National Renewable Energy Laboratory
Innovation for Our Energy Future

PHEV Battery Trade-Off Study
and Standby Thermal Control

26th International Battery Seminar & Exhibit
Fort Lauderdale, FL
March 16-19, 2009

Kandler Smith
Kandler.Smith@nrel.gov
Tony Markel
Tony.Markel@nrel.gov
Ahmad Pesaran
Ahmad.Pesaran@nrel.gov

NREL/PR-540-45048

Overview

- Motivation for PHEV battery trade-off analysis
- Battery life model
  - Calendar life vs. cycle life: Complex interdependency
  - An empirical model capturing major degradation factors (temperature, time, # cycles, ΔDOD*, voltage)
- Battery life/cost interactions
  - Lowest cost system that meets technical requirements
  - Life sensitivity to different temperatures
- Battery standby thermal management
  - Concept
  - Vehicle-battery thermal interactions
  - Benefits of temperature management
- Conclusions
  - Future test needs

* DOD = depth of discharge

USABC PHEV Battery Goals

Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		High Power/Energy Ratio Battery	High Energy/Power Ratio Battery
Reference Equivalent Electric Range	miles	**10**	**40**
Peak Pulse Discharge Power - 2 Sec / 10 Sec	kW	**50 / 45**	**46 / 38**
Peak Regen Pulse Power (10 sec)	kW	**30**	**25**
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	**3.4**	**11.6**
Available Energy for CS (Charge Sustaining) Mode	kWh	**0.5**	**0.3**
Minimum Round-trip Energy Efficiency (USABC HEV Cycle)	%	**90**	**90**
Cold cranking power at -30°C, 2 sec - 3 Pulses	kW	**7**	**7**
CD Life / Discharge Throughput	Cycles/MWh	**5,000 / 17**	**5,000 / 58**
CS HEV Cycle Life, 50 Wh Profile	Cycles	**300,000**	**300,000**
Calendar Life, 35°C	year	**15**	**15**
Maximum System Weight	kg	**60**	**120**
Maximum System Volume	Liter	**40**	**80**
Maximum Operating Voltage	Vdc	**400**	**400**
Minimum Operating Voltage	Vdc	**>0.55 x Vmax**	**>0.55 x Vmax**
Maximum Self-discharge	Wh/day	**50**	**50**
System Recharge Rate at 30°C	kW	**1.4 (120V/15A)**	**1.4 (120V/15A)**
Unassisted Operating & Charging Temperature Range	°C	**-30 to +52**	**-30 to +52**
Survival Temperature Range	°C	**-46 to +66**	**-46 to +66**
Maximum System Production Price @ 100k units/yr	$	**$1,700**	**$3,400**

USABC PHEV Battery Goals

Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		High Power/Energy Ratio Battery	High Energy/Power Ratio Battery
Reference Equivalent Electric Range	[illegible]	[illegible]	40
Peak Pulse Discharge Power - 2 Sec / 10 S	[illegible]	[illegible]	46 / 38
Peak Regen Pulse Power (10 sec)	[illegible]	[illegible]	25
Available Energy for CD (Charge Depleti	[illegible]	[illegible]	11.6
Available Energy for CS (Charge Sustaini	[illegible]	[illegible]	0.3
Minimum Round-trip Energy Efficiency (	[illegible]	[illegible]	90
Cold cranking power at -30°C, 2 sec - 3 Pu	[illegible]	[illegible]	7
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17	5,000 / 58
CS HEV Cycle Life, 50 W	[illegible]	300,000	300,000
Calendar Life, 35°C	[illegible]	[illegible]	15
Maximum System Weight	kg	60	120
Maximum System Volume	[illegible]	40	80
Maximum Operating Voltag	[illegible]	400	400
Minimum Operating Voltage	[illegible]	>0.55 x Vmax	>0.55 x Vmax
Maximum Self-discharge	[illegible]	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature Range	°C	-30 to +52	-30 to +52
Survival Temperature Range	[illegible]	[illegible]	-46 to +66
Maximum System Production Price @ 100k units/yr	[illegible]	[illegible]	$3,400

Available Energy = 11.6 kWh
SOC Swing = 70%
Total EOL Energy = 16.6 kWh
Fade over Life = 20%
Total BOL Energy = 20.7 kWh

Calendar Life at 35°C = 15 Years

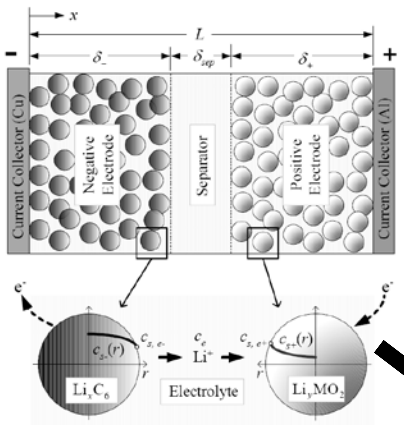
Max Weight = 120 kg
Max Volume = 80 L

System Price = $3,400

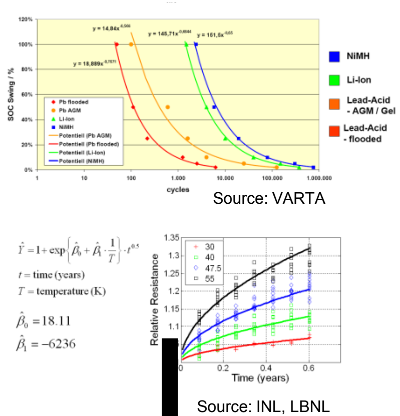
PHEV Battery Design Optimization

Design/size PHEV batteries to meet USABC technical goals/requirements at minimum cost.

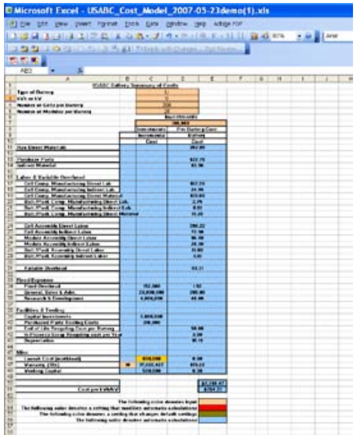
Battery Performance



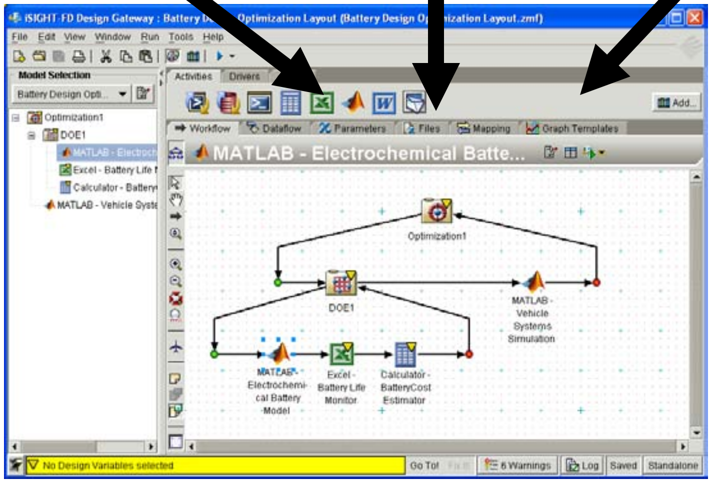
Battery Life



Battery Cost



Optimization
with vehicle simulations under realistic driving cycles and environments



Life prediction represents greatest uncertainty.

Complex dependency on $t^{1/2}$, t, # cycles, T, V, ΔDOD

Motivation: Minimize Battery Cost, Maximize Life

How?

Component design/ selection

0) Select a high-quality, low-cost cell.

1) **Size battery appropriately so as not to overstress/over-cycle, but with minimum cost and mass**
   1) Accelerated calendar & cycle life testing
   2) Accurate life and DOD predictive models

2) **Minimize time spent at high temperatures**
   1) Standby thermal management (vehicle parked!)
   2) Active thermal management (vehicle driving)

System design

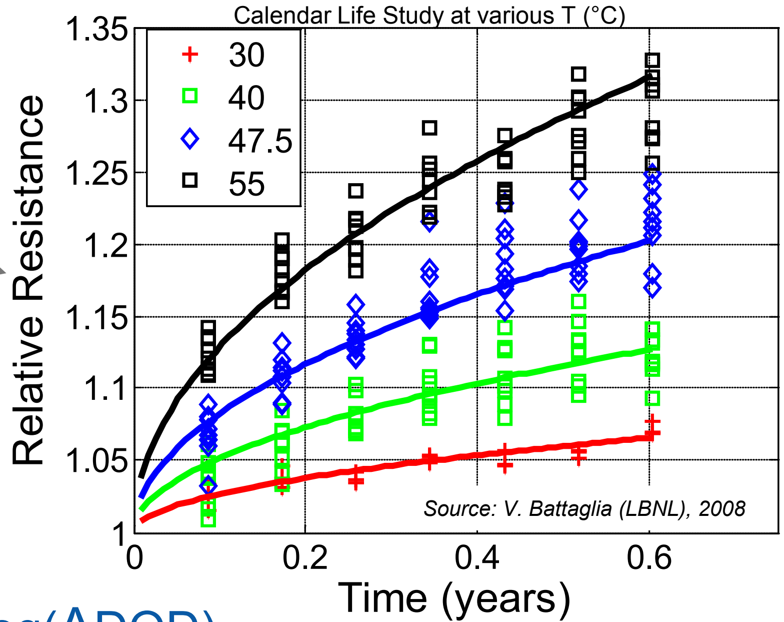
3) Proper electrical management, control design

:

How Can We Predict Battery Life?

