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

Kandler Smith • Kandler.Smith@nrel.gov, Gi-Heon Kim • Gi-Heon.Kim@nrel.gov, Ahmad Pesaran • Ahmad.Pesaran@nrel.gov – National Renewable Energy Laboratory

Abstract

An empirical degradation model, capturing the effects of both storage and cycling, was developed for the Li-ion Nickel-Cobalt-Aluminum chemistry[3]. The degradation model is coupled with NREL's multi-dimensional multi-scale (MSMD) cell model to explore the impacts of nonuniform cycling and temperature inside a cylindrical 20 Ah PHEV cell over the course of an accelerated cycle-life test. Results show significant differences compared to a lumped analysis that neglects the cell's real geometry.

Background and Approach

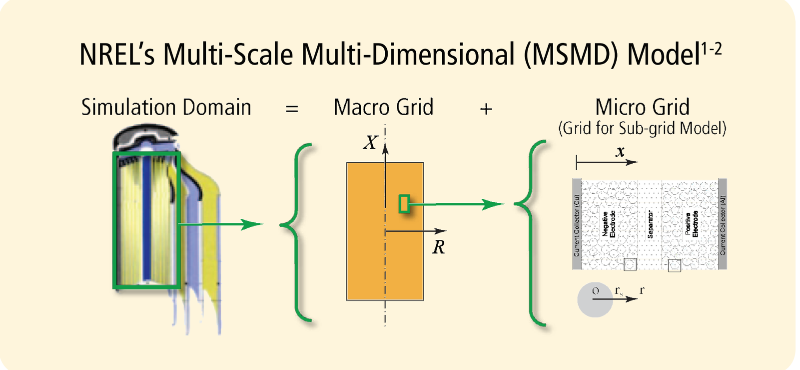
Background

- Context: Trend towards larger cells
  - 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 realistic geometry and physics
  - Reduce make-and-break iterations, accelerate design cycle

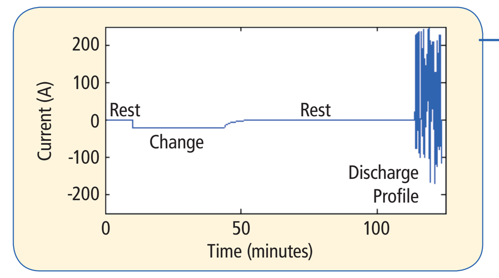
Multiscale approach for computational efficiency

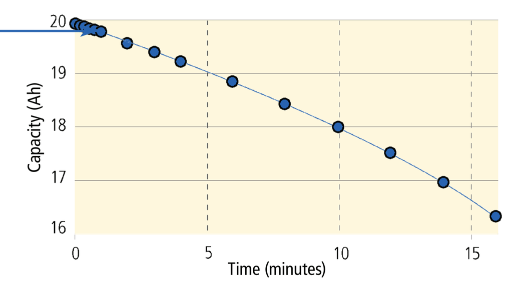
- Length scales:
  1. Li-transport (1~100 μm)
  2. Heat & electron transport (<1~20 cm)

NREL's Multi-Scale Multi-Dimensional (MSMD) Model[1,2]



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

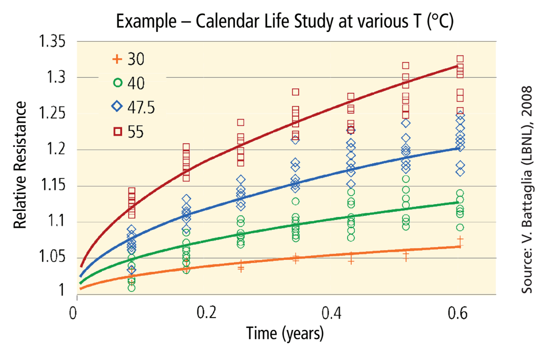


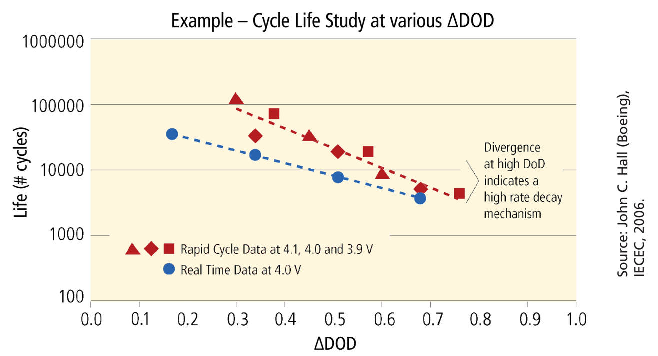


* Neglects sudden degradation caused by misuse (Li plating, over-discharge/charge, etc.)

