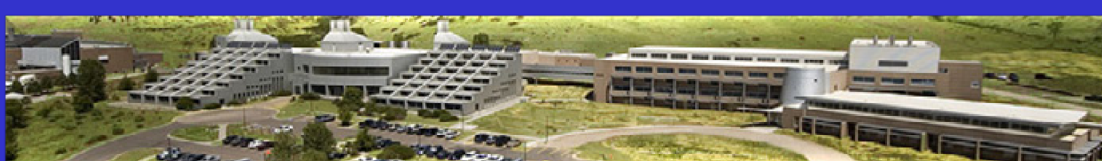
Design of Electric Drive Vehicle Batteries for Long Life and Low Cost

Robustness to Geographic and Consumer-Usage Variation



NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

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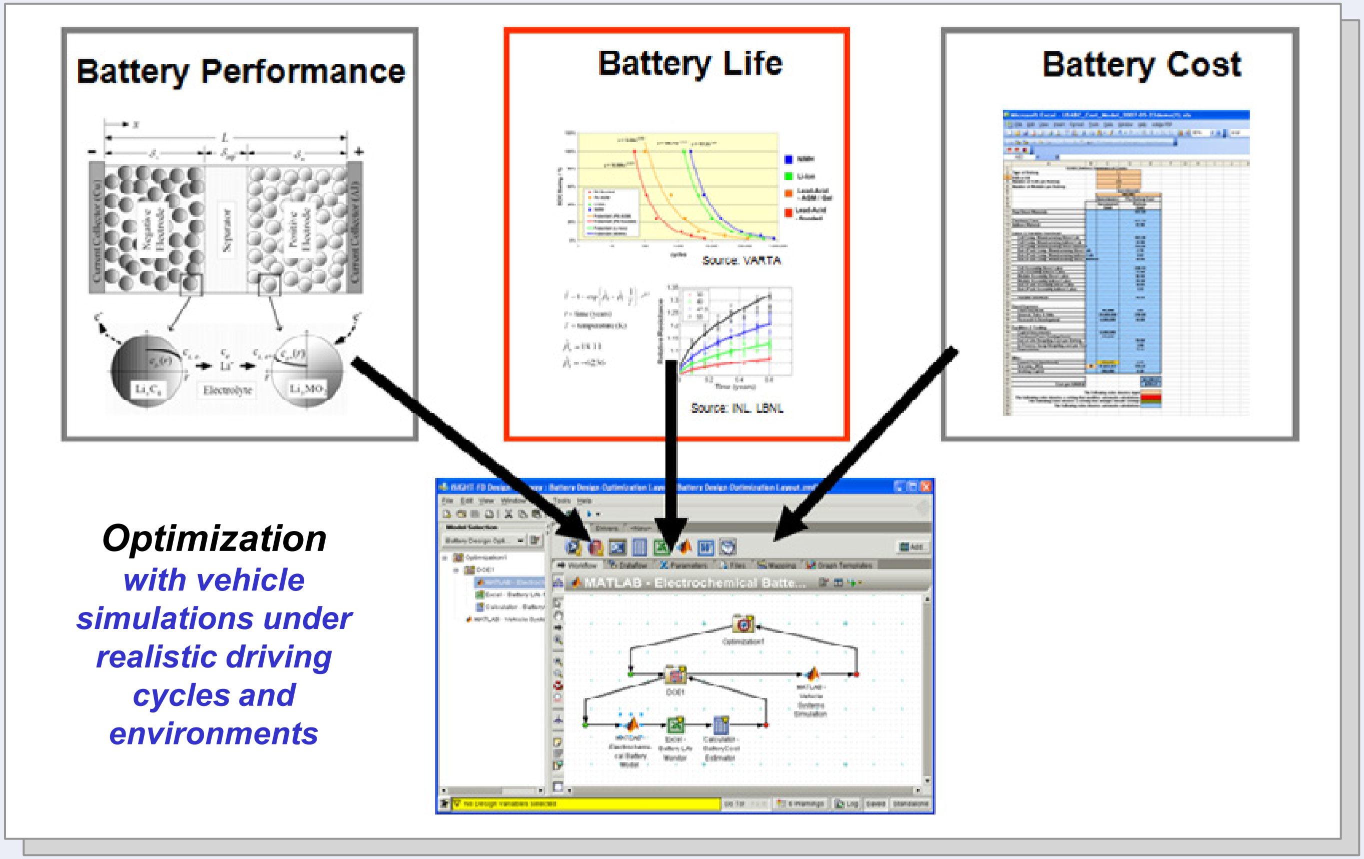
Motivation

- The fuel-displacement potential of EVs and PHEVs is elusive
  - Cost reduction needed for significant market penetration to be achieved
  - Batteries are the most expensive component of the vehicle
  - Consumers expect >10 years vehicle life
    - Periodic battery replacement (e.g., every 5 years) not warranted
- Battery life and cost are intimately related
  - Batteries are substantially oversized to meet power and energy performance requirements at the end-of-life
  - HEVs: only 10% to 25% of energy is used
    - Toyota Prius HEV: 1.2 kWh total energy, typically < 300 Wh is used
  - PHEVs: only 50% of energy is used
    - Chevy Volt PHEV: ~16 kWh total energy, only 8 kWh is used
- Need to understand worst-case conditions for battery aging
  - Worst-case duty cycles and environments drive the need to oversize batteries
  - Systems solutions and controls can be added to overcome some of these conditions
  - Life-predictive models are preferable to rules-of-thumb

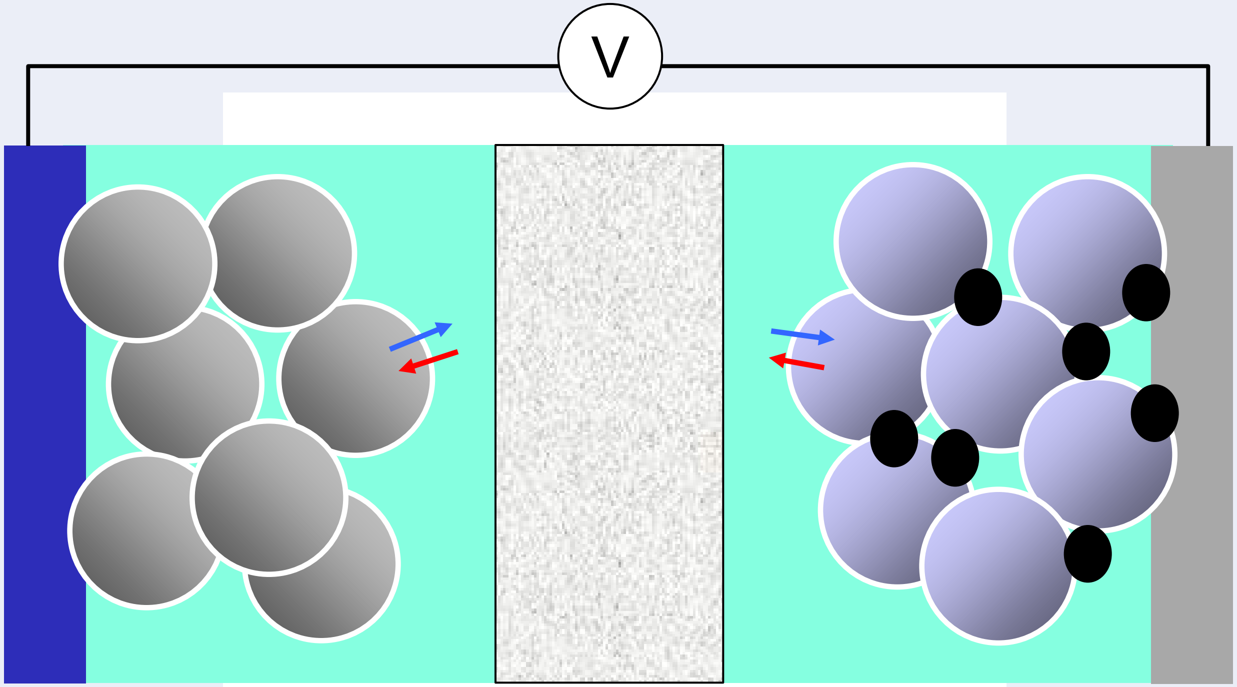
NREL Battery Optimization & Trade-off Analysis