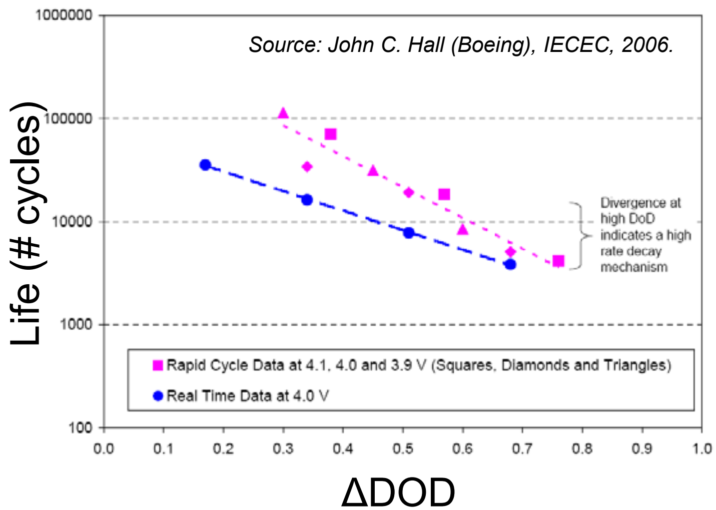
Calendar (Storage) Fade

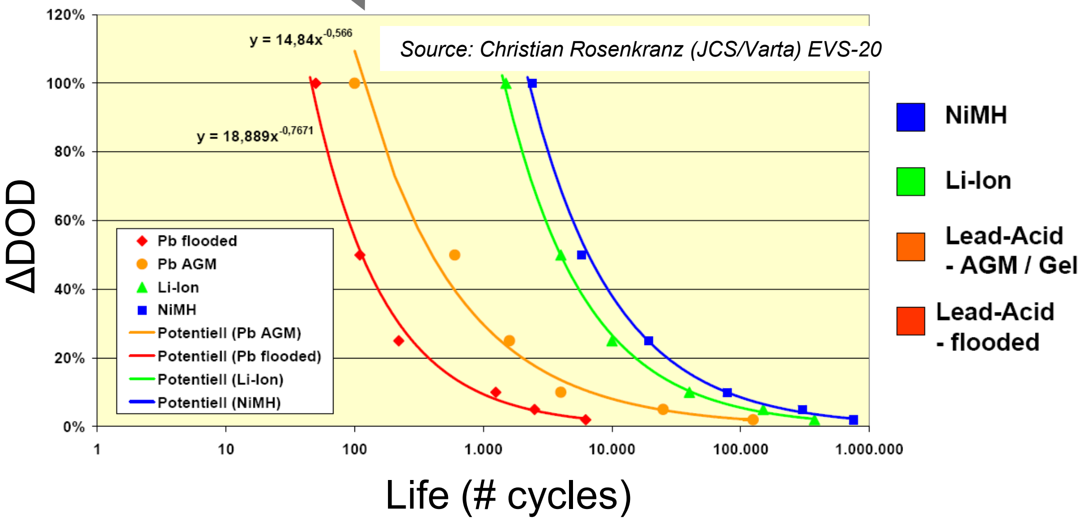
- Relatively well established & understood
- Typical $t^{1/2}$ time dependency
- Arrhenius relation describes T dependency



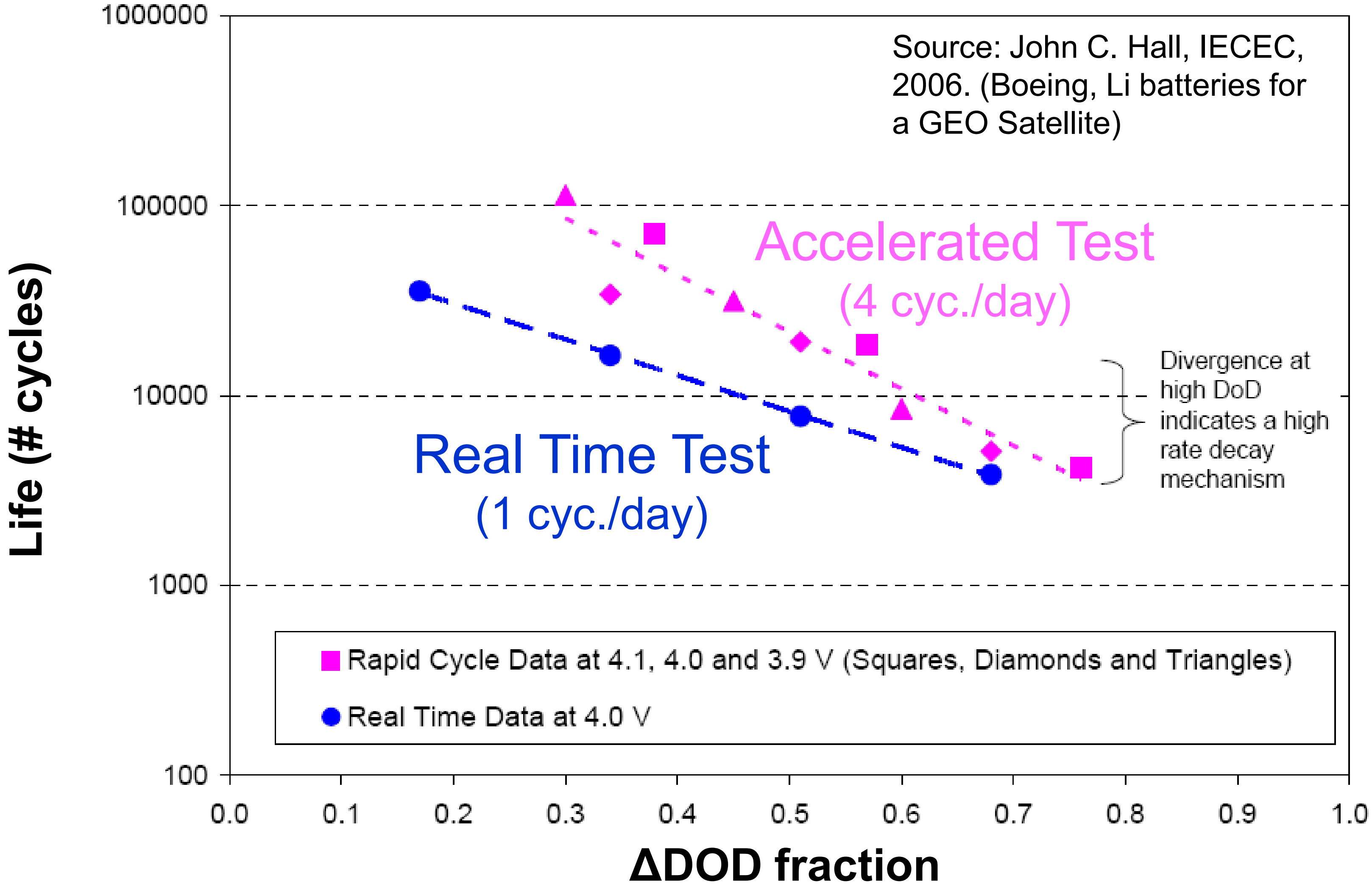
Cycling Fade

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





Accelerated Cycle Life Tests Are Not Always Conservative!

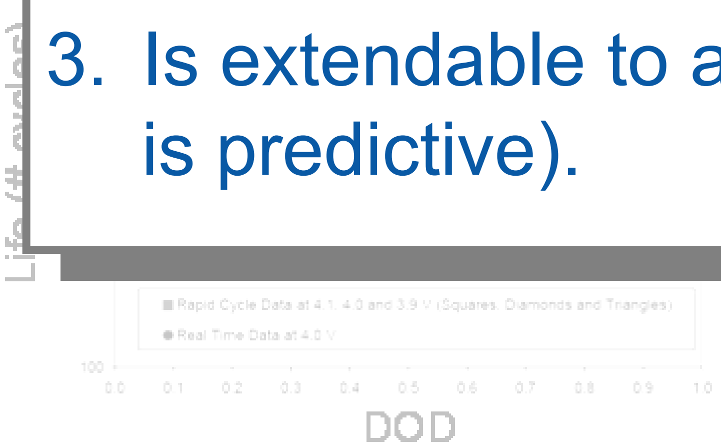


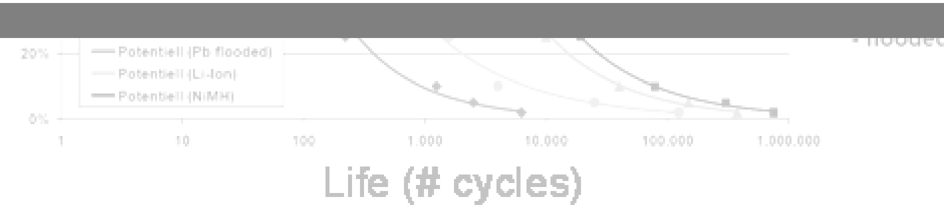
- Li-ion – high-voltage, nonaqueous chemistry – calendar life effect important
- Real-time tests necessary for proper extrapolation of accelerated results

Our Objectives for Battery Life Modeling

Develop a power and energy degradation model that —

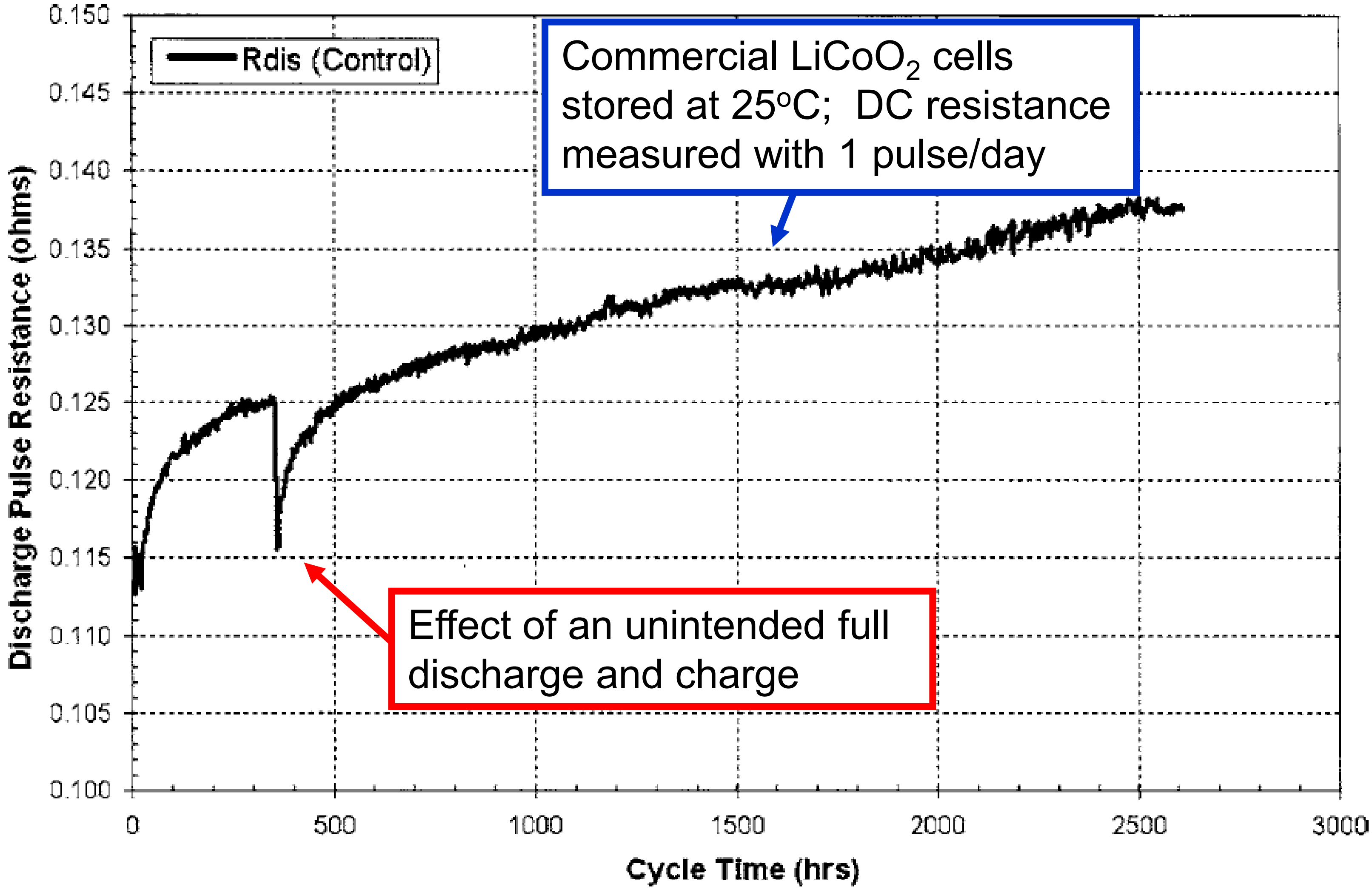
1. Uses both accelerated and real-time calendar and cycle life data as inputs.
2. Is mathematically consistent with all calendar and cycle life empirical data.
3. Is extendable to arbitrary usage scenarios (i.e., it is predictive).





