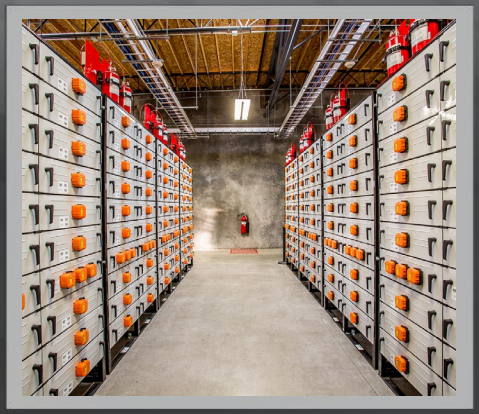

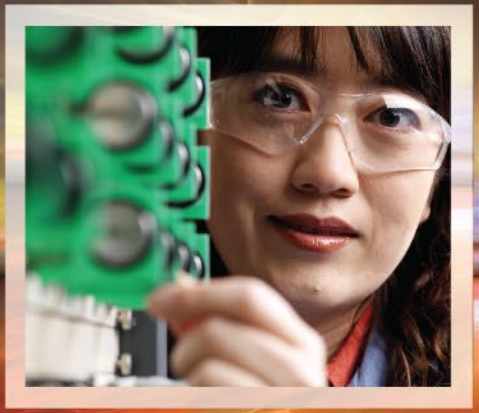

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# Battery Storage State of Health Model

Vilayanur V. Viswanathan, Alasdair J. Crawford, Daiwon Choi,
Patrick Balducci, David M. Reed, Vincent L. Sprenkle

DOE OE Energy Storage Peer Review
Santa Fe, New Mexico
September 25, 2018

DISCOVERY *in Action*

U.S. DEPARTMENT OF ENERGY

# Scope & How it Ties to DOE-OE Mission



- Develop reliable battery state of health model
  - Identify gaps in current state of the art
  - Plug in those gaps
- Use top-down approach to identify key degradation parameters
  - Leverage on in-house data being gathered (Reliability)
  - Feed key results to bottom-up model
- Develop path to reliable Battery Management System
  - OE mission - reliable & high energy storage penetration

# Outline

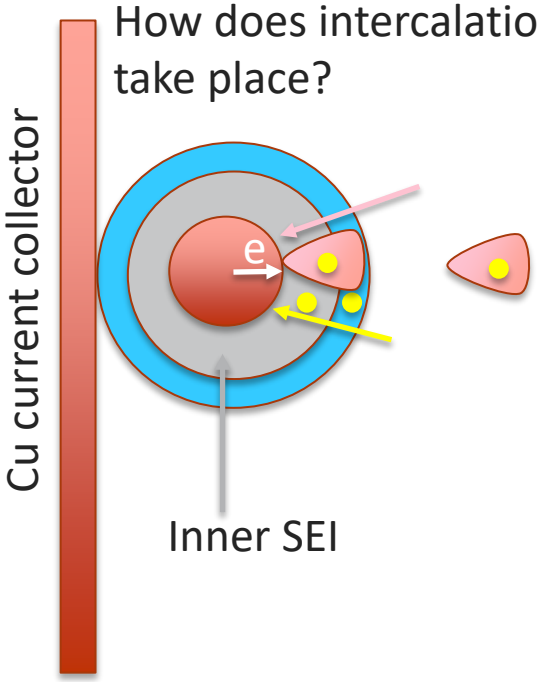


- Degradation mechanisms
- Findings
- Type of models
- Our approach
- Top down model results – in-house and literature data
- Bottom up model results
- Conclusions
- Future work

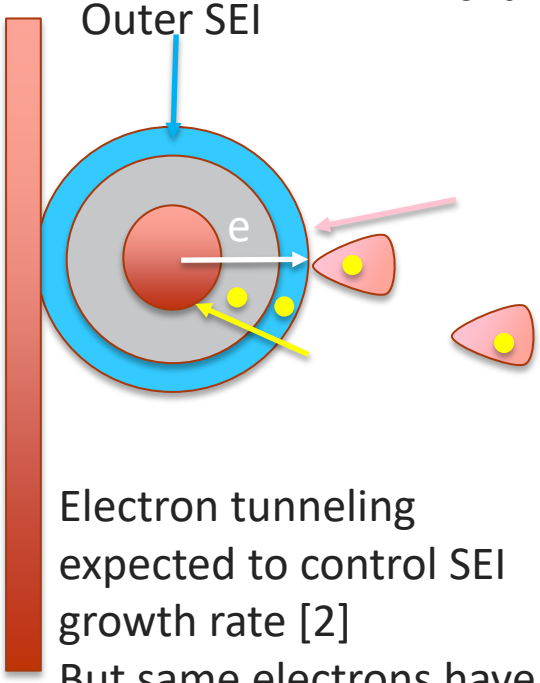
# Degradation Mechanism



SEI insulator, Solvent diffusion [1]
How does intercalation take place?

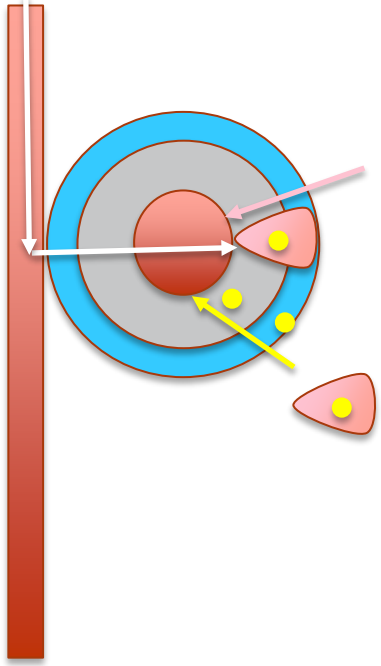


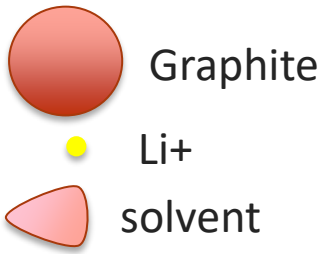

Outer SEI




Electron tunneling expected to control SEI growth rate [2]
But same electrons have to reach graphite - so intercalation is also slowed down

Our approach: SEI forms at graphite surface – diffusion + charge transfer – mixed kinetics

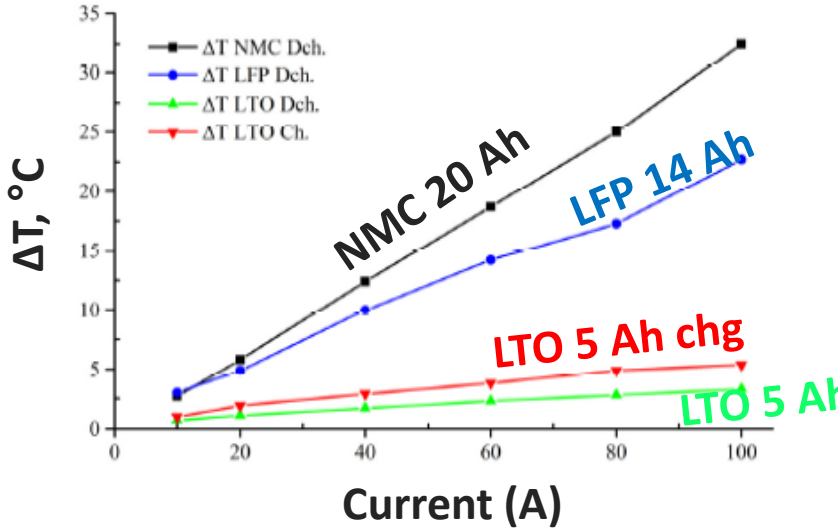


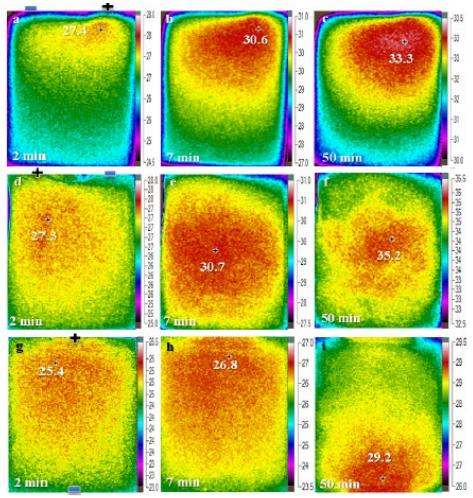



[1] M. Pinson et al, J. Electrochem. Soc., 160 (2) (2013) A243-A250
[2] F. Kindermann et al, J. Electrochem. Soc., 164 (12) (2017) E287-E294

# Findings

- Temperature is most important degradation parameter
  - Materials selection
  - Cell design
  - Temperature (T) distribution
- Interaction term between SOC and T
- Interaction between current (I) and dV/dQ
- Solid Electrolyte Interphase (SEI) growth mechanism hypothesis validated
  - Mixed kinetics – solvent diffusion/charge transfer
  - Pathway towards
    - Safe cell design
    - Battery Management System




*Energies* **2015**, *8*, 8175-8192; doi:10.3390/en8088175

# Types of Models and Gaps



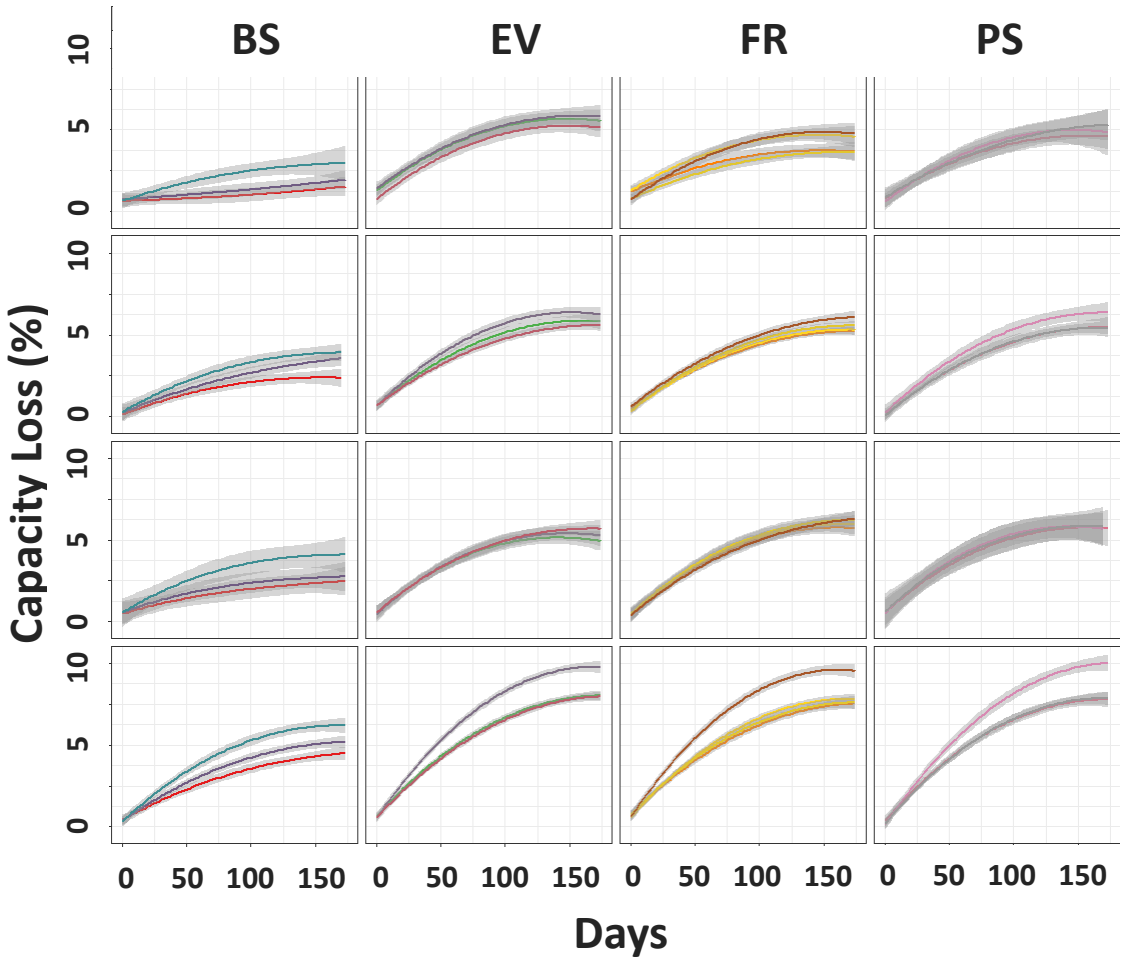
- Types
  - Empirical – fit to entire data set
  - Semi empirical – equivalent circuit
    - In both approaches, interactions not considered
  - Finite difference or finite element
- Gaps in top down model
  - Aging and cycling related effects calculated separately
    - Greater of the two used to estimate degradation - underestimation
    - Aging related degradation subtracted from total to estimate cycling degradation - overestimation of aging related losses
  - Use interaction terms that account for aging and operation
- Gaps in bottom up model
  - SEI layer is electronic insulator, hence solvent has to diffuse to graphite
    - How can intercalation place if this is true?
  - SEI considered to be impermeable to solvent, reaction rate controlled by slow electron tunneling through SEI
    - This would impede intercalation also – use mixed kinetics, account for SEI layer related overpotential for both intercalation and SEI growth reaction