Empirical degradation model considers both storage and cycling 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





Degradation Model[3]

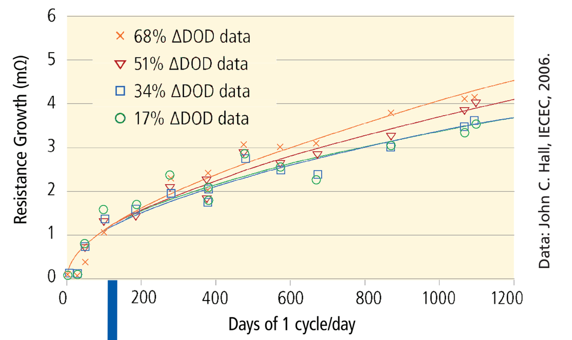
Empirical model fit to test data for the Li-ion NCA chemistry[4-9]

ΔDOD Effect

- Model includes $t^{1/2}$ (~storage) and N (~cycling) dependencies
- a_1 (~storage) and a_2 (~cycling) coefficients vary with ΔDOD

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

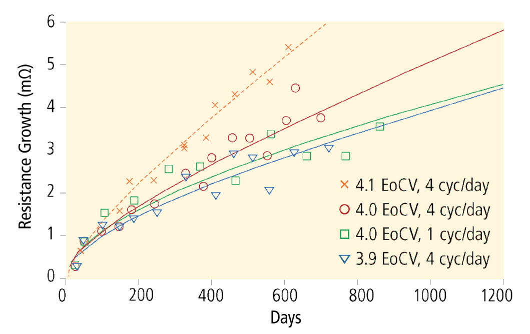
(Note: For 1 cycle/day, N = t)

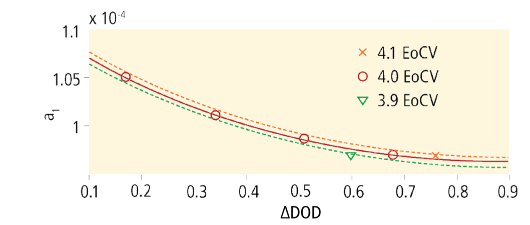


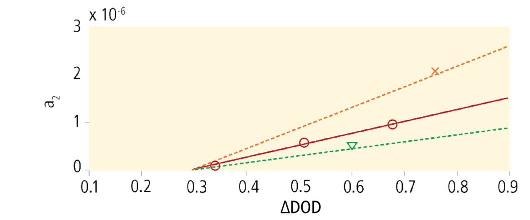
ΔDOD	a_1 (Ω/day$^{1/2}$)	a_2 (Ω/cyc)	R^2
× 68%	0.98245e-4	9.54812e-7	0.9667
▽ 51%	1.00001e-4	5.70972e-7	0.9684
□ 34%	1.02414e-4	0.988878e-7	0.94928
○ 17%	1.26352e-4	-7.53354e-7	0.9174

Voltage and temperature acceleration

- Increased degradation due to elevated voltage and temperature described using Tafel and Arrhenius equations







Li-ion (C/NCA) degradation model summary

Impedance Growth Model

- Temperature
$$k_1 = k_{1,ref} \exp(-E_{a1} \times (T^{-1} - T_{ref}^{-1})/R)$$
$$k_2 = k_{2,ref} \exp(-E_{a2} \times (T^{-1} - T_{ref}^{-1})/R)$$
- Voltage
$$a_1 = a_{1,ref}\, k_1 \exp(\alpha_1 F/RT \times V)$$
$$a_2 = a_{2,ref}\, k_2 \exp(\alpha_2 F/RT \times V)$$
$$a_{2,t} = a_2 (1 - \alpha_N)$$
$$a_{2,N} = a_2\, \alpha_N$$
- ΔDOD
$$a_1 = b_0 + b_1 (1 - \Delta DOD)^{b2}$$
$$a_2 / a_1 = \max[0, c_0 + c_1 (\Delta DOD)]$$
- Calendar Storage ($t^{1/2}$ term)
- Cycling (t & N terms)

