NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

Modeling of Nonuniform Degradation in Large-Format Li-ion Batteries

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Kandler Smith
Kandler.Smith@nrel.gov
Gi-Heon Kim
Gi-Heon.Kim@nrel.gov
Ahmad Pesaran
Ahmad.Pesaran@nrel.gov

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Background

- Context: Trend towards larger cells
  - Higher capacity applications (HEV → PHEV → EV)
  - Reduced cell count reduces cost & complexity
  - Drawback: Greater internal nonuniformity
    - Elevated temperature,
    - Regions of localized cycling

  } → Degradation

?

- Objectives
  - Understand impact of large-format cell design features on battery useful life
  - Improve battery engineering models to include both realistic geometry and physics
  - Reduce make-and-break iterations, accelerate design cycle

Overview

- Previous work
- Multiscale approach
  - Multidimensional echem/thermal model
  - Coupled with empirical degradation model
- Empirical degradation model
  - NCA chemistry
  - Degradation factors: $t^{1/2}$, t, # cycles, T, V, ΔDOD
  - Impedance growth, capacity loss
- Modeling investigation of nonuniform degradation
  - 20 Ah cell
  - Accelerated cycling for PHEV10-type application

Some previous work

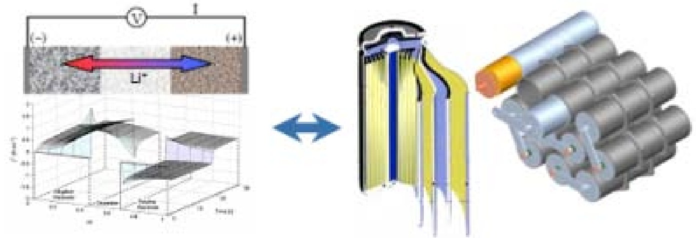
- Multidimensional Li-ion cell modeling
  - Thermal only, w/ uniform heat generation (Chen 1994)
  - 2-D echem model of Li-plating (Tang 2009)
  - 2-D echem/thermal w/simplified geometry (Gu 1999)
  - <u>2-D & 3-D multiscale electrochemical/thermal models</u> (Kim & Smith 2008-2009)
- Li-ion degradation modeling
  - Physical corrosion/SEI growth (Ramadass 2002; Christensen 2004)
  - Physical cycling stress/fracture (Christensen 2006; Sastry 2007)
  - <u>Empirical corrosion & cycling stress model</u> (Smith 2009)

Present work couples the <u>underlined models</u> above.

Multiscale approach for computational efficiency

- Length scales:

  1) Li-transport (1~100 μm)   2) Heat & electron transport (<1~20 cm)

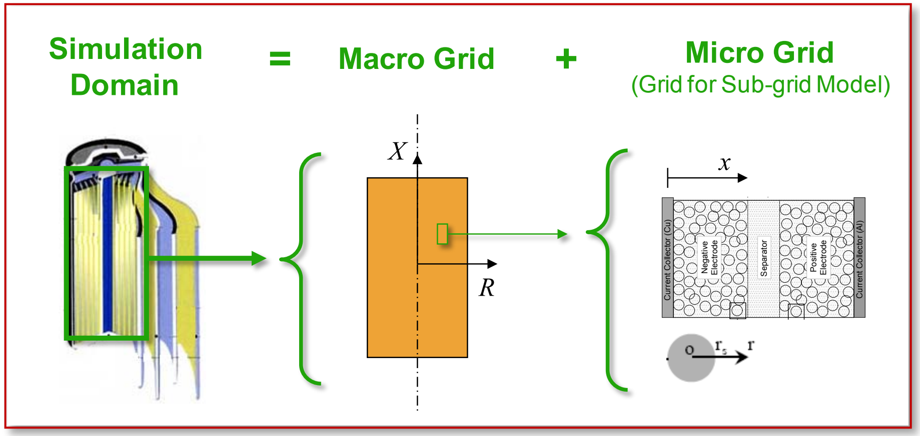


Li Transport & Charge Transfer Kinetics

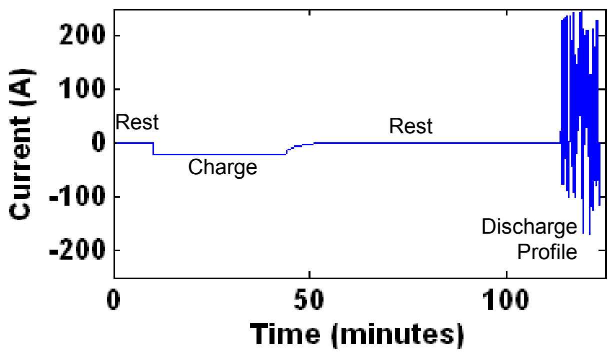
Electron Transport & Heat Transport

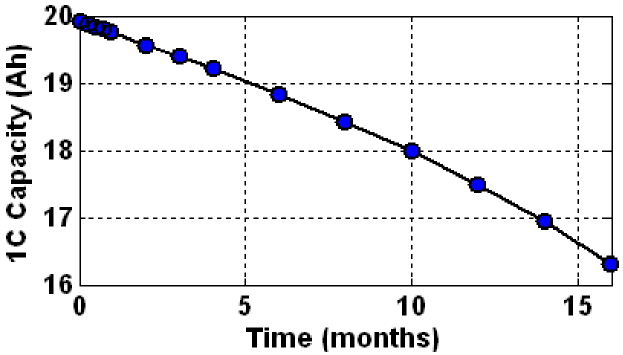
Multiscale approach for computational efficiency

- Length scales:
  1) Li-transport (1~100 μm) 2) Heat & electron transport (<1~20 cm)



- Time scales:
  1) Repeated cycling profile (minutes) 2) Degradation effects (months)*





* Neglects sudden degradation caused by misuse (Li plating, overdischarge/charge, etc.)

Empirical Degradation Model*

* Presented in full :
  - K. Smith, T. Markel, A. Pesaran, FL Battery Seminar, March 2008.

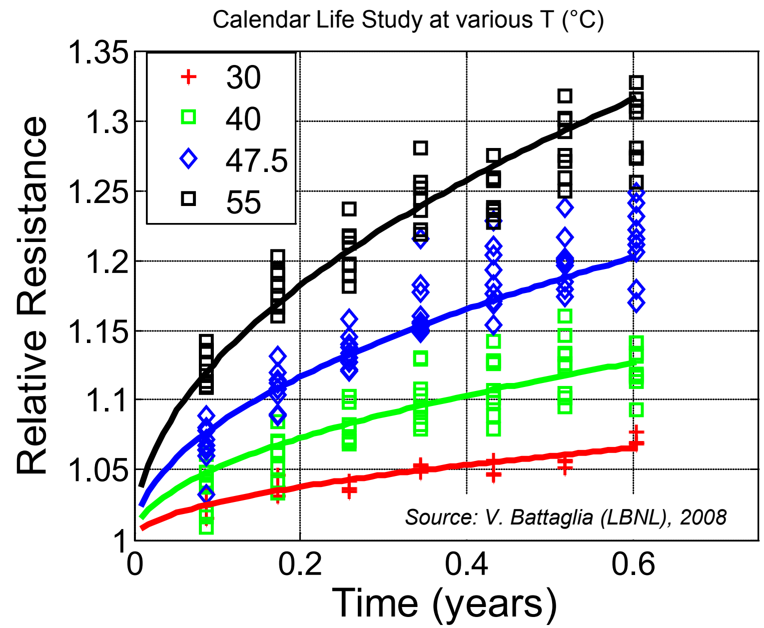
Model fit to Li-ion carbon/NCA cell data from the following :

1. J. Hall, T. Lin, G. Brown, IECEC, 2006.
2. J. Hall, A. Schoen, A. Powers, P. Liu, K. Kirby, 208th ECS Mtg., 2005.
3. DOE Gen 2 Performance Evaluation Final Report (INL/EXT-05-00913), 2006.
4. M. Smart, et al., NASA Aerospace Battery Workshop, 2006.
5. L. Gaillac, EVS-23, 2007.
6. P. Biensan, Y. Borthomieu, NASA Aerospace Battery Workshop, 2007.

