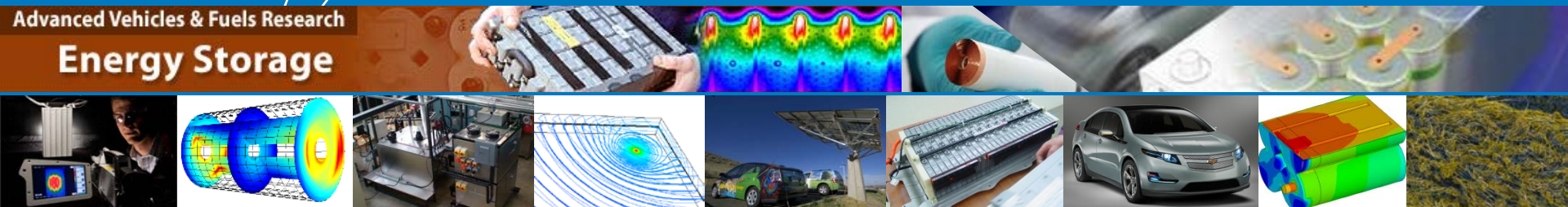


# Life Prediction Model for Grid-Connected Li-ion Battery Energy Storage System

Advanced Vehicles & Fuels Research  
**Energy Storage**



**Kandler Smith\*, Aron Saxon, Matthew Keyser, Blake Lundstrom**  
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**American Control Conference**  
**Seattle, WA May 23-26, 2017**

# Applications of Energy Storage (ES) on the Grid

*Focus of present ES system life study*

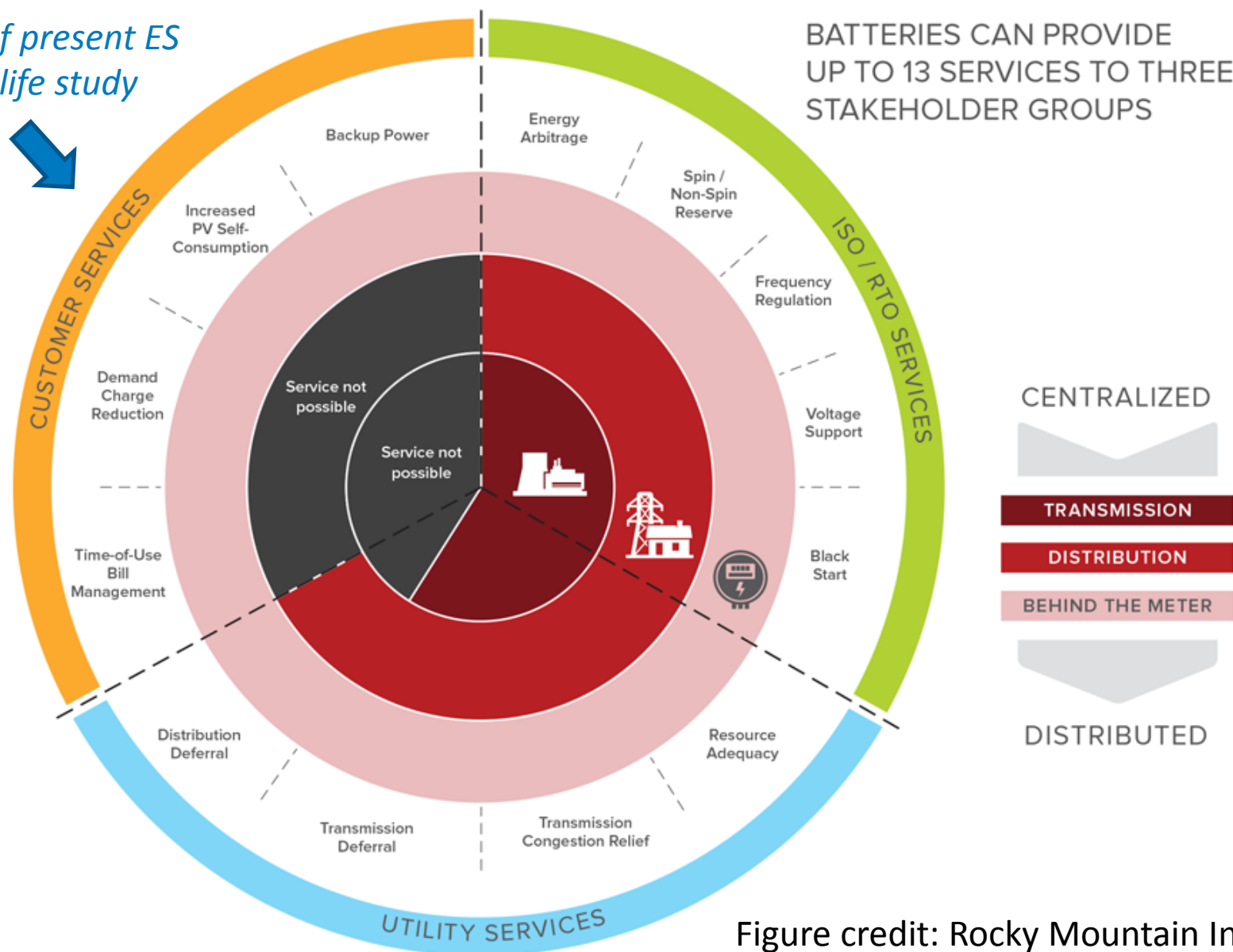


Figure credit: Rocky Mountain Institute

# Example Application: Behind-the-meter ES enables PV use in locations such as Hawaii (where power export is prohibited)

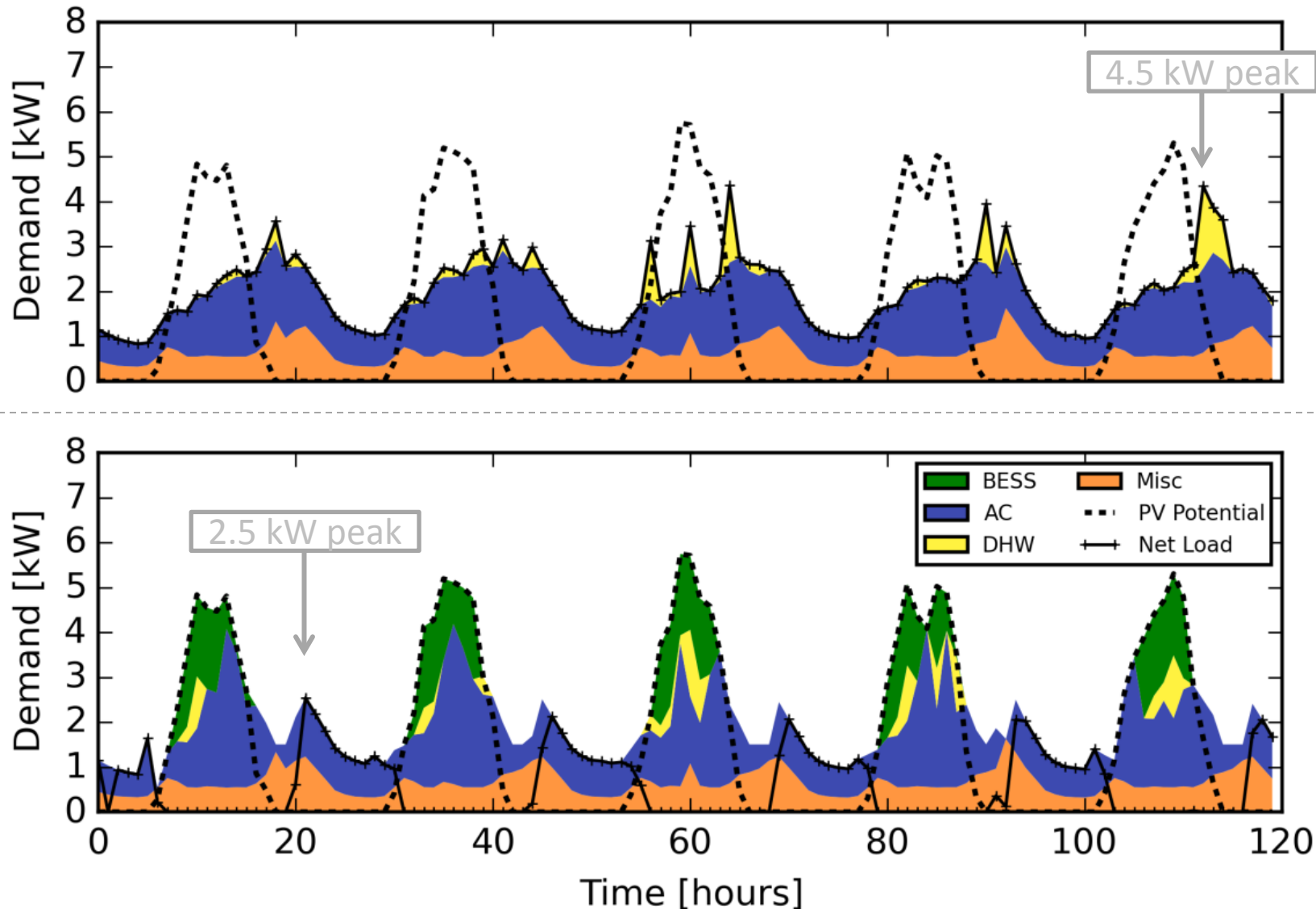


Figure: "Solar Plus: An Holistic Approach to Distributed Solar PV" Eric O'Shaughnessy, Kristen Ardani, Dylan Cutler, Robert Margolis (NREL Pub #68371)