- Explore strategies to extend life and/or reduce cost
  - Battery sizing, thermal preconditioning and standby cooling, 2nd use, battery ownership, vehicle-to-grid…
- Missing : Life model capable of analyzing arbitrary real-world scenarios

Typical Structure of Li-ion Batteries

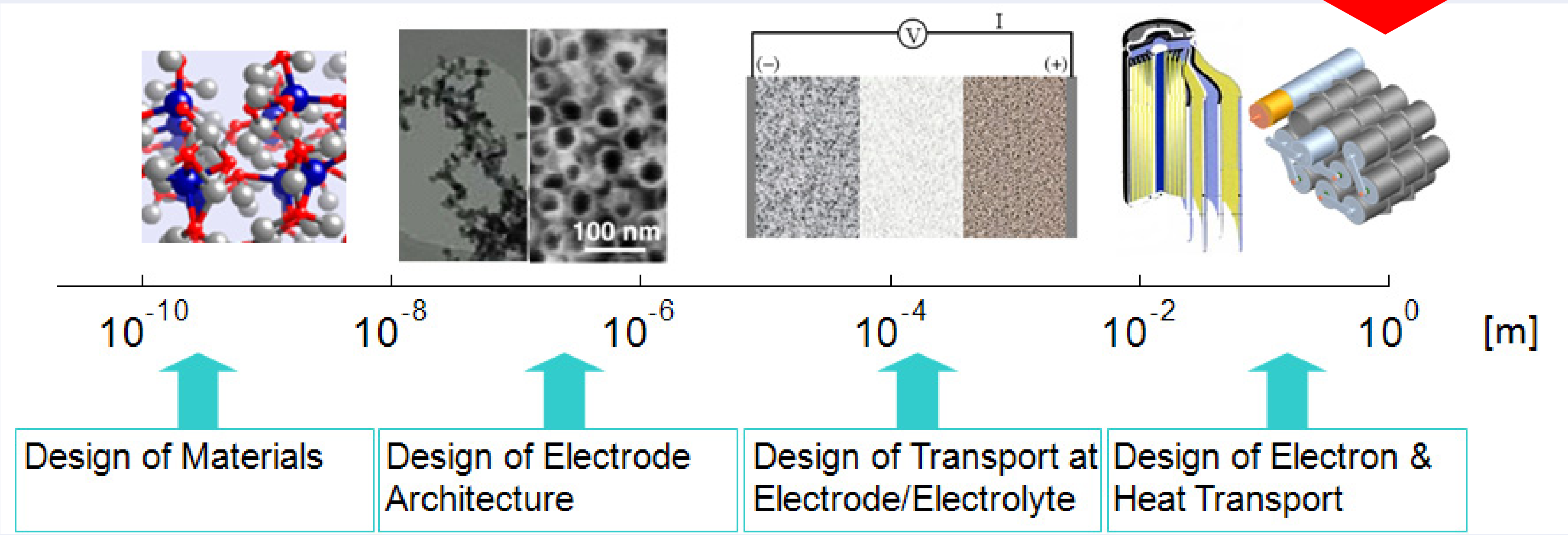
Designing Thermodynamics
Designing Kinetics



Multi-Scale Physics in Li-ion Battery

Requirements

Performance
Life
Cost
Safety



Outline

- Aging mechanisms in Li-ion batteries
- Aging models based on accelerated testing
- Robust design for long life, low cost

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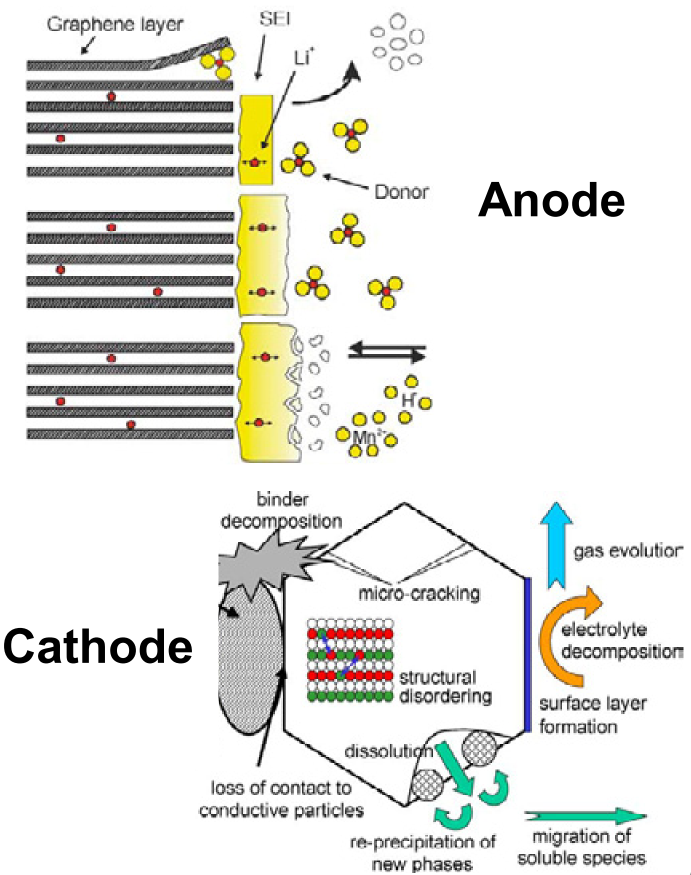
…from the electrochemist's point of view



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

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: graphitic carbons
Li_xC_6

Cathode: metal oxides
Li_yCoO_2, $Li_y(Ni,Co,Mn,Al)O_2$, Li_yMnO_4,

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 → a_s & D_e^{eff} ↓
- 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

