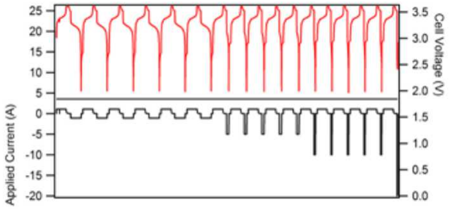
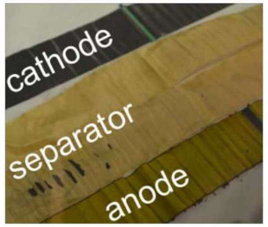
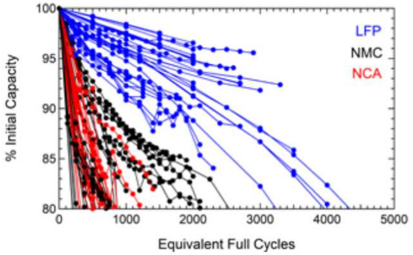
SAND2019-14129PE

# Degradation of Commercial Li-ion Cells Beyond 80% Capacity




*PRESENTED BY*

Yuliya Preger

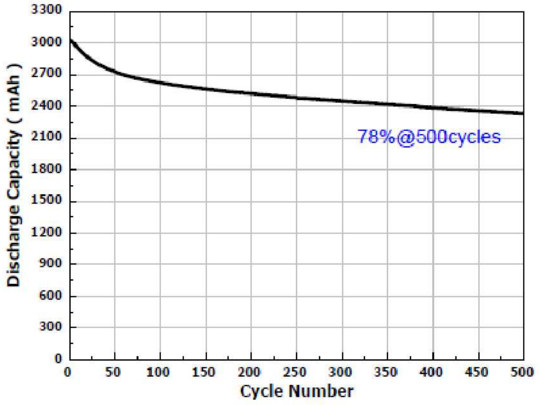
Battery Safety Council Forum 8

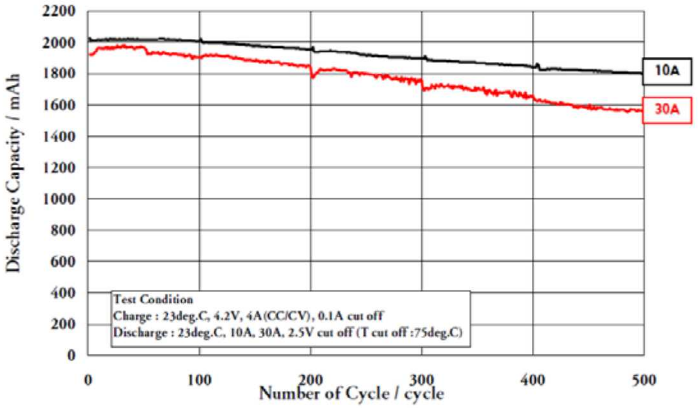
November 20, 2019

# Moving Beyond 80% Capacity for Grid Applications

- 80% capacity is common reference point in manufacturer spec sheets

**Examples:**



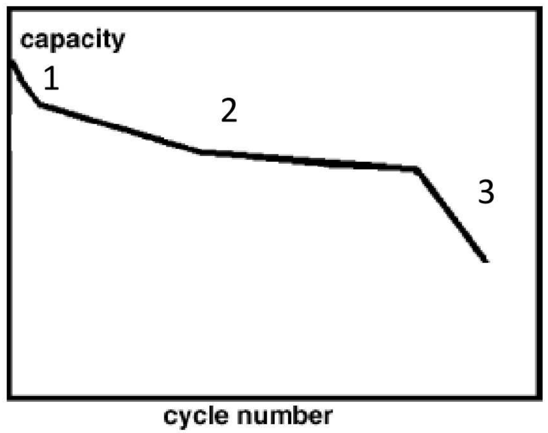

- 80% capacity is a holdover from the EV world
  - USABC 1996: "*EV batteries should be removed from automotive use when* ***current battery capacity is 80% of initial battery capacity*** *and current battery power capability is 80% of initial battery power capability*"
  - at this time, EVs were primarily powered by Ni-based batteries

- Unrealistic criteria for Li-ion batteries with higher energy density and power capability?