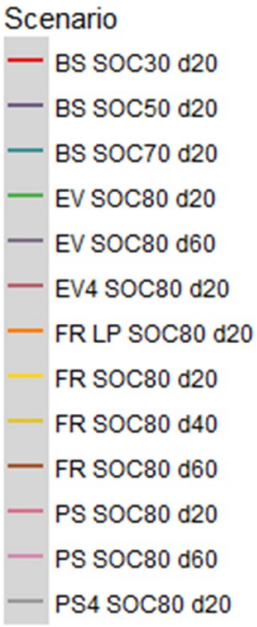
# Top Down Model Approach



- Fit randomized data set, and verified the fit to remaining data
- Examples of predictors used
  - Product of various powers of time t - $t^{0.5}$, $t^{1}$, $t^{2}$ with various terms such as various powers of T, SOC, T&SOC, I&dV/dQ
- Above approach used for each chemistry to get a global list of parameters with decreasing order of importance
  - Individual data set analyzed, and the global order of importance for parameters used in conjunction with order of importance for individual data set

# In-house Data Capacity Loss Trends




**NMC2 highest degradation LFP lowest**

**NMC2 highest degradation**

**NMC2 highest degradation**

**NMC2 highest degradation**

- Total losses higher for nickel based cathodes
- Duty cycle losses for LFP > NMC1 and NCA
- Duty cycle losses for NMC2 highest

# Comparison of Degradation for PS Grid Service – 80% to 60% SOC Range

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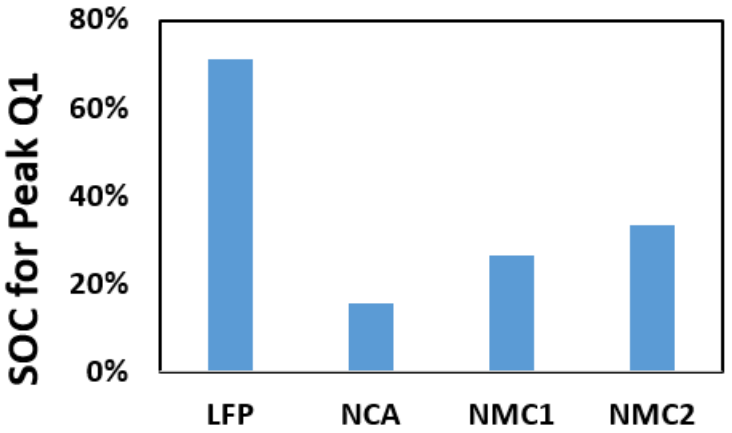
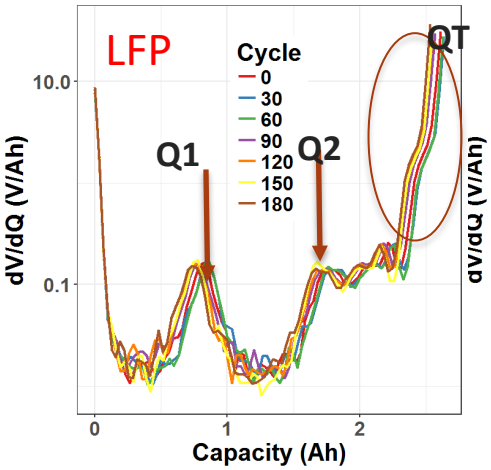
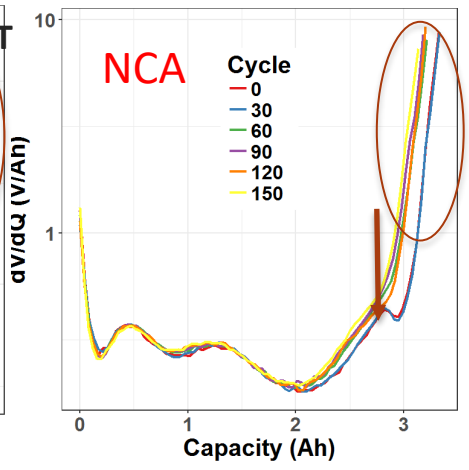
- Duty cycle losses for LFP slightly > NMC1 and NCA (since baseline losses lowest)
- For LFP, Q1 peak occurs at 71% SOC, for nickel based at much lower SOC
- Hence, this peak traversed only for LFP for this PS duty cycle

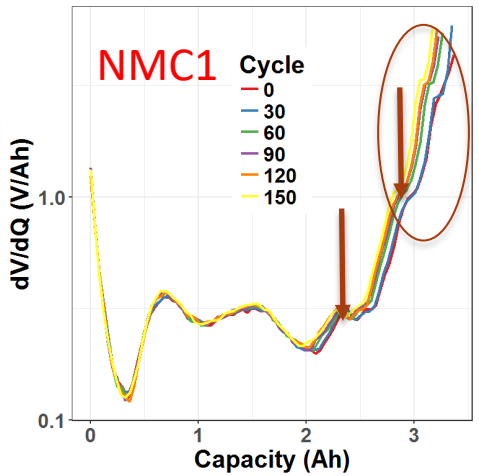
| | |
|---|---|
| ΔQ1 = | Loss of lithium (Li) |
| Δ(Q2-Q1) = | Loss of graphite (G) |
| ΔQT = | Total loss |
| ΔQT – (Li+G)= | Loss of cathode / other |

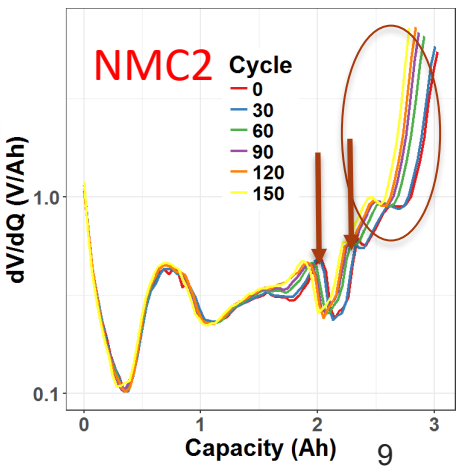



PS 20% DOD



# Comparison of Degradation for PS Grid Service – 80% to 20% SOC Range

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- NCA and NMC1 Q1 peaks occur at 15.6% and 26.6% SOC
- NMC2 Q1 peak at 33.3% SOC
  - NMC2 degrades much more than NCA and NMC1
- LFP cycle related degradation > NCA and NMC1 as Q1 at 71% SOC
- dV/dq term shows up for LFP & NMC2

Expressions for capacity loss from Reliability data

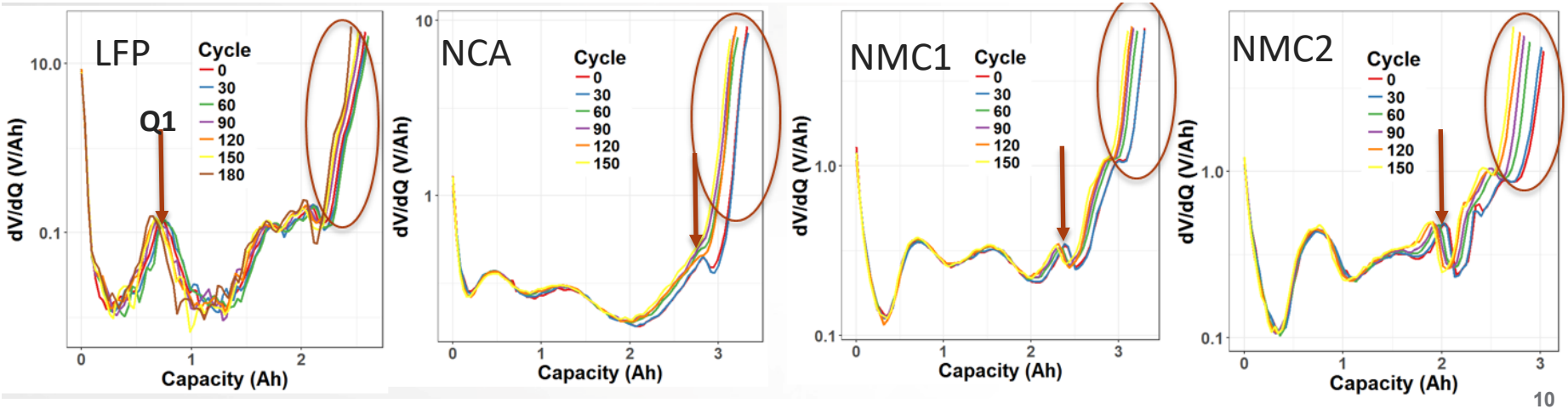
LFP: $k_1 * t^{0.5} + k_2 \int i^2 (dV/dQ) dt$

NCA: $k1 * t^{0.5}$

NMC1: $k1 * t^{0.5}$

NMC2: $k_1 * \int i * (1-SOC)^2 (dV/dQ) dt + k2 * \int (dV/dQ) dt$

PS 60% DOD



# In-house Data Fitting

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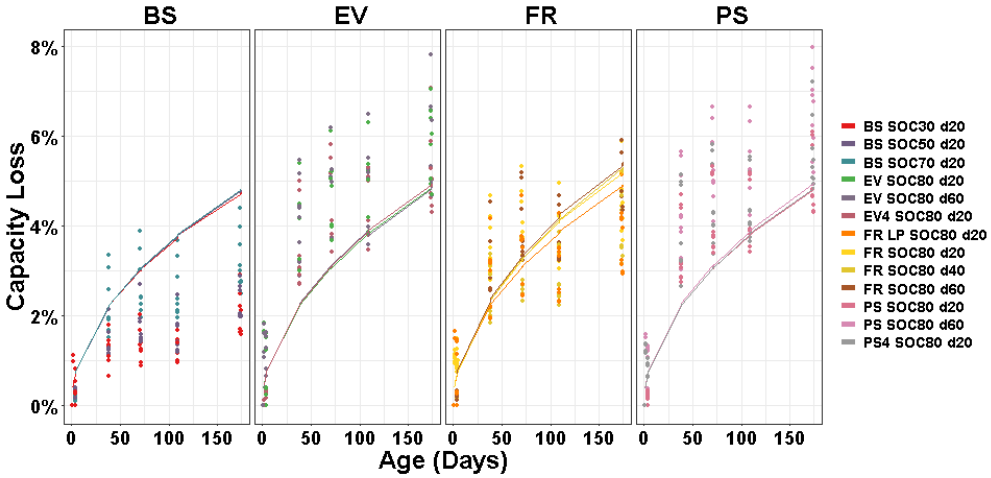
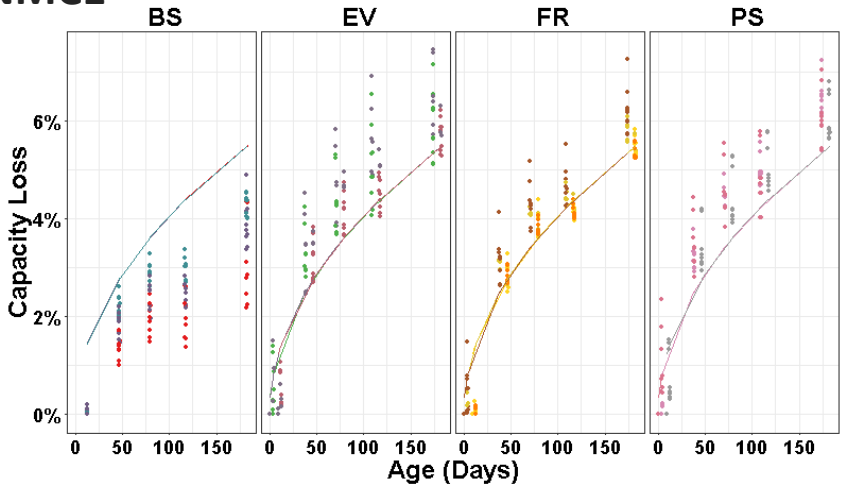
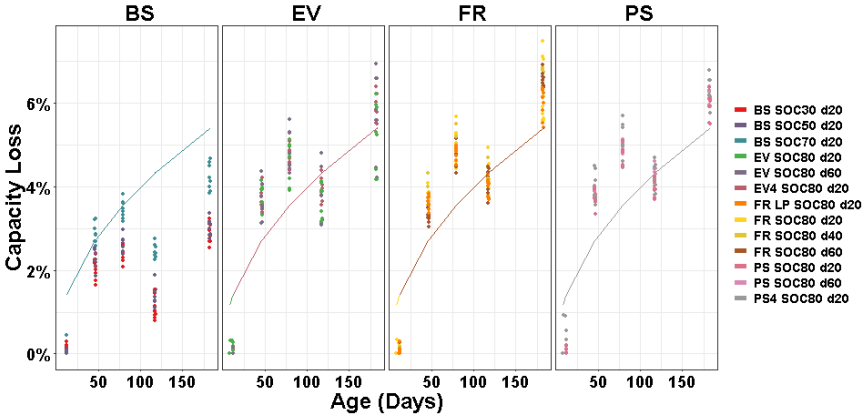
## LFP