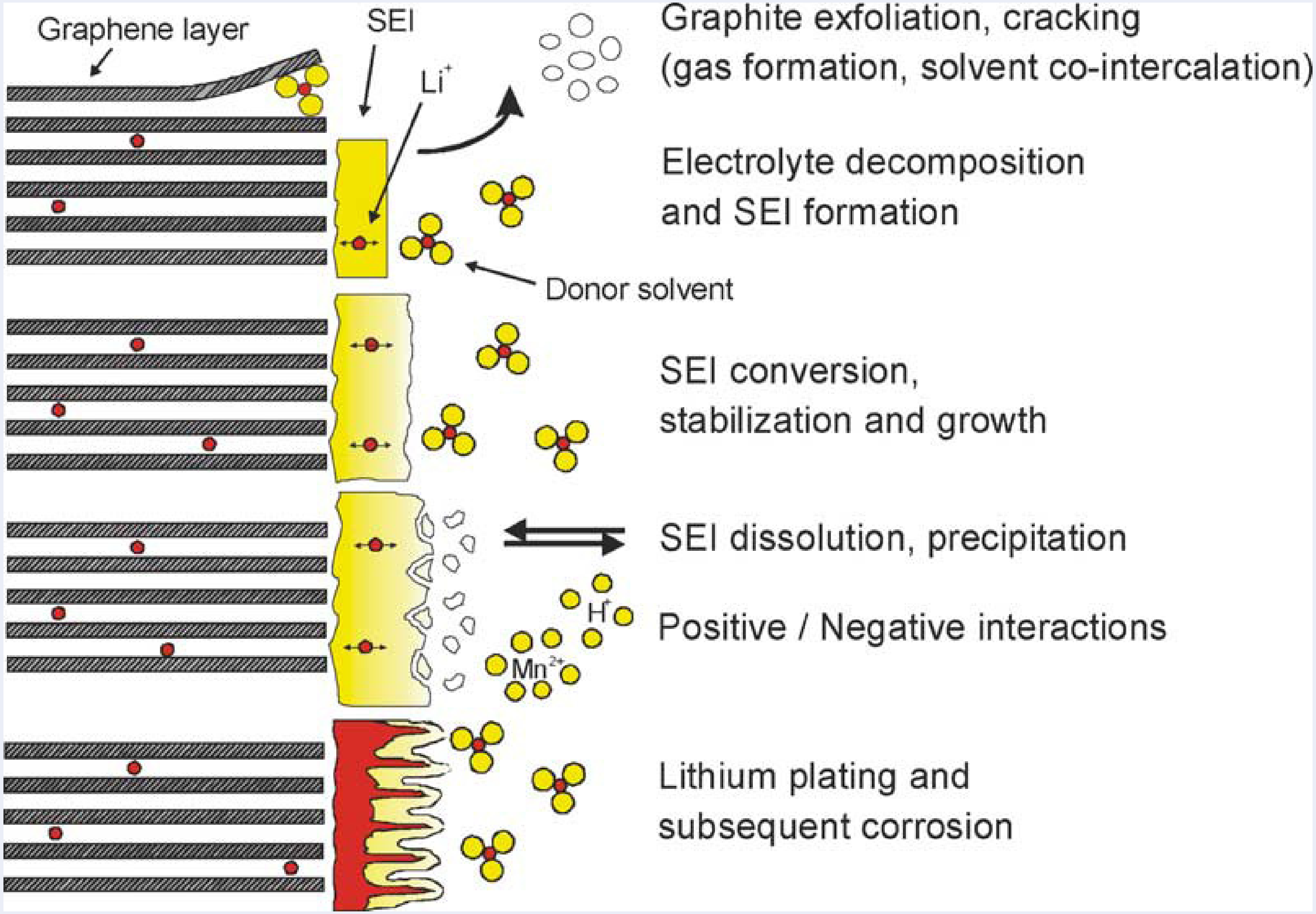


Image: Vetter et al., “Ageing mechanisms in lithium-ion batteries,” *J. Power Sources,* 147 (2005) 269-281

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
- 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 σ, D_s
  - Gas evolution

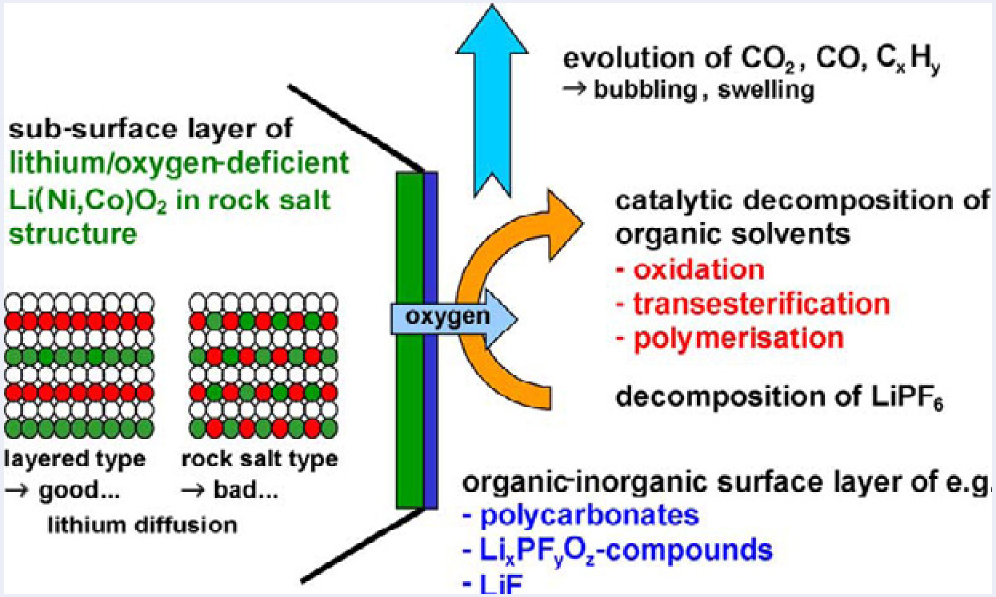
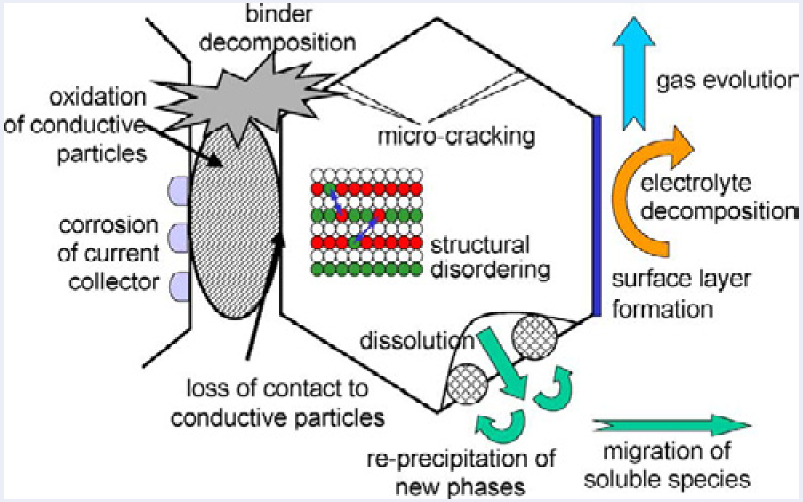


Image: Vetter et al., "Ageing mechanisms in lithium-ion batteries," *J. Power Sources*, 147 (2005) 269-281

Cathode Aging



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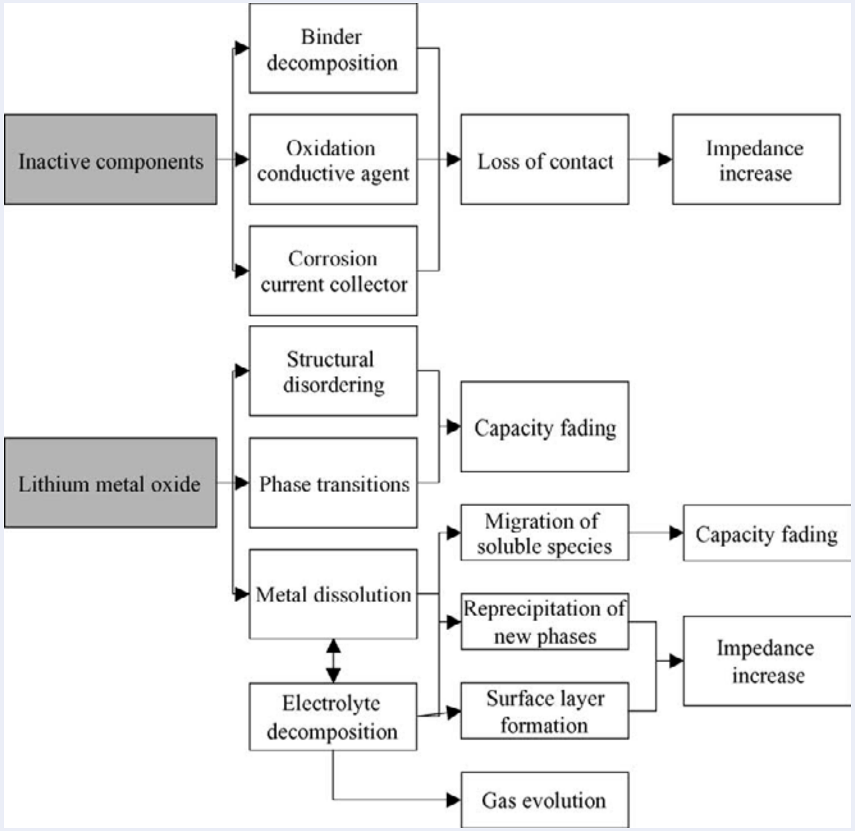


Source: Wohlfahrt-Mehrens et al., “Aging mechanisms of lithium cathode materials,” *J. Power Sources*, 127 (2004) 58-64

Summary of Aging

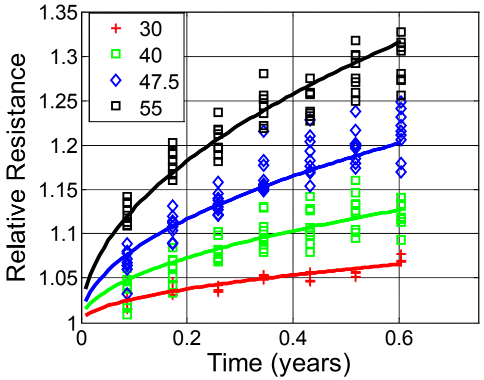
Aging influenced by:

- Both high and low SOC
- High temperatures
- Low temperatures during charging
- Surface chemistry (anode and cathode)
- Phase transitions/structural changes (cathode)

Outline

- Aging mechanisms in Li-ion batteries
- **Aging models based on accelerated testing**
- Robust design for long life, low cost

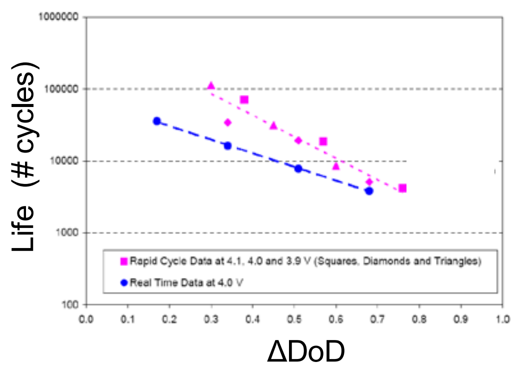
…from the automotive engineer's point of view



Calendar Life

Source: V. Battaglia (LBNL), 2008

Cycle Life

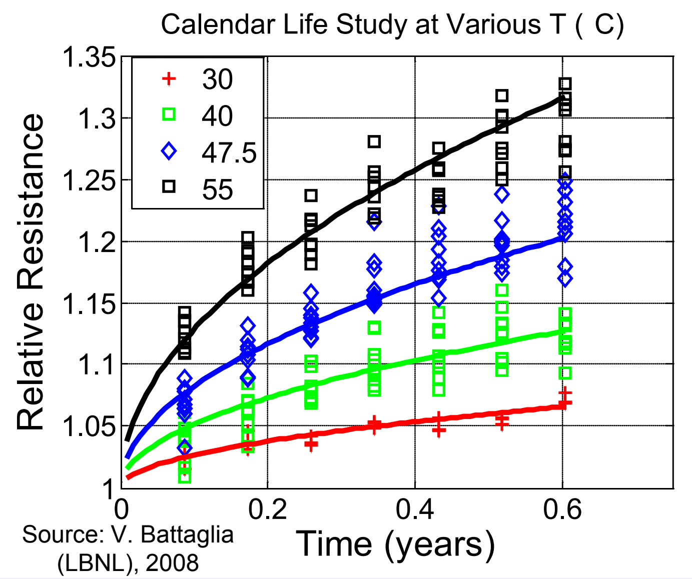


Source: J. Hall (Boeing), 2006

How Can We Predict Battery Life?

Accelerated storage tests

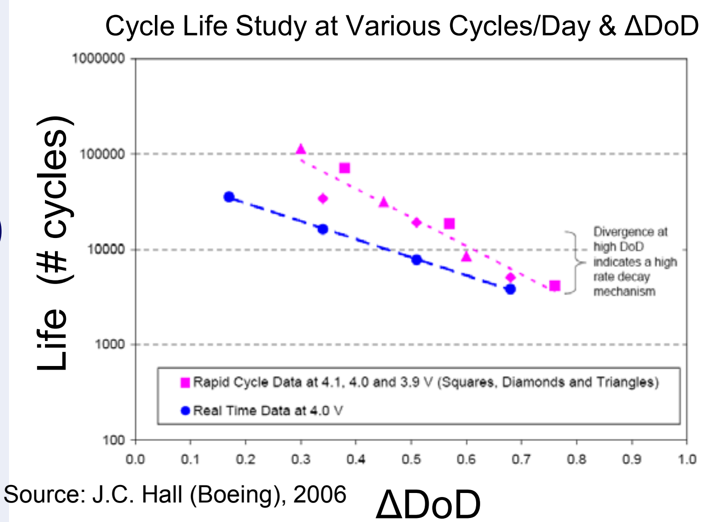
- **Relatively well understood**
- Mechanism: SEI growth, Li loss
- Model:
  - $t^{1/2}$ time dependency
  - Arrhenius T dependency



Source: V. Battaglia (LBNL), 2008

Accelerated cycling tests

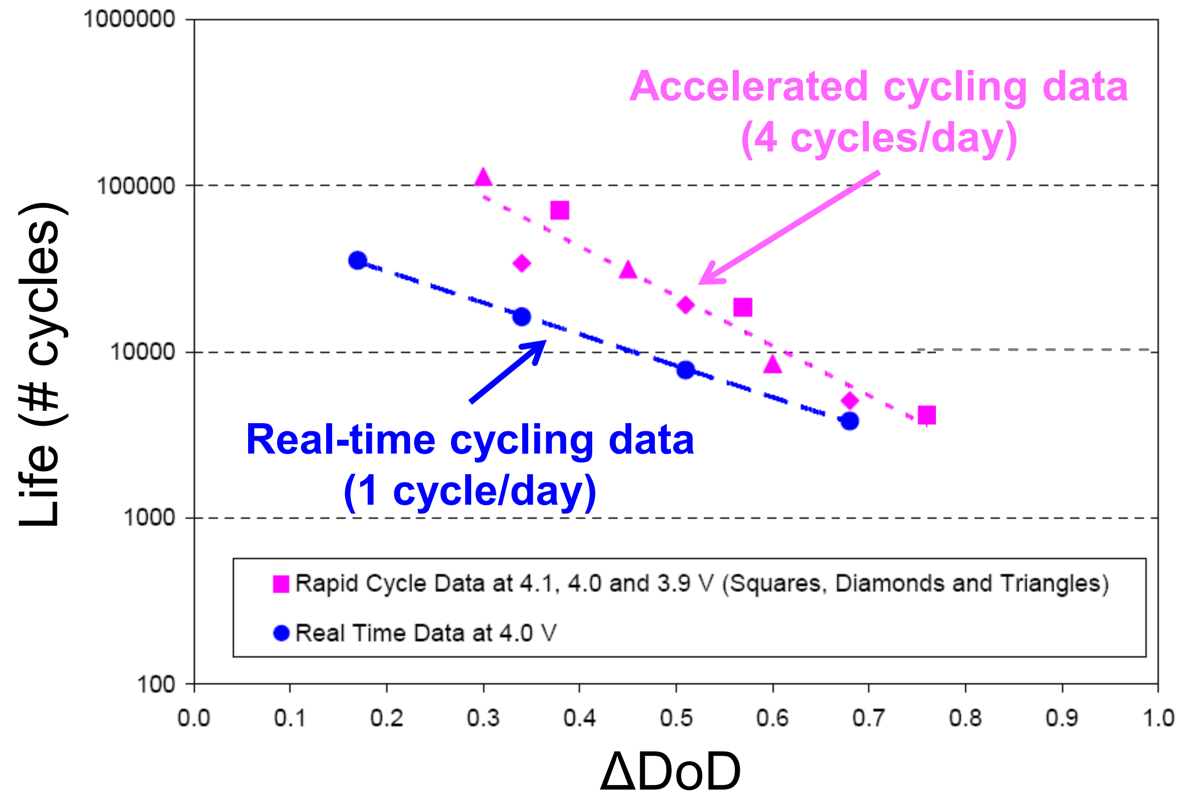
- **Poorly understood**
- Mechanism: Mechanical stress & fracture (may be coupled with SEI fracture+regrowth)
- Model:
  - Typical t or N dependency
  - Often correlated log(# cycles) with ΔDOD



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

Accelerated Tests May Not Predict Correct Real-Time Result

- Cycle-life study for geosynchronous satellite battery shows possible change in degradation mechanisms depending upon how frequently the battery is cycled



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

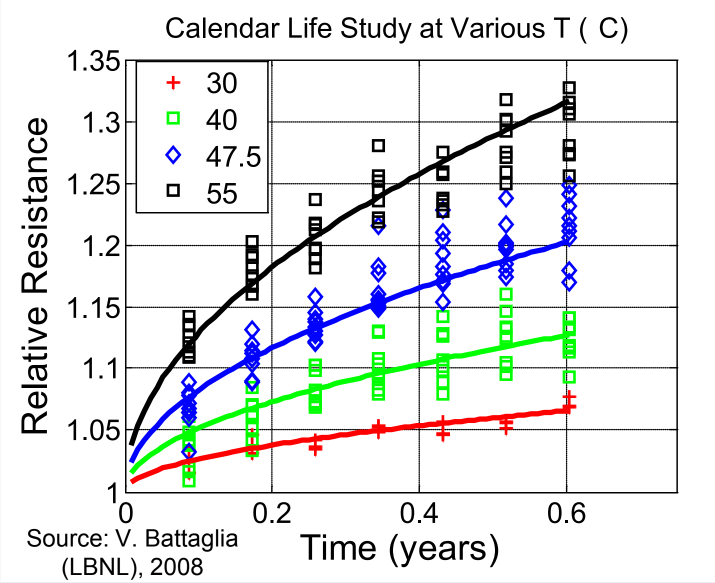
End-of-life defined when ΔDoD times actual capacity exceeds available capacity.