# Outline

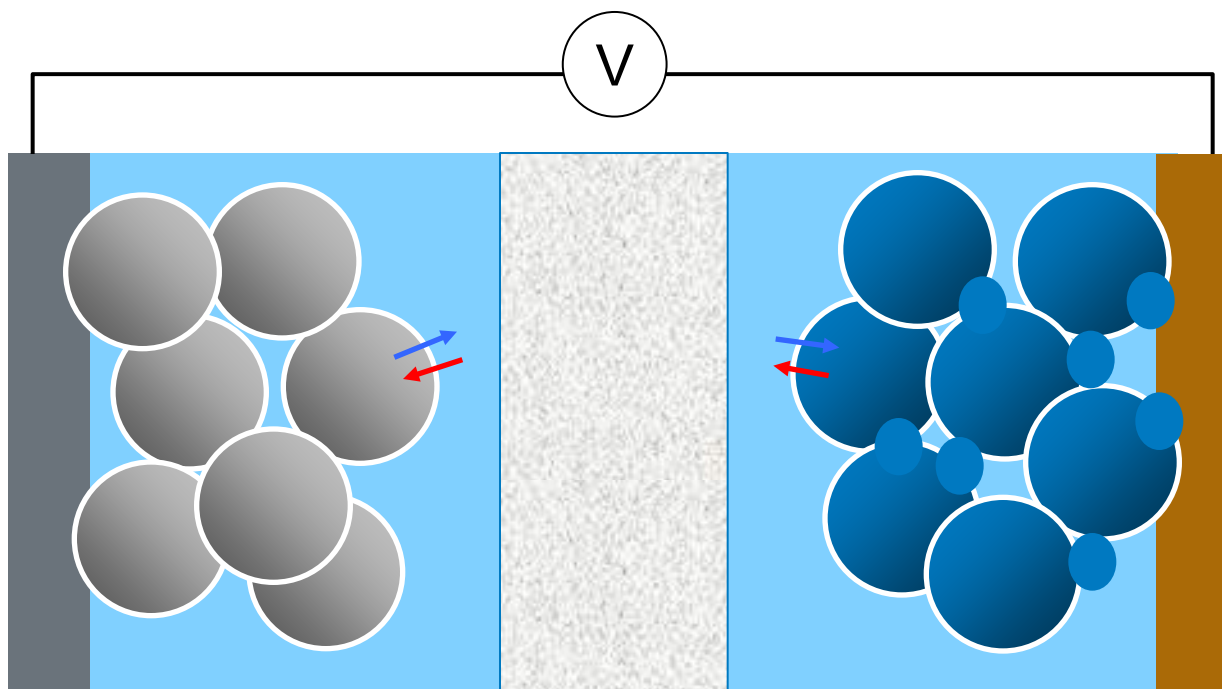
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- **Degradation mechanisms**
- **Modeling approach**
- **Aging tests**
- **Model and parameter identification**
- **Example life prediction**

# Li-ion Working Principles

## Neg. Electrode

Graphite  
Hard carbon  
Silicon  
Titanate  
Li metal



## Pos. Electrode

$\text{LiXO}_2$ ,  
X = NiMnCo  
Co  
NiCoAl  
 $\text{LiMn}_2\text{O}_4$ ,  
 $\text{LiFePO}_4$

Figure credit: Gi-Heon Kim

# Electrochemical Operating Window

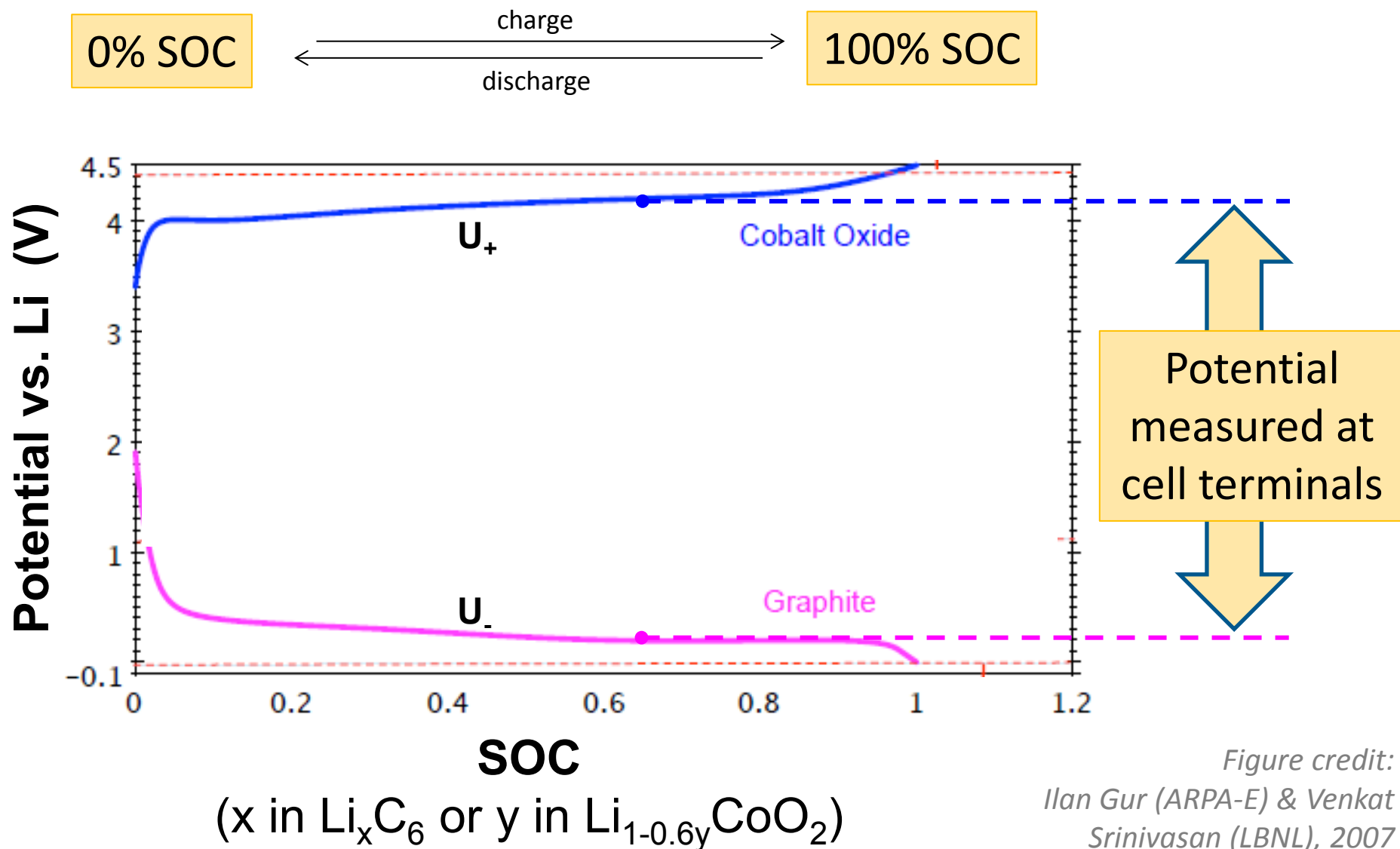
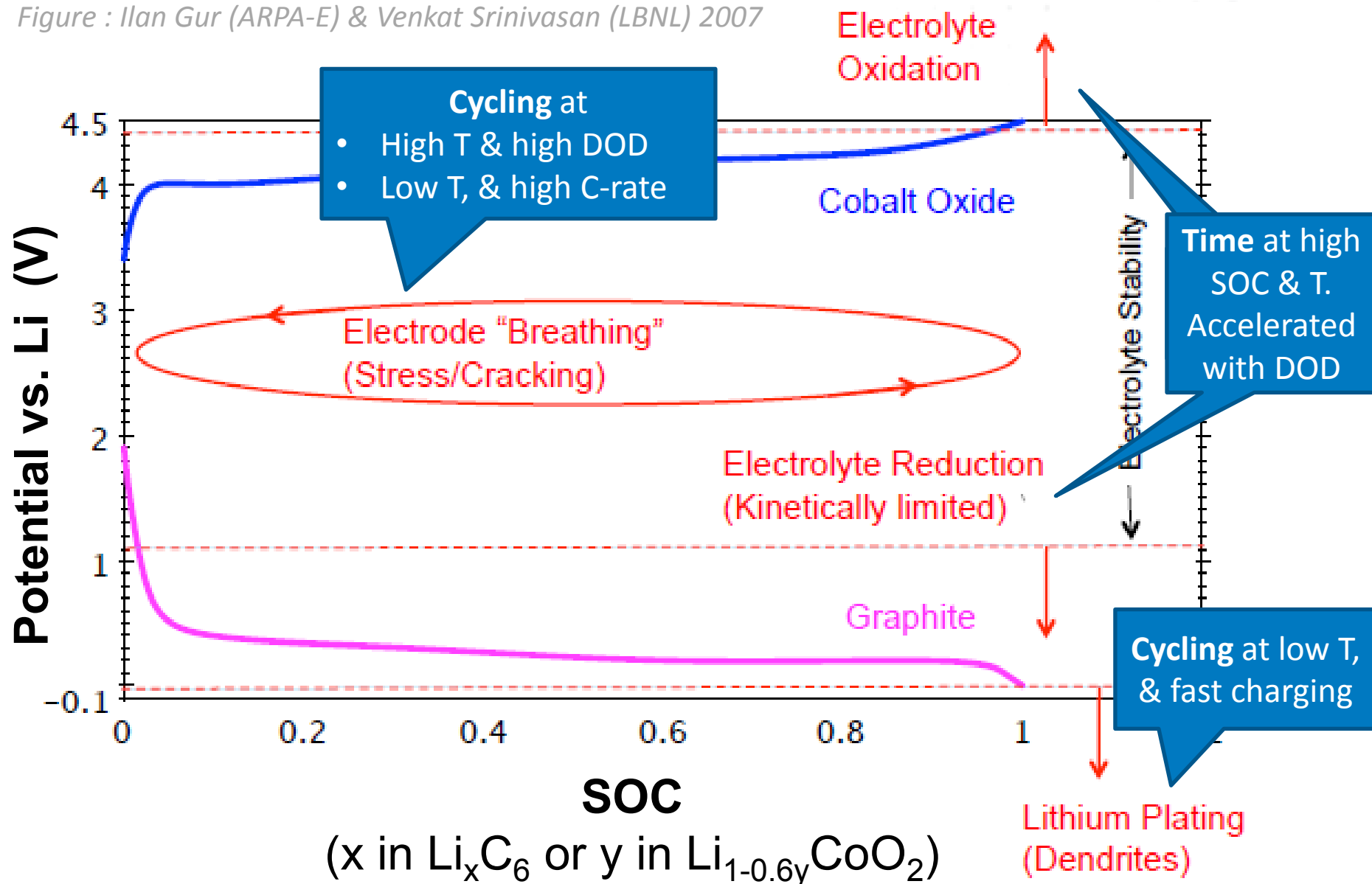