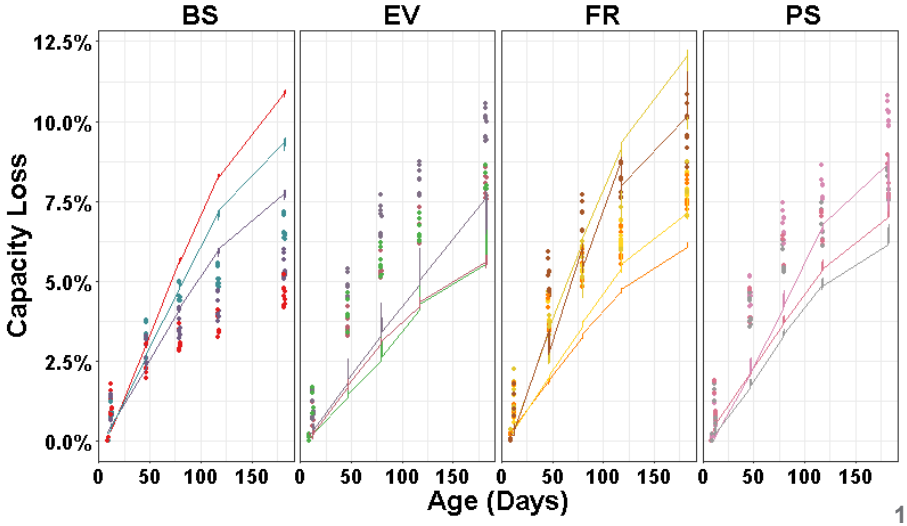

## NMC1




## NCA

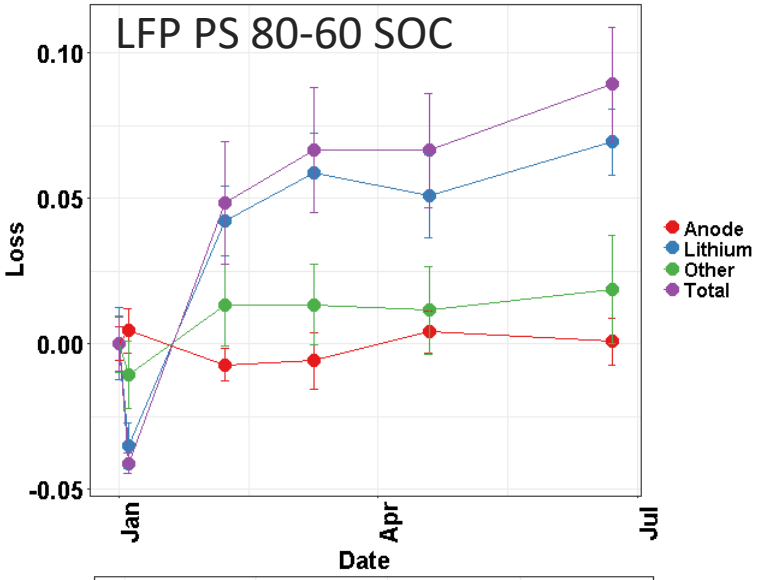


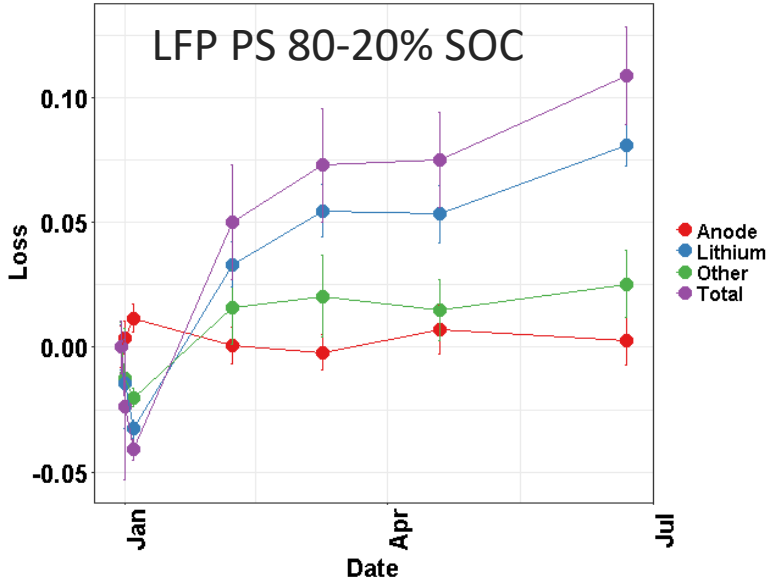

## NMC2



# Various Losses from dV/dQ Analysis



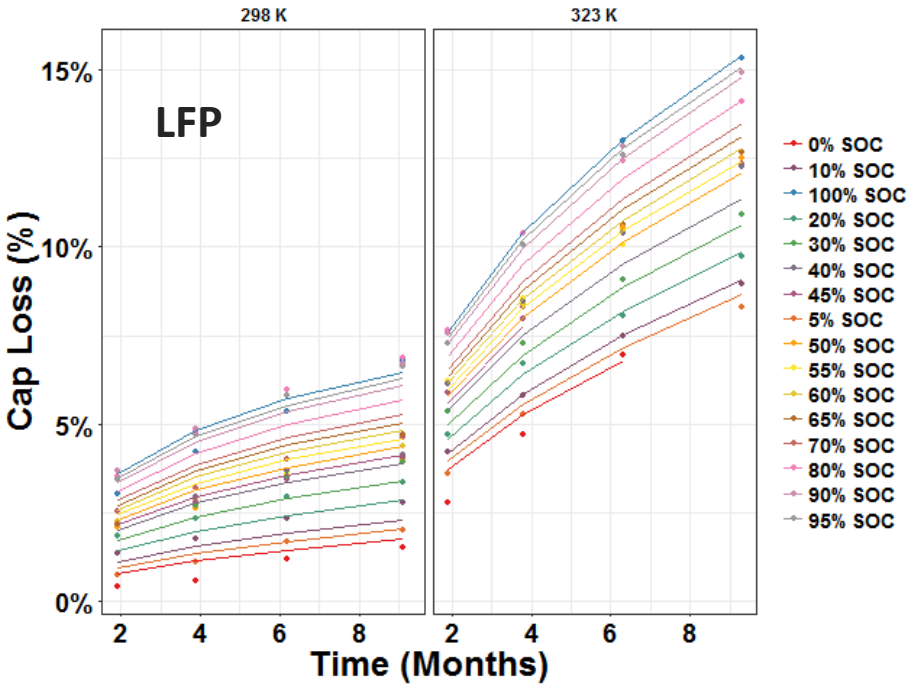



- Loss of lithium main source of degradation
- Loss of graphite anode negligible
- Total loss nearly equal to loss of lithium
- Work ongoing to analyze other chemistries

# Literature Data - Aging at Various T & SOC

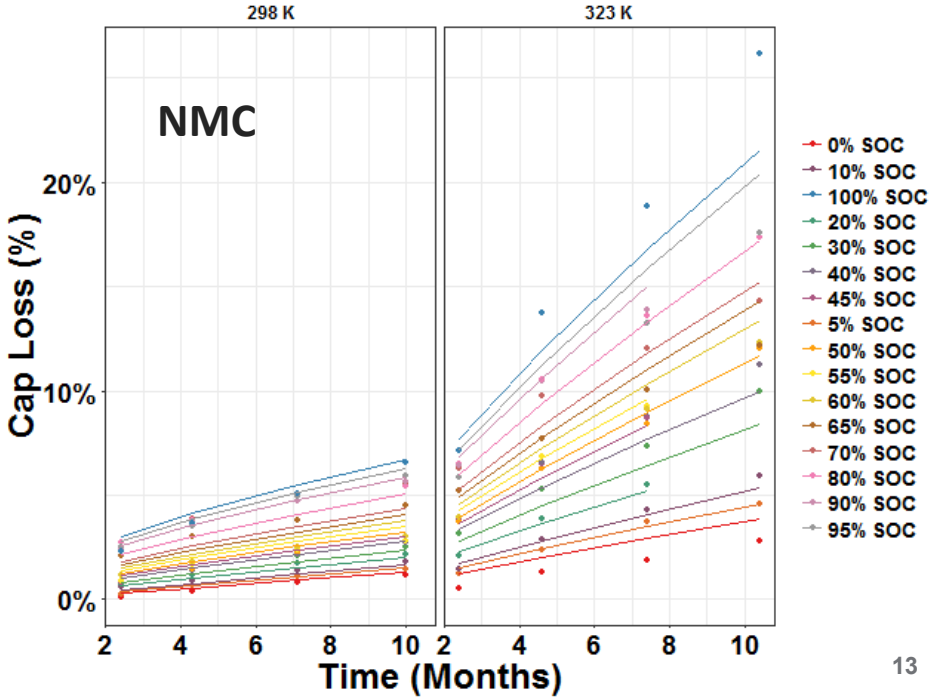





- Temperature terms dominate
- SOC-T interaction important
- Increase in degradation at 100% SOC for NMC reflected in SOC term prominence
  - Electrolyte oxidation
  - Transition metal dissolution
  - High degree of delithiation

*Keil et al, J. Electrochem. Soc.*, **163** (9) A1872-1880 (2016)

| LFP | NMC | NCA |
|---|---|---|
| $t^{0.5}$ | $t^{0.5}$ | $t^{0.5}$ |
| $T^2$ | $T^3$ | $T^2$ |
| $t^{0.5}T^3$ | $t^{0.5}T^3SOC^3$ | $t^{0.5}T$ |
| $t^{0.5}$ | $t^{0.5}T^2$ | $t^{0.5}T^3$ |
| $t^{0.5}T^3SOC$ | $t^{0.5}SOC$ | $t*T^3SOC$ |
| $t^{0.5}SOC^2$ | $t*T^3$ | $t^{3}*T^3SOC$ |



# Bottom-up Model Approach



- Parameters list for cell components used from literature
- **Loss of lithium at anode SEI layer assumed to be degradation mode**
- Rate constant for SEI growth and solvent diffusion coefficient in SEI from literature

