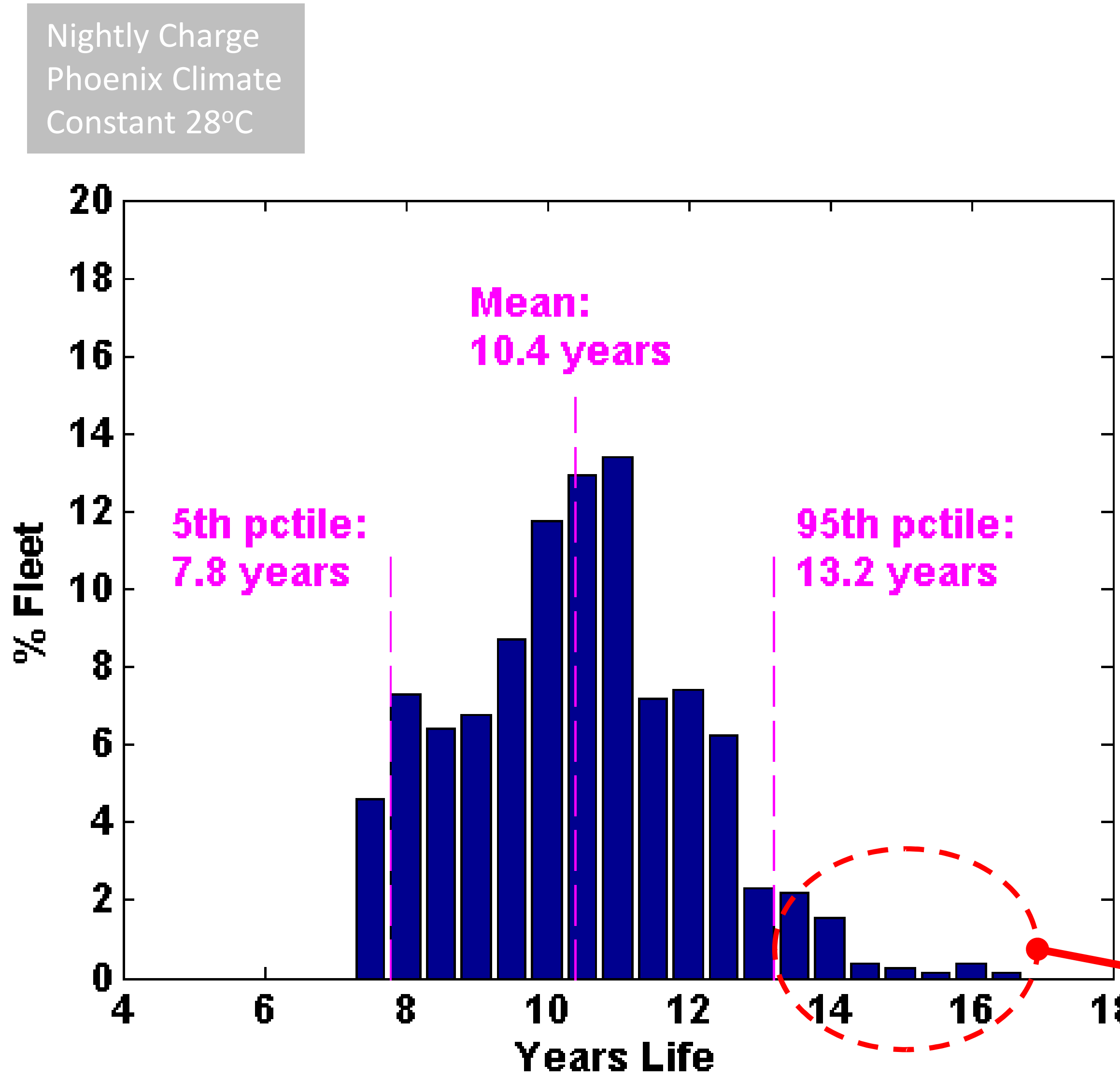
Charging Profiles**

- Nightly charge (baseline)
- Opportunity charge

** Level I charging rates.

* Worst-case hot climate, Phoenix Arizona ~28°C

Expected Life for various drive-cycle aging scenarios at constant temperature – PHEV10