# How Far Beyond 80% Should We Go?

**One possible criteria: until a battery undergoes rapid degradation**

- Typical model of LiB degradation assumes a transition from linear behavior
  - Phase 1: SEI formation
  - Phase 2: linear degradation
  - Phase 3: rapid capacity fade (80% capacity assumed in this region)



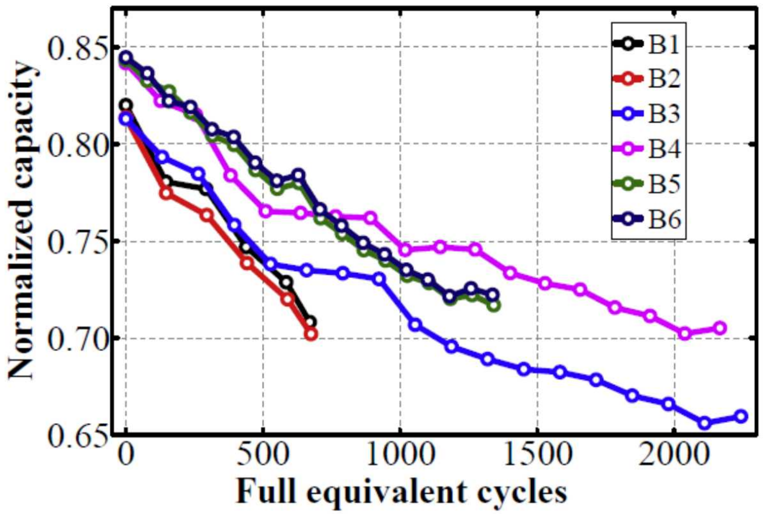

Spotnitz et al. *J. Power Sources* **2003**, *113*, 72.

- Transition to rapid capacity fade has many names
  - Transition point, tipping point, knee, rollover

- Transition to rapid capacity fade has many nuanced explanations
  - General resistance increase at anode
  - Li plating at anode
  - Electrode dry-out
  - Cathode processes (degradation or resistance increase)

# Position of Knee Highly Dependent on Cycling Conditions

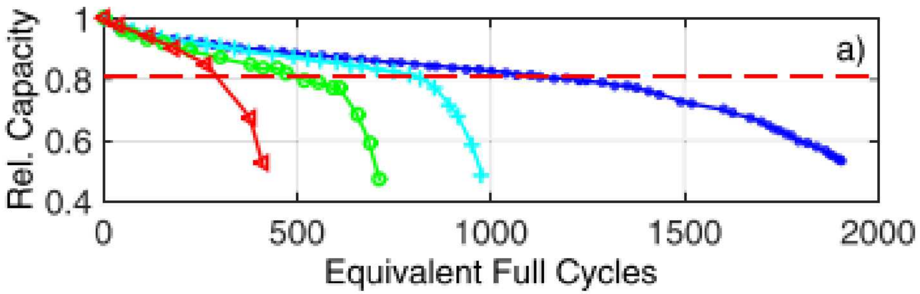
No knee down to 65% capacity

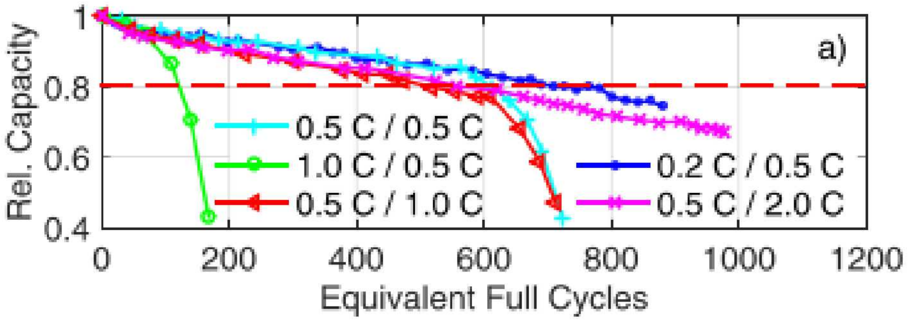



60Ah LFP cells cycled with various load profiles

Jiang et al. *J. Clean. Prod*. **2018**, *205*, 754.