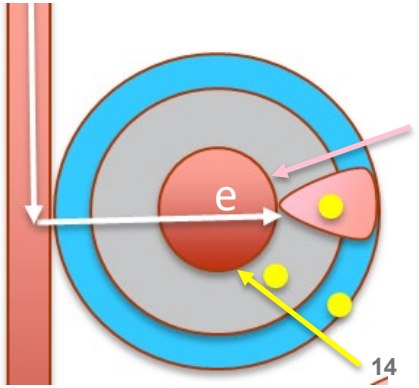
Gap in literature:

- Approach 1
  - SEI layer impermeable to electron
  - Solvent diffusion through SEI needed for SEI formation at graphite/SEI interface

- Approach 2
  - Electron tunneling through SEI layer applied only to SEI formation
    - Graphite assumed to be in contact with the copper current collector
  - Reaction occurs at SEI/electrolyte interface

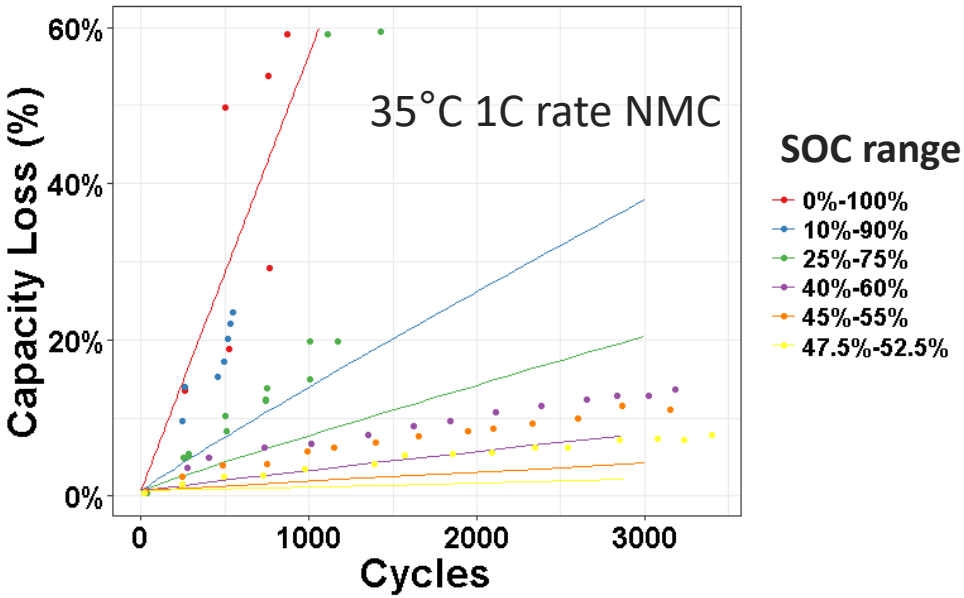
Our approach:

- SEI forms all around graphite
- Electron transport through SEI for intercalation and SEI formation
- Use mixed kinetics – solvent diffusion/charge transfer
- Assigned stress values as f(Li content in graphite) – dV/dQ

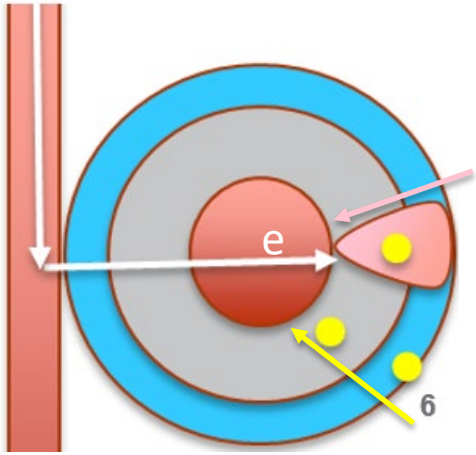


# Bottom-up Model






M. Ecker et al, J. Power Sources, 248 (2014)




- SEI layer growth assumed to occur on graphite surface
- Need electron transport and solvent transport to graphite surface
  - Triple phase boundary (fuel cells)
- Electrode, electrolyte, separator, SEI electronic conductivity, SEI equilibrium potential from literature
- Vary kinetic rate constant to fit data
  - $2.43 \times 10^{-16}$ m/s

# Conclusions



- Top down model predicts degradation well
- Interaction terms important
  - High T + High SOC for example
- dV/dQ analysis provides guidance on degradation for various SOC ranges
  - Repeated excursion of SOC range where graphite peak occurs detrimental to SOH
- Nickel based cathodes lead to greater degradation possibly due to transition metal dissolution
- Bottom up mixed kinetics model validated vs. literature data
  - Room for improvement with better input parameters for kinetic rate constant and solvent diffusion coefficient

# Future Work



- Incorporate more accurate parameters  from single particle model
  - Incorporate cathode degradation, electrolyte oxidation
- Investigate effect of lithium plating on performance
- Use in-house FY19 data – incorporating 3-electrode results
- PNNL Pouch fabrication to study effect of anode to cathode capacity ratio
  - affects SOC at which dV/dQ peaks occur.
- Quantify various losses for different grid services from dV/dQ analysis
- Correlate losses with anode to cathode (A/C) ratio and SOC operation range
- Investigate effect of A/C on cathode degradation – high A/C drives up cathode V
  - Cathode degradation, electrolyte oxidation, passivation layer on cathode

# Acknowledgements

**Dr. Imre Gyuk** - Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability, U.S. Department of Energy

# Additional Slides

# Degradation Mechanisms



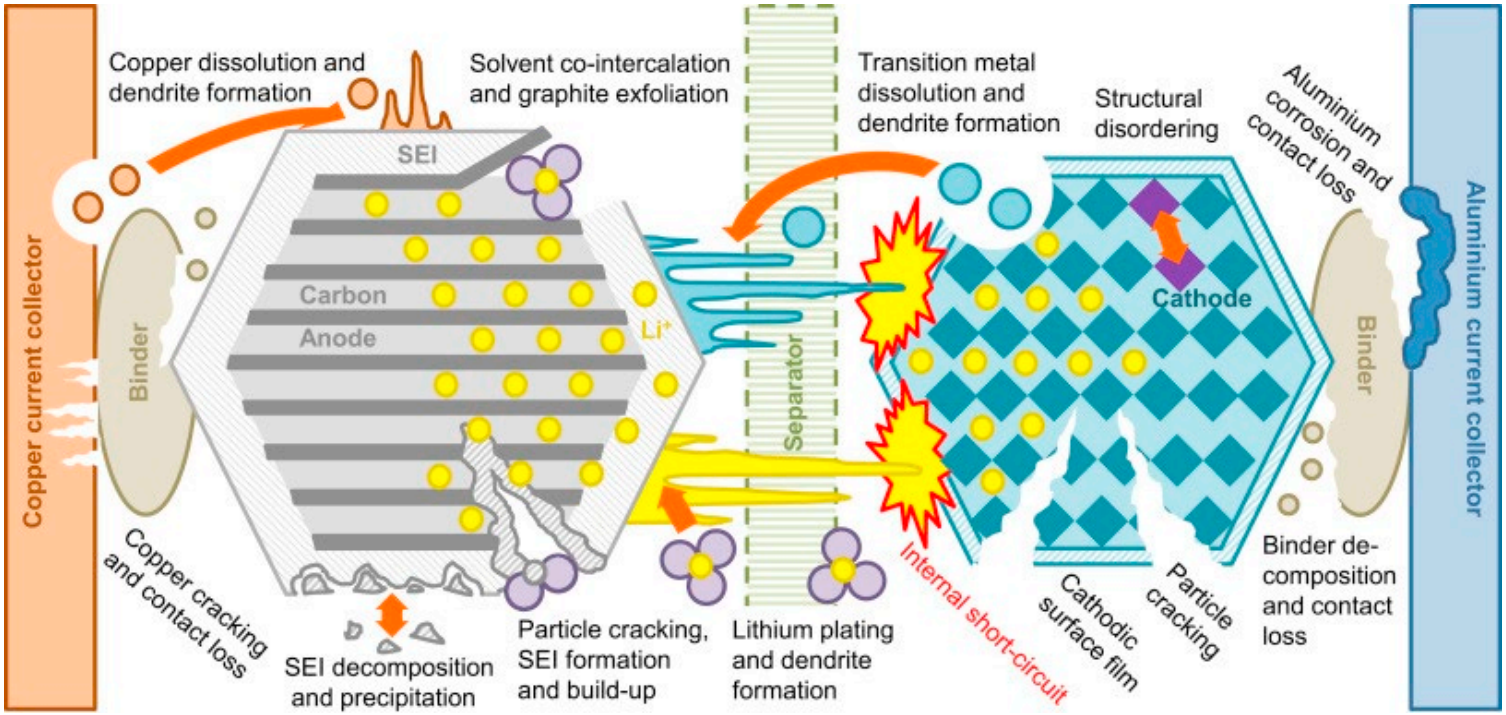
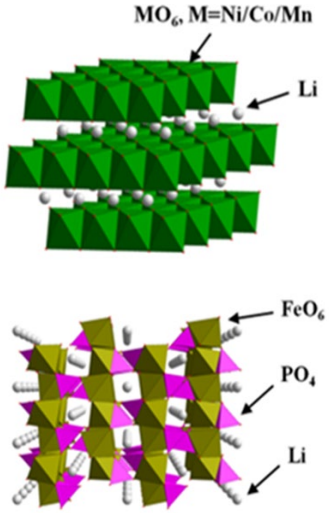
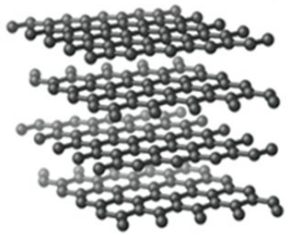



**Figure 2**. Degradation mechanisms in Li-ion batteries.

## Cathode



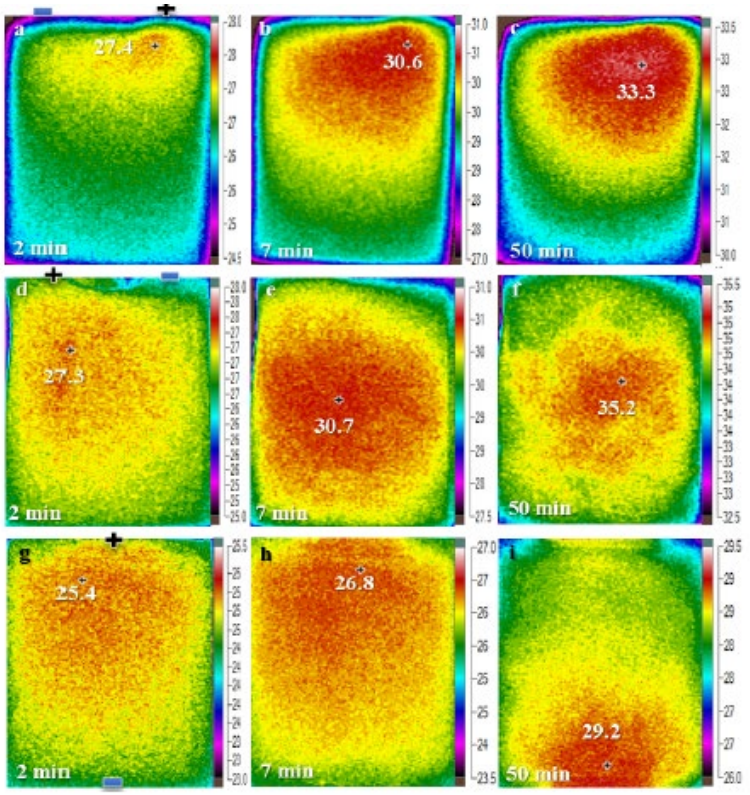

## Anode

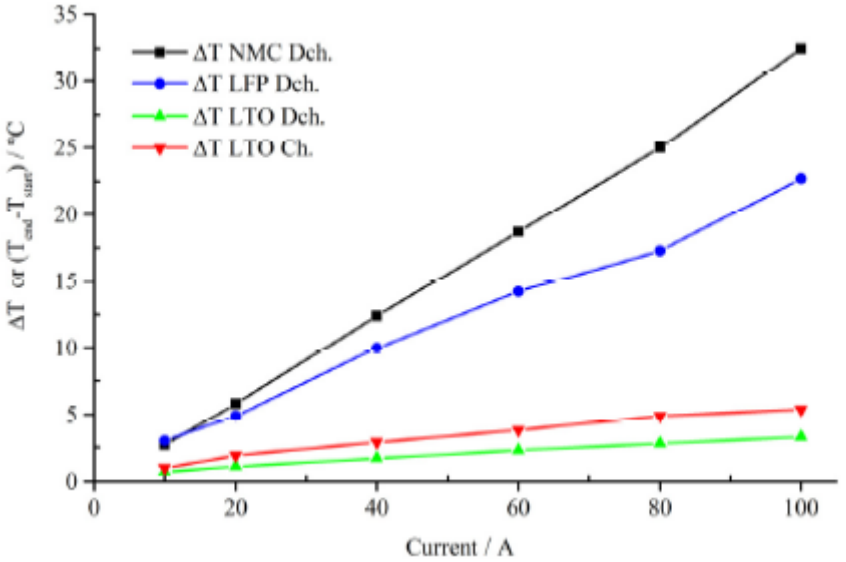


**Ref)** Birkl *et al*., "Degradation diagnostics for lithium ion cells", *J. Power Sources* 341 (2017) 373-386

# Temperature Effect






Non-uniform surface temperature
20C rate for LTO less delta T than 5C for NMC

Nickel Manganese Cobalt oxide (NMC)-based 20 Ah cell, Lithium Iron Phosphate (LFP) 14 Ah, and Lithium Titanate Oxide (LTO) 5 Ah cell