Accurate life prediction must consider both storage and cycling degradation effects

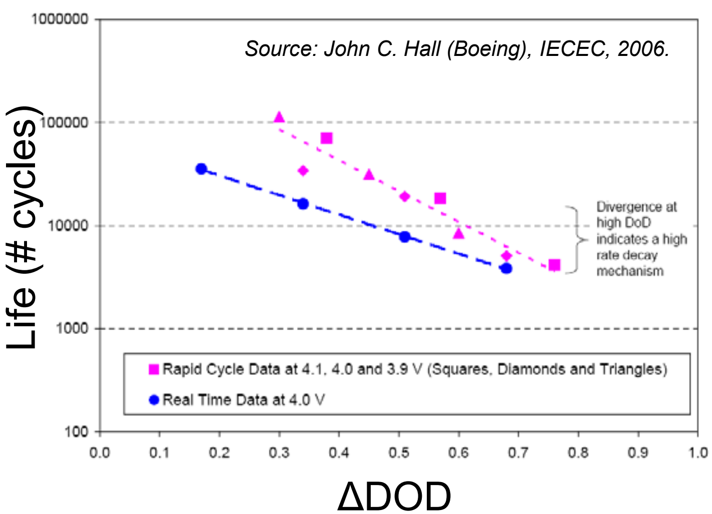
Storage (Calendar) Fade

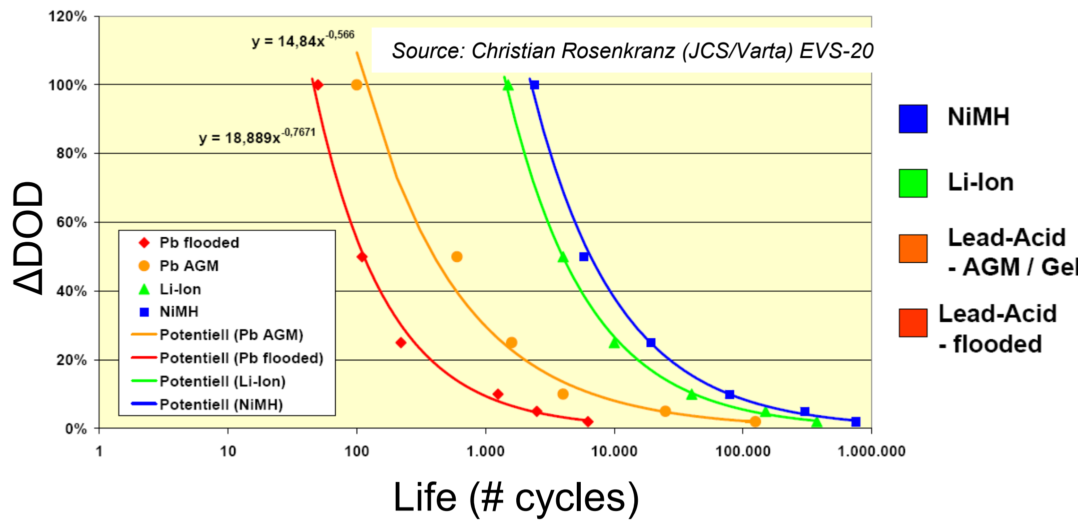
- Typical $t^{1/2}$ time dependency
- Arrhenius relation describes T dependency



Cycling Fade

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





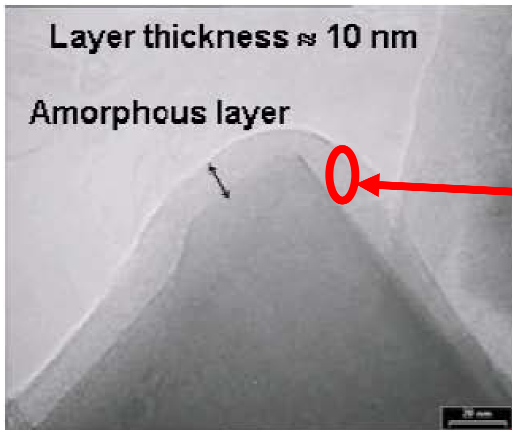
Impedance growth mechanisms: Complex calendar and cycling dependency