Impedance Growth Mechanisms: Complex Calendar and Cycling Dependency

Cycling has been shown to suppress impedance growth.



Source: J.P.Christopersen, J. Electrochem. Society, 2006.

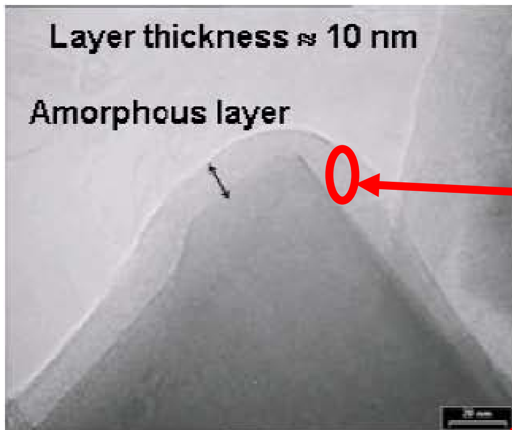
Impedance Growth Mechanisms: Complex Calendar and Cycling Dependency

NCA chemistry: Different types of electrode surface film layers can grow.

(1) “Electrolyte film” (2) “Solid film”

SEM Images: John C. Hall, IECEC, 2006.

Cell stored
at 0°C

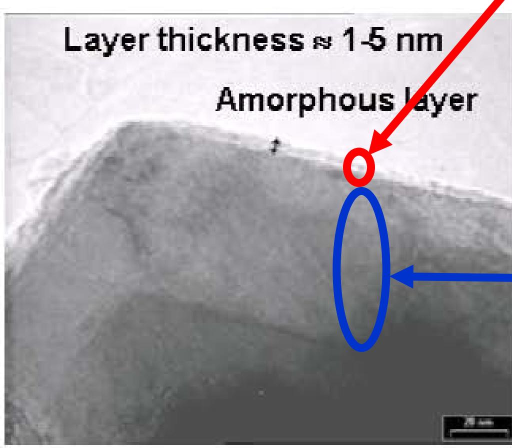


Electrolyte film*

- grows during storage α $t^{1/2}$
- suppressed by cycling

*Often called Solid-Electrolyte Interphase (SEI) layer

Cell cycled
1 cycle/day
at 80% DOD



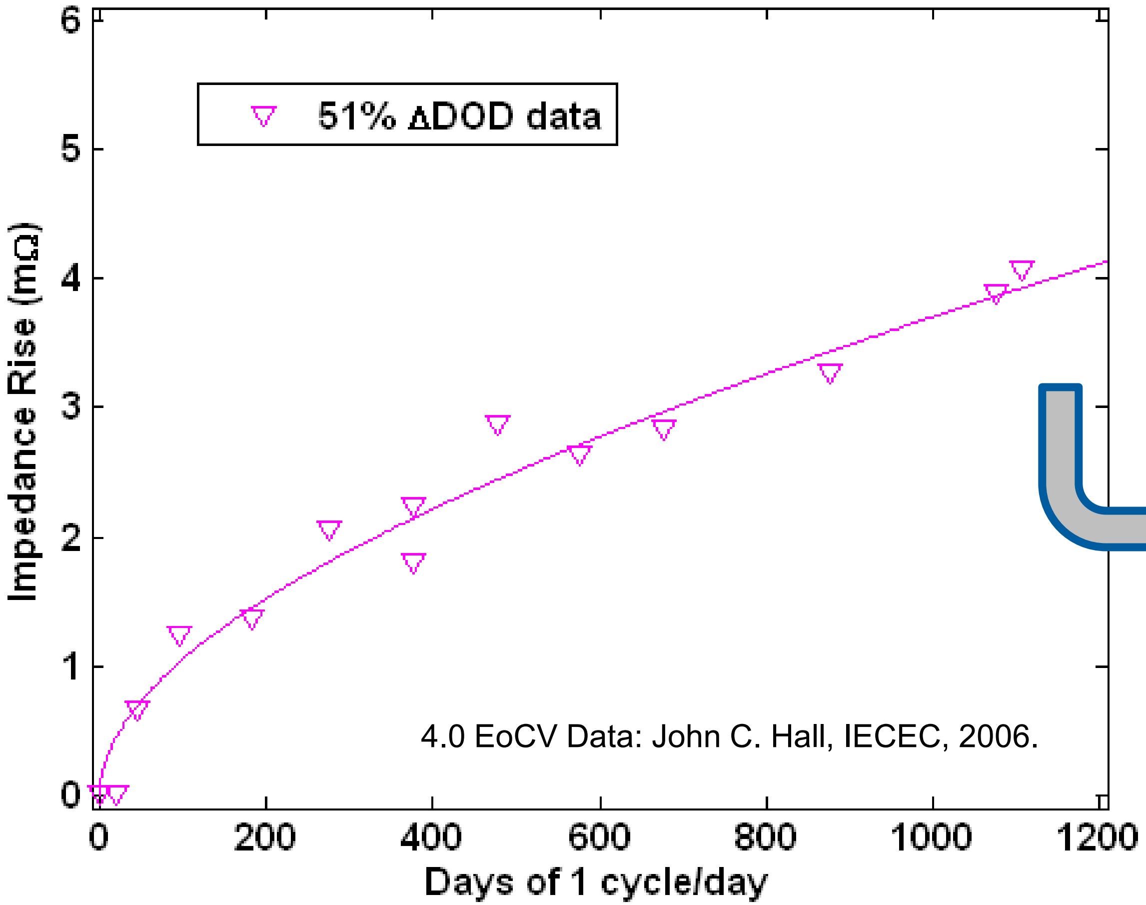
Solid film

- grows only with cycling α t or N

Impedance (R): Cycling at Various ΔDODs

Fitting $t^{1/2}$ and N Components

- Simple model fit to cycling test data: Boeing GEO satellite application, NCA chemistry
- Model includes $t^{1/2}$ (~storage) and N (~cycling) component.



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

(Note: For 1 cycle/day, N = t*)*

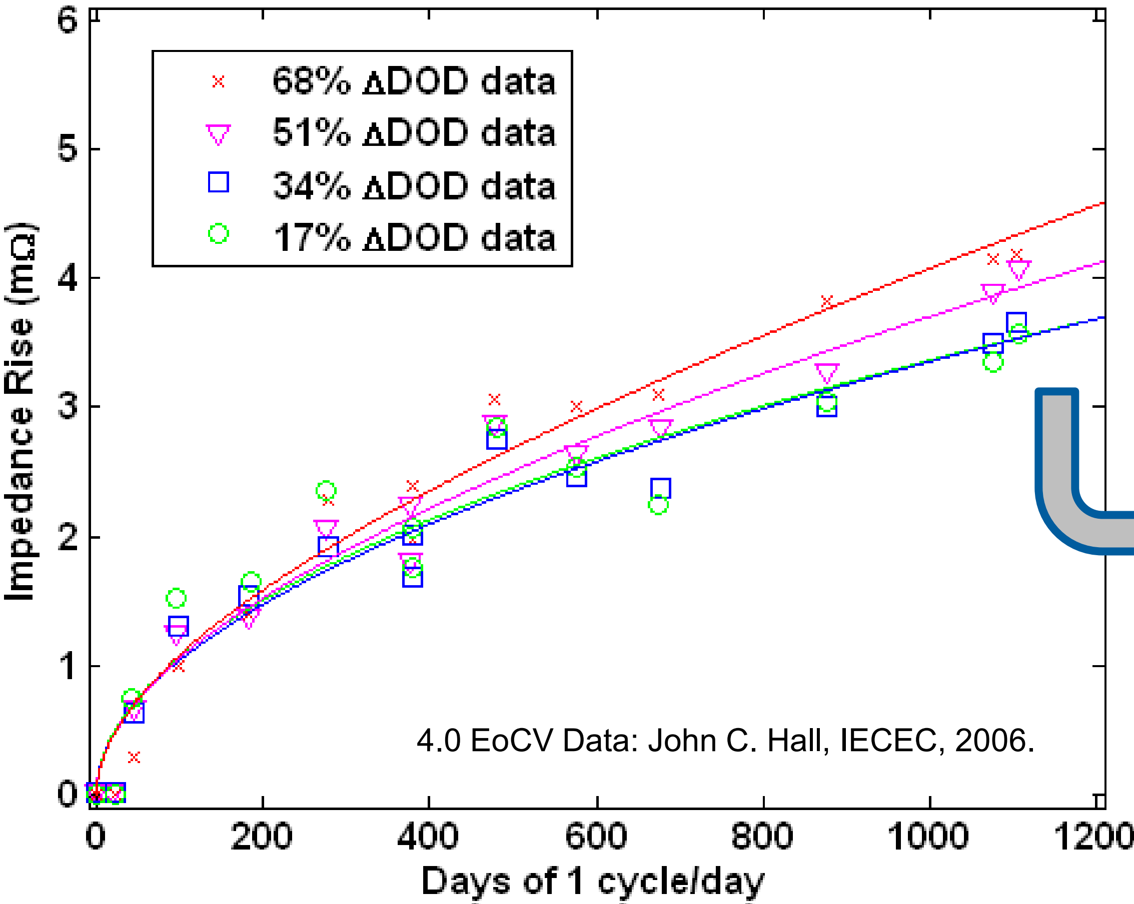
Curve-fit at 51% ΔDOD:

a_1 = 1.00001e-4 Ω/day$^{1/2}$
a_2 = 5.70972e-7 Ω/cyc
R^2 = 0.9684

Impedance (R): Cycling at Various ΔDODs

Fitting $t^{1/2}$ and N Components

- Simple model fit to cycling test data: Boeing GEO satellite application, NCA chemistry
- Model includes $t^{1/2}$ (~storage) and N (~cycling) component.