Figure credit:  
Ilan Gur (ARPA-E) & Venkat  
Srinivasan (LBNL), 2007

# Electrochemical Window – Degradation

Figure : Ilan Gur (ARPA-E) & Venkat Srinivasan (LBNL) 2007

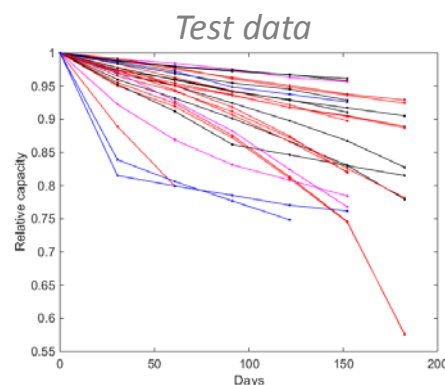
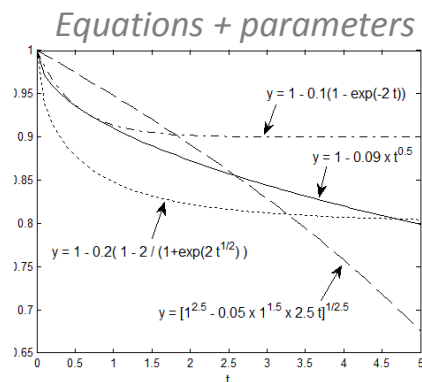


# NREL Battery Life Predictive Model Framework

## Reduced-order models for physical fade mechanisms, e.g.

- SEI growth & damage
- Particle fracture
- Electrode isolation
- Electrolyte decomposition
- Gas generation, delamination
- Li plating

## Semi-automated software aids model equation selection and parameter identification



Mechanism	Trajectory equation	State equation	Parameters
Diffusion-controlled reaction	$x(t) = kt^{1/2}$	$\dot{x}(t) = \frac{k}{2} \left( \frac{k}{x(t)} \right)$	$k$ - rate ( $p=1/2$ )
Kinetic-controlled reaction	$x(t) = kt$	$\dot{x}(t) = k$	$k$ - rate ( $p=1$ )
Mixed diffusion/kinetic	$x(t) = kt^p$	$\dot{x}(t) = kp \left( \frac{k}{x(t)} \right)^{\frac{1-p}{p}}$	$k$ - rate $p$ - order, $0.3 < p < 1$
Diffusion controlled reaction with mechanical damage	See Appendix A	$\dot{D} = \frac{dN}{dt} k_D \cdot (\sqrt{D})^p$ $\dot{x}_0(t) = \frac{k}{2} \left( \frac{k}{x(t)} \right)$ $\dot{x}_j(t) = D \frac{k}{2} \left( \frac{k}{x(t)} \right)$	$k$ - rate $p$ - order
Cyclic fade-linear	$x(N) = kN$	$\dot{x}(N) = k$	$k$ - rate ( $p=0$ )
Cyclic fade-accelerating	$x(N) = [x_0^{1+p} + kx_0^p(1+p)N]^{\frac{1}{1+p}}$	$\dot{x}(N) = k \left( \frac{x_0}{x(N)} \right)^p$	$k$ - rate $p$ - order, $0 \leq p > 3$
Break-in process	$x(t) = M(1 - \exp(-kt))$ or $x(N) = \dots$	$\dot{x}(t) = k(M - x(t))$	$M$ - maximum fade $k$ - rate
Sigmoidal reaction	$x(t) = M \left[ 1 - \frac{2}{1 + \exp(kt^p)} \right]$ or $x(N) = \dots$	$\dot{x}(t) = \frac{2MkpX(t)\exp(kX(t))}{[1 + \exp(kX(t))]^2}$ $X(t) = \left\{ \frac{1}{k} \ln \left( \frac{2}{1 - x(t)/M} - 1 \right) \right\}^{\frac{1}{p}}$	$M$ - maximum fade $k$ - rate $p$ - order

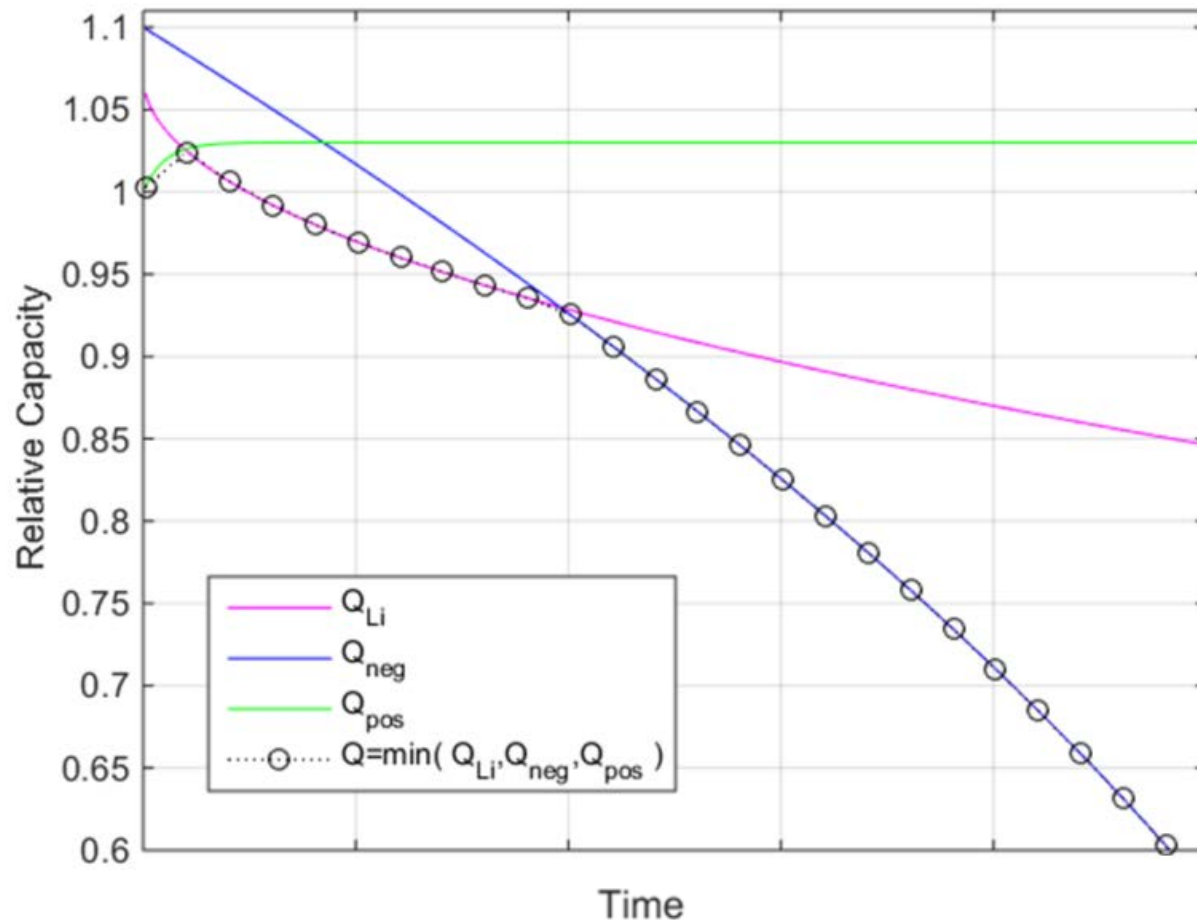
$x, D$ : state variables  
 $k, k_D$ : fade rates  
 $p$ : order  
 $M$ : maximum extent of fade

S. Santhanagopalan, K. Smith, J. Neubauer, G.-H. Kim, A. Pesaran, M. Keyser, Design and Analysis of Large Lithium-Ion Battery Systems, Artech House, 2015.