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

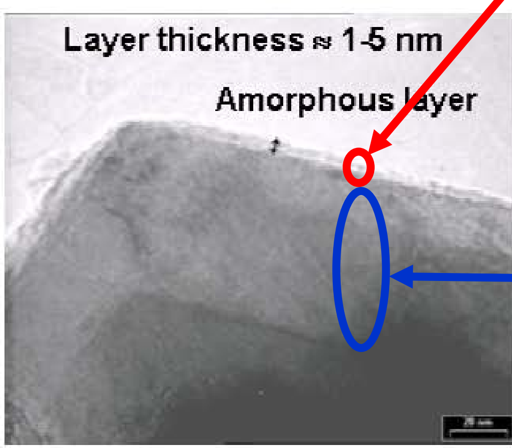
(1) SEI film (2) Solid surface film

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

Cell stored
at 0°C



Cell cycled
1 cycle/day
at 80% DOD



SEI film

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

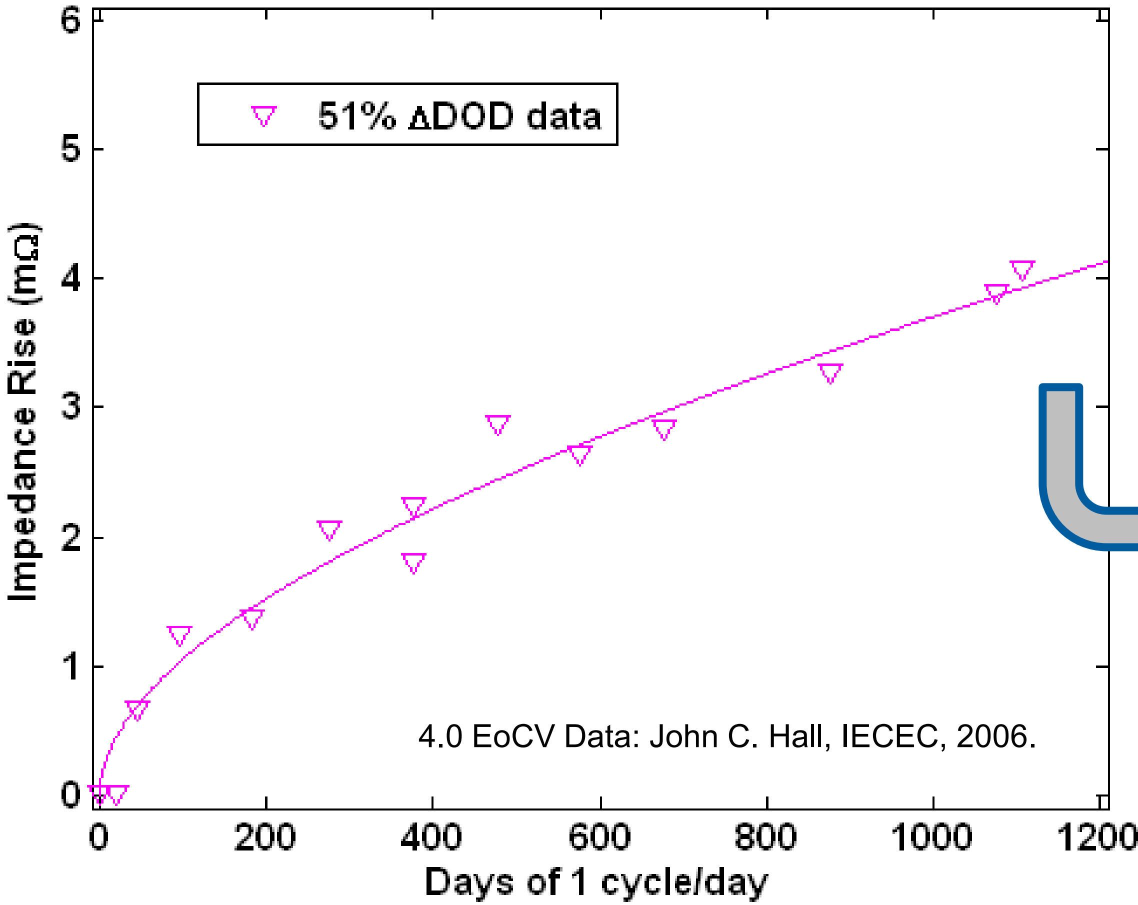
Solid surface film

- 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*)*

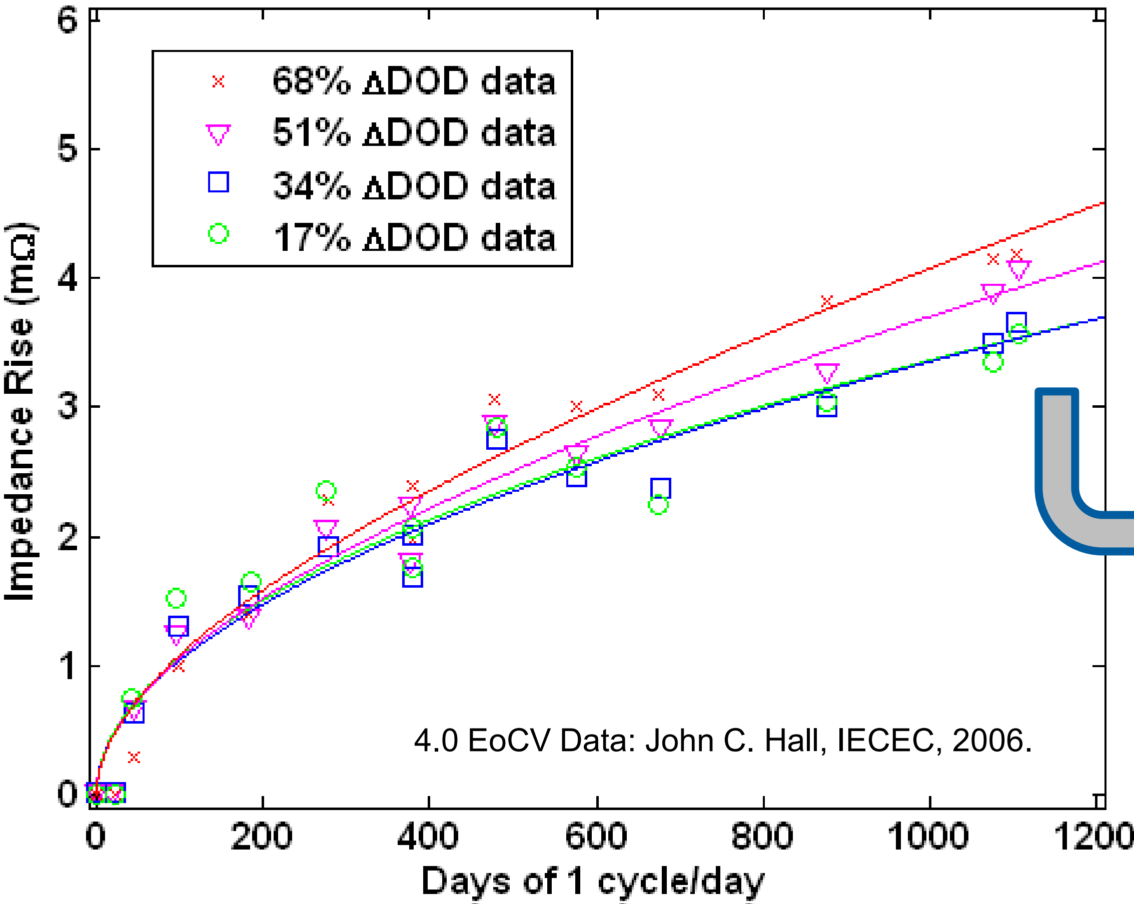
Curve-fit at 51% ΔDOD:

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*)*

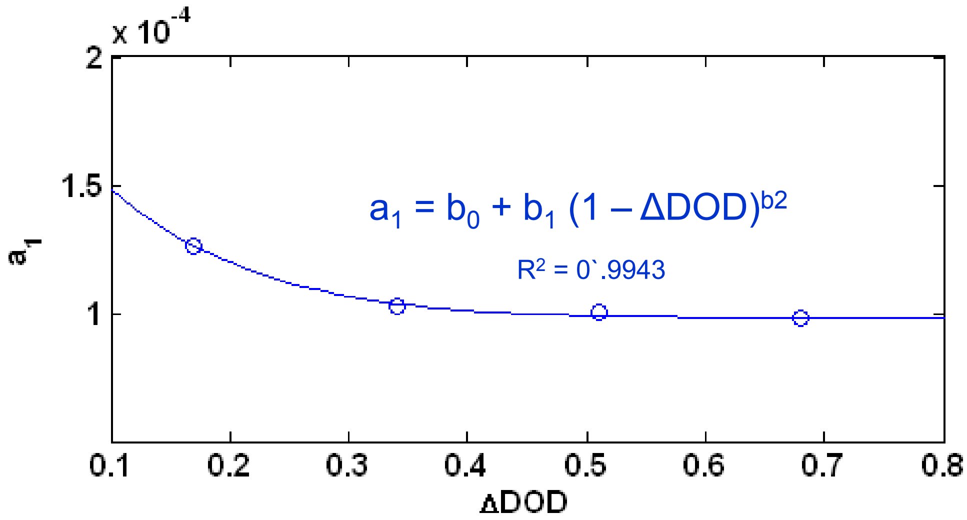
ΔDOD	a_1 (Ω/day$^{1/2}$)	a_2 (Ω/cyc)	R^2
68%	0.98245e-4	9.54812e-7	0.9667
51%	1.00001e-4	5.70972e-7	0.9684
34%	1.02414e-4	0.988878e-7	0.94928
17%	1.26352e-4	-7.53354e-7	0.9174

Impedance (R): Cycling at various ΔDODs

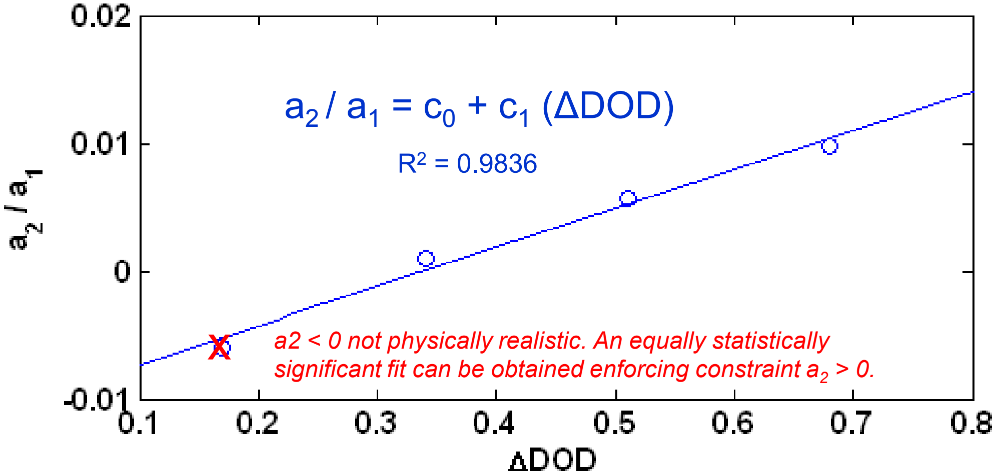
Capturing parameter dependencies on ΔDOD