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

(Note: For 1 cycle/day, N = t*)*

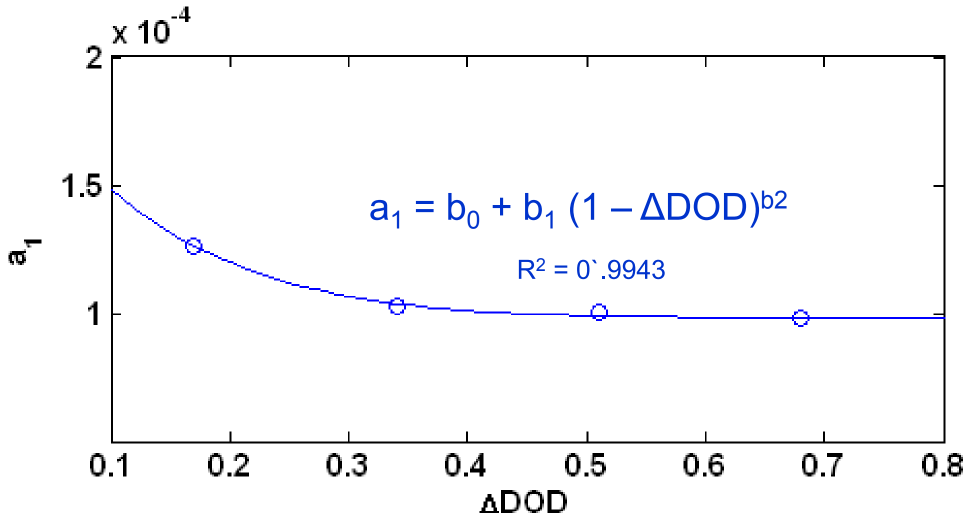
ΔDOD	a_1 (Ω/day$^{1/2}$)	a_2 (Ω/cyc)	R^2
68%	0.98245e-4	9.54812e-7	0.9667
51%	1.00001e-4	5.70972e-7	0.9684
34%	1.02414e-4	0.988878e-7	0.94928
17%	1.26352e-4	-7.53354e-7	0.9174

Impedance (R): Cycling at Various ΔDODs

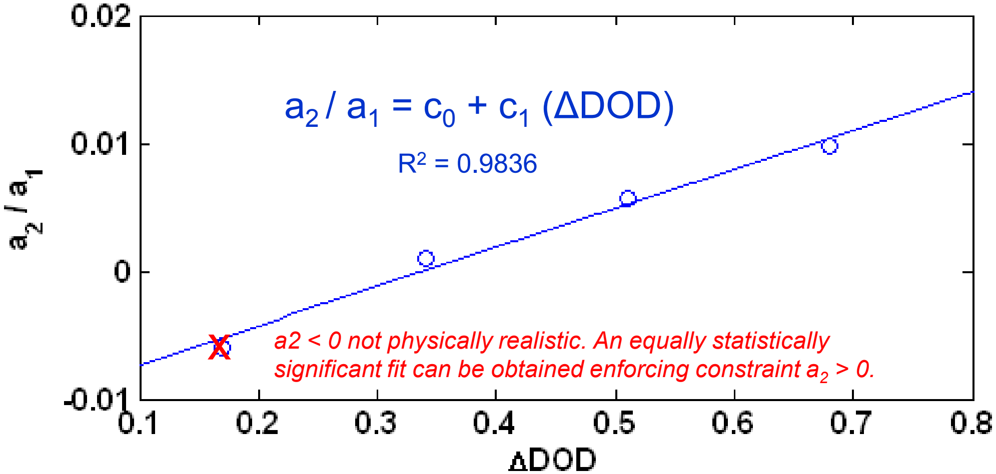
Capturing Parameter Dependencies on ΔDOD

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

Additional models are fit to describe a_1 and a_2 dependence on ΔDOD.



High $t^{1/2}$ resistance growth on storage is suppressed by cycling.



High DOD cycling grows resistance α N.

Low DOD cycling reduces resistance α N.

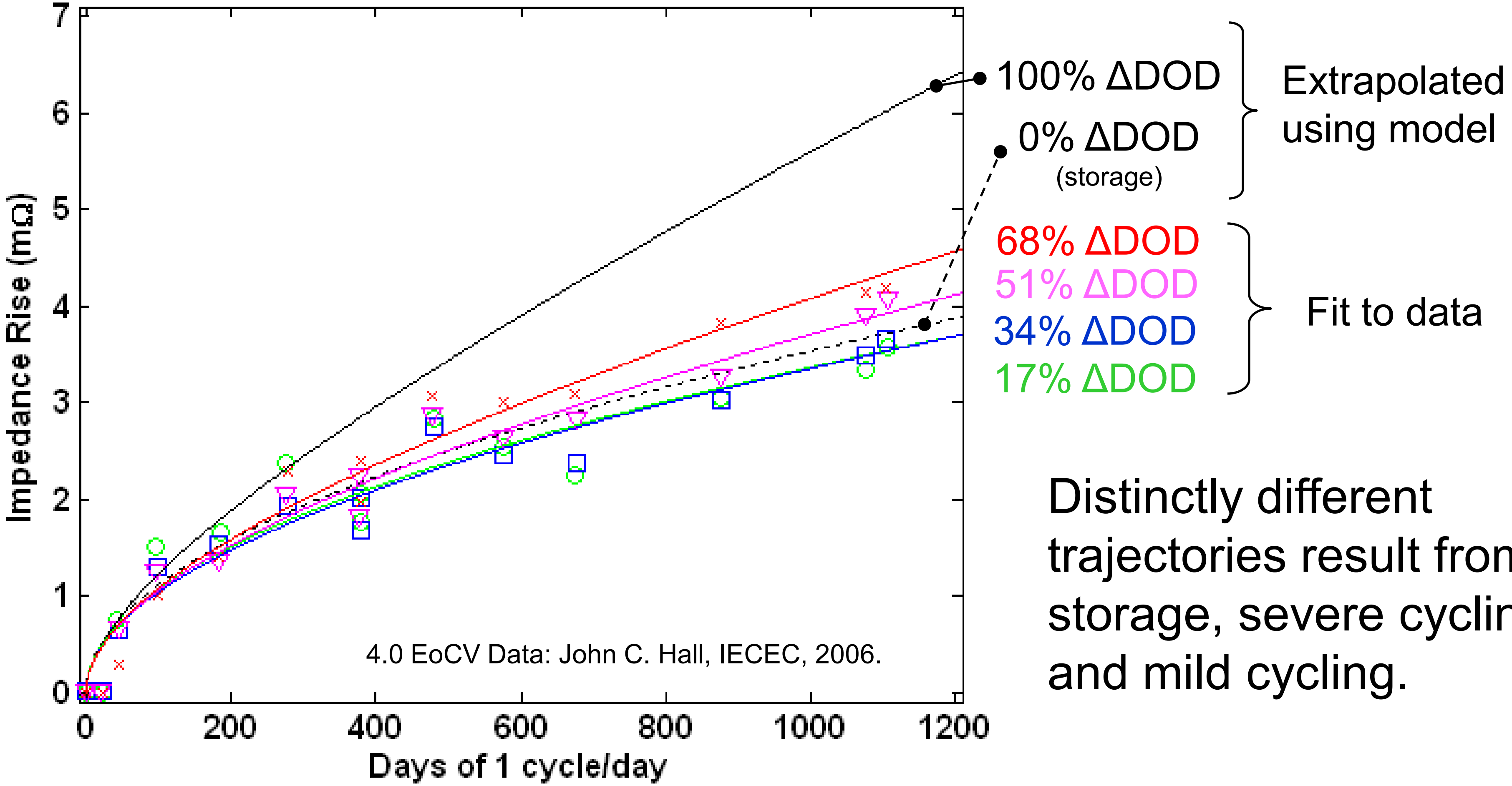
Impedance: Cycling at Various ΔDODs

Example Model Projections

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

$$a_1 = b_0 + b_1\,(1 - \Delta DOD)^{b2}$$

$$a_2 / a_1 = \max[0,\ c_0 + c_1\,(\Delta DOD)]$$

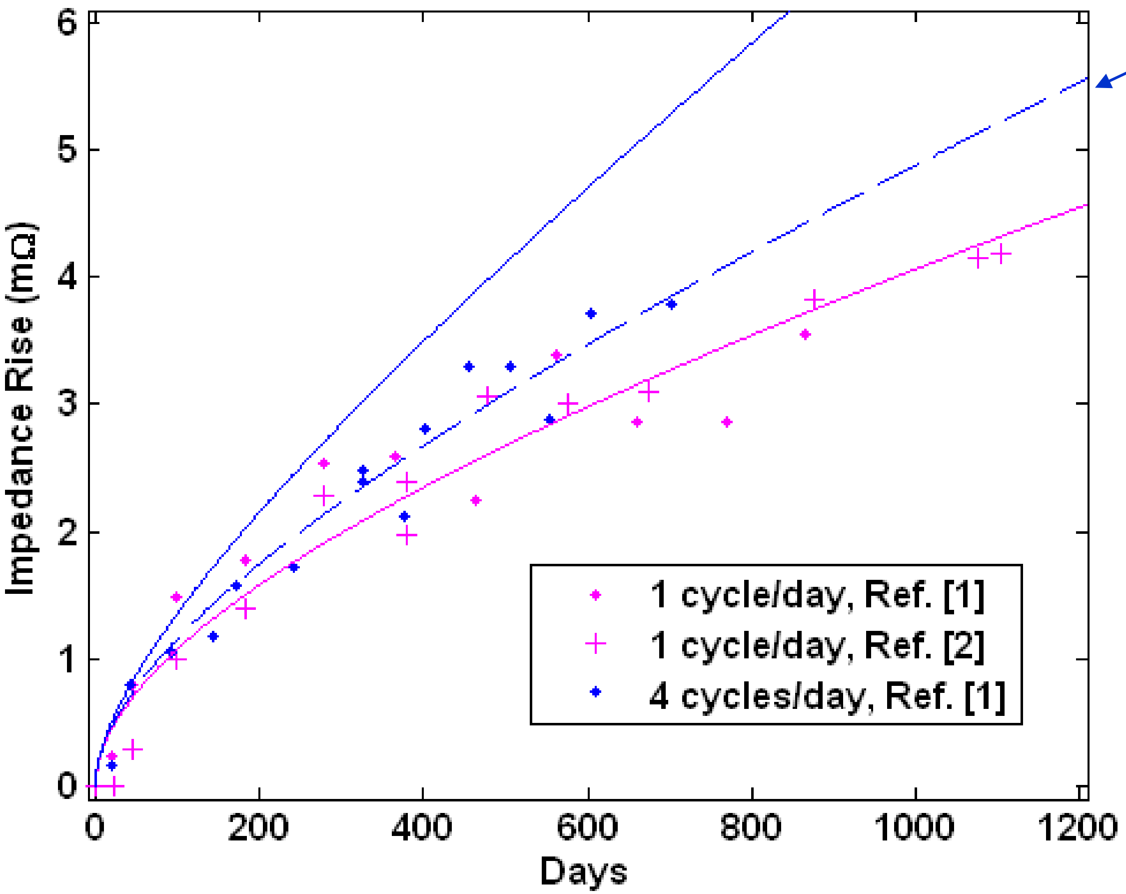


Distinctly different trajectories result from storage, severe cycling and mild cycling.