*Energies* **2015**, *8*, 8175-8192; doi:10.3390/en8088175

# Battery Test Method

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## ❑ Variables

- Time : 24h grid cycle (1day)
- State-of-Charge (SOC) : 20~80%
- Depth of Discharge (DOD or ΔSOC) : 20, 40, 60%
- Power (C-rate): within cell specifications (voltage window)
- Temperature : 25°C
- Number of cells: 3 under same test condition (total: 156 cells)

## ❑ Schedules (# of conditions)

- BS : Baseline (3) – holding (aging) at different SOC levels
- FR : Frequency Regulation (4)
- PS : Peak Shaving (3)
- EV : Electric Vehicle (3)

# Degradation of Performance Metrics per Cycle

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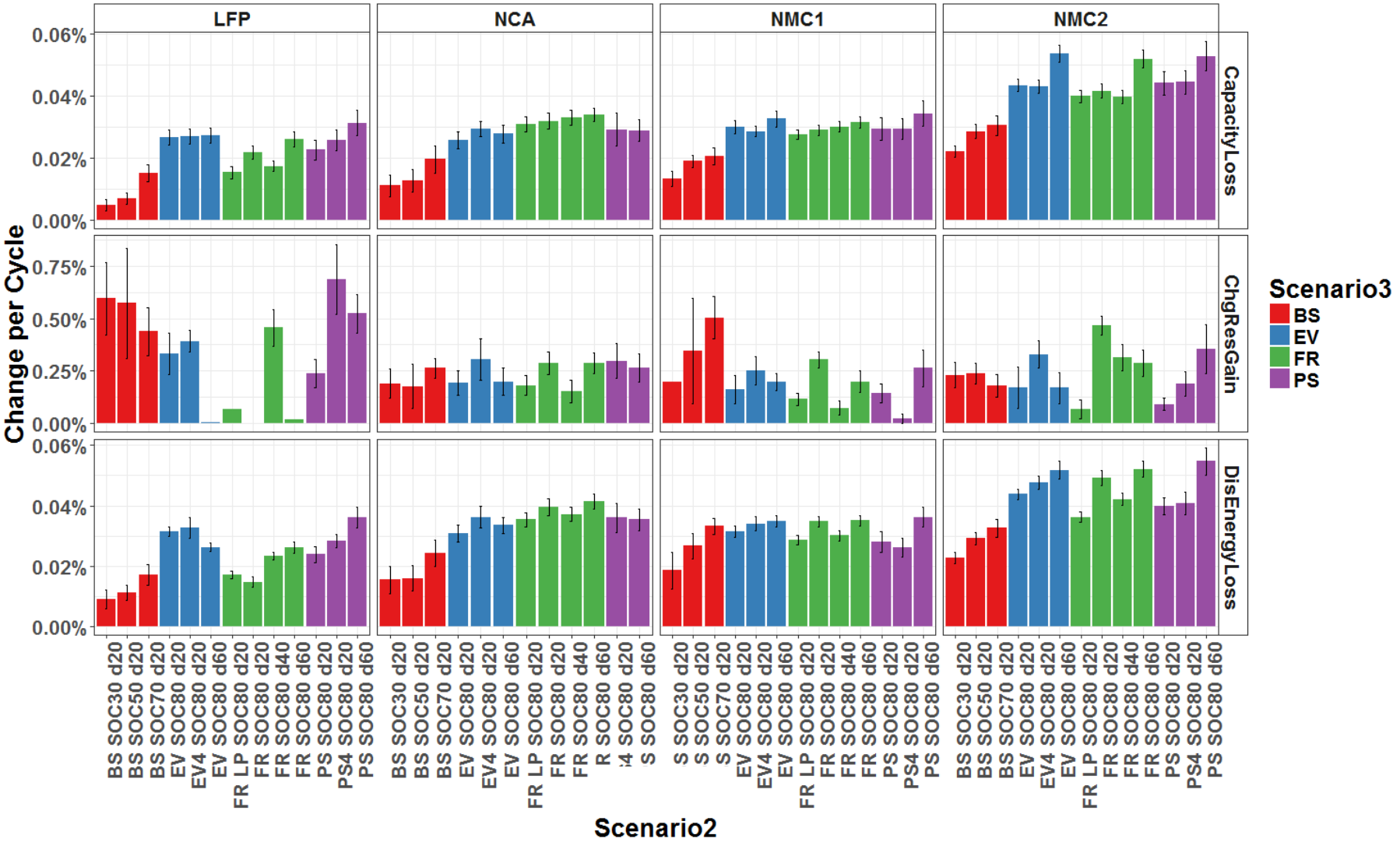


**Degradation rate - NMC2>NMC1>NCA>LFP**

**Great energy throughput leads to greater degradation**

# Comparison of Aging at 30% and 70% SOC

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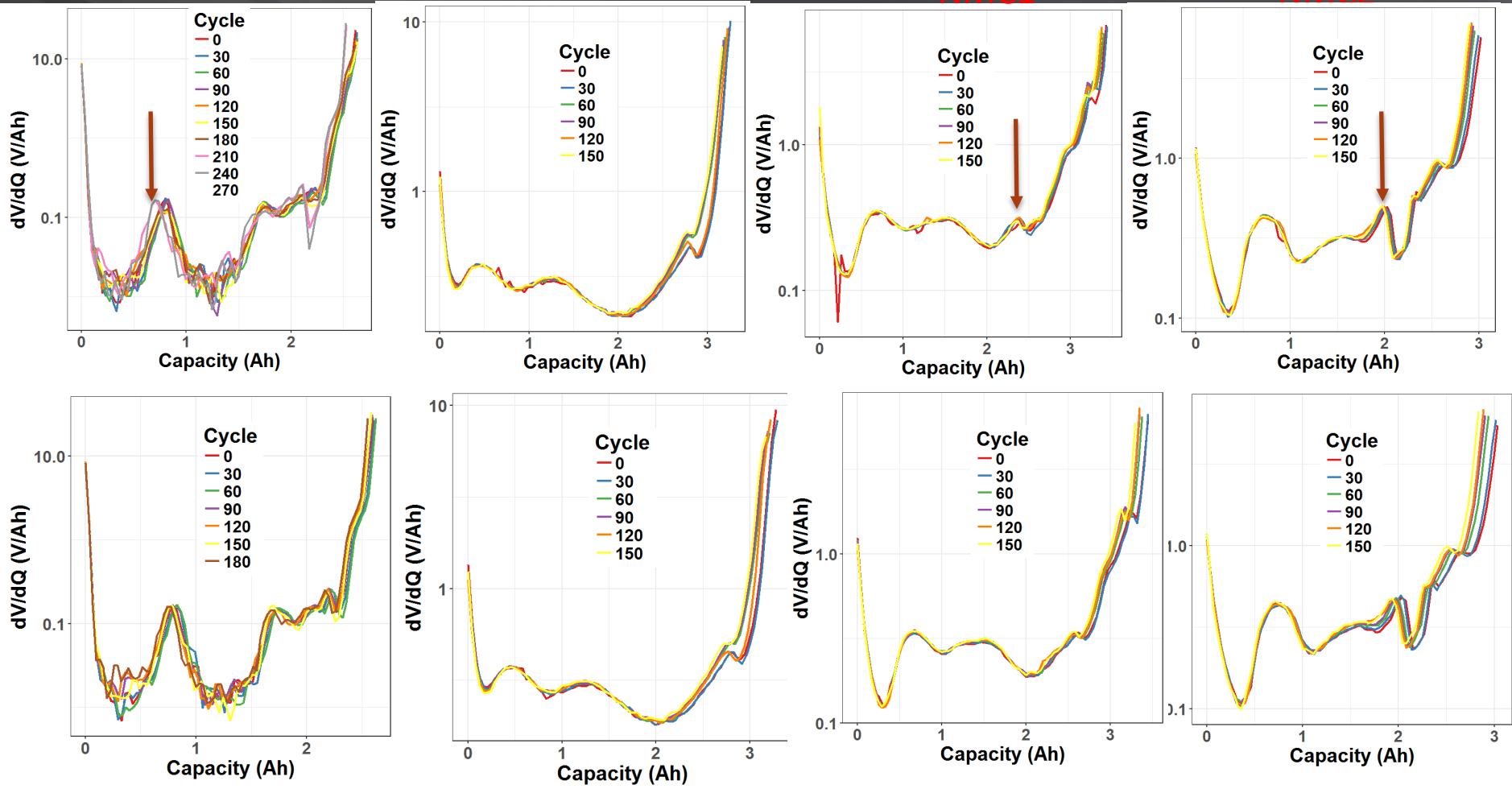
LFP NCA NMC1 NMC2

BS 30% SOC

BS 70% SOC




**First peak of anode occurs at higher SOC for LFP, high excess anode leads to low x in LixC6 at end of charge**
**Anode peaks shift due to loss of lithium. NMC2 ages fastest at 70% SOC. Little difference at 30% SOC**

# Comparison of Degradation for Electric Vehicle (EV) Drive Cycle

Pacific Northwest NATIONAL LABORATORY
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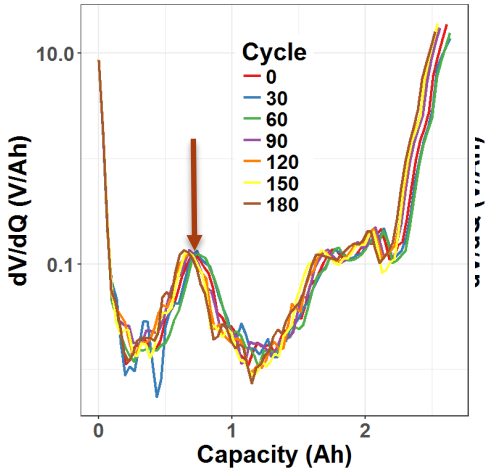
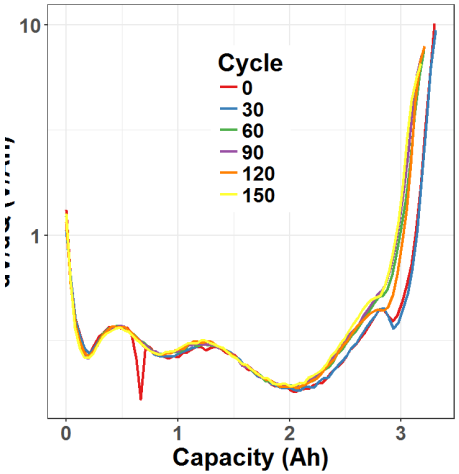
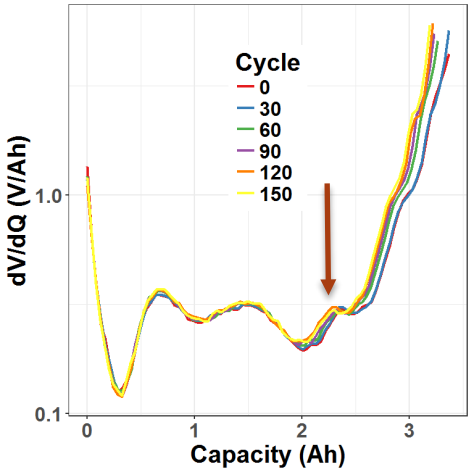
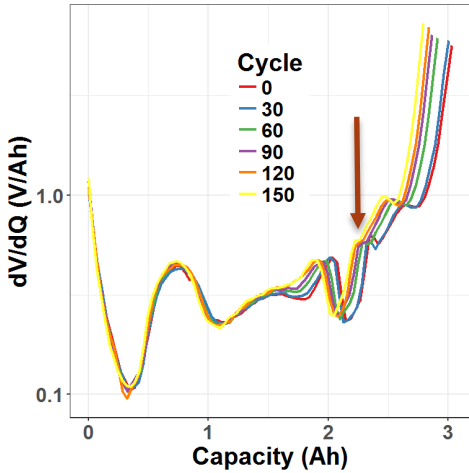
LFP NCA NMC1 NMC2