Life expectancy across 782 driving cycles in a hot climate is 7.8 to 13.2 years

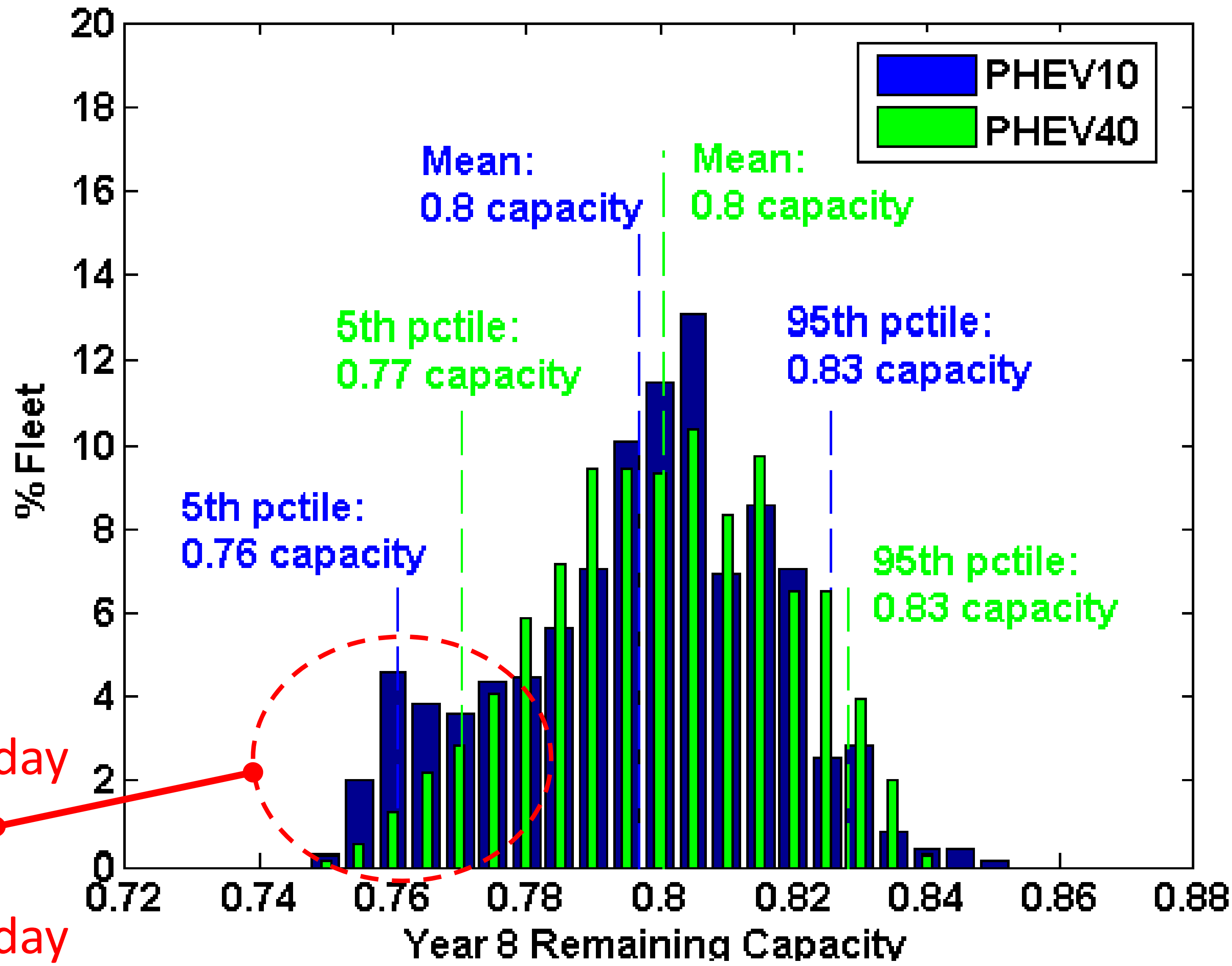
Reminder of key assumptions:

- NCA chemistry
- End-of-life condition: 75% remaining capacity
- 80% SOC_{max}
- 30% $SOC_{min\ @\ BOL}$

Opportunities for V2G, 2^{nd} use?