Impedance: Multiple Cycles per Day

Dependence on $t^{1/2}$, N model overpredicts effect of accelerated cycling.
(not used)

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



$R = a_1 t^{1/2} + a_{2,t}\, t + a_{2,N}\, N$

$a_{2,t} = a_2 (1 - \alpha_N)$

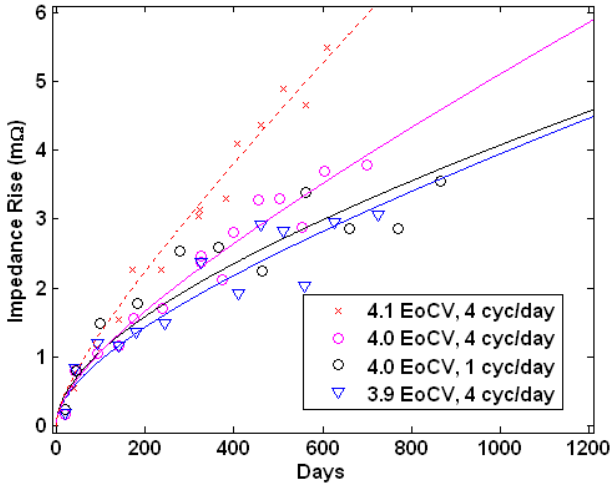
$a_{2,N} = a_2\, \alpha_N$

$\alpha_N = 0.285$, $R^2 = 0.9488$

Dependence on $t^{1/2}$, **t**, N model predicts accelerated and real-time cycling much better.

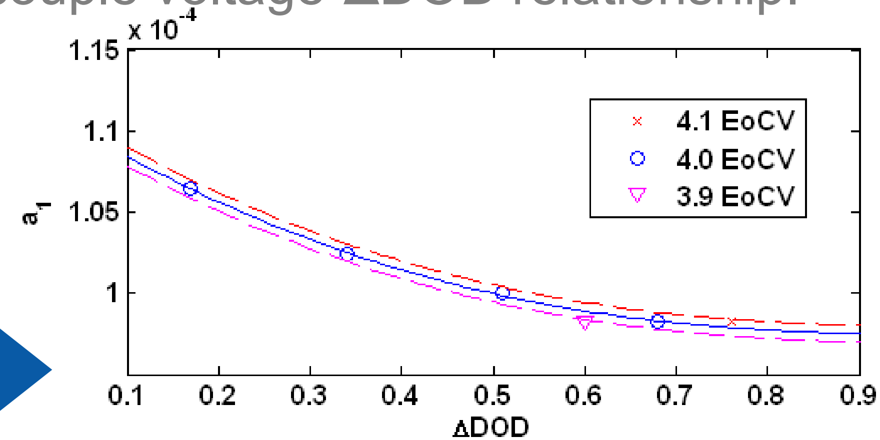
[1] Corrected data from J.C. Hall et al., 208th ECS Mtg., Oct. 16-21, Los Angeles, CA. [2] Data from J.C. Hall et. al., 4th IECEC, June 26-29, San Diego, CA.

Impedance: Voltage and Temperature Acceleration



- Increased impedance growth due to elevated voltage & temperature fit using Tafel & Arrhenius-type equations.

- Dedicated lab experiments required to fully decouple voltage-ΔDOD relationship.

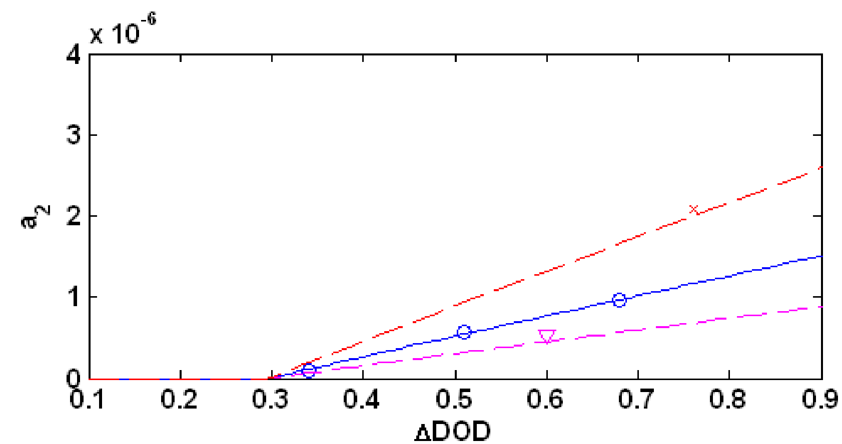


$$a_1 = a_{1,ref}\, k_1 \exp(\alpha_1 F/RT \times V)$$

$$a_2 = a_{2,ref}\, k_2 \exp(\alpha_2 F/RT \times V)$$

$$k_1 = k_{1,ref} \exp\left(-E_{a1} \times (T^{-1} - T_{ref}^{-1}) / R\right)$$

$$k_2 = k_{2,ref} \exp\left(-E_{a2} \times (T^{-1} - T_{ref}^{-1}) / R\right)$$

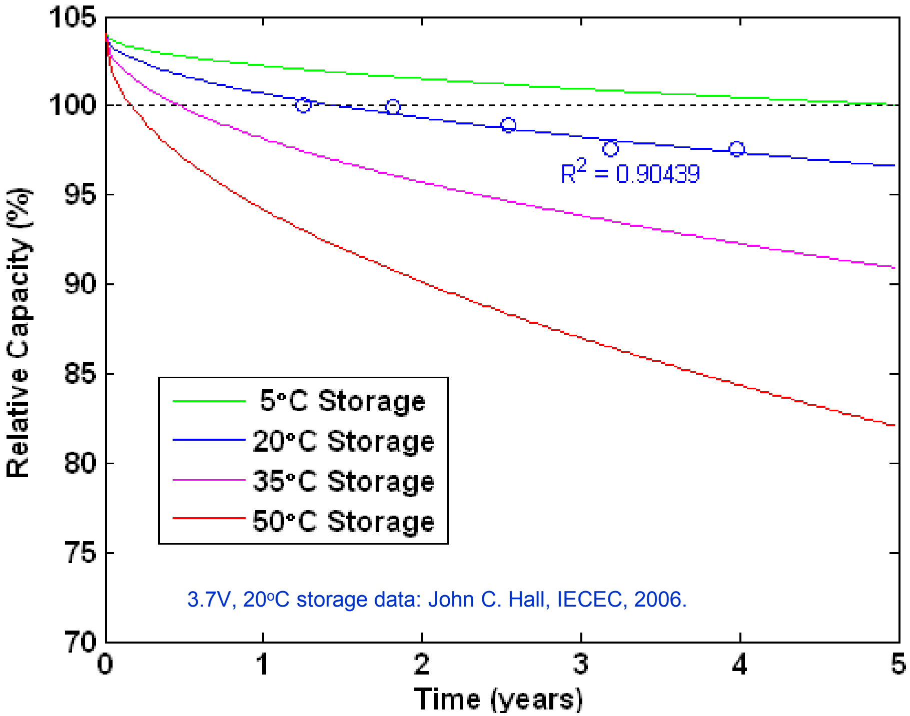


- This work assumes values for k_1 & α_1.
- Activation energies, E_{a1} and E_{a2}, are taken from similar chemistry.

Capacity Fade: Calendar (storage) and Cycling Effects

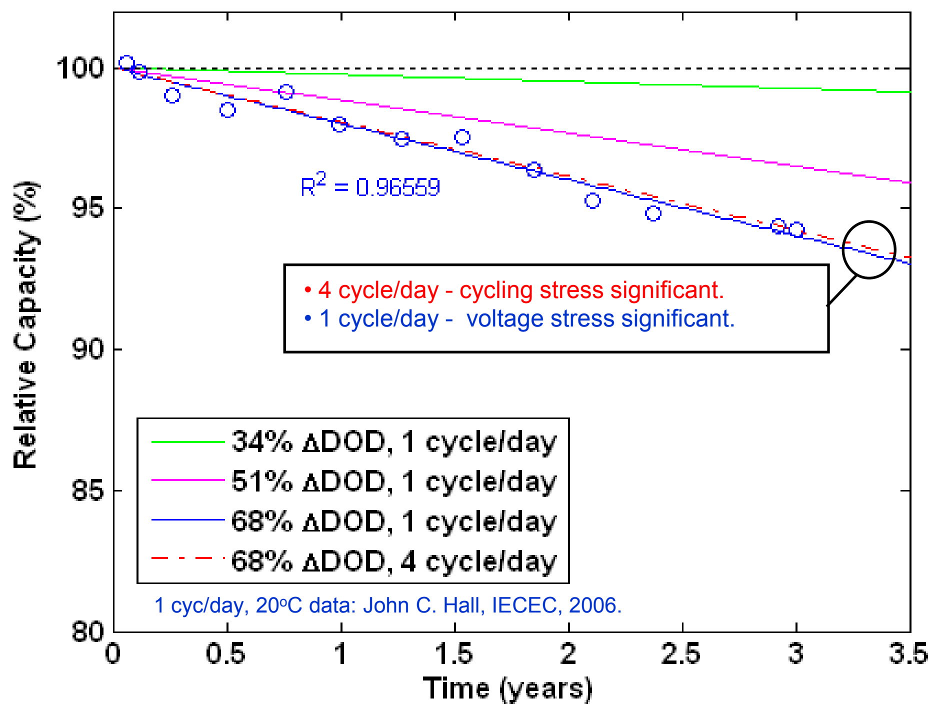
Capacity Loss During Storage

Loss of cyclable Li



Capacity Loss During Cycling

Isolation of active sites



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

$$Q_{sites} = e_0 + e_1 \times (a_{2,t}\, t + a_{2,N}\, N)$$

Q = Relative Capacity

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

a_1 and a_2 capture temperature, ΔDOD, and voltage dependencies (previous slides).

Life Model Summary (equations & coefficients)

Impedance Growth Model

- Temperature
- Voltage
- ΔDOD
- Calendar Storage ($t^{1/2}$ term)
- Cycling (t & N terms)

$$k_1 = k_{1,ref} \exp\left(-E_{a1} \times (T^{-1} - T_{ref}^{-1}) / R\right)$$
$$k_2 = k_{2,ref} \exp\left(-E_{a2} \times (T^{-1} - T_{ref}^{-1}) / R\right)$$

$$a_1 = a_{1,ref}\, k_1 \exp(\alpha_1 F/RT \times V)$$
$$a_2 = a_{2,ref}\, k_2 \exp(\alpha_2 F/RT \times V)$$

$$a_1 = b_0 + b_1 (1 - \Delta DOD)^{b2}$$
$$a_2 / a_1 = \max[0, c_0 + c_1 (\Delta DOD)]$$

$$a_{2,t} = a_2 (1 - \alpha_N)$$
$$a_{2,N} = a_2 \alpha_N$$

$$R = a_1 t^{1/2} + a_{2,t}\, t + a_{2,N}\, N$$

Capacity Fade Model

- Temperature
- Voltage
- ΔDOD
- Calendar Storage (Li loss)
- Cycling (Site loss)

From impedance growth model

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

$$Q_{sites} = e_0 + e_1 \times (a_{2,t}\, t + a_{2,N}\, N)$$

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

Reasonably fits available data

Actual interactions of degradation mechanisms may be more complex.