Important for a life-predictive model to accurately capture both cycling conditions.
Prediction based on accelerated cycling results would over-estimate life!

How Can We Predict Battery Life?

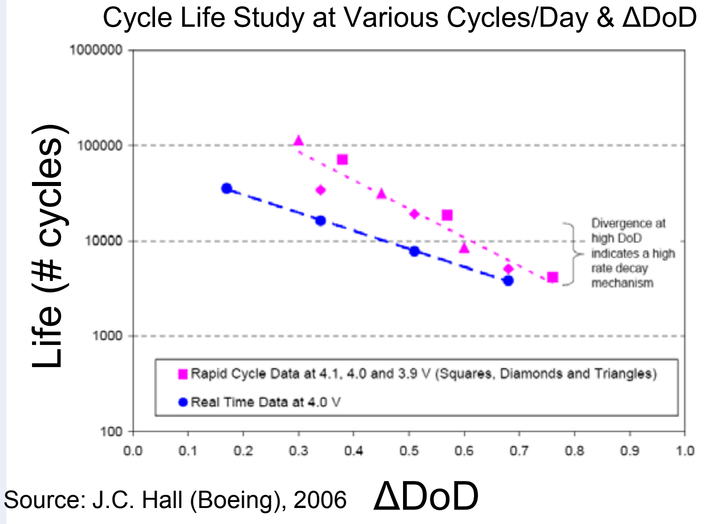
Accelerated storage tests

- Relatively well understood
- Mechanism: SEI growth, Li loss
- Model: (e.g., DOE TLVT)
  - $t^{1/2}$ time dependency
  - Arrhenius T dependency



Accelerated cycling tests

- Poorly understood
- Mechanism: Mechanical stress & fracture (may be coupled with SEI fracture + regrowth)
- Model: (e.g., VARTA)
  - Typical t or N dependency
  - Often correlated log(# cycles) with ΔDOD



Real-world cycling & storage

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

Life Modeling Approach

NCA datasets fit with empirical, yet physically justifiable formulas

*K. Smith, T. Markel, A. Pesaran, "PHEV Battery Trade-off Study and Standby Thermal Control," 26th International Battery Seminar & Exhibit, Fort Lauderdale, FL, March, 2009.

Calendar fade
- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1(\Delta DOD, T, V)$

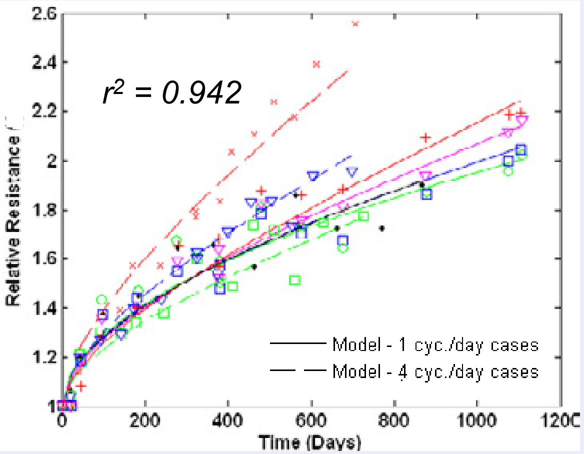
Cycling fade
- Active material structure degradation and mechanical fracture
- $a_2(\Delta DOD, T, V)$

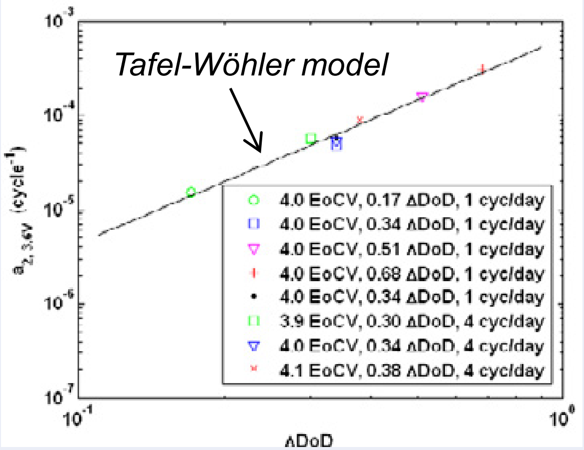
Resistance Growth
$$R = a_1 t^{1/2} + a_2 N$$

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

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

$$Q_{active} = e_0 + e_1 \times (a_2 N)$$





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

Predictive model that considers effects of real-world storage and cycling scenarios

Fitting of NCA/Graphite Baseline Life Model to Lab Data

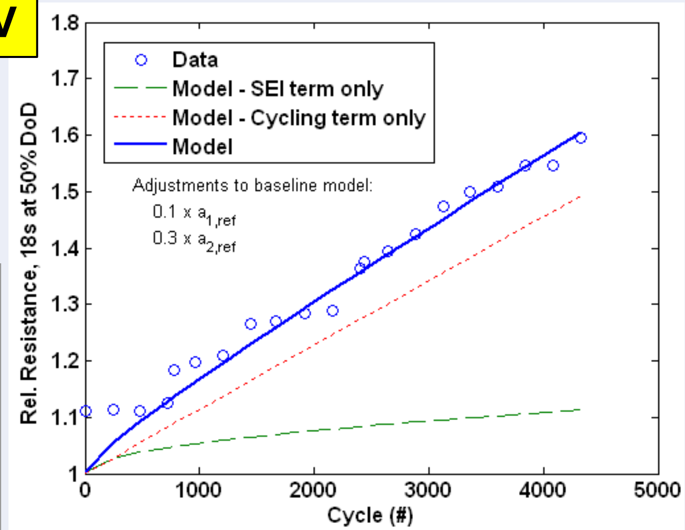
1. Resistance growth during storage
   - ♦ Broussely (Saft), 2007:
     - T = 20°C, 40°C, 60°C
     - SOC = 50%, 100%
2. Resistance growth during cycling
   - ♦ Hall (Boeing), 2005-2006:
     - DoD = 20%, 40%, 60%, 80%
     - End-of-charge voltage = 3.9, 4.0, 4.1 V
     - Cycles/day = 1, 4
3. Capacity 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)

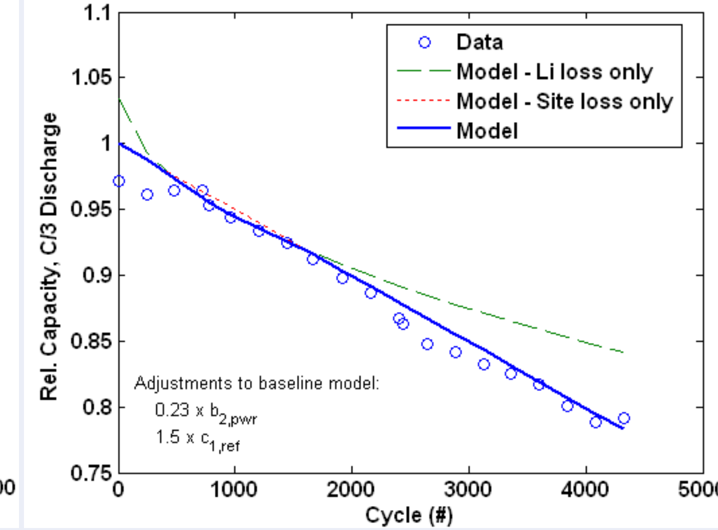
- ***30 different tests***
- ***>$1M in test equipment***
- ***1-4 years duration***