Knee at ~80% capacity, but also earlier or later



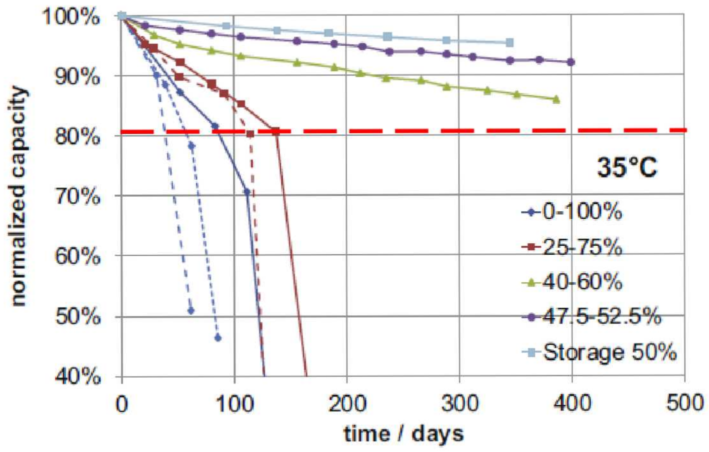



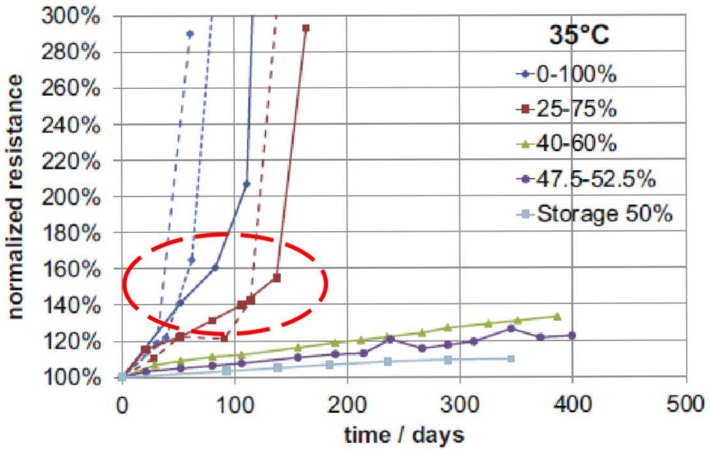

18650 1.95Ah NMC cells cycled with various temperatures, DOD, charge/discharge rate

Schuster et al. *J. Energy Storage* **2015**, *1*, 44.

# Rapid Capacity Fade Due to Resistance Increase

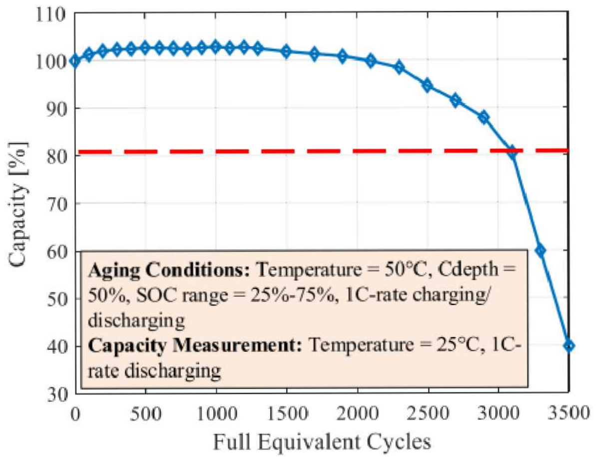
Tipping point coincides with resistance increase of ~150%