Life/Cost Trade-Offs: Approach

- Life model adjusted slightly to reflect experience with present-day PHEV battery technology (NCA chemistry).
- Cost model from previous work:
  - Manufacturing cost of a complete pack at high volume production

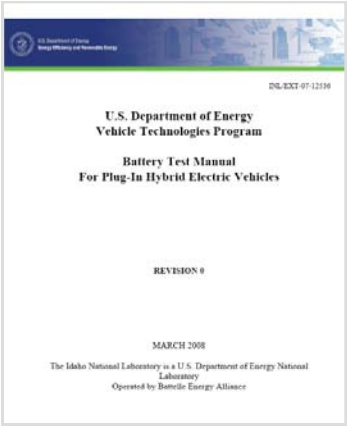
$$\$/pack = 11.1*kW + 224.1*kWh + 4.53*BSF + 340$$

BSF = Battery Size Factor

Nominal Energy (kWh)	P/E	Detailed Model: [3] NCM	Detailed Model: [3] NCA	Simple Model: [1,2] $=11*kW+224*kWh+680
6.88	5.8	$3120	**$2600**	**$2660**
8.46	4.7	$3510	**$2860**	**$3020**
11.46	3.5	$4290	**$3500**	**$3680**

NCA - Nickel Cobalt Alumina; NCM- Nickel Cobalt Manganese

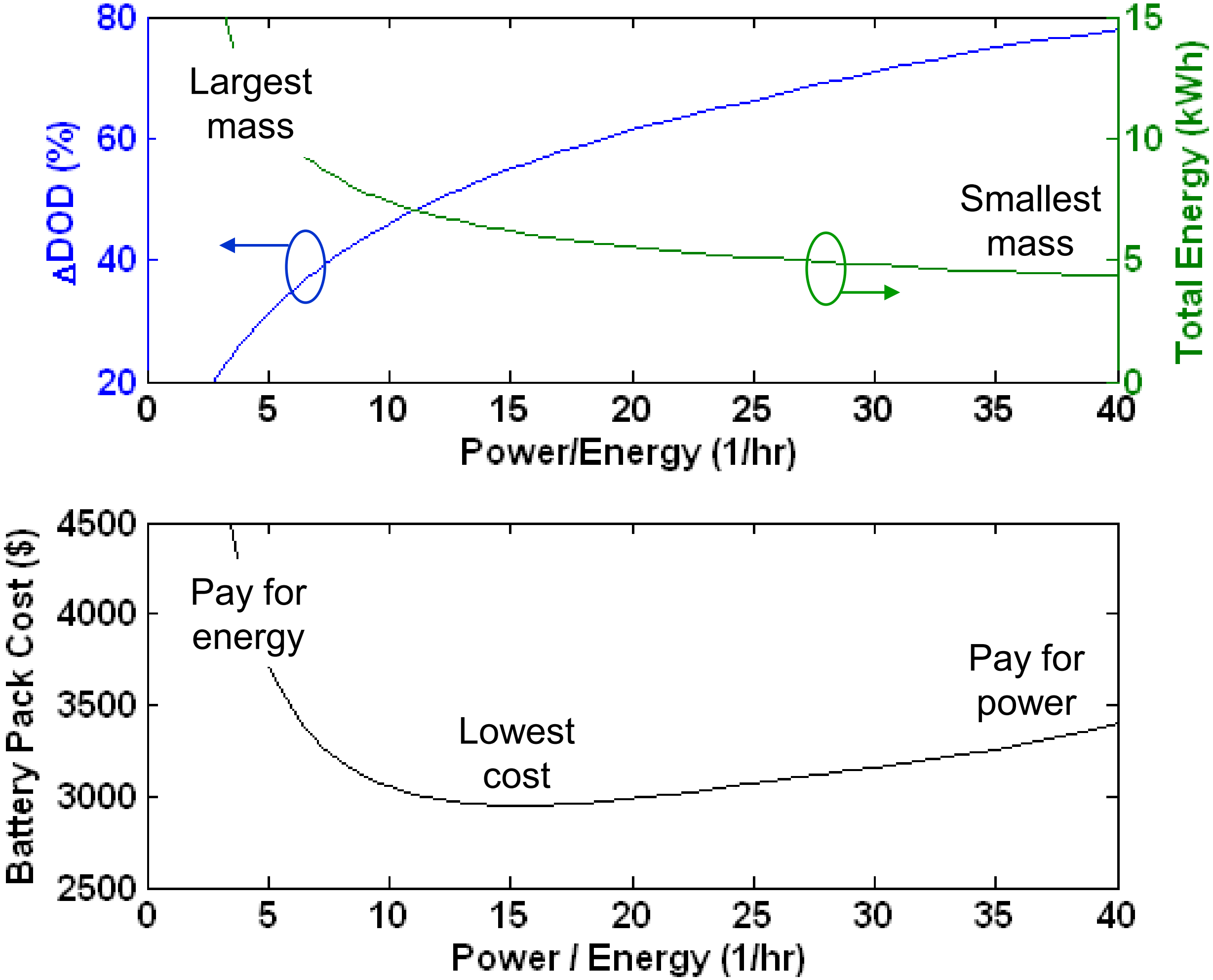
- Requirements from USABC/DOE
  - Energy: 3.4 kWh PHEV10; 11.6 kWh PHEV40
  - CD Cycle Life: 5000 CD cycles
  - Calendar Life: 15 years at 35°C
    - Too aggressive for present-day technology
    - Instead used 10 years at 30°C for analysis (next two slides)
- Questions:
  - What ΔDOD & P/E meet life at minimum cost?
  - Which controls life? Calendar or cycle life?
  - What environmental parameters cause greatest life sensitivity?



1. Graham, R. et al. "Comparing the Benefits and Impacts of Hybrid Electric Vehicle Options," Electric Power Research Institute (EPRI), 2001.
2. Simpson, A., "Cost Benefit Analysis of Plug-In Hybrid Electric Vehicle Technology," *22nd International Electric Vehicle Symposium*, Yokohama, Japan, Oct. 2006.
3. "Cost Assessment for Plug-In Hybrid Vehicles," *TIAX LLC*, Oct. 2007.

Life/Cost Trade-Offs: Usable ΔDOD

<u>PHEV10</u> battery sized for
10 years at 30°C, 1 cycle/day*

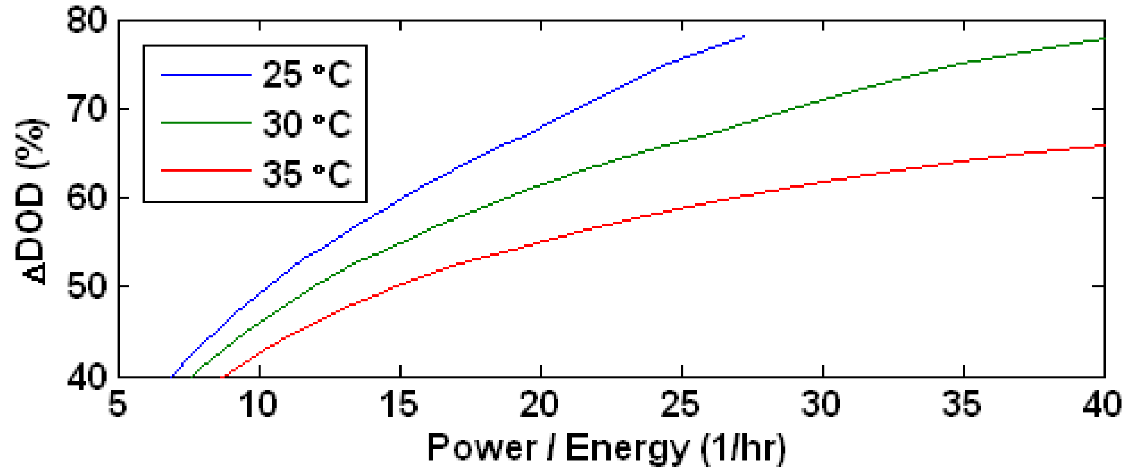


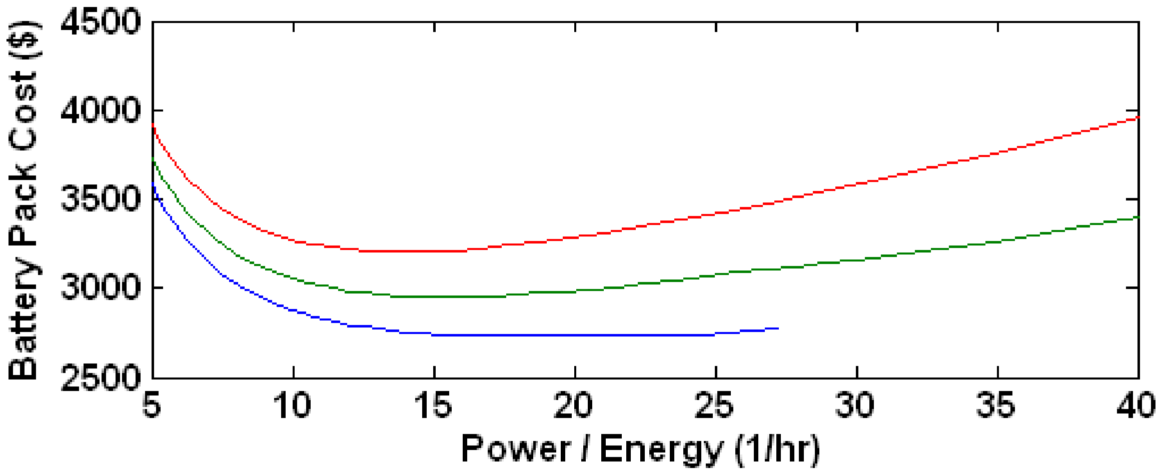
* using 3.9 EoCV (90% SOC_{max})

- Expanding ΔDOD window
  - reduces total battery energy & mass
  - requires higher P/E to meet power requirements at low SOC
- Optimal P/E ratio (~15 hr^{-1}) yields lowest cost battery
- Too much P/E is preferred to too little P/E
  - small increase in cost
  - reduces mass

Life/Cost Trade-Offs: Temperature Sensitivity

PHEV10 battery sized for
10 years at 25°C, 30°C, & 35°C*





- Temperature exposure drastically impacts system size necessary to meet goals at end of life.
  - 25°C: 70% to 80% ΔDOD is usable
  - 35°C: 50% to 65% ΔDOD is usable