EV 20% DOD

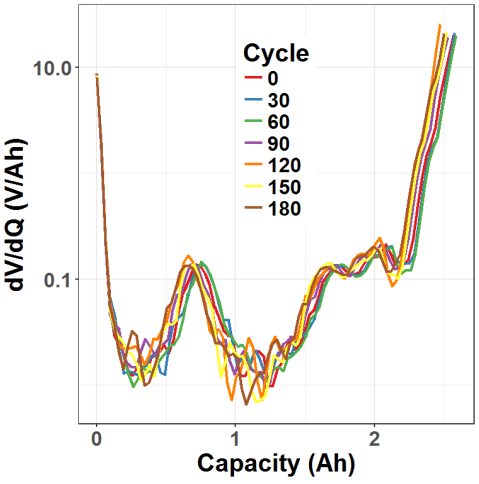


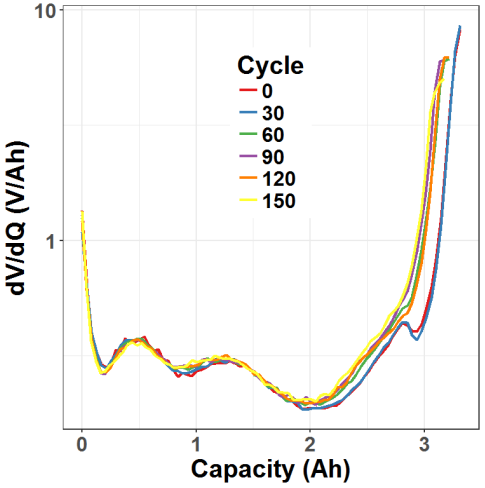



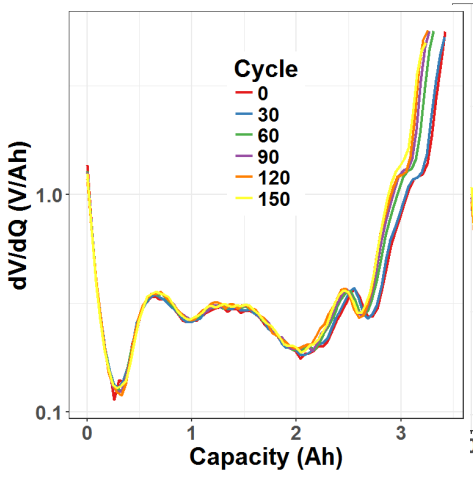



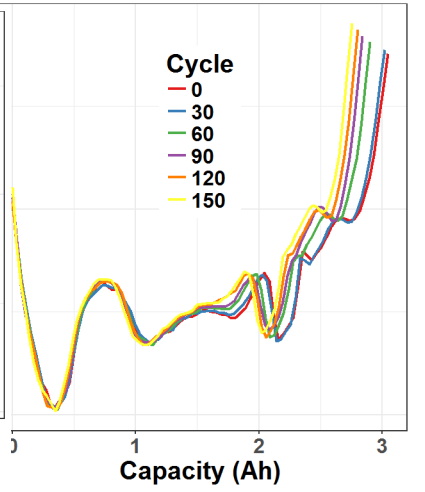




EV 60% DOD



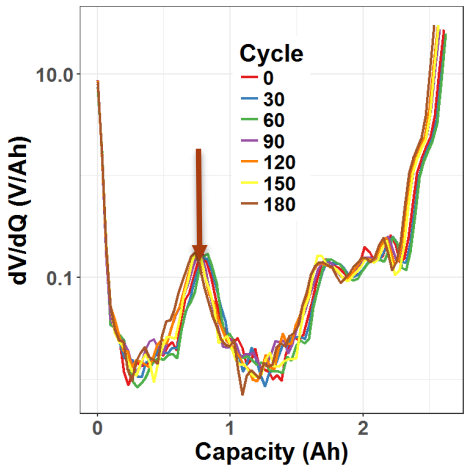

**Anode peaks shift due to loss of lithium. NMC2 ages fastest. Loss of capacity possibly due to transition metal dissolution. Little difference among other chemistries.**

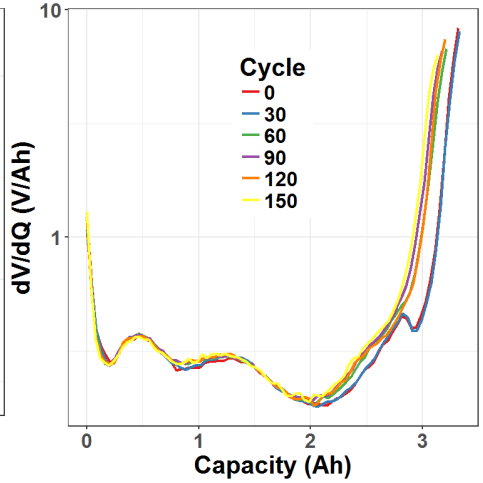
# Comparison of Degradation for FR Grid Service

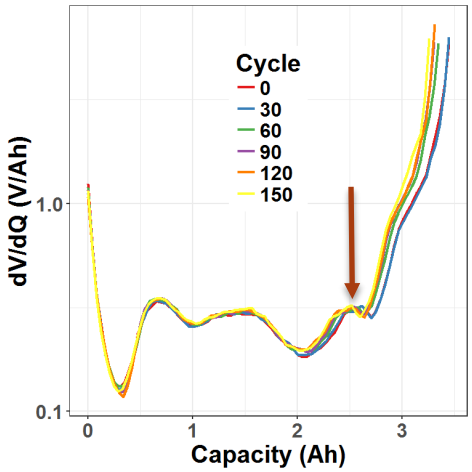
Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

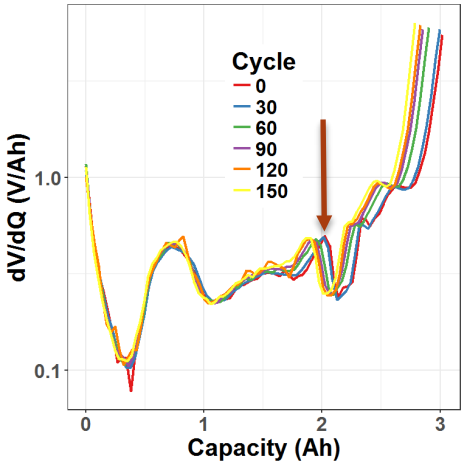
LFP NCA NMC1 NMC2

FR 20% DOD

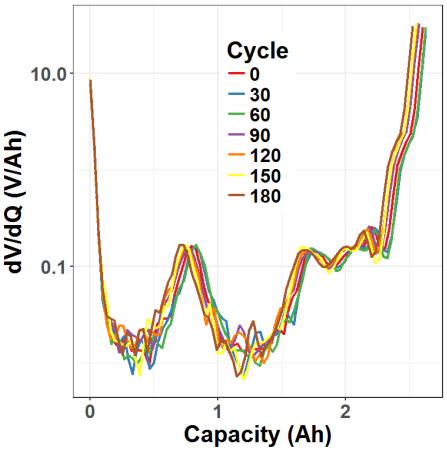


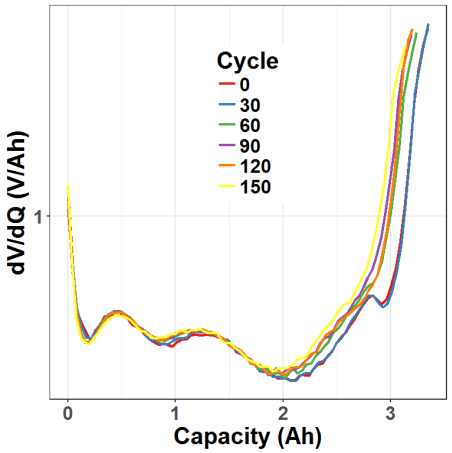



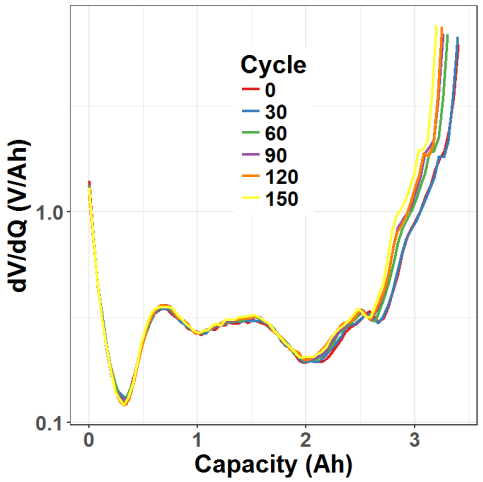



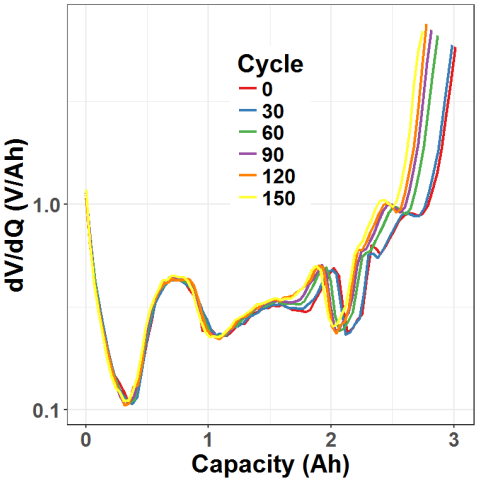




FR 60% DOD



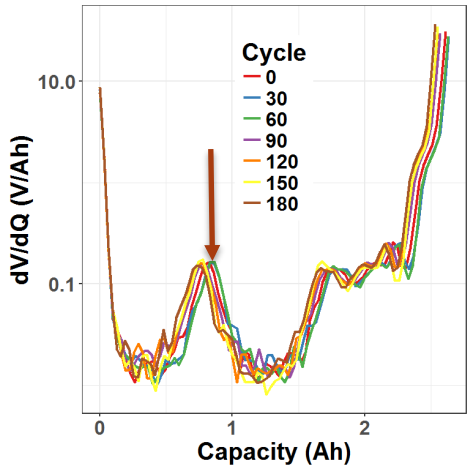

**Anode peaks shift due to loss of lithium. NMC2 ages fastest. Loss of capacity possibly due to transition metal dissolution. Little difference among other chemistries**

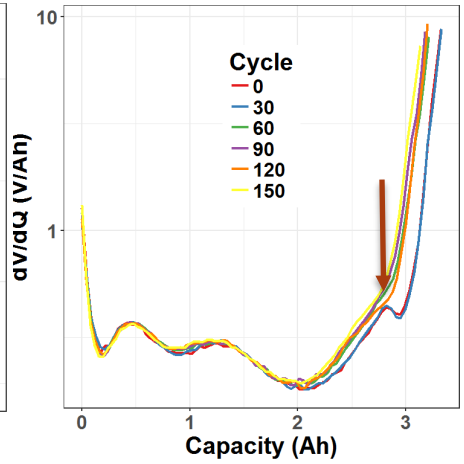
# Comparison of Degradation for PS Grid Service