→ ***Expensive!!***

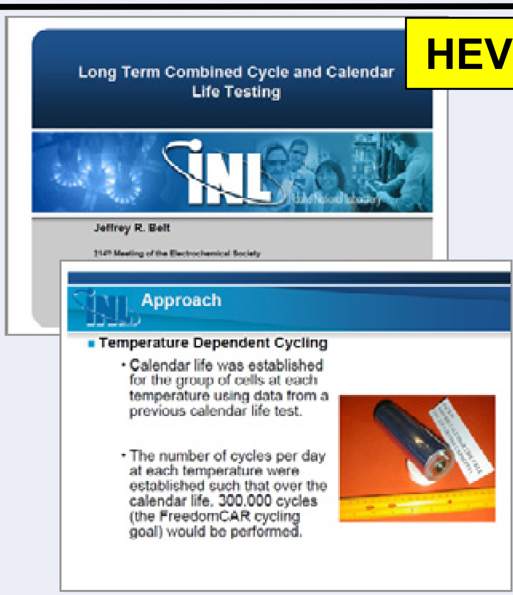
Model Comparison with Vehicle Battery Laboratory Data

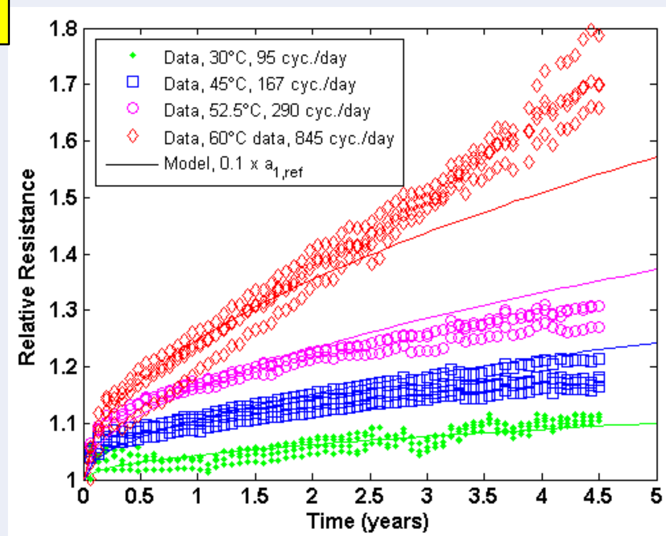
PHEV

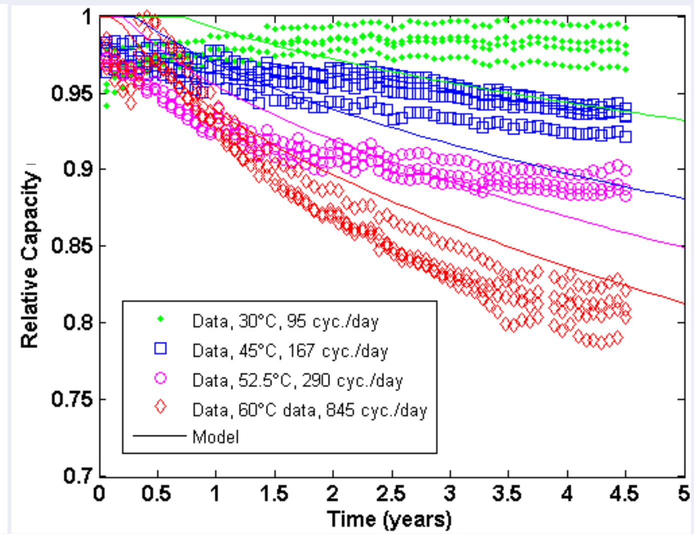




HEV



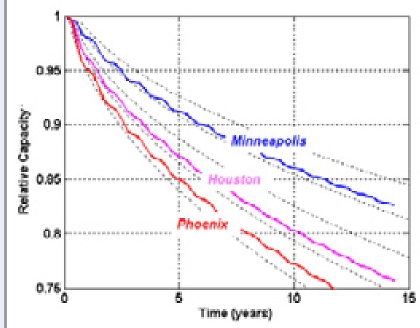




Outline

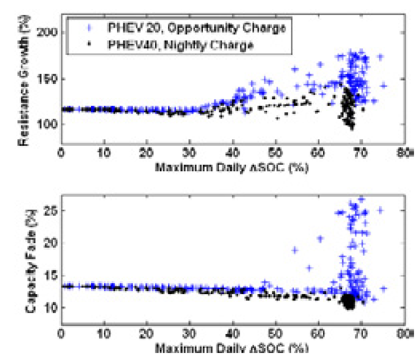
- ♦ Aging mechanisms in Li-ion batteries
- ♦ Aging models based on accelerated testing
- ♦ Robust design for long life, low cost

…for the vehicle systems integrator



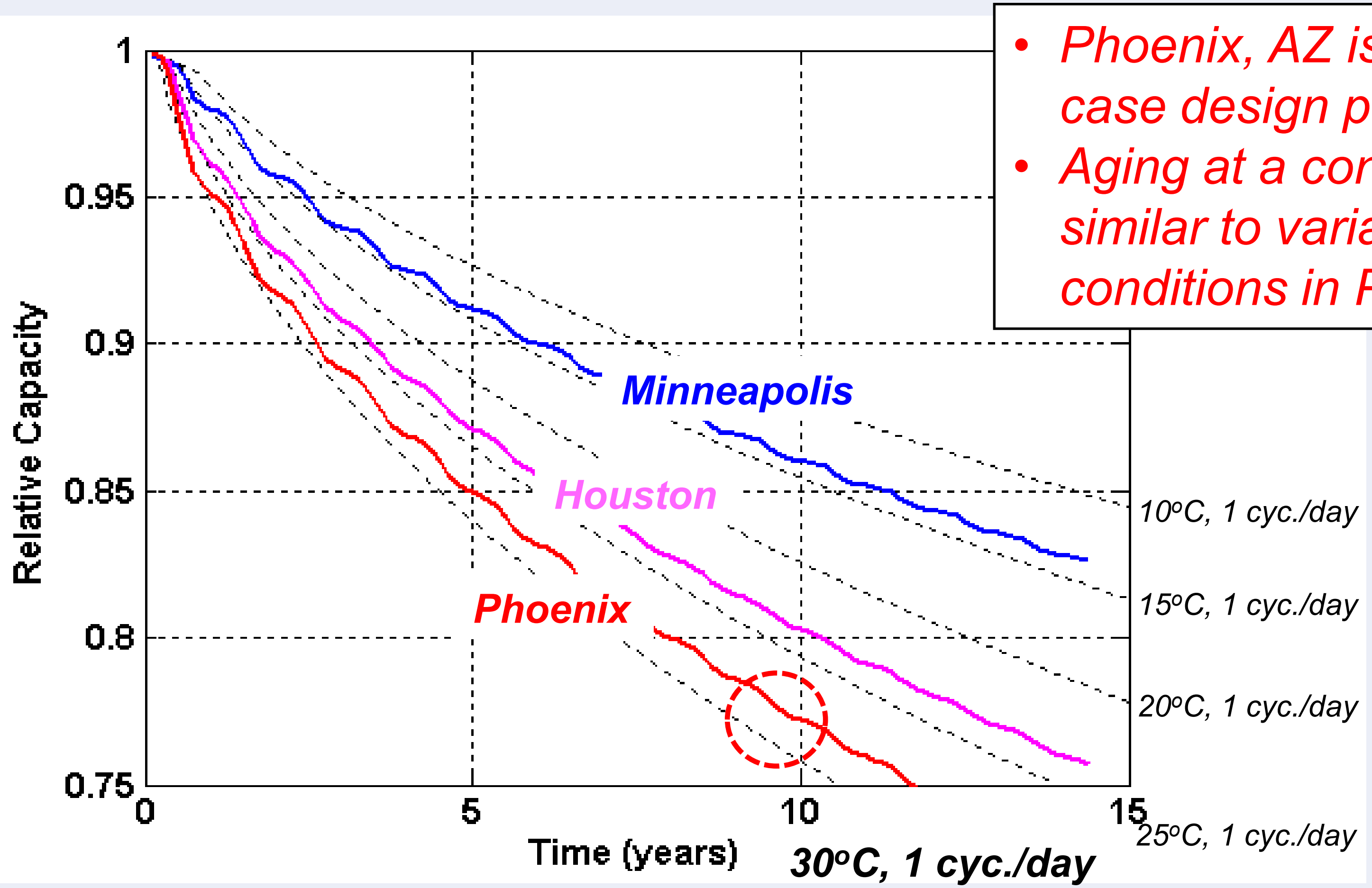
Temperature Effects

Duty-cycle Effects



Impact of Geographic Region

- Example: PHEV20 battery, 1 cycle/day, ΔDoD=0.54, various climates
  - NREL Typical Meteorological Year data used to simulate ambient conditions for each city