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

Capacity Fade Model

- Temperature
- Voltage
- ΔDOD

Dependencies from impedance growth model

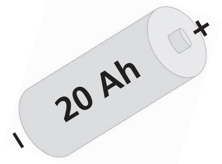
- Calendar Storage (Li loss)
$$Q_{Li} = d_0 + d_1 \times (a_1 t^{1/2})$$
- Cycling (Site loss)
$$Q_{sites} = e_0 + e_1 \times (a_{2,t}\, t + a_{2,N}\, N)$$

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

Results

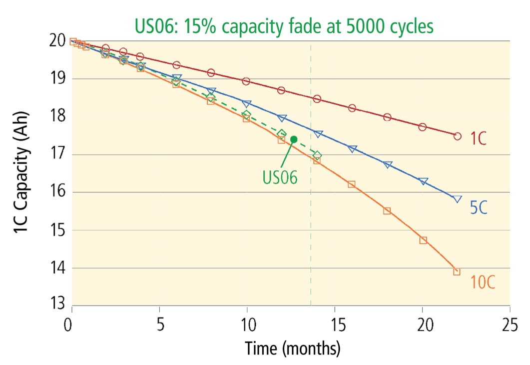
Modeling investigation: Accelerated cycling of 20 Ah PHEV-type cylindrical cell

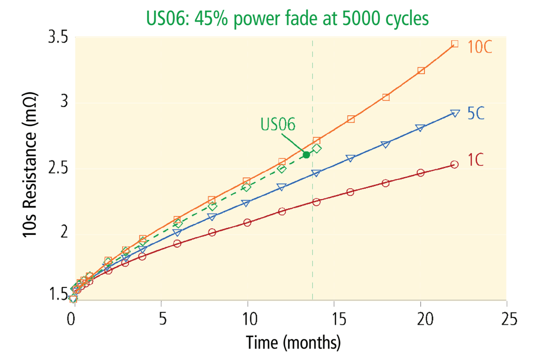
- Cell Dimensions: 48 mm diameter, 120 mm height
  - Well designed for thermal & cycling uniformity, low capacity fade rate
- Thermal: 30°C ambient, h = 20 W/m²K
- ΔDOD: 90% SOC_{max} to 30% SOC_{min}
- Accel. Cycling: Various *discharge* (shown below), 10 min rest, 1C charge, 60 min rest, repeat.



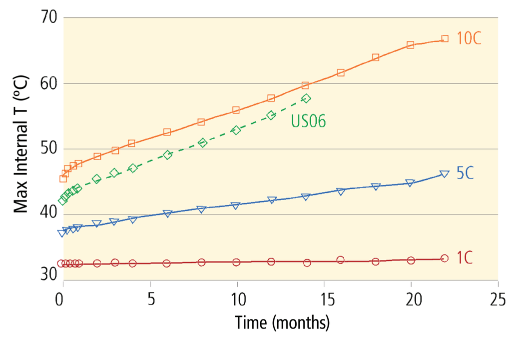
Capacity fade & resistance growth for various repeated discharge profiles (1C, 5C, 10C, US06)

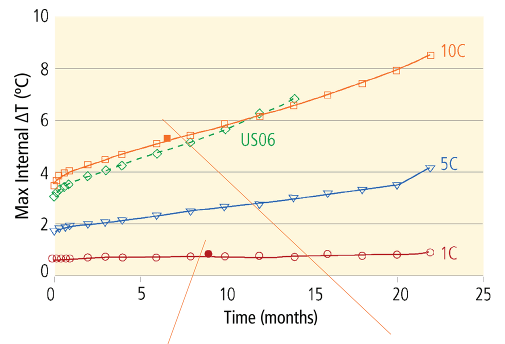
Temperature rise accelerates degradation