Expected Life – PHEV10 vs. PHEV40

Nightly Charge
Phoenix Climate
Constant 28°C



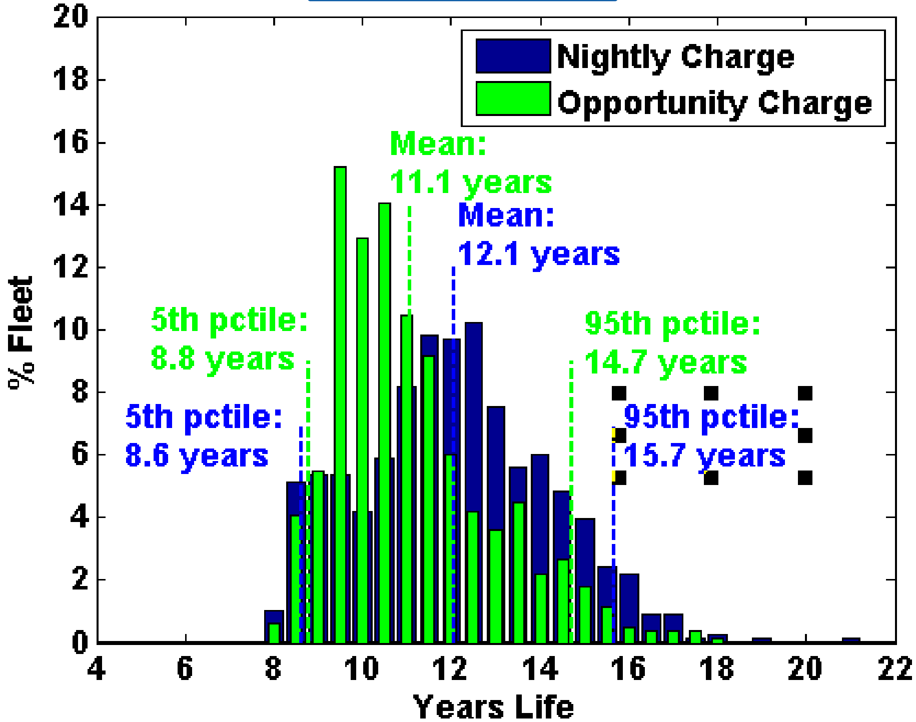
86% of driving cycles > 10 mi/day

34% of driving cycles > 40 mi/day

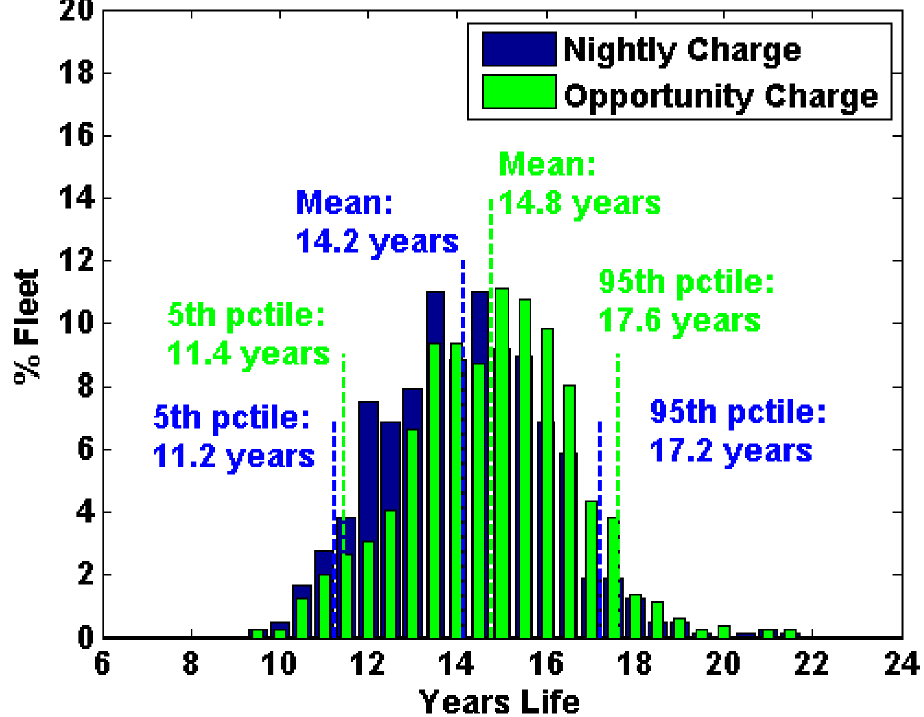
Impact of Opportunity Charging (Level 1)