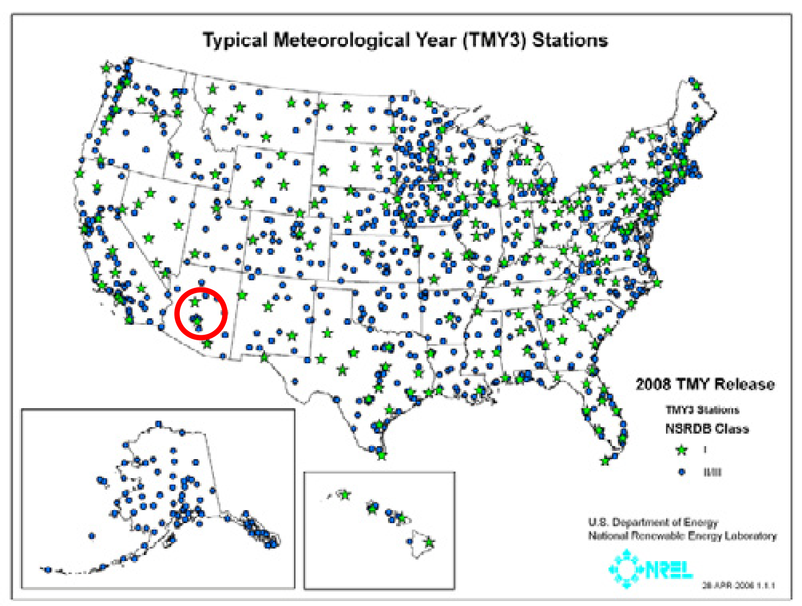


- *Phoenix, AZ is typical worst-case design point for OEMs*
- *Aging at a constant 30°C is similar to variable ambient conditions in Phoenix*

Impact of Thermal Management in Phoenix

♦ Cooling strategies investigated:

1. **No cooling**
2. **Air cooling**
   - $h = 15\ W/m^2K$
   - $T_{inf} = 30^oC$ (passenger cabin air)
3. **Liquid cooling**
   - $h = 80\ W/m^2K$
   - $T_{inf} = 20^oC$ (refrigerated ethylene glycol)
4. **Air cooling, with low impedance cell**
   - $h = 15\ W/m^2K$
   - $T_{inf} = 30^oC$ (passenger cabin air)
   - Use of a high power/low impedance cell reduces heat generation rates by 50%

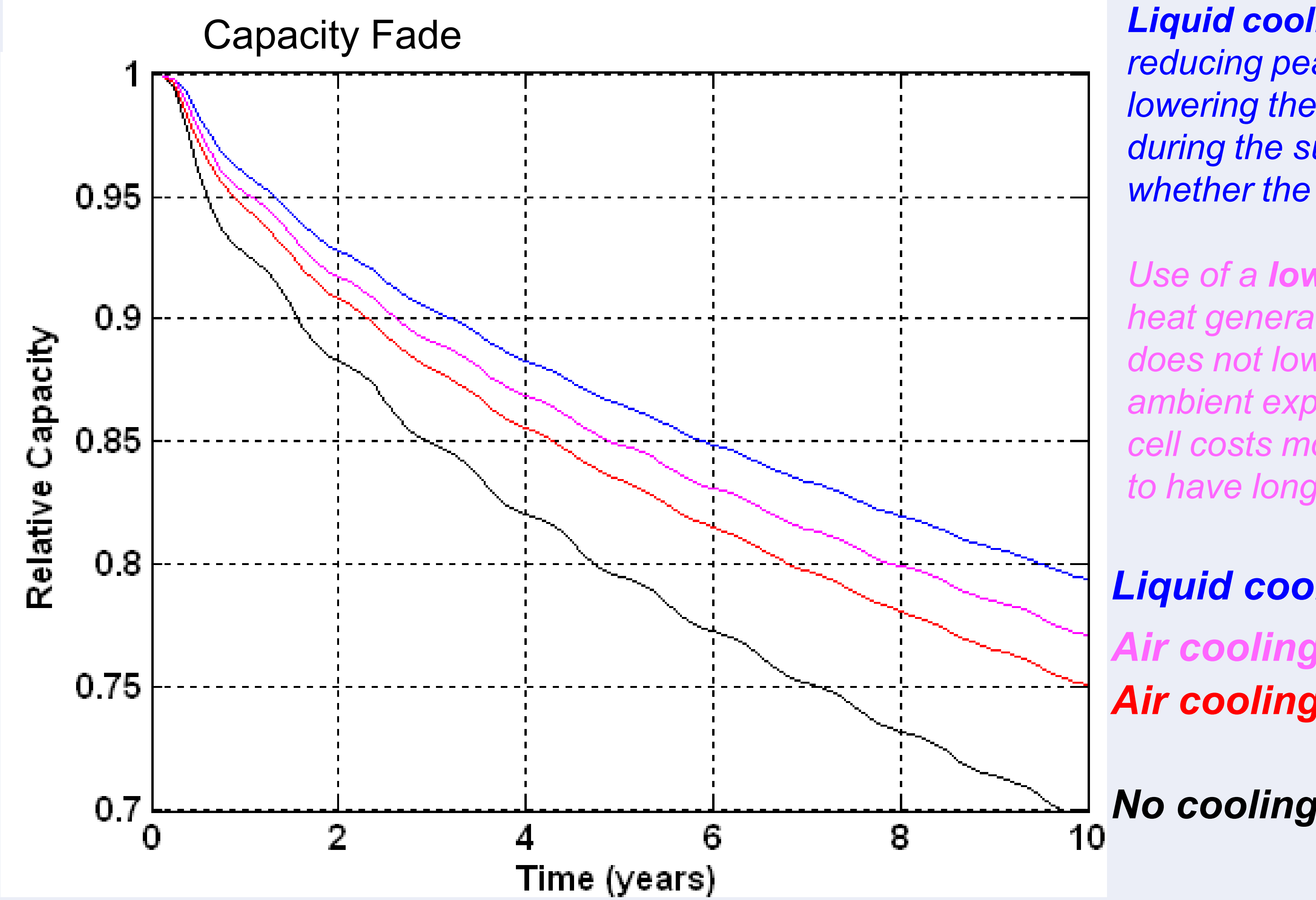


Other assumptions used to generate temperature profiles for the various cases:

- CD and CS heat generation rates chosen to represent average driving (between US06 and city driving measurements taken in the NREL lab)
- Two trips per day
  - 8:00-8:30 a.m. morning commute
  - 5:00-5:30 p.m. evening commute
- 34 mph average speed

Impact of Thermal Management in Phoenix

- Battery life differs depending on how the battery is cooled
  - Example below: PHEV20, 1 cycle/day at ΔDoD=0.54