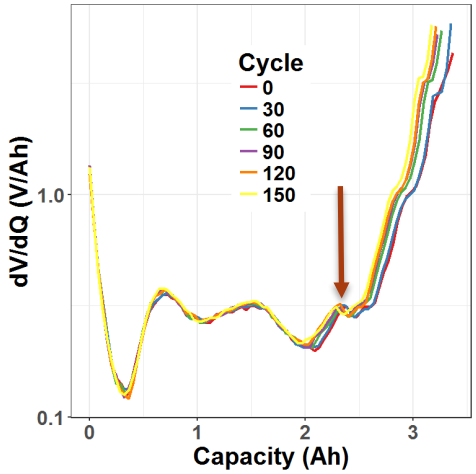
Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

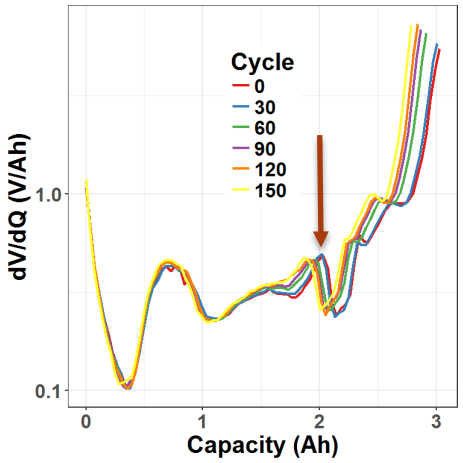
LFP NCA NMC1 NMC2

PS 20% DOD

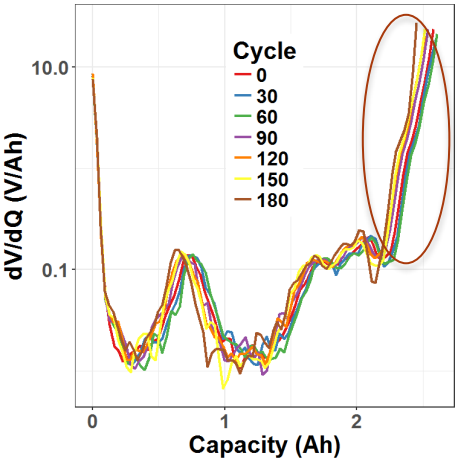


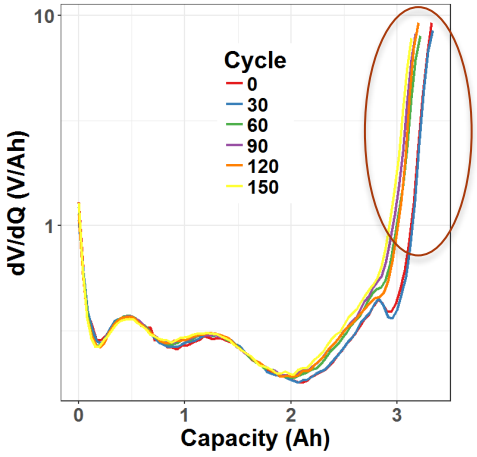



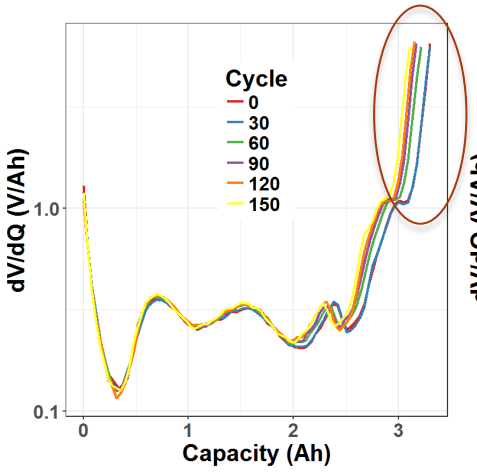



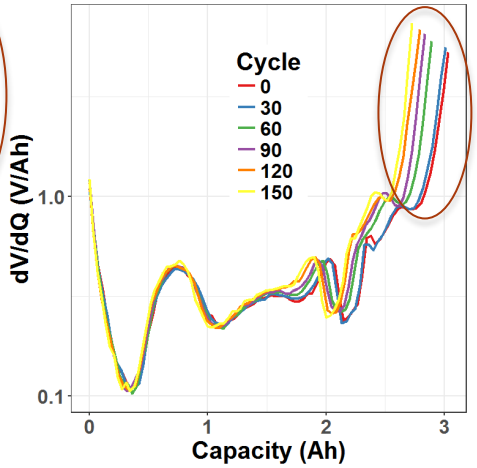




PS 60% DOD



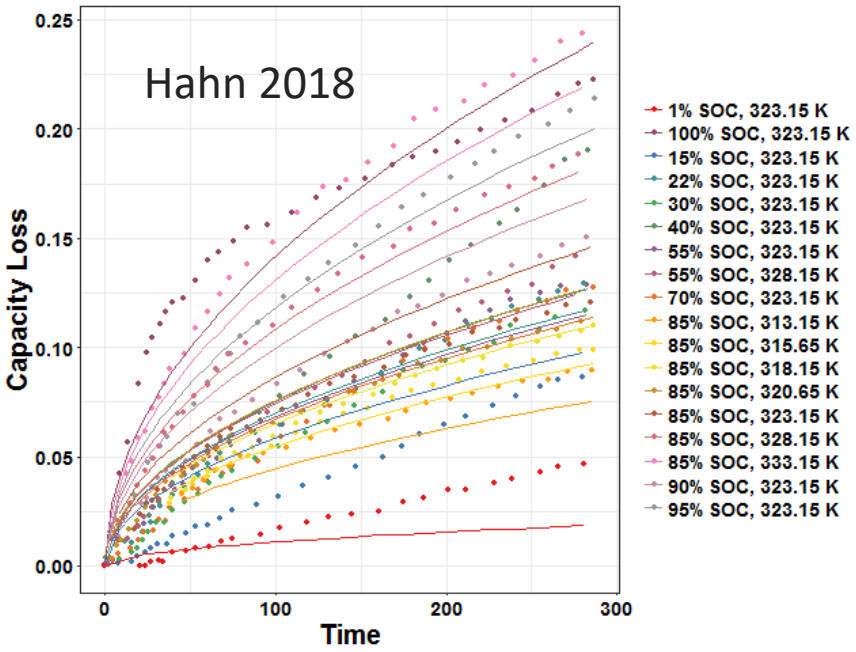



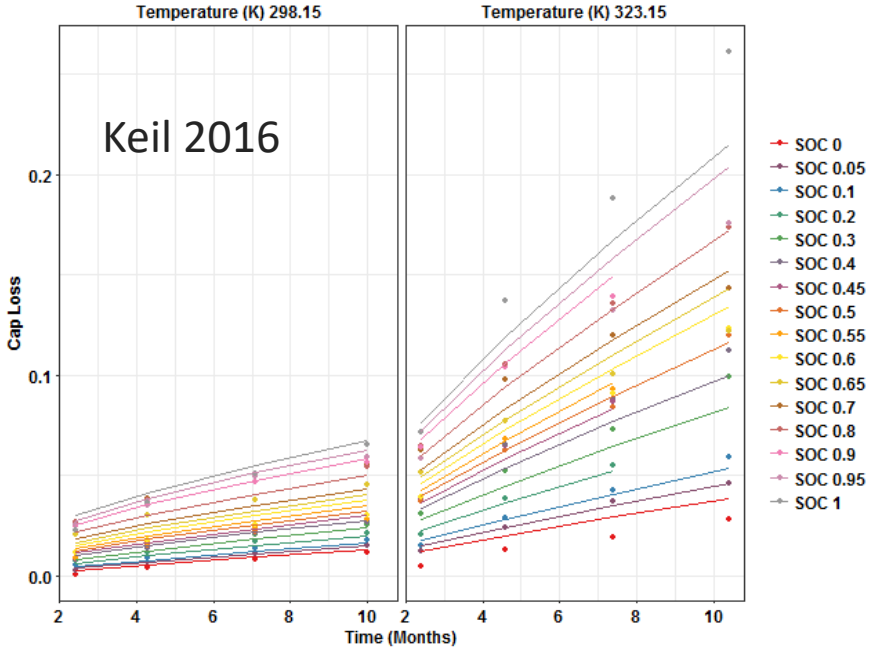




**Anode peaks shift due to loss of lithium. NMC2 ages fastest. Loss of capacity possibly due to transition metal dissolution. Little difference among other chemistries.**

# NMC Rest at Various SOC, T





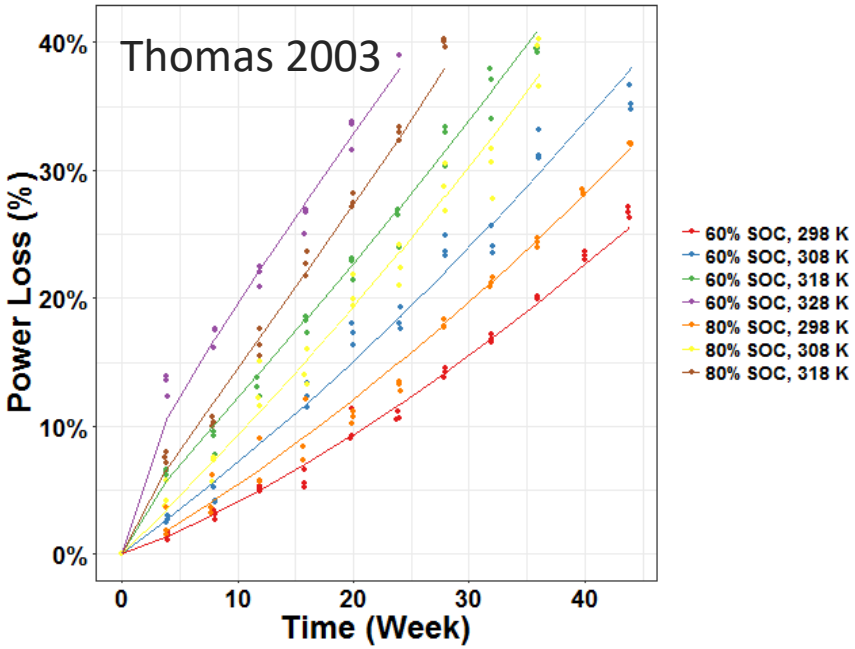

$t^{0.5}T^3SOC^3$
$t^{0.5}T^3$
$t^{0.5}SOC$
$t^{0.5}SOC^2$

$t^{0.5}T^3$, $t^{0.5}T^2$
$t*T^3$, $t^{0.5}*T$
$t^{0.5}SOC$, $t^{0.5}SOC*T$
$t*T^2$, $t^{0.5}T^3SOC^3$
$t*T^3SOC^3$, $t^{0.5}T^2SOC$

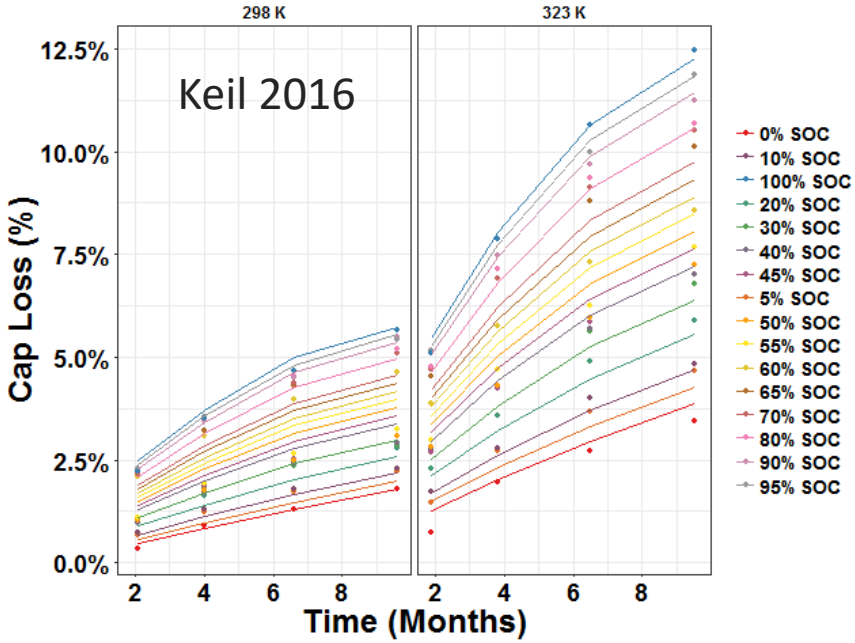
Hahn et al, J. Power Sources, **400** (2018) 402-414
Keil et al, J. Electrochem. Soc., **163** (9) A1872-1880 (2016)