# Model assumes measured capacity is minimum of:

1. Cycleable lithium,  $Q_{Li}$
2. Negative electrode sites,  $Q_{neg}$
3. Positive electrode sites,  $Q_{pos}$



# Aging tests – Kokam 75Ah Gr/NMC Li-ion cells

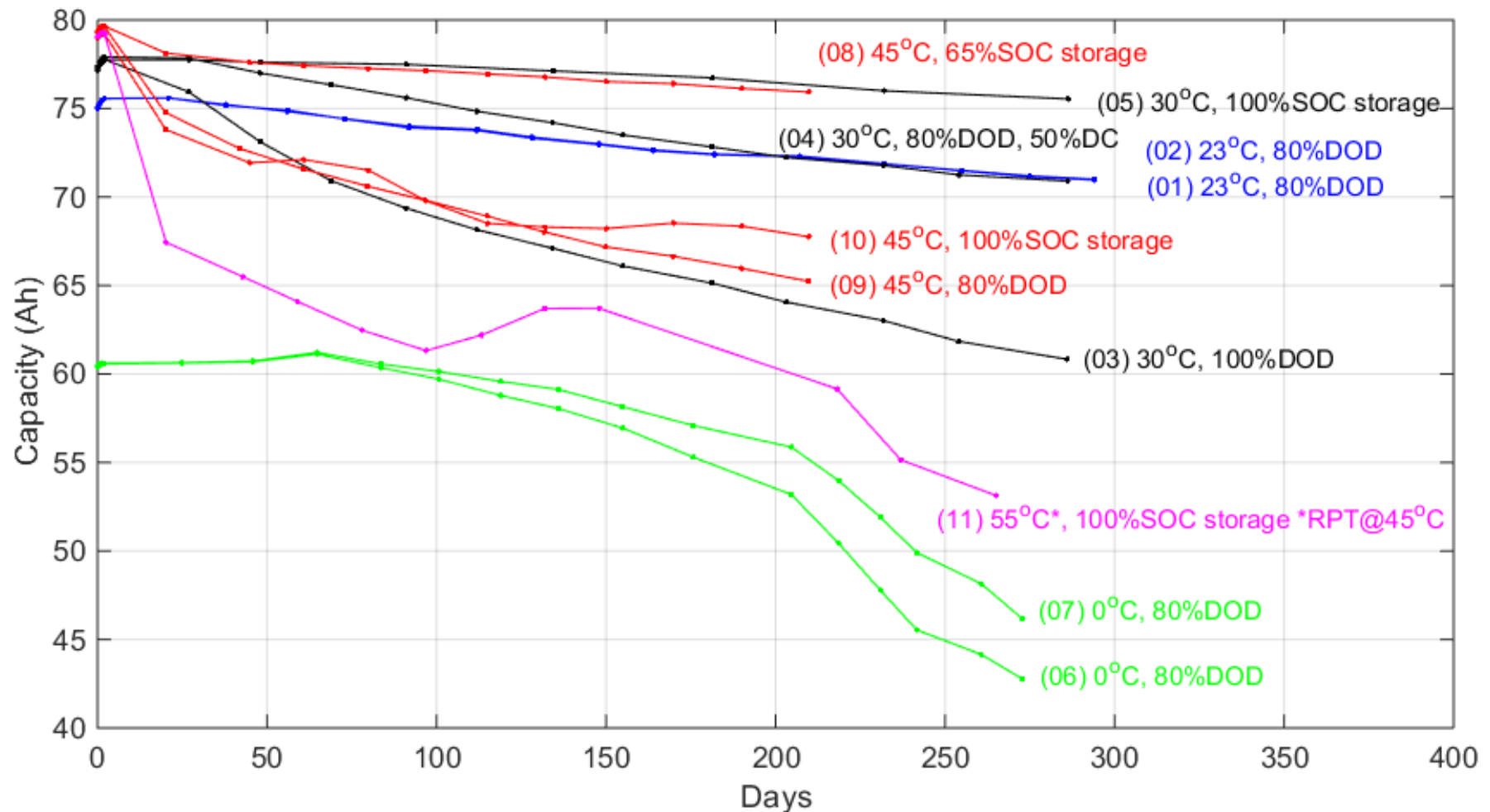
- **Tests design to include both benign and highly accelerated aging**
  - Some real-world, some reaching 30% capacity fade in 6-9 months
- **Pure storage (0%), partial cycling (50% DC\*), & fully accelerated cycling (100% DC)**
  - Separate calendar from cycling fade
- **Capacity check run at test temperature**
  - Simplifies testing but makes model ID more difficult
- **Ideal test matrix would include more aging conditions**

Cycling tests				
Temperature	DOD	Dis./charge rate	Duty-cycle*	# of cells
23°C	80%	1C/1C	100%	2
30°C	100%	1C/1C	100%	1
30°C	80%	1C/1C	50%	1
0°C	80%	1C/0.3C	100%	2
45°C	80%	1C/1C	100%	1
Storage tests				
Temperature	SOC			# of cells
30°C	100%			1
45°C	65%			1
45°C	100%			1
55°C	100%			1

Gr = Graphite negative electrode  
NMC = Nickel-Manganese-Cobalt positive electrode

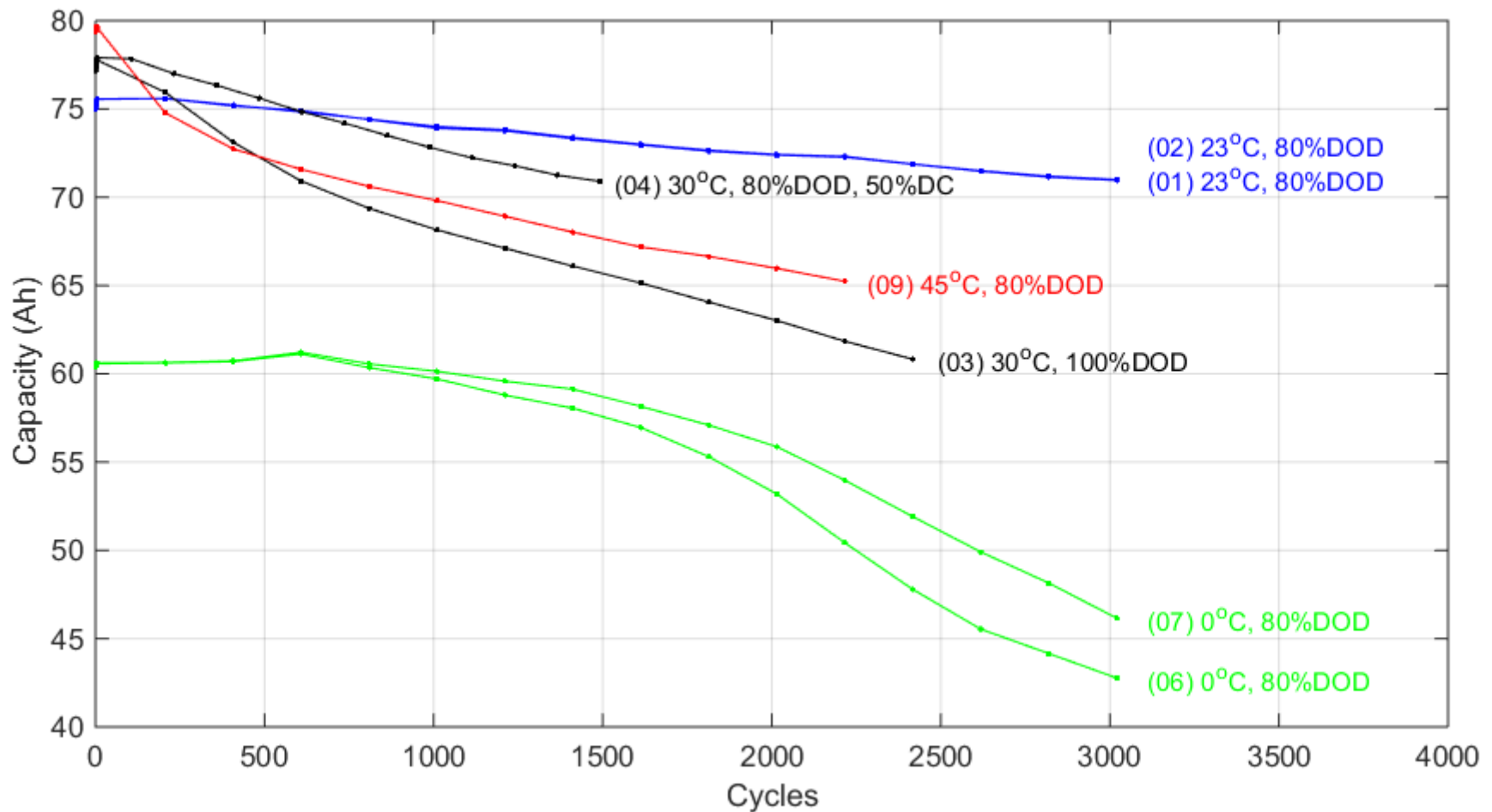
# C/5 Capacity vs. Time

- Tight agreement for replicate cells 1&2 at 23°C
- Some divergence for replicate cells 6&7 at 0°C
- Unexplained temporary capacity increase for 55°C storage cell