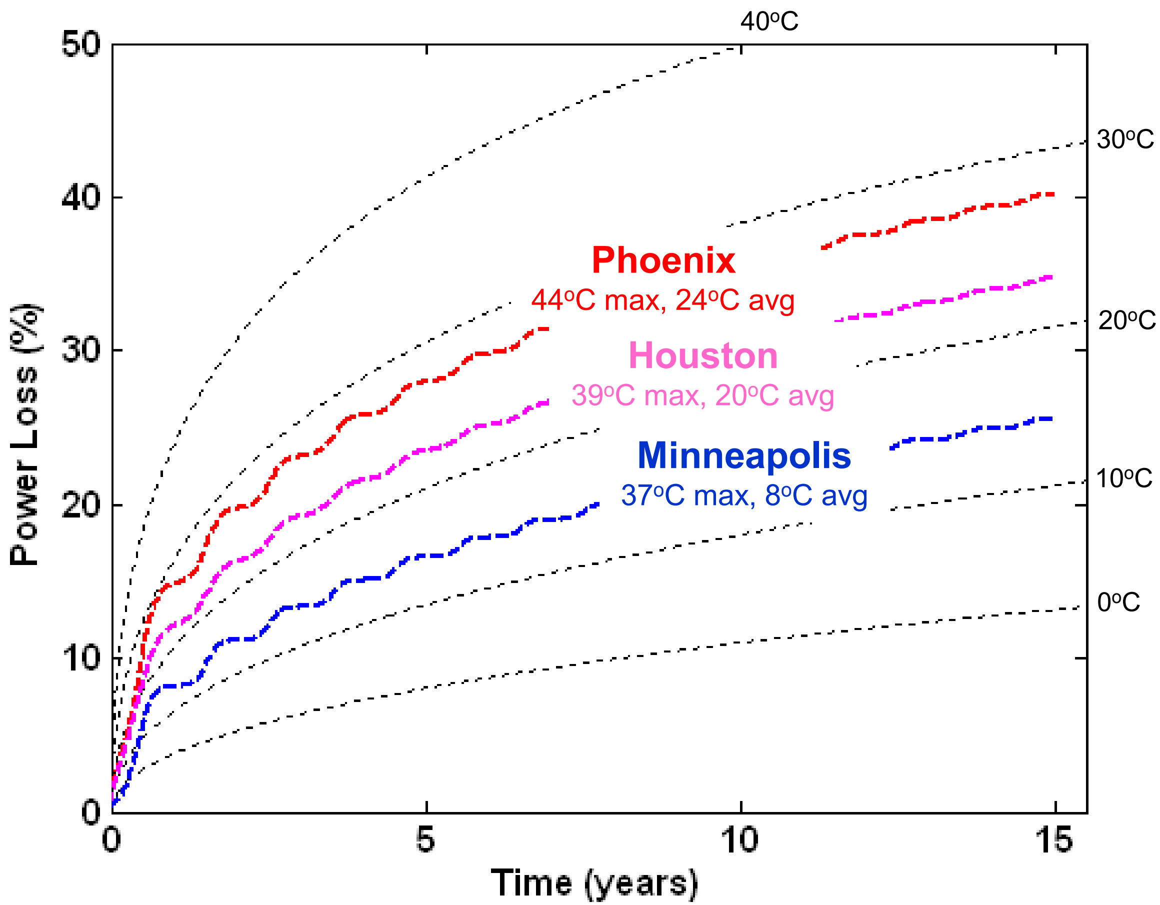
- Modifying life requirements from 10 years at 25°C to 10 years at 35°C increases battery cost by > $500.

* 1 cycle/day, 3.9 EoCV (90% SOC_{max})

The Case for Thermal Control of PHEV Batteries

Storage at elevated temperatures responsible for significant impedance growth; most passenger vehicles are parked >90% of the time.

- Assume vehicle is always parked (storage calendar life effect only).
- Typical Meteorological Year (TMY) hour-by-hour geographic dataset used to provide ambient conditions.
- Assume $T_{battery} = T_{ambient}$ *(Realistic? No. Solar loading on vehicle cabin & battery will cause even more power loss.)*



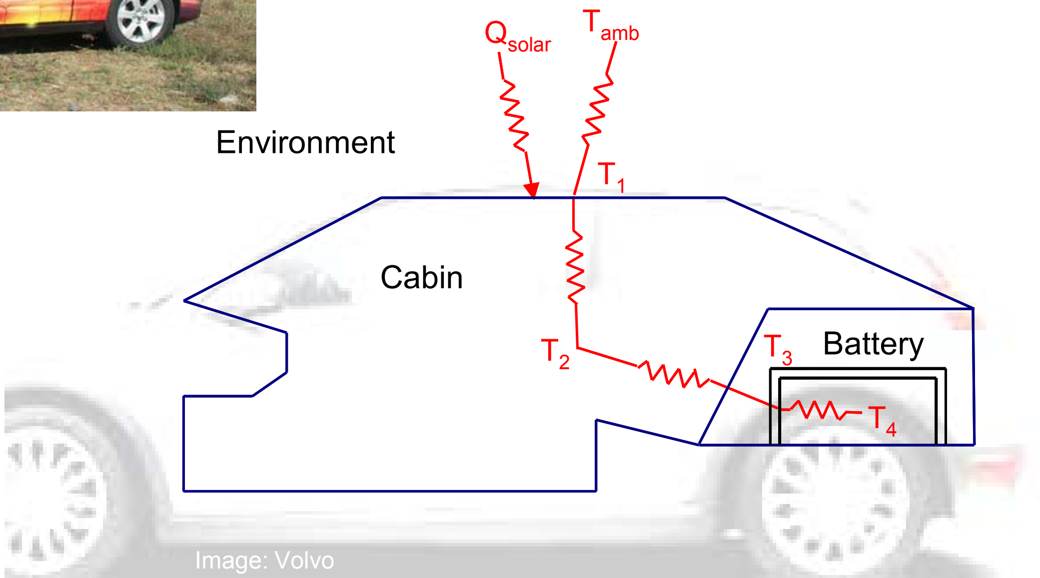
Current Li-ion technology can require 30% to 70% excess power to last 15 years.

Advanced Li-Ion technologies still could require 15% to 30% excess power to last 15 years.

Thermal control of PHEV batteries is needed even during standby.

Study of PHEV Battery Standby Thermal Control

- Investigate the technical and economic merits of various thermal control strategies during standby
  - Experiments using NREL PHEV Test Bed and other vehicles
  - Vehicle thermal modeling with various solar and ambient loads



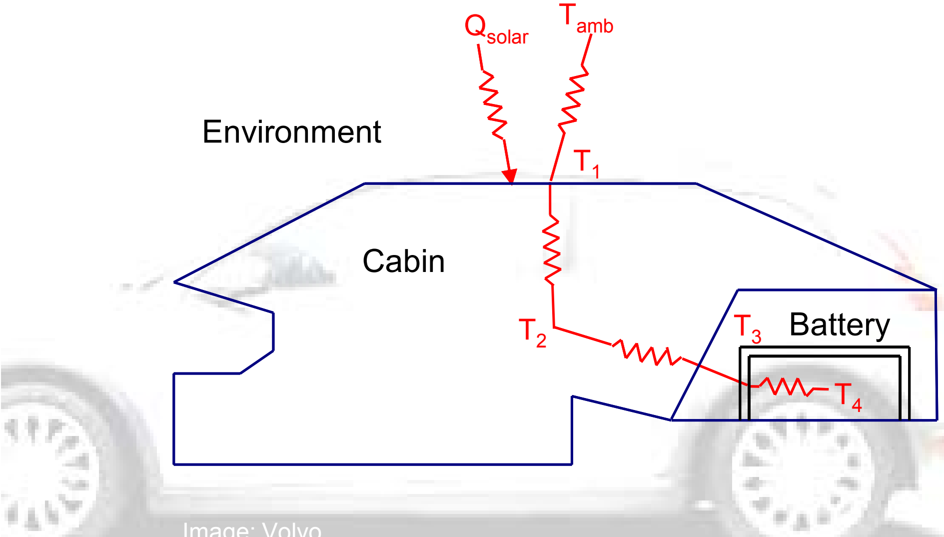
On Sunny Days, Solar Warming of Cabin Can Cause Battery Temperature to Be Much Hotter than Ambient

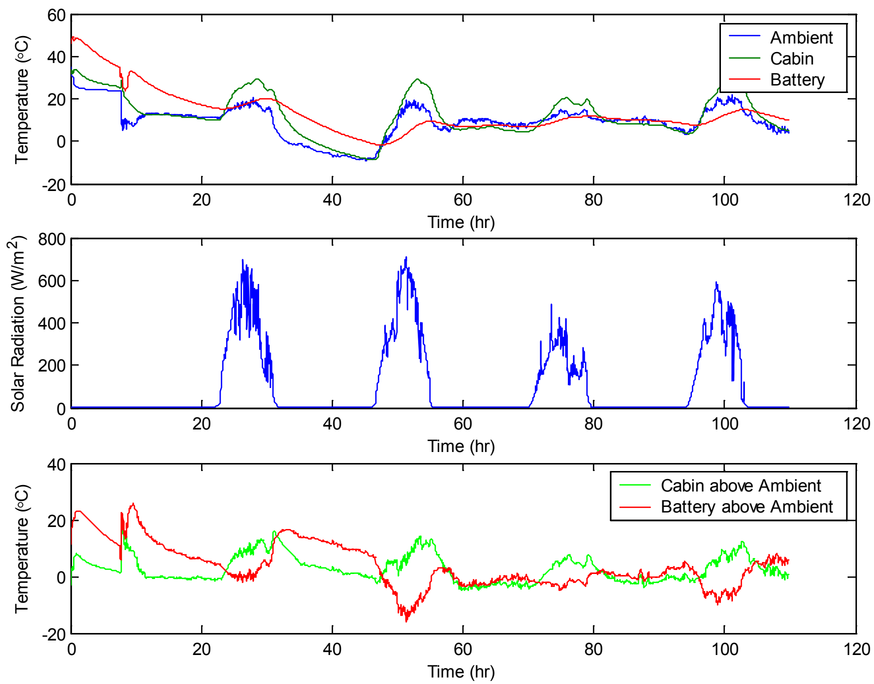
NREL PHEV Test Bed instrumented to correlate solar radiation & ambient temperature with battery temperature