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

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

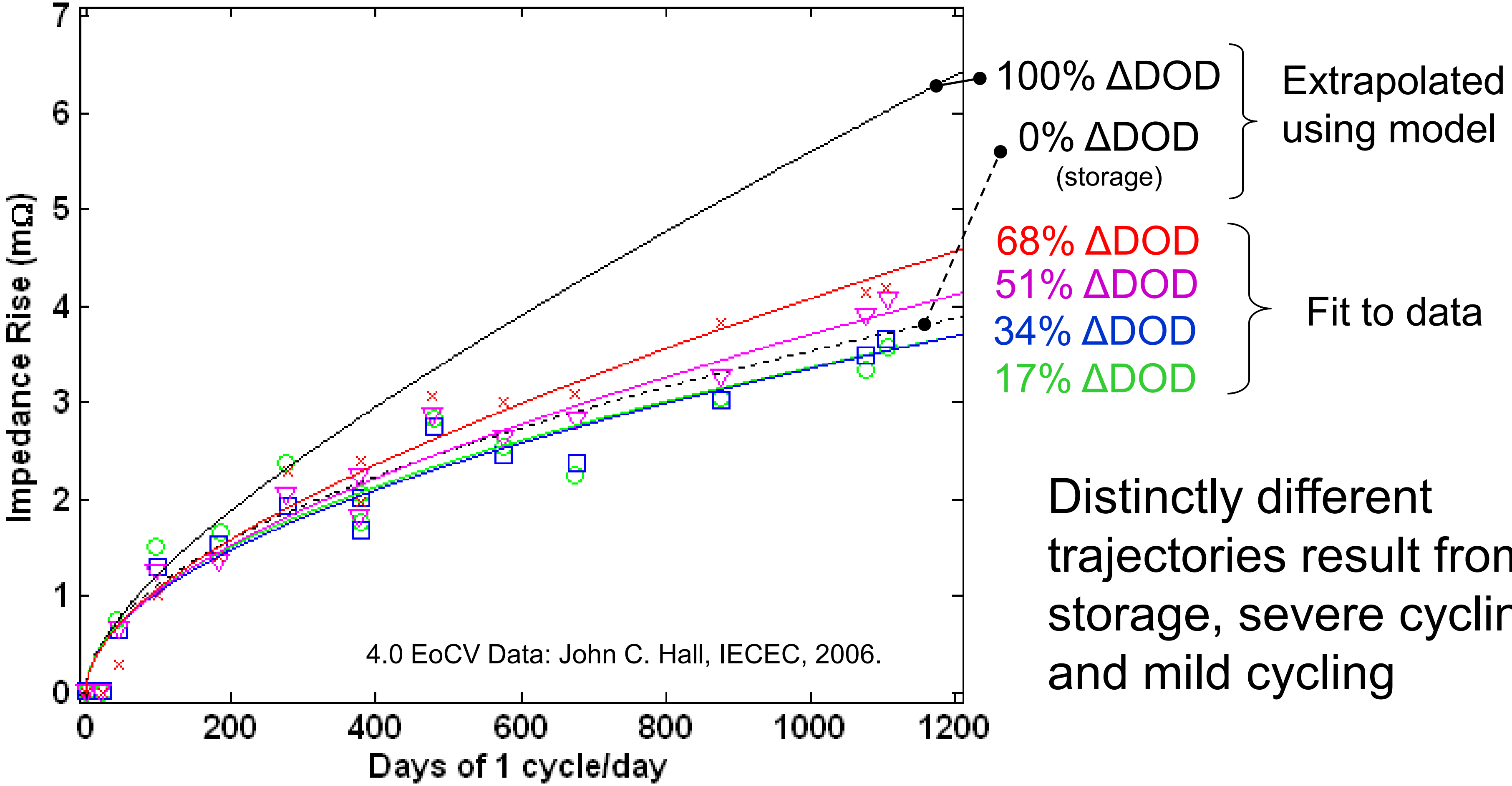
Impedance: Cycling at various ΔDODs

Example model projections

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

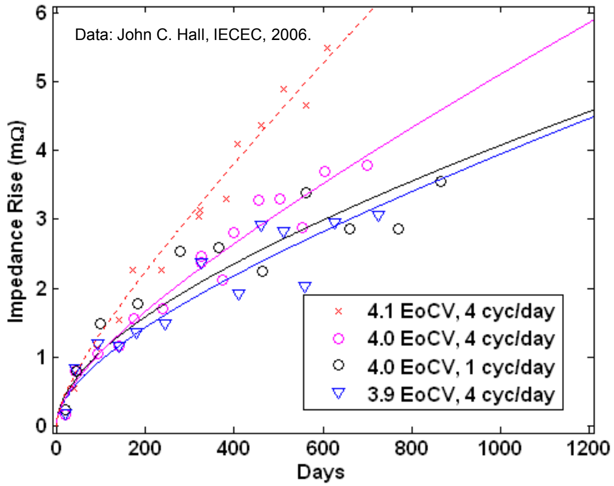
$$a_1 = b_0 + b_1 (1 - \Delta DOD)^{b2}$$

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



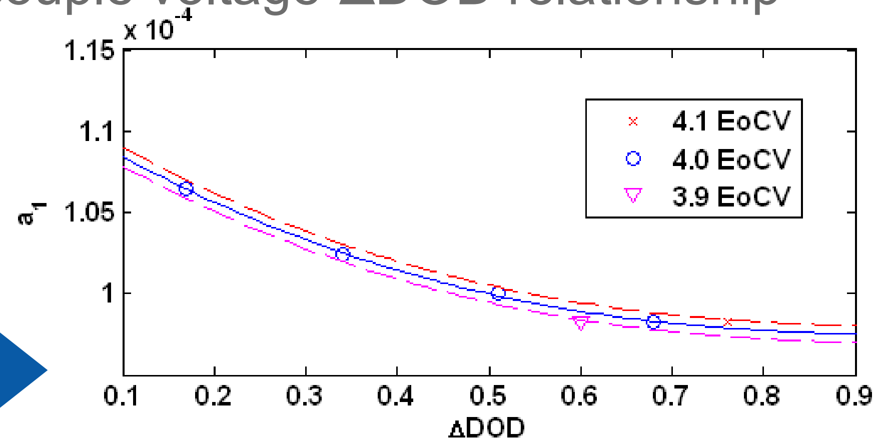
Distinctly different trajectories result from storage, severe cycling and mild cycling

Impedance: Voltage and temperature acceleration

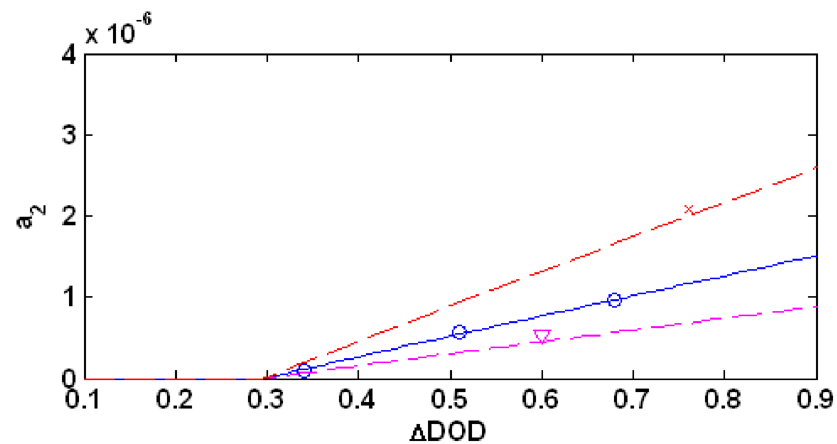


- Increased impedance growth due to elevated voltage & temperature fit using Tafel & Arrhenius-type equations
- Dedicated lab experiments required to fully decouple voltage-ΔDOD relationship

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



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



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

Li-ion (C/NCA) degradation model summary

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)