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

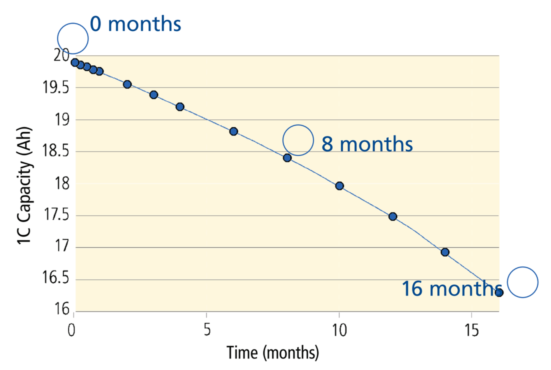




- Significant growth in internal temperature during US06 and 10C discharge cycling
- Internal temperature remains ~constant for 1C discharge cycling

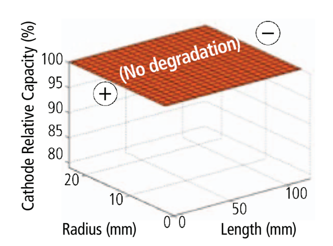
US06 – Nonuniform degradation

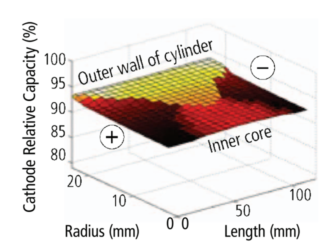
Relative Capacity

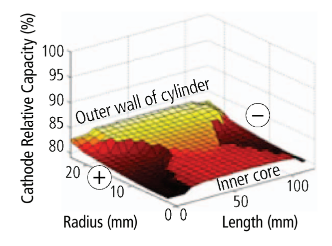


- Regions near terminals suffer most significant capacity loss
  Large overpotential ⟶ Excessive cycling
- Inner core loses capacity faster than outer cylinder wall
  High temperature ⟶ Material degradation

0 months: ⟶ 8 months: ⟶ 16 months:



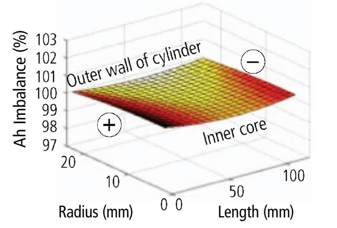


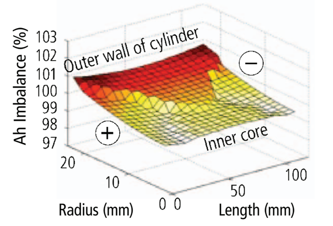


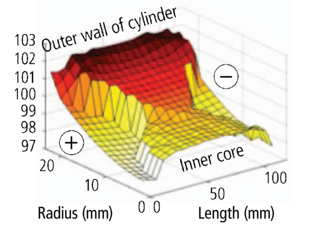
Ah Imbalance

- 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
- Imbalance continually grows throughout life

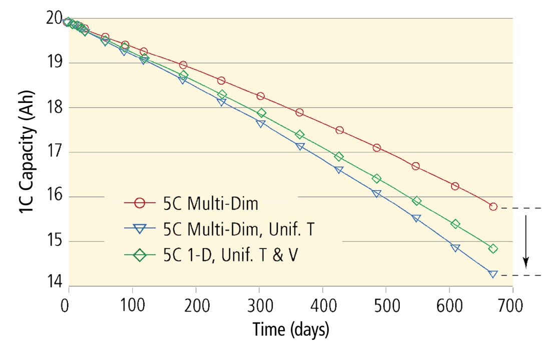
0 months: 0.7% Ah Imbalance ⟶ 8 months: 1.7% Ah Imbalance ⟶ 16 months: 4.8% Ah Imbalance

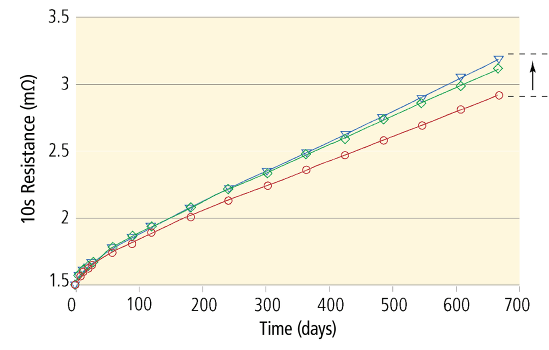






Nonuniform degradation effects important for predicting cell performance fade





- 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

Acknowledgements

- U.S. Department of Energy, Office of Vehicle Technologies
  - Dave Howell, Energy Storage Program

FreedomCAR & Fuel Partnership

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