Rooftop pyranometer & RTD

Battery Pack RTD

Vehicle thermal model extracted for geographic scenario analysis



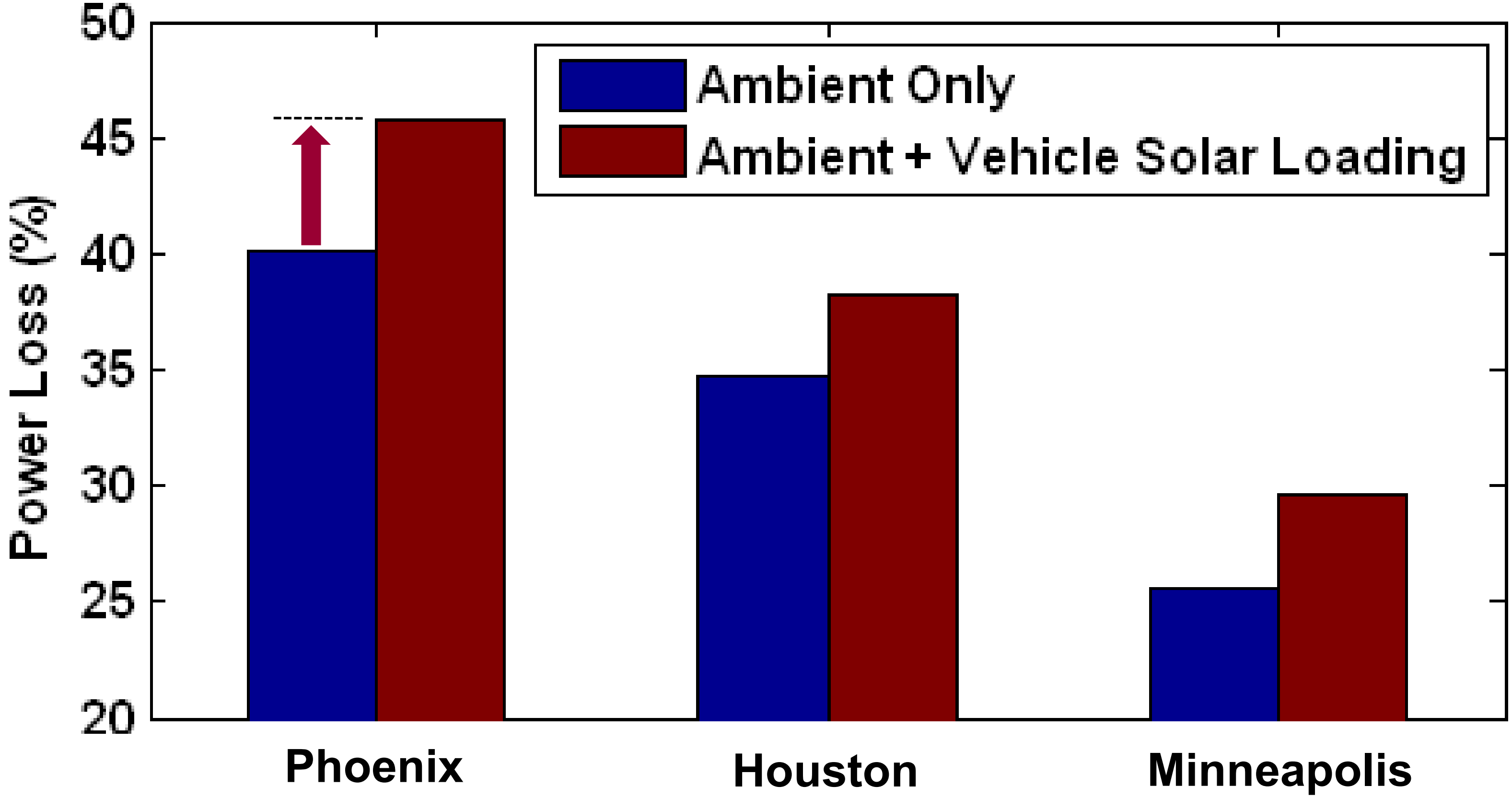


Model: Solar Warming of Cabin (and its effect on battery temperature) Is Important for Predicting Battery Degradation

PHEV10 – Power loss after 15 years

Degradation predictions with and without effects of vehicle solar loading.

Current Li-ion technology

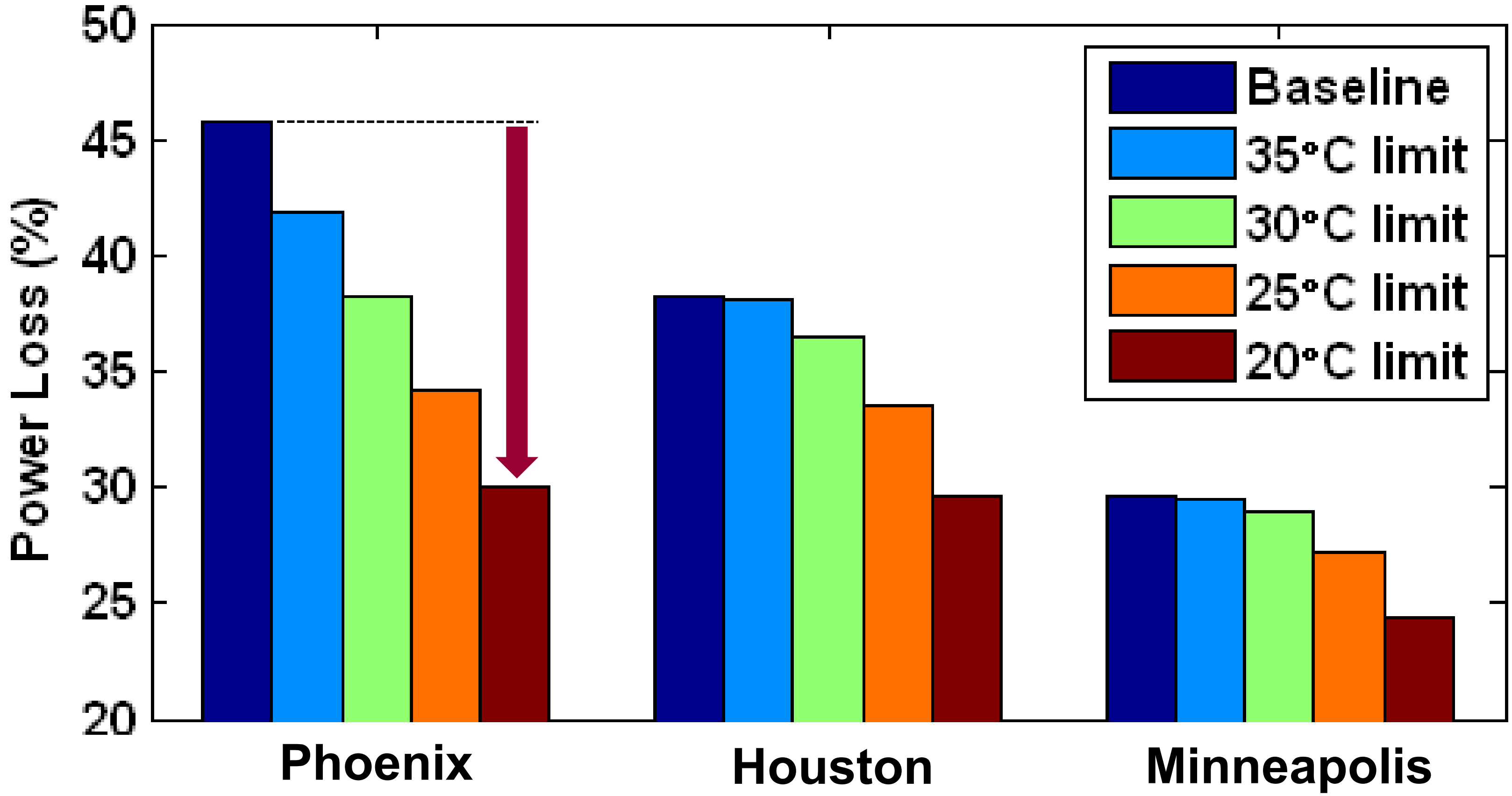


Eliminating Peak Battery Temperatures (e.g., battery insulation, active cooling, reducing solar load) **Can Greatly Improve Battery Life**

PHEV10 – Power loss after 15 years

Ambient temperature & solar radiation climate data input to vehicle/battery thermal model. Assume peak battery temperatures can be eliminated.

Current Li-ion technology



Conclusions

- Useful life of a given cell design is dictated by the complex interaction of parameters ($t^{1/2}$, t, N, T, V, DOD).
- Successful introduction of PHEV Li-ion technology requires careful consideration of
  - Design factors: battery DOD, end of charge voltage, …
  - Real-world use: # cycles/day, temperature exposure.
- Battery life is extremely sensitive to temperature exposure; solar loading on cabin can cause severe battery heating.
- PHEV battery standby thermal control can reduce power loss by >15% over baseline 15-year Phoenix, AZ, scenario.
- Accurate degradation prediction requires large parametric dataset at the cell level (next slide) plus dedicated laboratory tests at the material level.

Need for Parametric Data on Li-ion Technologies:

Battery life model is only as good as the dataset populating it.

Special Considerations:

- Expose possible accelerating mechanisms:
  - high T material degradation
  - low T mechanical stress.
- Low ΔDOD cycling is important for decoupling $t^{1/2}$ and t dependencies.
- Test to $>V_{max}$ to improve model fit at elevated voltages.
- When cells die:
  - destructive physical analysis, or
  - continue cycling at less severe rate (enable 2nd use/resale).

4 Cycles per Day at Average CD Current

- Size CD region

	Capacity (Ah)	30	34	38	42
	EoCV (V)	3.9	4	4.1	4.25
ΔDOD (%)	90	20˚C	-10˚C, 0˚C, 20˚C, 40˚C	20˚C	20˚C, 40˚C
	70	20˚C	20˚C	20˚C	
	30	20˚C	-10˚C, 0˚C, 20˚C, 40˚C	20˚C	20˚C, 40˚C
	10	20˚C	20˚C	20˚C	

1 Cycle per Day at Average CD Current

- Allow proper extrapolation of 4 cycle/day accelerated tests

	Capacity (Ah)	30	34	38	42
	EoCV (V)	3.9	4	4.1	4.25
ΔDOD (%)	90		0˚C, 20˚C, 40˚C		20˚C, 40˚C
	80		20˚C		
	65		0˚C, 20˚C, 40˚C		20˚C, 40˚C
	30		20˚C		

Open Circuit Storage

- Choose OCV to match CD & CS cycling scenarios

OCV (V)	3.4	4	4.1	4.25
	40˚C	20˚C, 40˚C, 60˚C	40˚C	20˚C, 40˚C, 60˚C

Continuous Cycling in Various CS Windows

- Find optimum CS region and window

	Capacity (Ah)	30	34	38	42
	SOC (%)	5%	10%	20%	50%
ΔDOD (%)	2	0˚C, 20˚C	0˚C, 20˚C	20˚C	20˚C
	5	0˚C, 20˚C	0˚C, 20˚C	20˚C	20˚C

Acknowledgements

- Battery life modeling and trade-off study supported by DOE's Office of Vehicle Technologies
  - Dave Howell, Energy Storage Program

- Thermal standby analysis supported by NREL's Strategic Initiative
  - Funding: Dale Gardner, Director, NREL Renewable Fuels and Vehicle Systems
  - Technical support: Larry Chaney and Anhvu Le