Dependencies 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

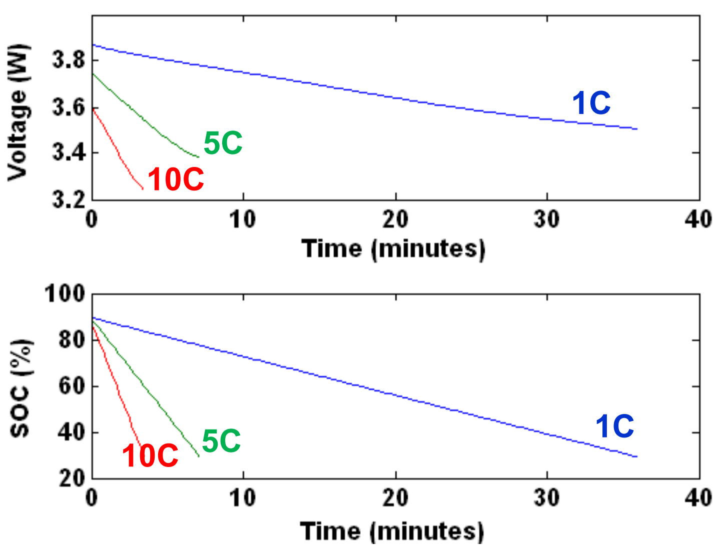
Actual interactions of degradation mechanisms may be more complex.

Modeling Investigation of Nonuniform Degradation

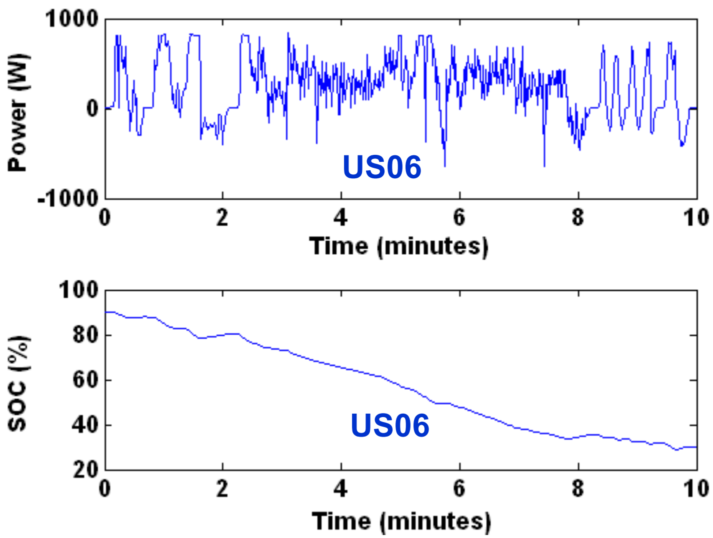
Modeling investigation: Accelerated cycling of 20 Ah PHEV-type cylindrical cell

- Cell Dimensions: 48 mm diameter, 120 mm height
  - Well designed for thermal & cycling uniformity, low capacity fade rate
- Thermal: 30^{o}C ambient, h = 20 W/m^{2}K
- ΔDOD: 90% SOC_{max} to 30% SOC_{min}
- Accel. Cycling: Various *discharge* (shown below), 10 min rest, 1C charge, 60 min rest, repeat.