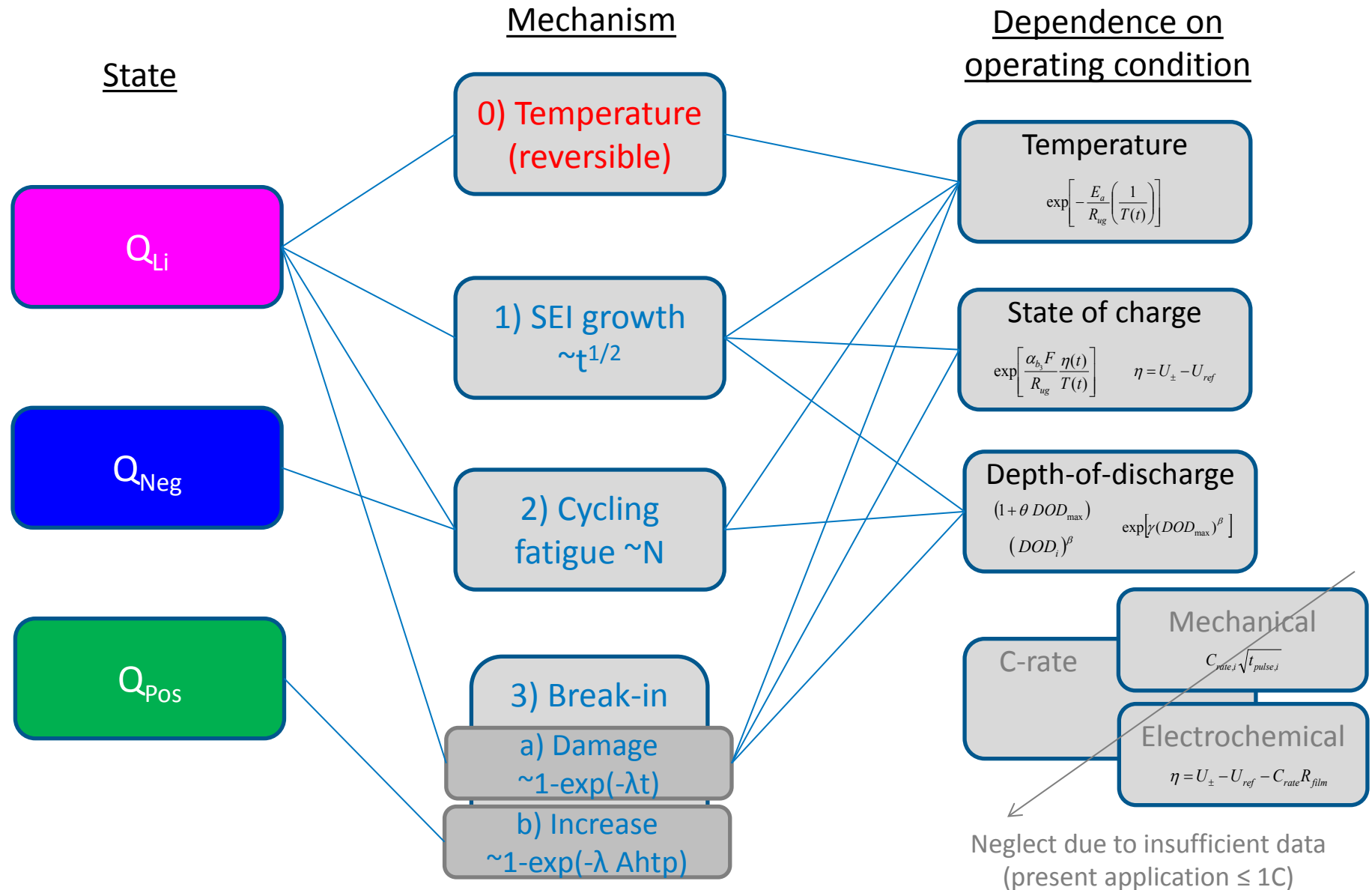


# C/5 Capacity vs. Cycles

- Storage data omitted
- Just 6% capacity loss after 3000 cycles at 23°C, 80% DOD



# Capacity Evolution—Reversible and Irreversible



# $Q_{pos}$ Capacity Break-in & Initial Temperature Dependence

- Hypothesize initial cycles induce microcracks in NMC particles, increasing electrolyte wetting and surface area

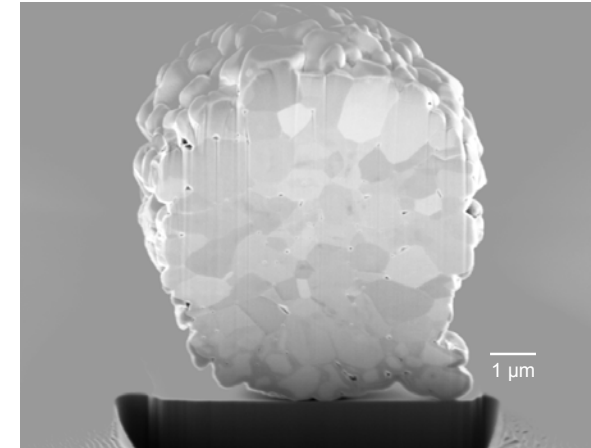
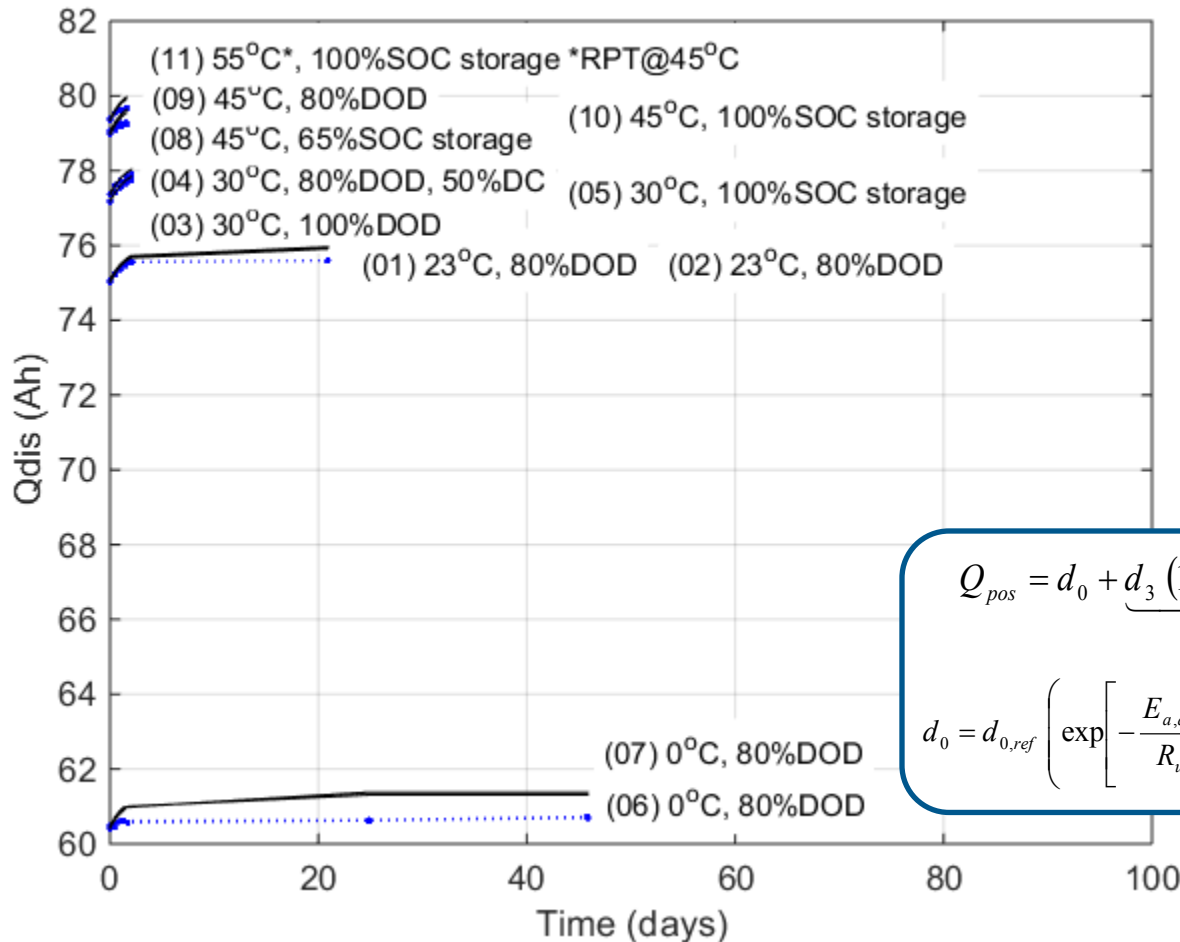


Image: Dean Miller & Daniel Abraham, Argonne National Laboratory

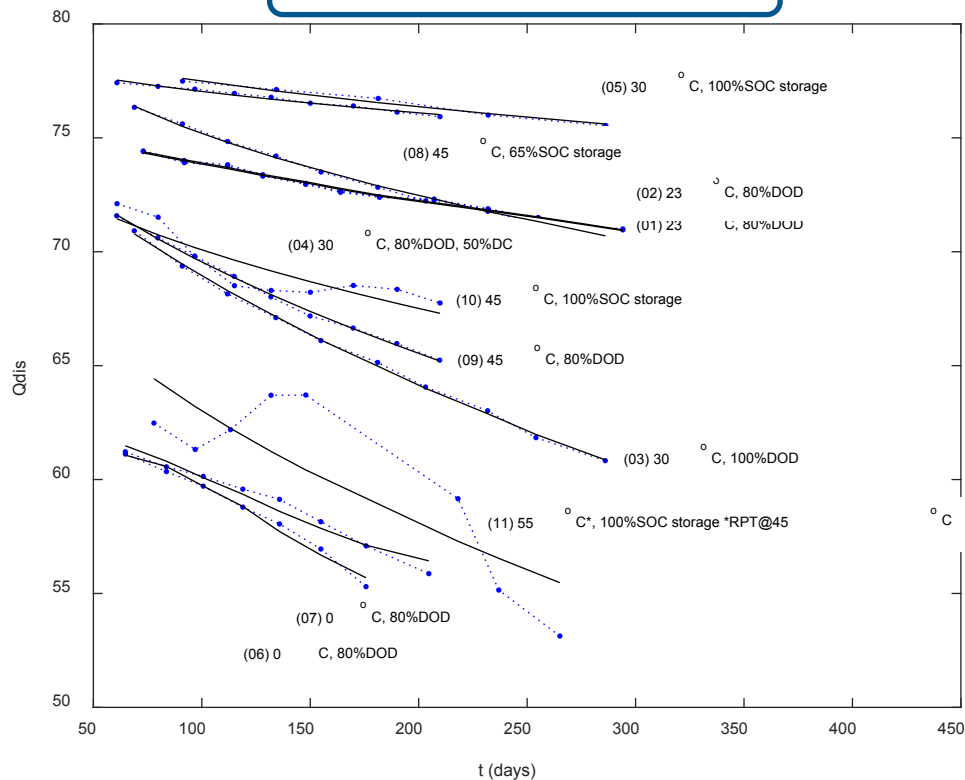
$$Q_{pos} = d_0 + \underbrace{d_3 (1 - \exp(-Ah_{dis}/228))}_{\text{Increase in capacity at BOL}}$$

$$d_0 = d_{0,ref} \left[ \exp \left[ -\frac{E_{a,d_0,1}}{R_{ug}} \left( \frac{1}{T_{RPT}(t)} - \frac{1}{T_{ref}} \right) - \left( \frac{E_{a,d_0,2}}{R_{ug}} \right)^2 \left( \frac{1}{T_{RPT}(t)} - \frac{1}{T_{ref}} \right)^2 \right] \right]$$