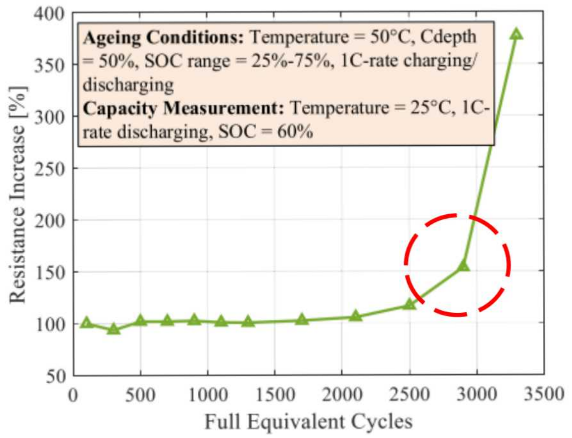



Sanyo 18650 2.05Ah NMC/graphite cells

Ecker et al. *J. Power Sources* **2014**, *248*, 839.

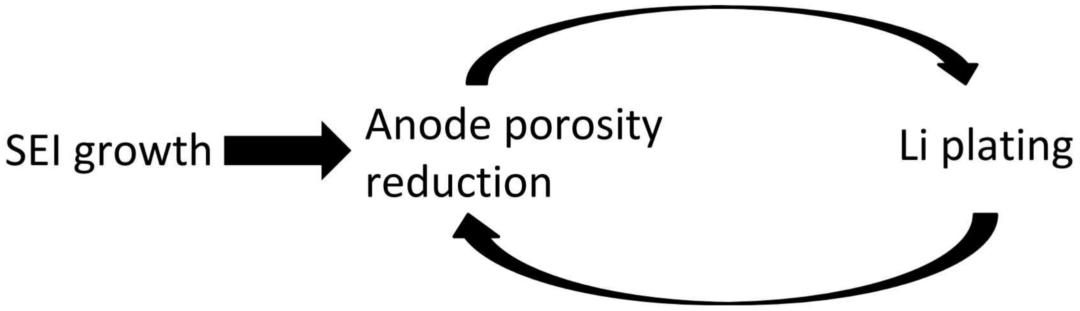


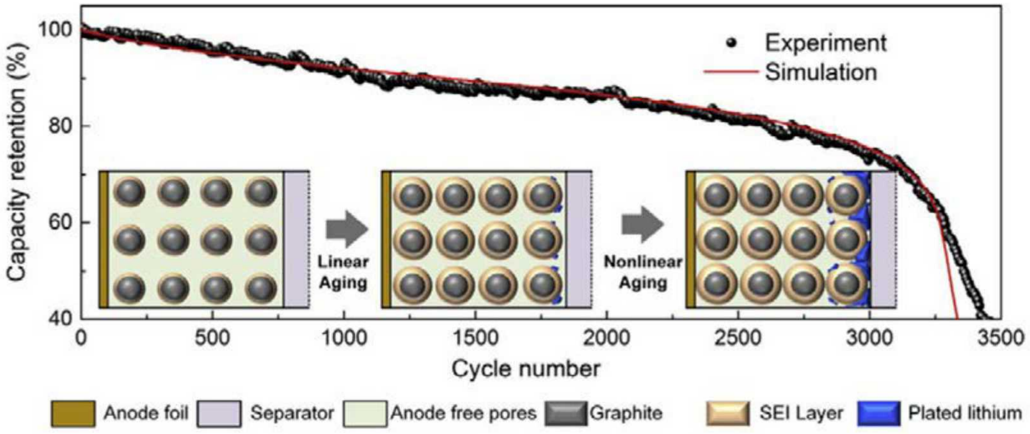




13Ah NMC/LTO cells

Stroe et al. *Microelectron. Reliab.* **2018**, *88-90*, 1251.