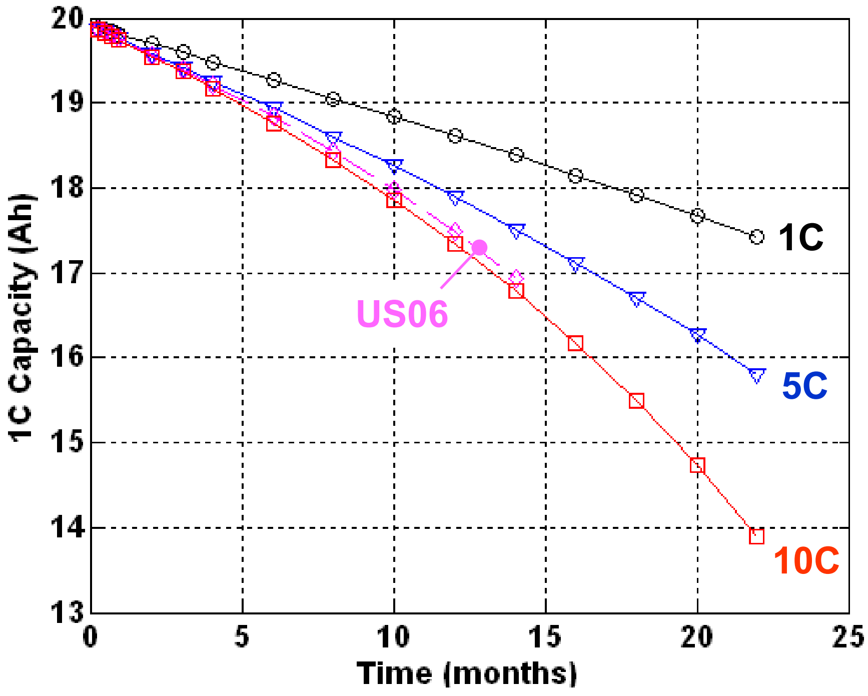
Constant Current Discharge

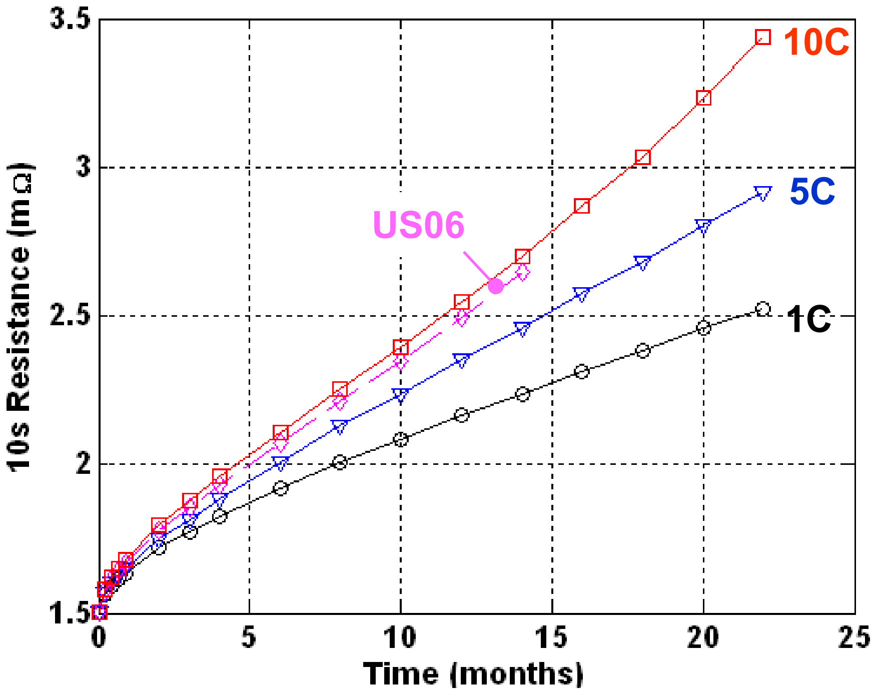


US06 Power Profile Discharge

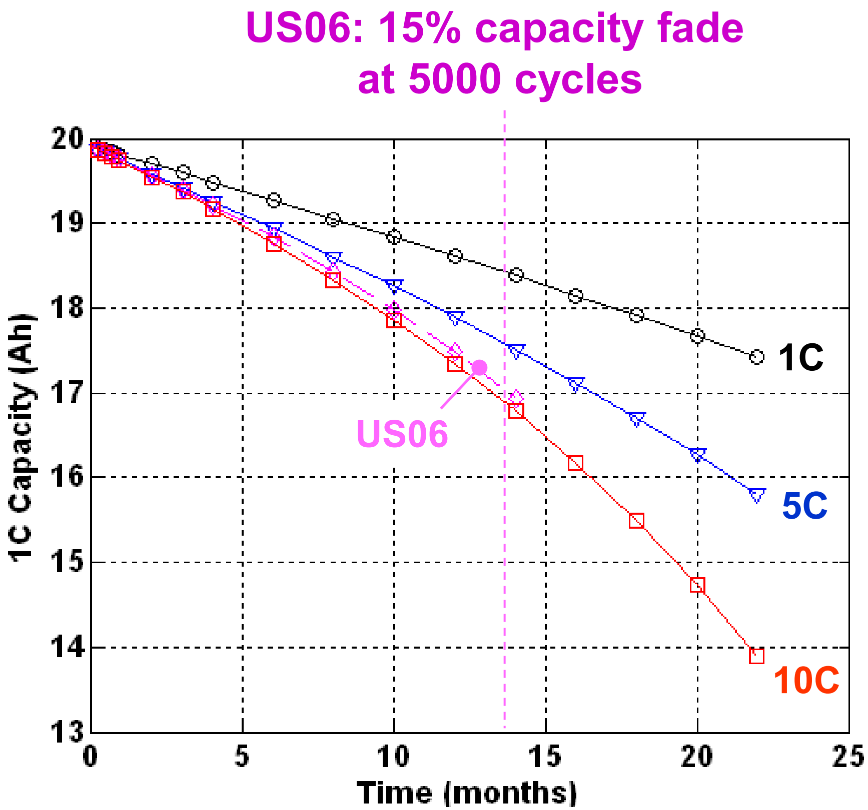


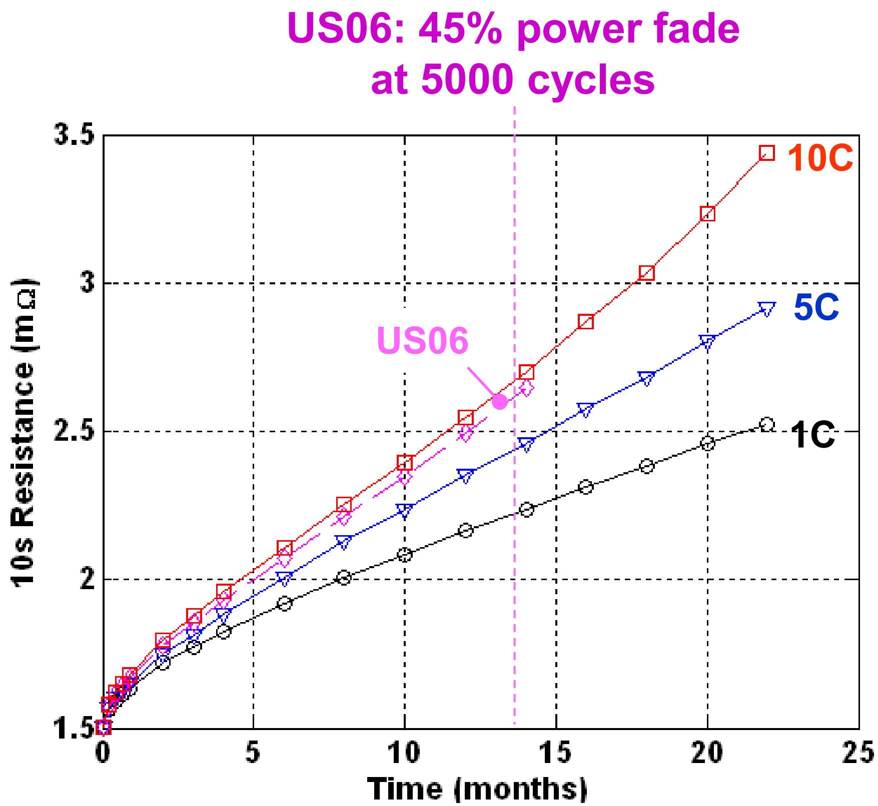
Capacity fade & resistance growth for various repeated discharge profiles (1C, 5C, 10C, US06)





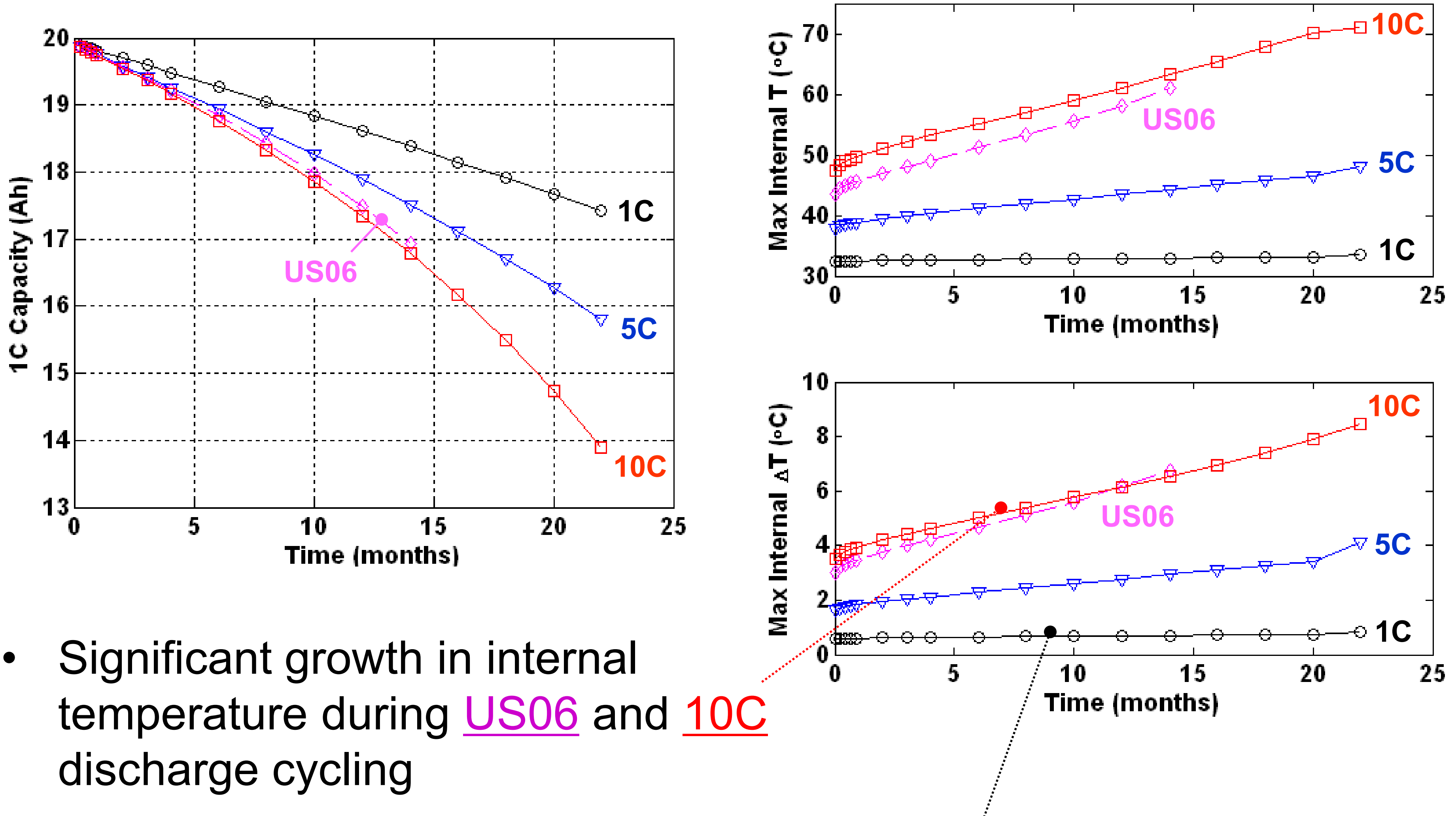
Capacity fade & resistance growth for various repeated discharge profiles (1C, 5C, 10C, US06)