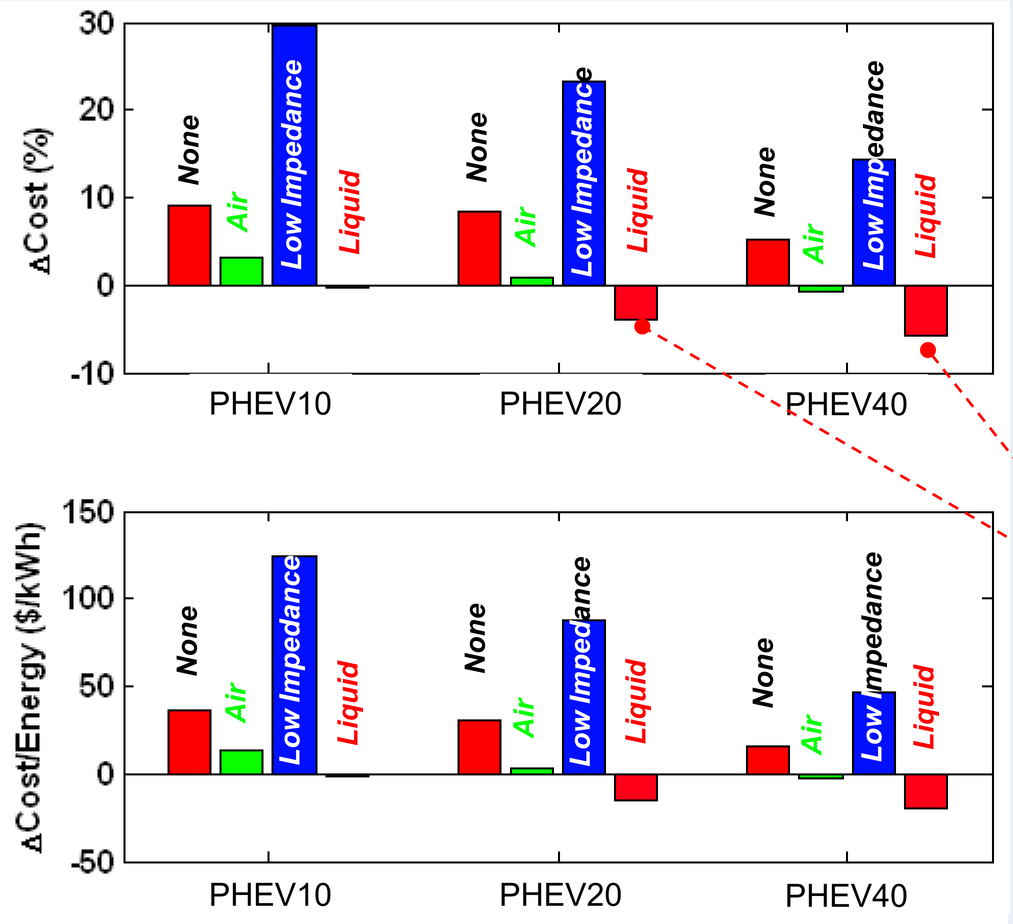


***Liquid cooling** is very effective at reducing peak temperatures as well as lowering the average daily temperature during the summer. It is uncertain whether the extra expense is warranted.*

*Use of a **low impedance cell** reduces heat generation rates while driving, but does not lower temperature due to ambient exposure. This higher power cell costs more upfront, but does appear to have longer life.*

$$ Value of Thermal Management in Phoenix

- Slower degradation saves battery cost by allowing smaller battery to meet end-of-life performance requirements
  - All values below are compared to a baseline battery pack designed for 1 cycle/day at 30°C.



No thermal management increases baseline battery cost by 5% to 10%.

Slower fade rate of low impedance cell does not justify the upfront cost of extra power in this design.

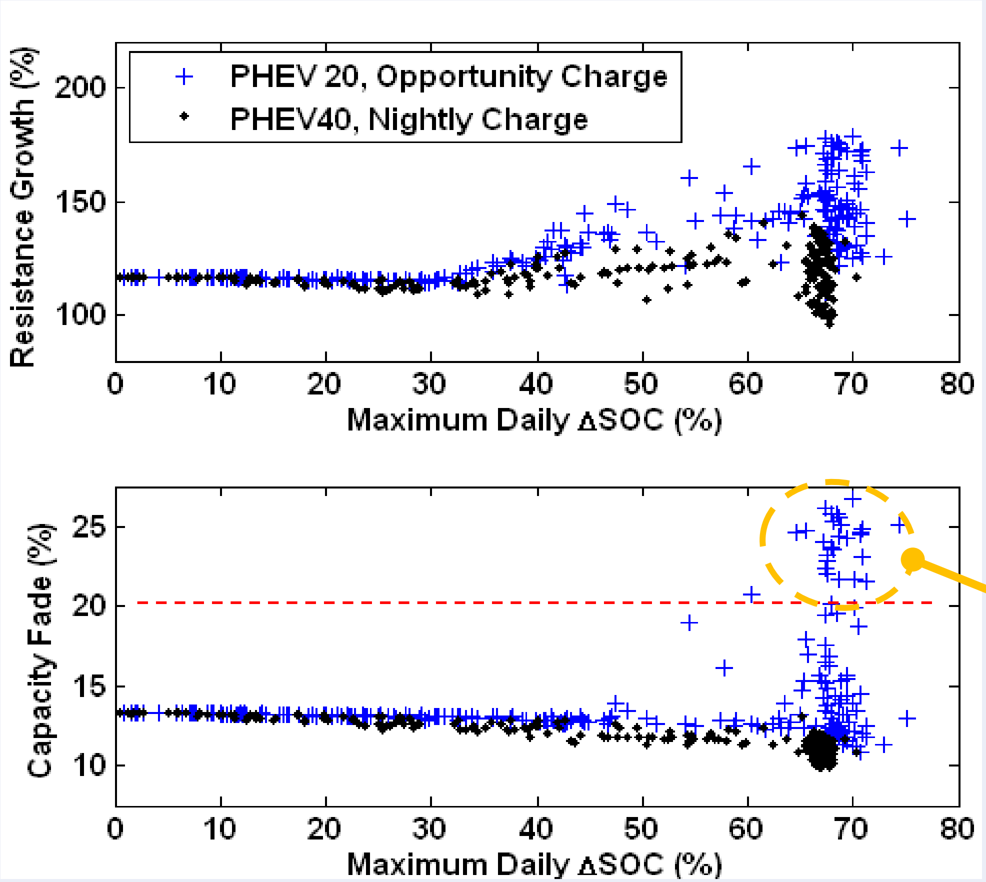
Effective thermal management decreases baseline pack costs by 5%.

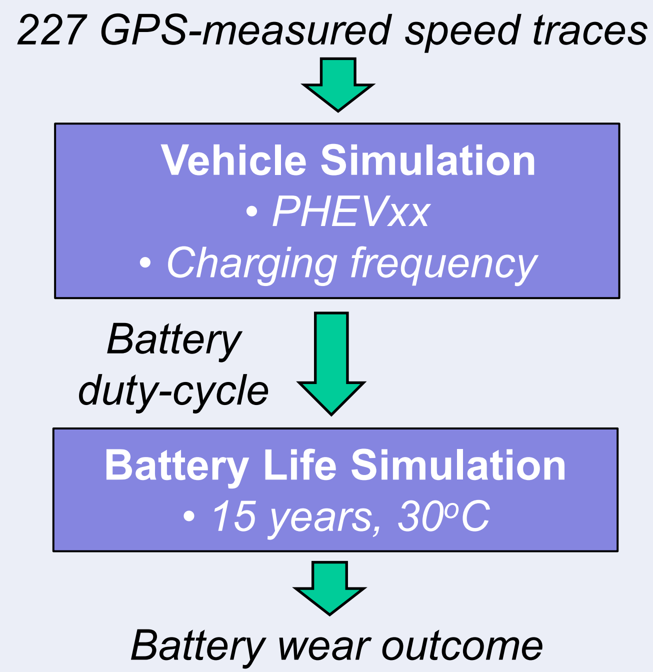
- PHEV40 shows most benefit from liquid-cooled system that lowers daily average temperatures during the summer.

Impact of Duty-Cycle

Two scenarios with similar petroleum displacement

1. PHEV 20, opportunity charge
2. PHEV 40, nightly charge





Frequent deep cycling can lead to early failure.

Conclusions

- Battery degradation is complex
  - Stressors: Chemical, electrochemical, thermal, and mechanical
  - Physics-based models do not yet capture all relevant mechanisms
- Aging tests are expensive and time consuming
  - Accelerated tests do not always reveal real-time fade rates!
  - Models useful for proper interpretation and extrapolation
    - Present: Semi-empirical, requires large test matrix
    - Future: Physics-based, requires fewer tests + useful as battery design tool
- Robust design tools require accurate battery life prediction under multiple scenarios
  - Knowledge must be efficiently passed from electrochemists to vehicle systems engineers
- Significant cost savings may be achieved through streamlined battery life verification methods and robust design

Acknowledgements

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  - Dave Howell, Energy Storage Program Manager

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  - Marshall Smart, NASA-Jet Propulsion Laboratory