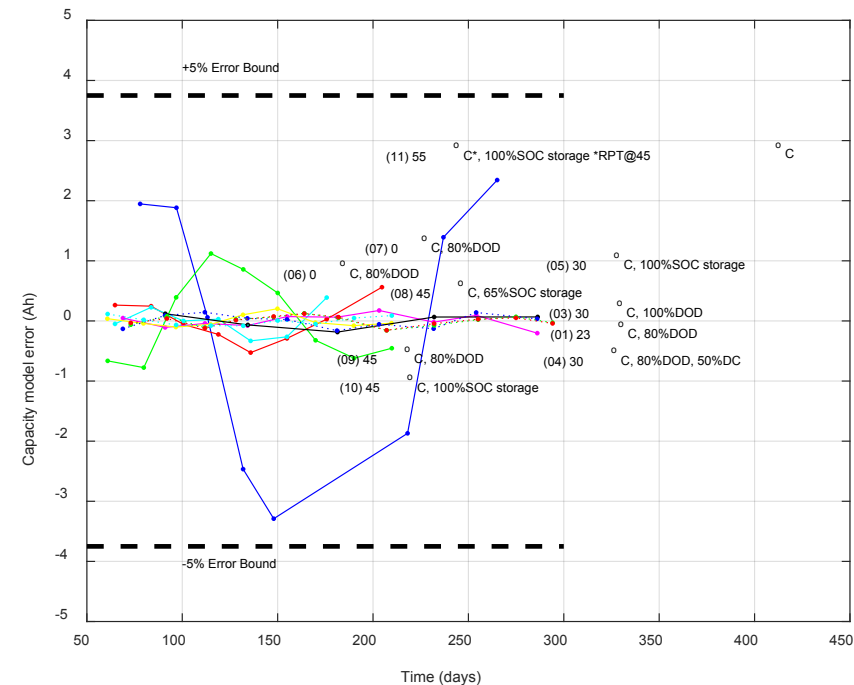
# $Q_{Li}$ Local Models

- Local models: Separately fit  $b_0$ ,  $b_1$ ,  $b_2$  for each data set, excluding
  - First 50 days of data (allows y-intercept to vary with break-in)
  - Knee at  $0^\circ\text{C}$  (to be captured later with  $Q_{neg}$  model)

$$Q_{Li} = d_0 [b_0 - b_1 t^{1/2} - b_2 N]$$

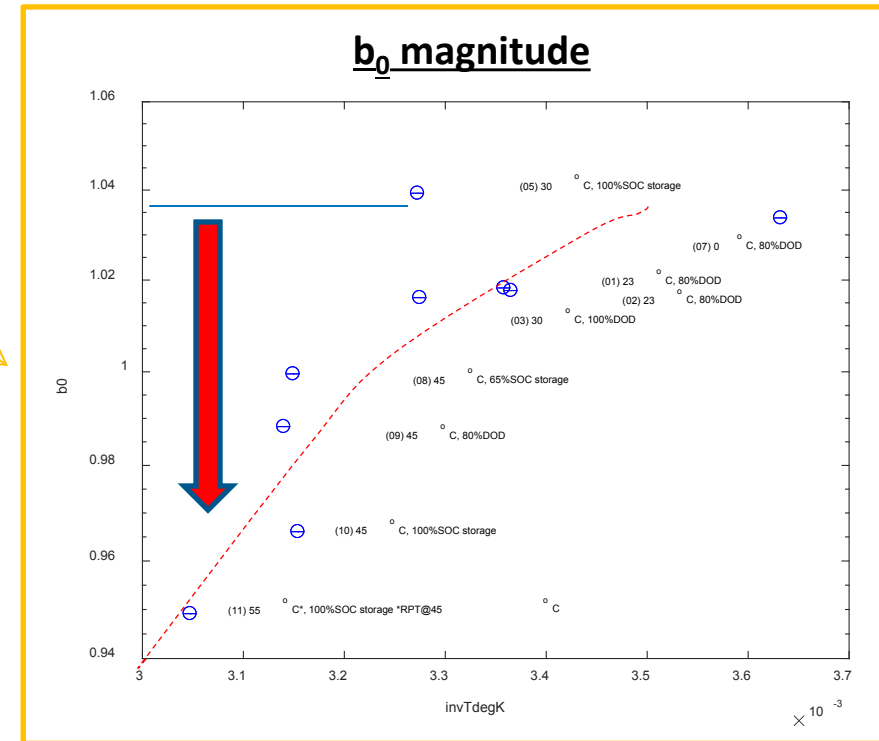
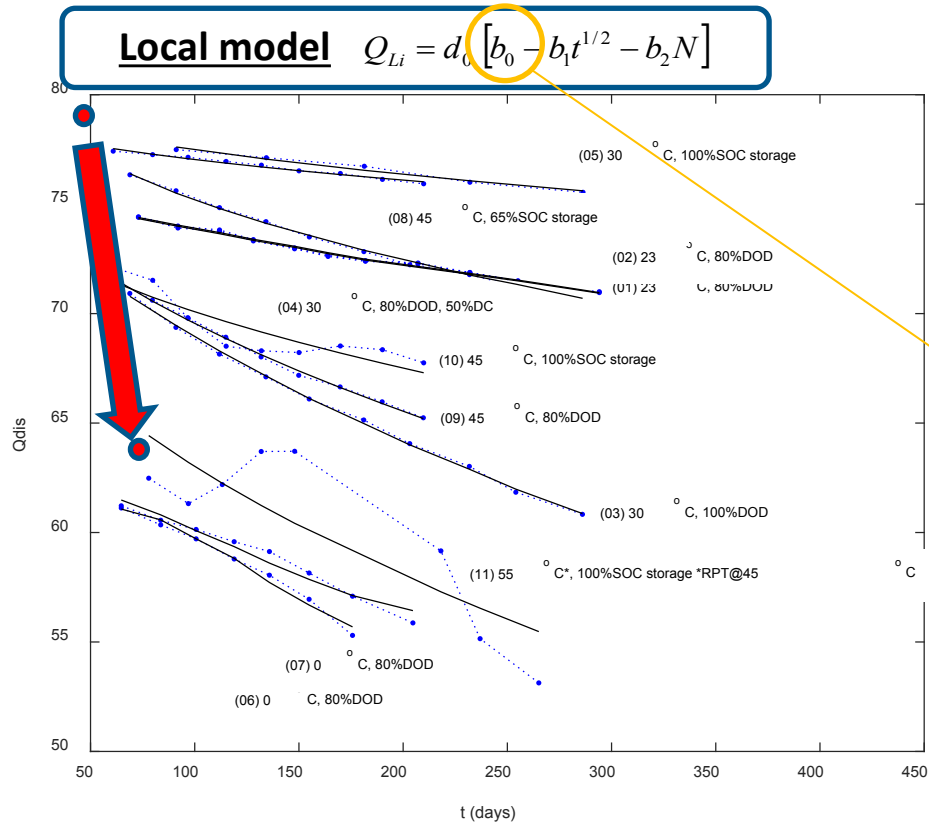


Error = Model - Data



- Choice of mechanisms justified by  $R^2=0.990$  and flat residuals

# $Q_{Li}$ Magnitude of break-in Li-loss



- Least degraded cells show ~3-4% excess Li capacity
- High temperature causes rapid loss in first 50 days
  - Open-circuit voltage and DOD also increase loss
  - Evidence of film layer formation at positive electrode?

## **$b_0$ magnitude model**

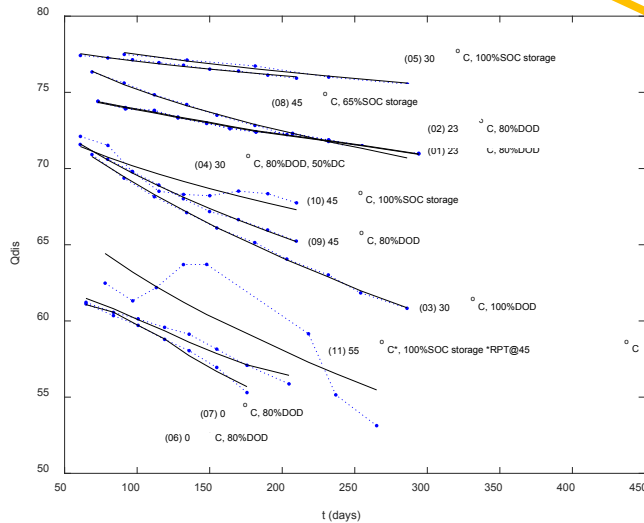
$$y_0 - b_3(1 - \exp(-t / \tau_{b3}))$$

$$b_3 = b_{3,ref} \exp\left[-\frac{E_{a,b3}}{R_{ug}}\left(\frac{1}{T(t)} - \frac{1}{T_{ref}}\right)\right] \exp\left[\frac{\alpha_{b3} F}{R_{ug}}\left(\frac{V_{OC}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}}\right)\right] (1 + \theta DOD_{max})$$