- No accelerating trend observed for low-rate 1C discharge cycles
- Clear accelerating trend observed for high-rate US06 and 10C cases

Temperature rise due to resistance growth accelerates degradation for high-rate US06 & 10C cycling cases

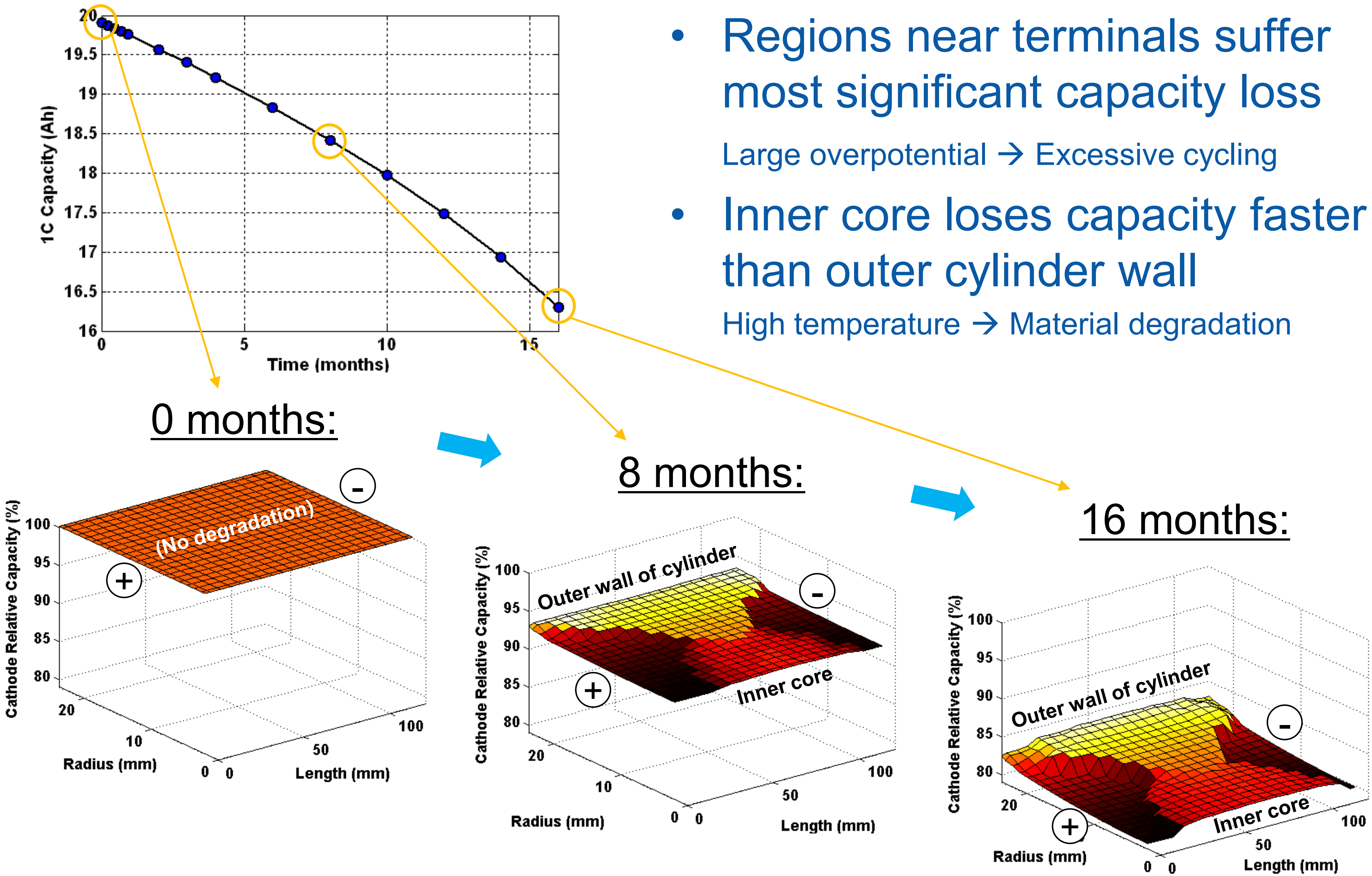


- Significant growth in internal temperature during US06 and 10C discharge cycling

- Internal temperature remains ~constant for 1C discharge cycling

US06 – Nonuniform capacity loss

- Regions near terminals suffer most significant capacity loss
  Large overpotential → Excessive cycling
- Inner core loses capacity faster than outer cylinder wall
  High temperature → Material degradation

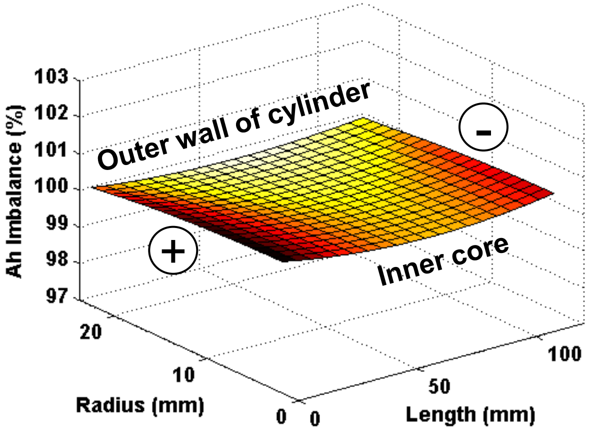


US06 – Ah imbalance (nonuniform cycling)

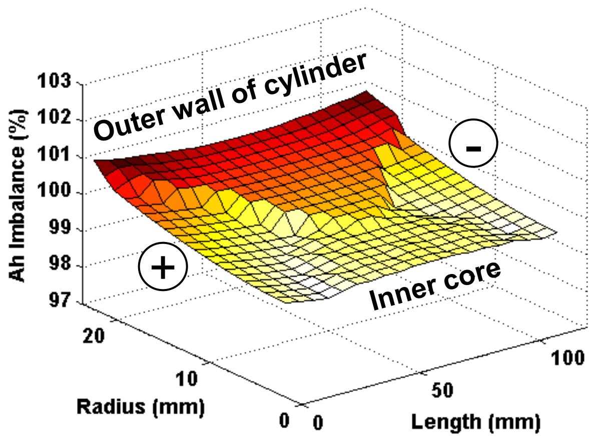
Preferentially cycled regions shift early in life

Imbalance continually grows throughout life

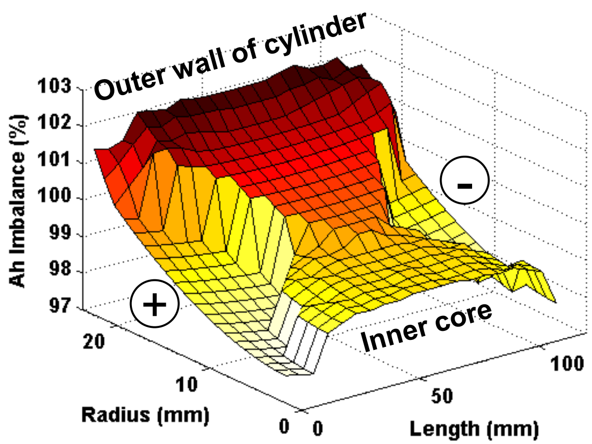
<u>0 months:</u>
0.7% Ah Imbalance



<u>8 months:</u>
1.7% Ah Imbalance



<u>16 months:</u>
4.8% Ah Imbalance



- Early in life, inner core and terminal areas are cycled the most
- Later in life, those same areas are most degraded and are cycled least