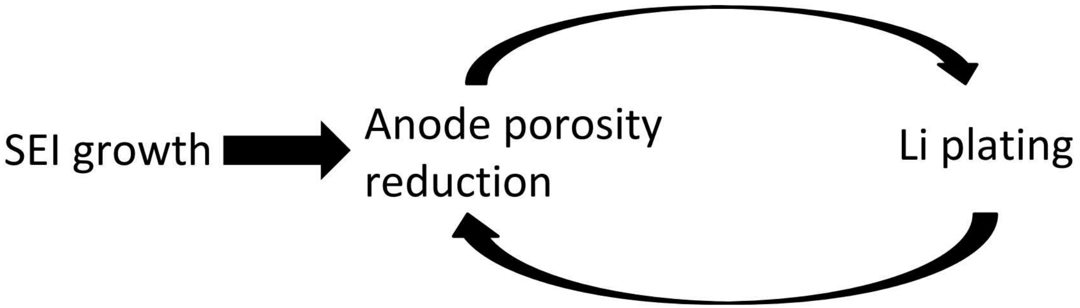
# Li Plating as Cause of Rapid Resistance Increase

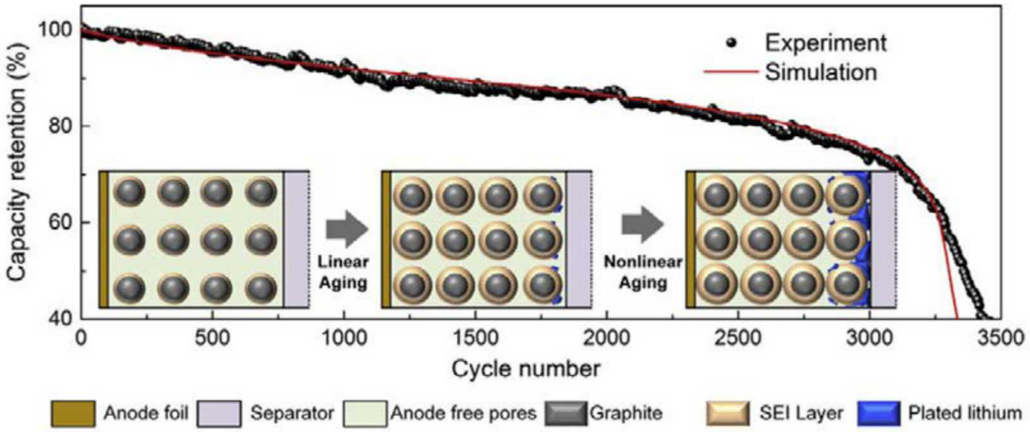



Yang et al. *J. Power Sources* **2017**, *360*, 28.

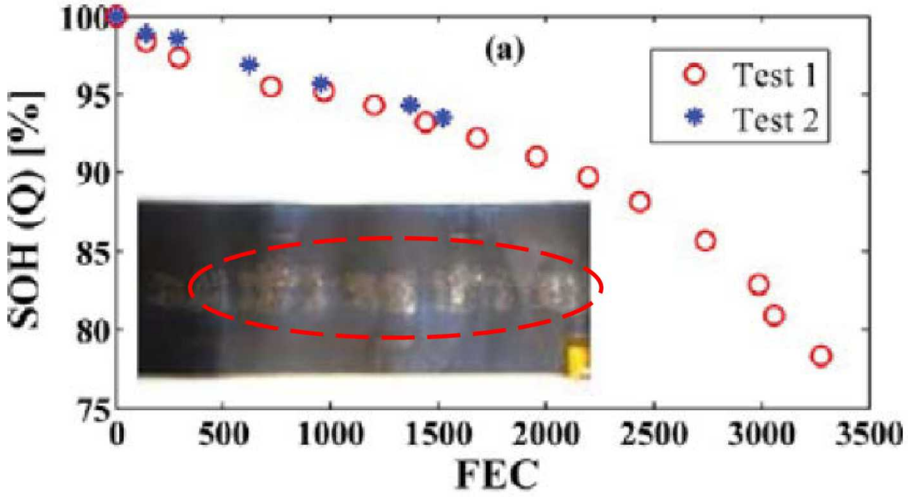
# Li Plating as Cause of Rapid Resistance Increase