# $Q_{Li}$ Calendar fade rate

**Local model**  $Q_{Li} = d_0 [b_0 - b_1 t^{1/2} - b_2 N]$

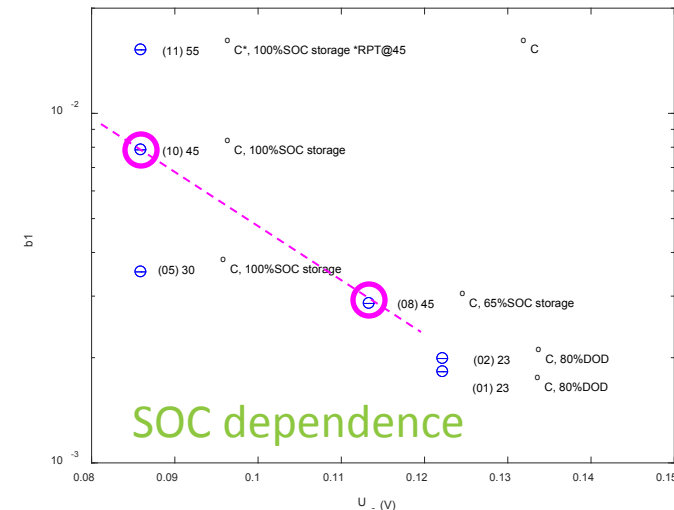
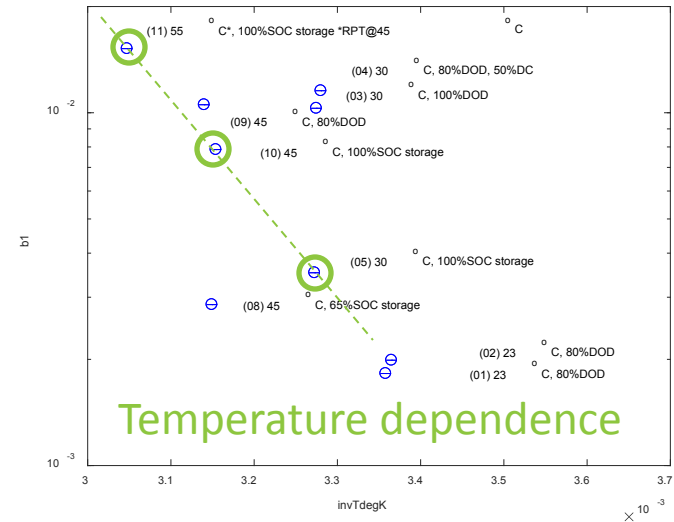


## **$b_1$ rate model**

$$b_1 = b_{1,ref} \exp \left[ -\frac{E_{a,b_1}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right] \exp \left[ \frac{\alpha_{b_1} F}{R_{ug}} \left( \frac{U_-(t)}{T(t)} - \frac{U_{ref}}{T_{ref}} \right) \right] \exp [\gamma_{b_1} (DOD_{max})^{\beta_{b_1}}]$$

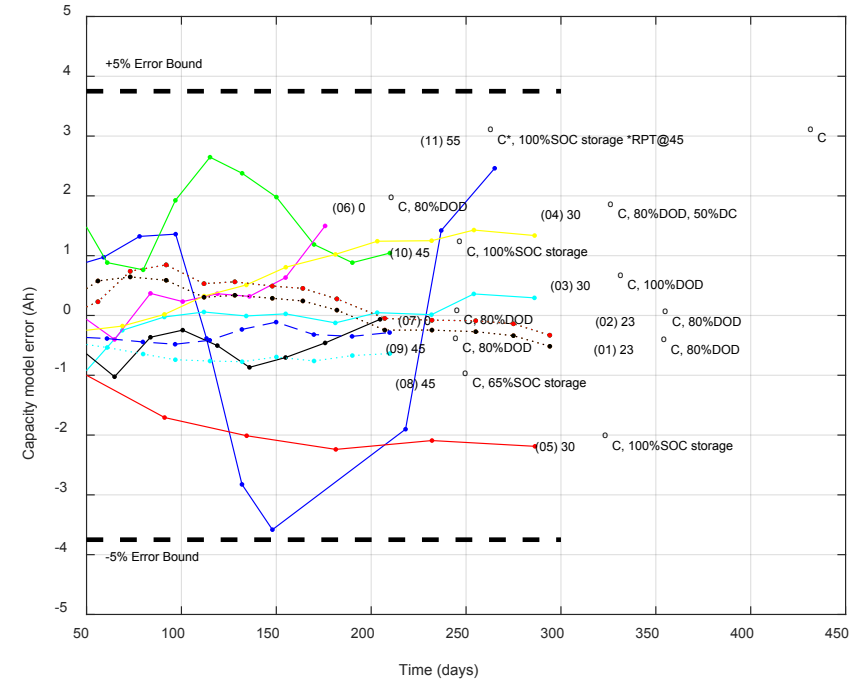
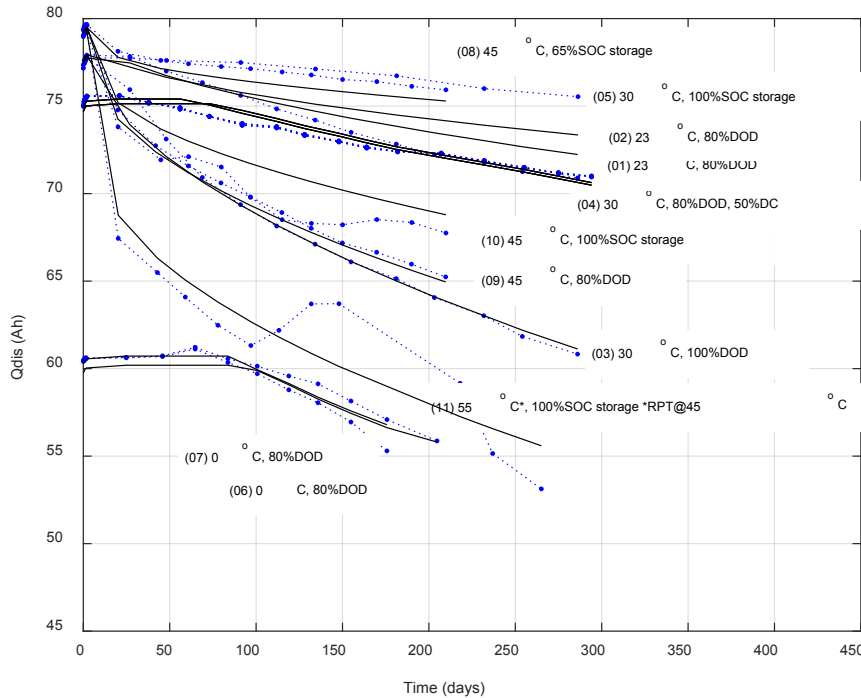
- Visualization of rates suggests rate model equations
- Fitted rate model parameters provide initial guess for global model parameters

## **$b_1$ rate**



# Q<sub>Li</sub> Global Model

- With equations known, parameters fit to all data simultaneously
- $R^2 = 0.985$ , RMSE = 1% of capacity, flat residuals



## Q<sub>Li</sub> global model

$$Q_{Li} = d_0 \left[ b_0 - \underbrace{b_1 t^{1/2}}_{\text{SEI growth with calendar time}} - \underbrace{b_2 N}_{\text{Loss with cycling}} - \underbrace{b_3 (1 - \exp(-t/\tau_{b3}))}_{\text{Break-in mechanism at BOL}} \right]$$

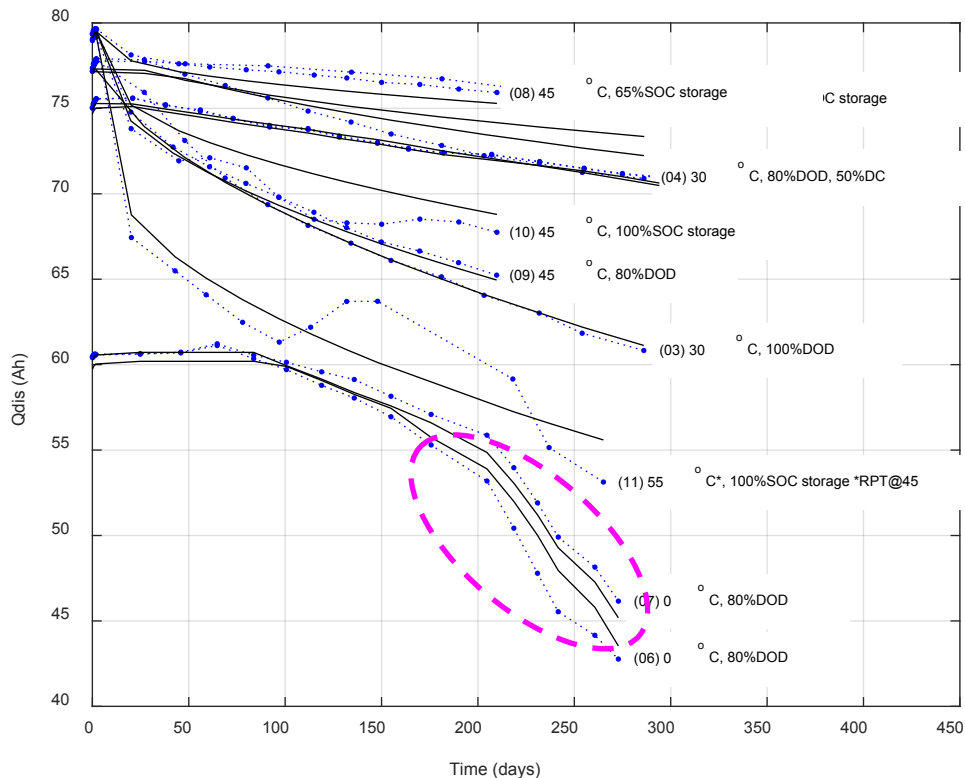
$$b_1 = b_{1,ref} \exp \left[ -\frac{E_{a,b_1}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right] \exp \left[ \frac{\alpha_{b_1} F}{R_{ug}} \left( \frac{U_{-}(t)}{T(t)} - \frac{U_{ref}}{T_{ref}} \right) \right] \exp [\gamma_{b_1} (DOD_{max})^{\beta_{b_1}}]$$

$$b_2 = b_{2,ref} \exp \left[ -\frac{E_{a,b_2}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right]$$

$$b_3 = b_{3,ref} \exp \left[ -\frac{E_{a,b_3}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right] \exp \left[ \frac{\alpha_{b_3} F}{R_{ug}} \left( \frac{V_{OC}(t)}{T(t)} - \frac{V_{ref}}{T_{ref}} \right) \right] (1 + \theta DOD_{max})$$