# NCA Storage at Various T and SOC






$t^{0.5}T^2$, $t^{0.5}T$
$t^{0.5}T^3SOC$, $t^{0.5}$
$t^{0.5}SOC$, $t^{0.5}T^2SOC$
$t^{0.5}T*SOC$, $t^2T^3$

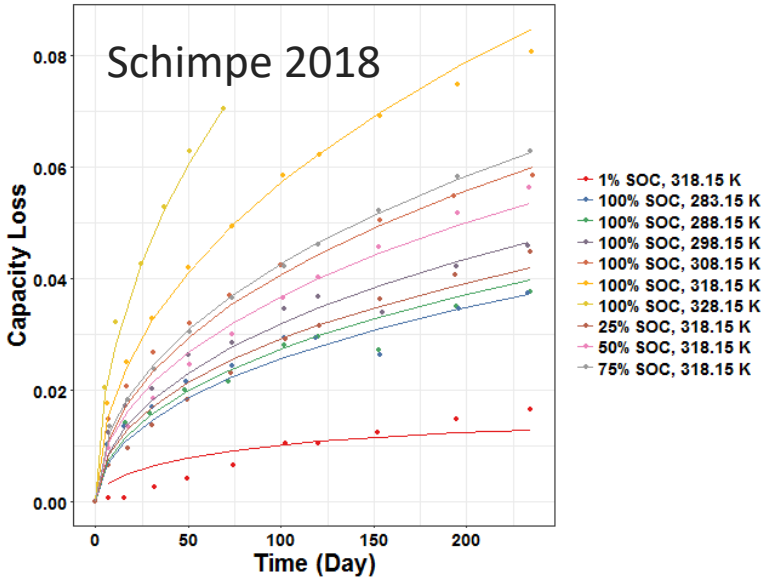


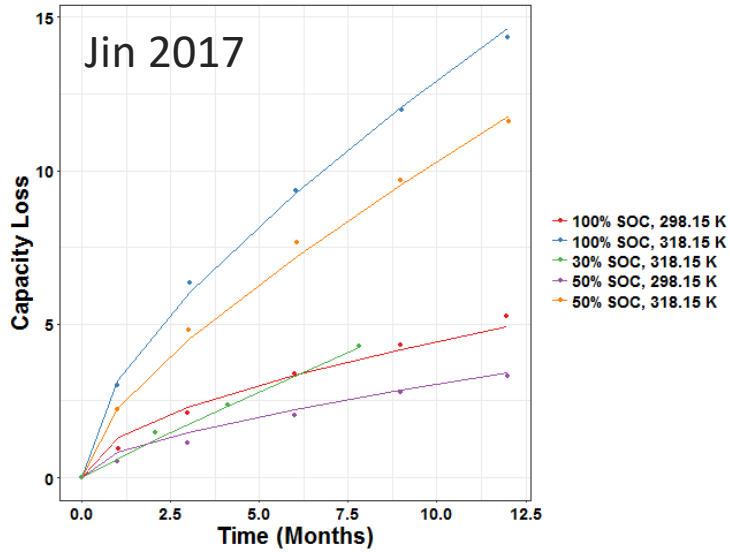

$t^{0.5}T^2$, $t^{0.5}T^3$
$t*T^3$, $t^3T^3SOC$
$t^{0.5}T$, $t^2SOC$
$t^{0.5}T^2SOC$

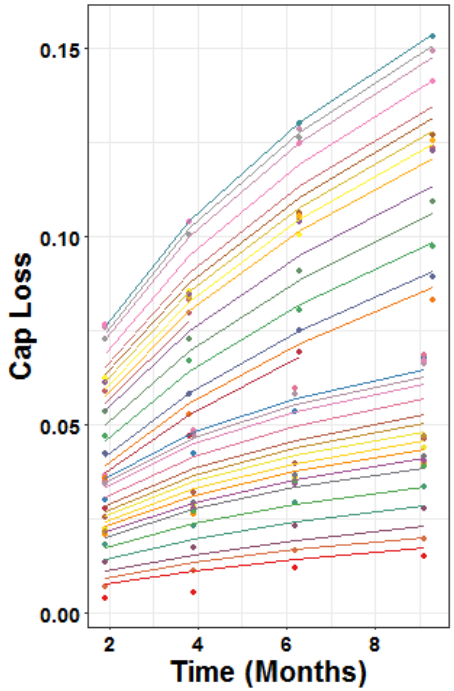
Thomas et al, Journal of Power Sources **124** (2003) 254–260
Keil et al, J. Electrochem. Soc., **163** (9) A1872-1880 (2016)

# LFP SOC and T





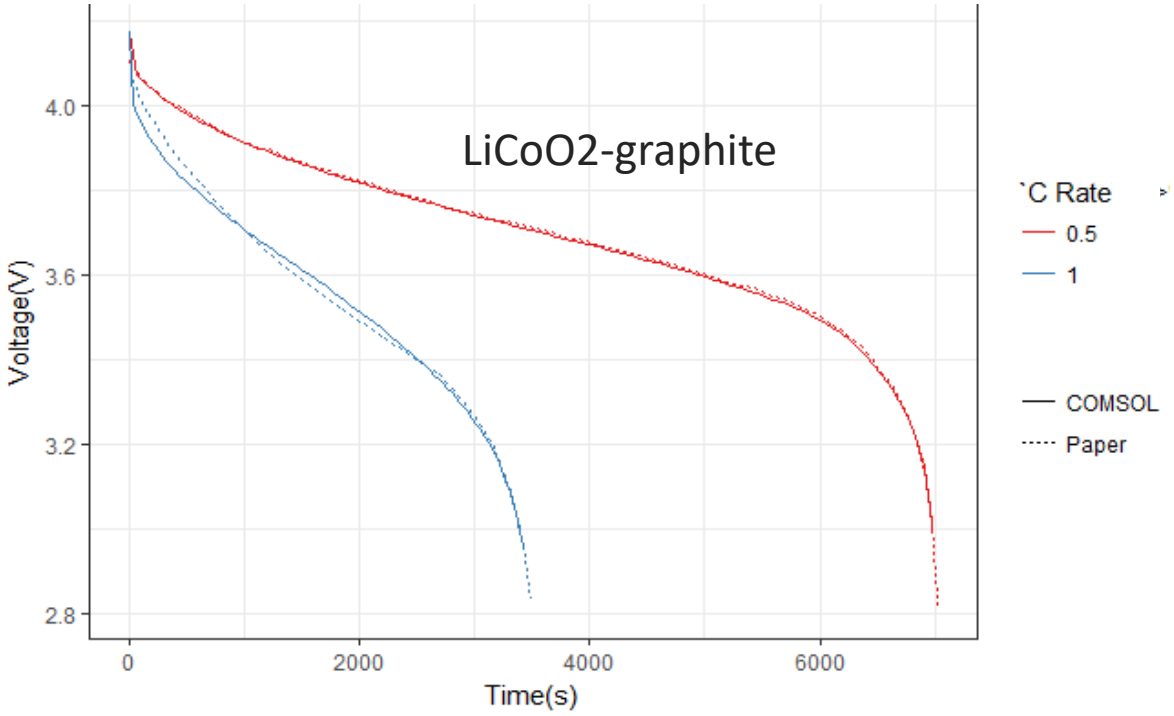

Keil 2016

0% SOC, 298.15 K
0% SOC, 323.15 K
10% SOC, 298.15 K
10% SOC, 323.15 K
100% SOC, 298.15 K
100% SOC, 323.15 K
20% SOC, 298.15 K
20% SOC, 323.15 K
30% SOC, 298.15 K
30% SOC, 323.15 K
40% SOC, 298.15 K
40% SOC, 323.15 K
45% SOC, 298.15 K
45% SOC, 323.15 K
5% SOC, 298.15 K
5% SOC, 323.15 K
50% SOC, 298.15 K
50% SOC, 323.15 K
55% SOC, 298.15 K
55% SOC, 323.15 K
60% SOC, 298.15 K
60% SOC, 323.15 K
65% SOC, 298.15 K
65% SOC, 323.15 K
70% SOC, 298.15 K
70% SOC, 323.15 K
80% SOC, 298.15 K
80% SOC, 323.15 K
90% SOC, 298.15 K
90% SOC, 323.15 K
95% SOC, 298.15 K
95% SOC, 323.15 K

Schimpe et al, J. Electrochem. Soc,, **165** (2) A181-A193 (2018)
Keil et al, J. Electrochem. Soc., **163** (9) A1872-1880 (2016)
Jin et al, Conference Paper, May 2017, DOI: 10.23919/ACC.2017.796293

# COMSOL Model Validation






Use electrode, electrolyte parameters from literature

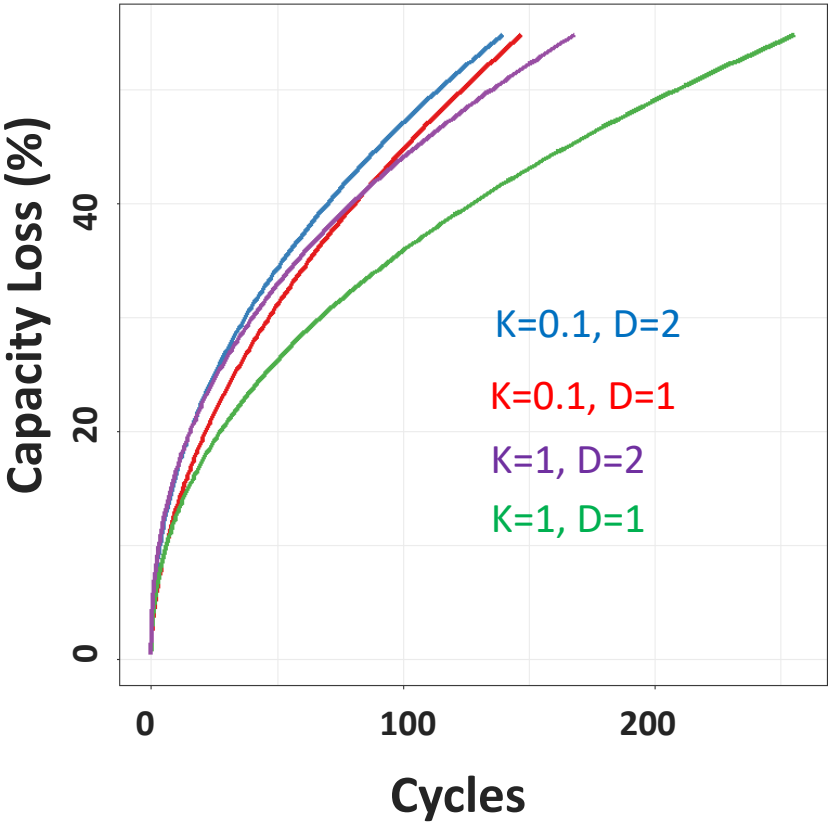
Modeled C/2 and C rate discharge

Dao et al, J. Power Sources 198 (2012) 329– 337

# Bottom up Model – Effect of Exchange Current and Diffusivity (SEI)



Vary diffusion coefficient of solvent through SEI $D_{solv}$
Vary kinetic rate constant for SEI reaction $k_{SEI}$
Multiples of $k_{SEI}$ and $D_{solv}$ used as parameters




- Decreasing rate constant increased capacity loss – unexpected
- Need to use total current times the SEI layer electronic resistance to calculate potential drop across SEI layer overpotential for both intercalation and SEI growth reactions
  - SEI reaction current was used for overpotential of SEI layer reaction
  - Intercalation reaction current was used for intercalation overpotential estimation
- Lessons learned!