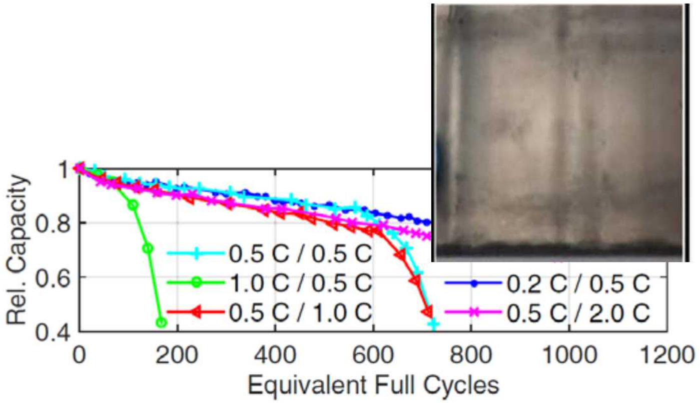




Yang et al. *J. Power Sources* **2017**, *360*, 28.

Deposits of Li observed on anode, while cathode unmodified



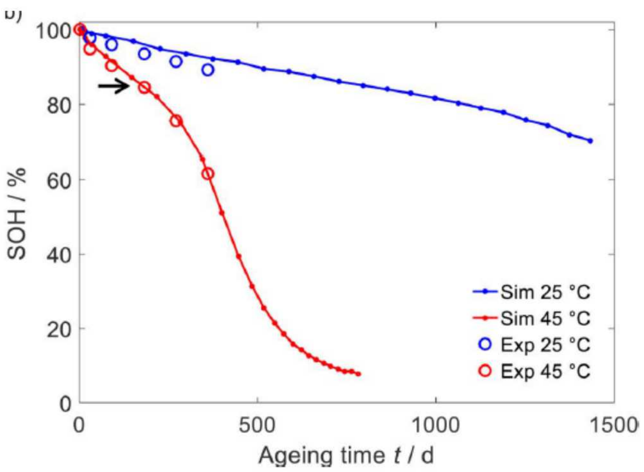

Sarasketa-Zabala et al. *J. Phys. Chem. C* **2015**, *119*, 896.