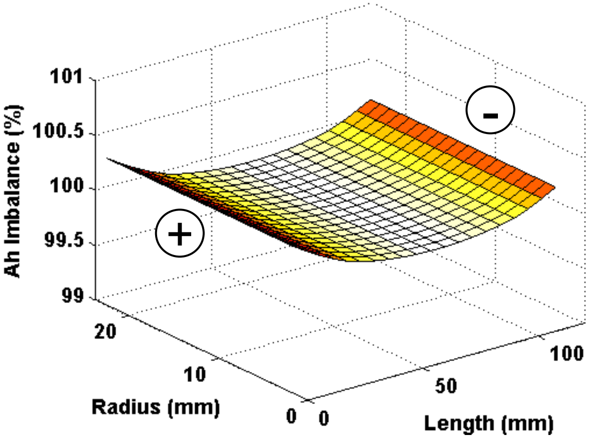
US06 Ah imbalance: Effect of uniform temperature

Multidimensional model rerun with temperature fixed to a spatially averaged value taken from nonuniform temperature simulations (previous slide)

<u>0 months:</u>

0.4% Ah Imbalance

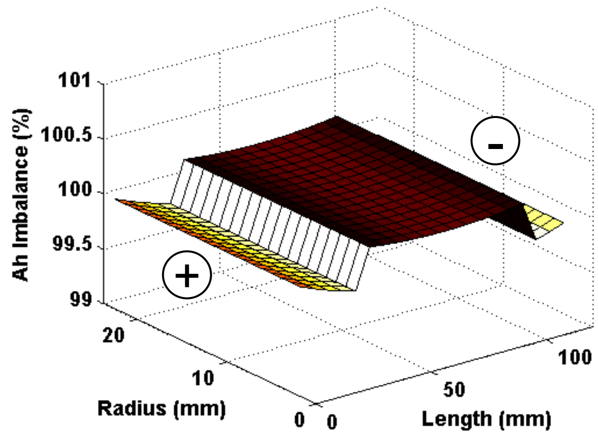
(vs. 0.7% for nonuniform T)



<u>8 months:</u>

0.4% Ah Imbalance

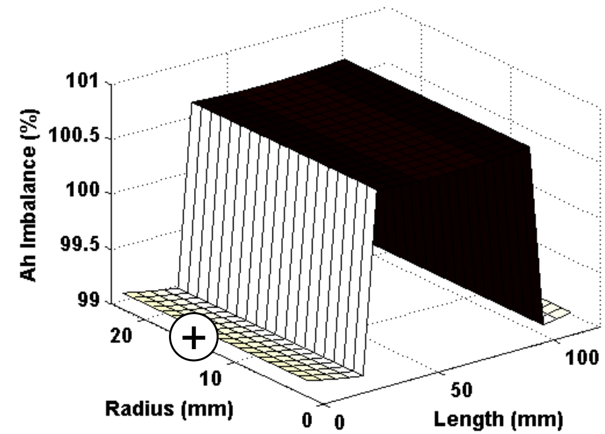
(vs. 1.7% for nonuniform T)



<u>16 months:</u>

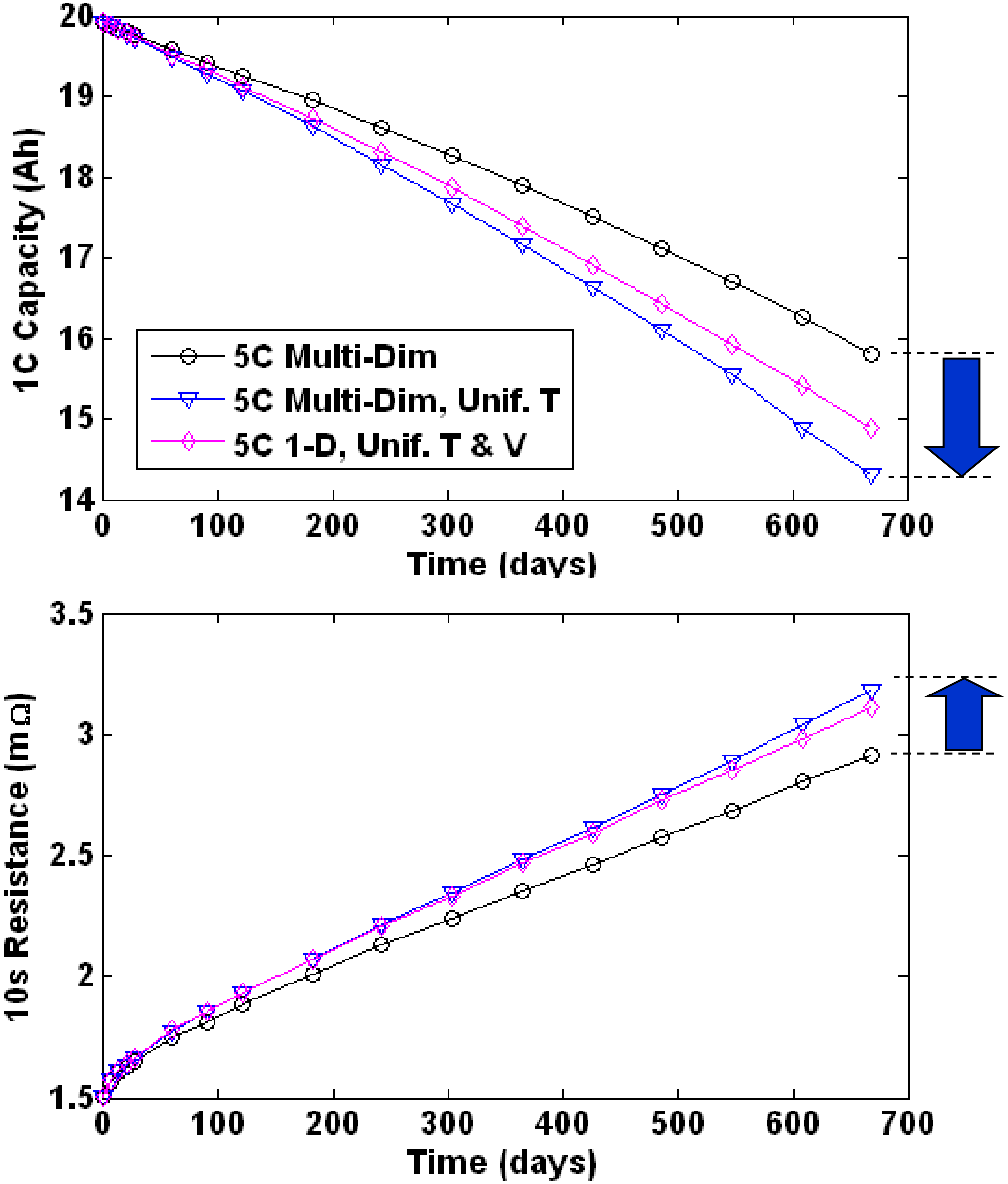
1.7% Ah Imbalance

(vs. 4.8% for nonuniform T)



- More clearly shows how degradation proceeds from terminals inward
- Compared with nonuniform temperature simulations …
  - Significantly reduces Ah imbalance (this slide)
  - But measured cell-level impedance and capacity will fade faster (next slide)

Nonuniform degradation effects important for predicting cell performance fade



- Lumped temperature model overpredicts cell level fade

  (1-D echem/thermal model also overpredicts fade)

- Illustrates strong coupling between multidimensional degradation and cell performance

Conclusions

For 20 Ah cylindrical cell with good thermal & cycling uniformity at beginning of life...

- Imbalance grows throughout life (T, Ah throughput, capacity loss)
- Acceleration mechanism apparent for high-rate cycling cases:
  - Higher impedance → Higher temperature → Faster degradation
- Major factors leading to nonuniform degradation
  - Nonuniform temperature (degrades inner core)
  - Nonuniform potential (degrades terminal regions)
- Regions heavily used at beginning of life (inner core, terminal regions) are used less and less as life proceeds
- 1-D echem/lumped thermal model not suited to predict performance degradation for large cells
  - For a given electrode-level degradation mechanism, overpredicts cell-level capacity fade and impedance growth