# $Q_{Neg}$ Model

- Captures **knee** with cold temperature cycling
- Minor importance in most real-world scenarios



## $Q_{Neg}$ global model

$$\frac{dQ_{neg}}{dN} = -\left(\frac{c_2}{Q_{neg}}\right)$$

$$Q_{neg} = \left[ c_0^2 - 2c_2c_0 N \right]^{\frac{1}{2}}$$

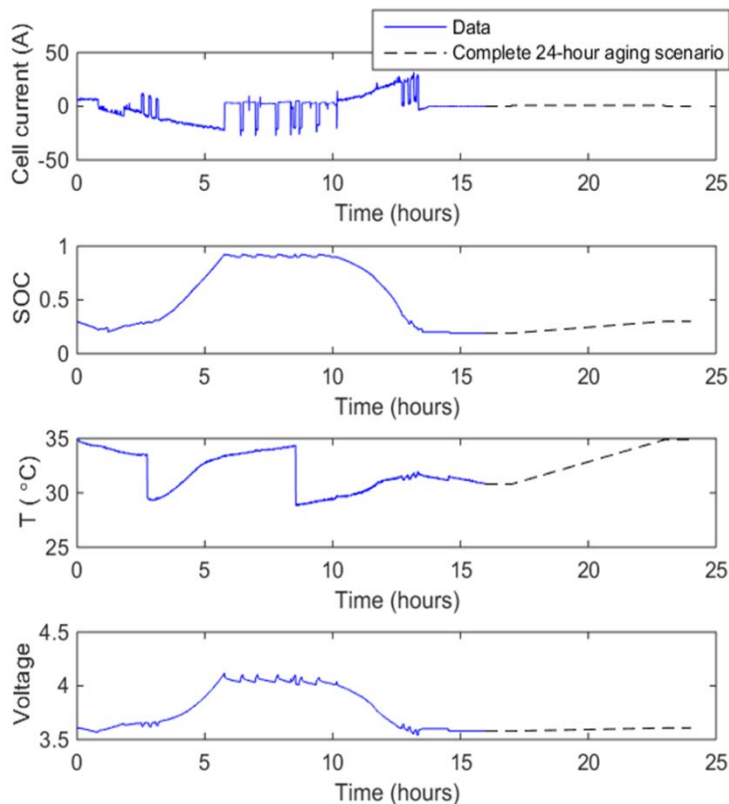
$$c_0 = c_{0,ref} \exp \left[ -\frac{E_{a,c0}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right]$$

$$c_2 = c_{2,ref} \exp \left[ -\frac{E_{a,c2}}{R_{ug}} \left( \frac{1}{T(t)} - \frac{1}{T_{ref}} \right) \right] (DOD)^{\beta_{c2}}$$

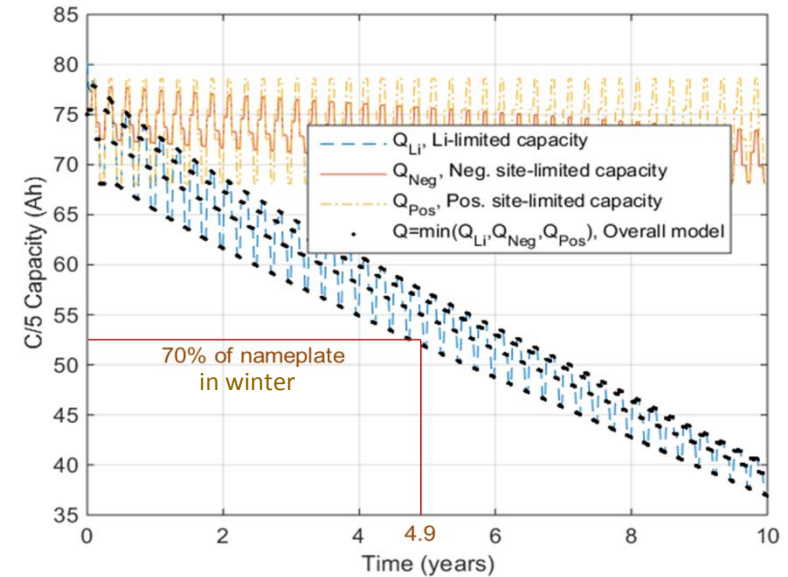
# Lifetime analysis – PV self consumption

- Model reformulated in rate-based form
- SOC(t) discretized into microcycles,  $DOD_i$ , using Rainflow algorithm

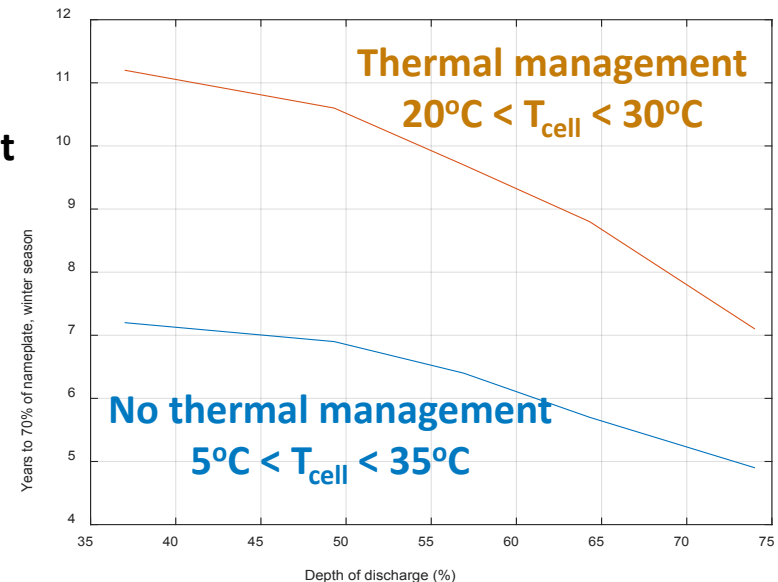
- Application data



- Multi-year, 4-season simulation
- Same cycle each



- Impact of DOD and thermal management



# Conclusions

- **Battery energy storage can enable increased integration of renewable power generation on the grid**
- **Battery life modeling methodology formalized, aiding systems design process**
  - Capacity error:  $L_2 = 1\%$ ,  $L_\infty = 5\%$
  - For studied Gr/NMC Li-ion ES technology, best to restrict daily cycles  $< 55\%$  DOD with occasional larger excursions
  - Thermal management extends life from 7 to 10 years
- **Battery aging experiments are time consuming & expensive**
- **Additional model validation needed**
  - Longer duration
  - Variable cycling & temperature
- **Life model accuracy may be enhanced in the future by coupling with electrochemical modeling & diagnostics**

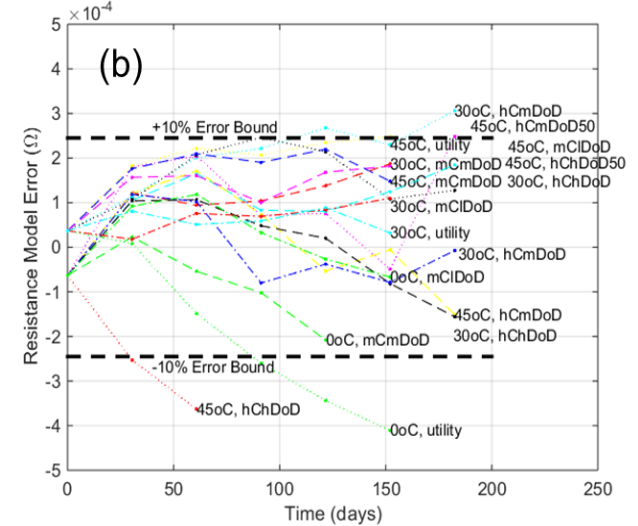
# Acknowledgements

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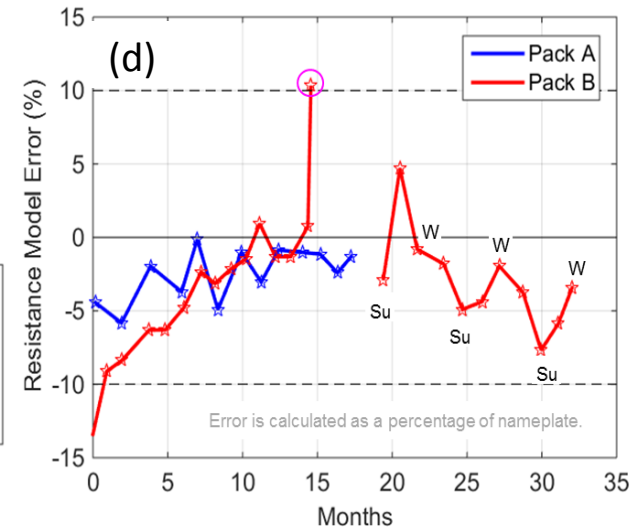
- **U.S. DOE Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Program**
- **SunPower Corporation**

# Extra Slides

*Eaton Corp. ARPA-E AMPED project  
resulting in 35% smaller HEV battery  
(PI: Dr. Chinmaya Patil/Eaton)*



A red EAT-N Hybrid Power truck is shown in profile, facing right. The truck has a white box trailer with the EAT-N logo and 'Hybrid Power' text. The cab is red with a large chrome grille. The background is a blurred green field.



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