Phoenix Climate
Aggressive Cooling

PHEV10



PHEV40

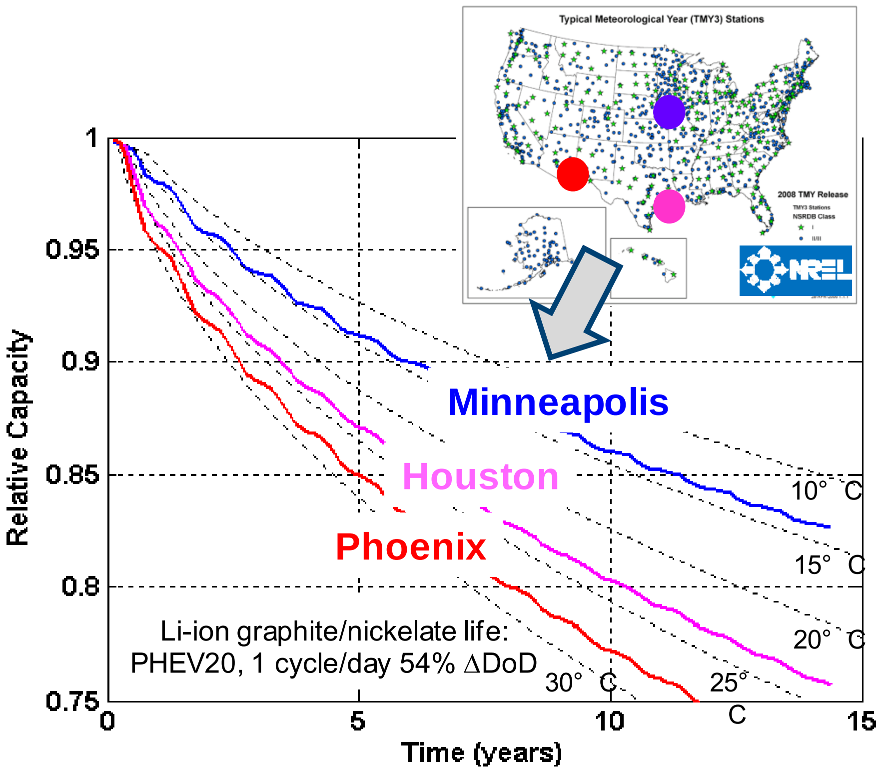


PHEV10: Frequent charging can reduce average life by 1 year

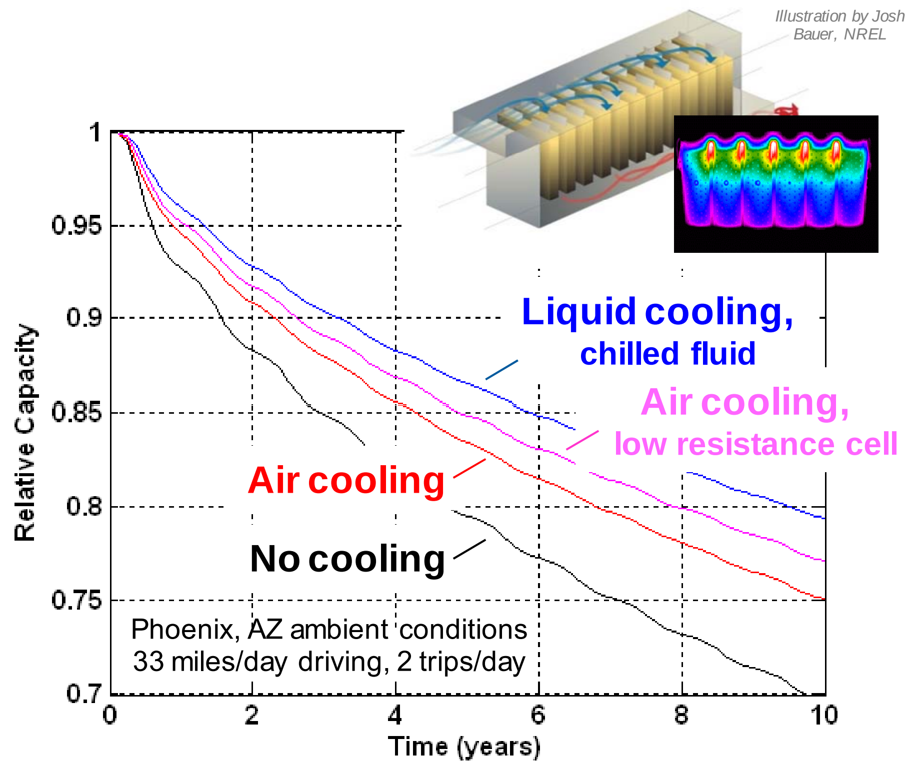
•PHEV40: Frequent charging can extend average life by ½ year

Impact of Battery Thermal Environment

Geographic Impact on Life



Thermal Management Impact on Life



Battery R&D

- Energy storage is already ubiquitous in electronics; many more vehicle and grid applications are in the pipeline
  - Cost, life, and safety all need improvement for greater market acceptance
- Multi-disciplinary, multi-physics nature of batteries:
  - Slow development process
  - Moore's Law does not apply
  - Easier to find a thesis topic!
- Student opportunities at NREL
  - Part-time test engineer; send resumes to kandler.smith@nrel.gov
  - Organize a thesis topic together with NREL
- More info: http://www.nrel.gov/vehiclesandfuels/energystorage/publications.html