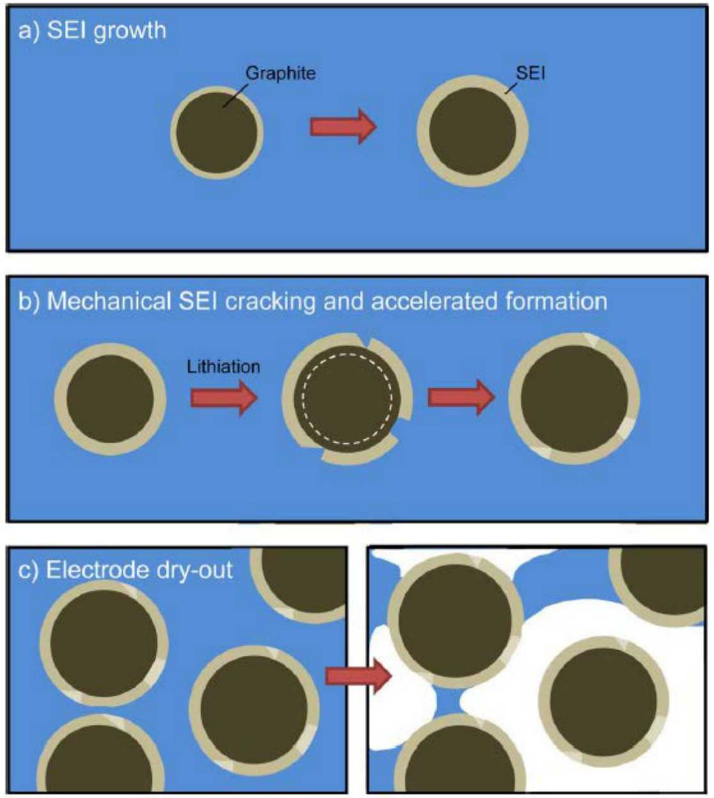



Bach et al. *J. Energy Storage* **2016**, *5*, 212.

# Rapid Capacity Fade due to Electrode Dry-Out

- SEI formation reactions generate gas
- Gas bubbles lead to a loss of contact between active material and electrolyte
- Model fits the data, but no explicit experimental confirmation of phenomenon



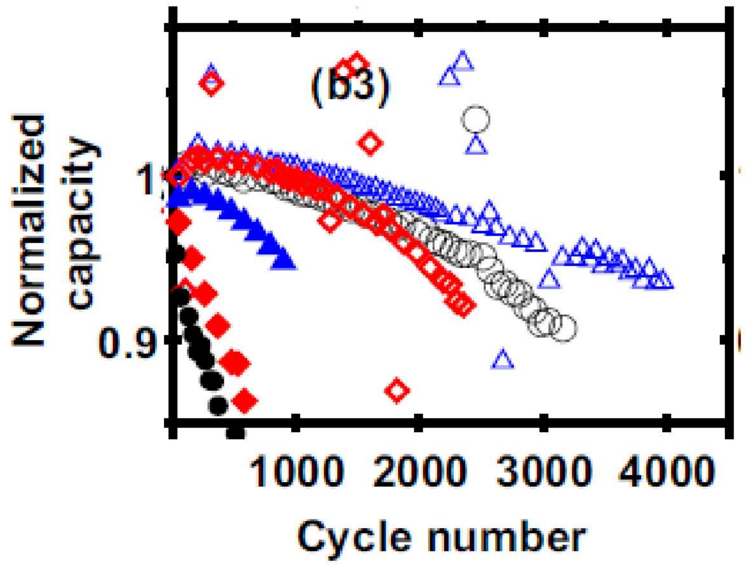

Kupper et al. *J. Electrochem. Soc.* **2018**, *165*, A3468.

# Rapid Capacity Fade due to Cathodic Processes

- Rollover due to impedance growth at positive electrode

- Impedance growth associated with higher charging voltage and electrolyte oxidation

- No change in anode impedance and no Li plating observed on cells past tipping point





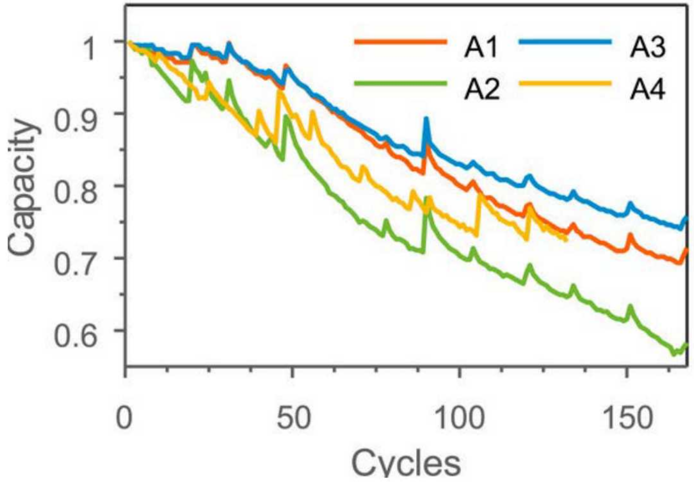
Ma et al. *J. Electrochem. Soc.* **2019**, *166*, A711.

# Limited Materials Insight and Cycling Data Means Limited Predictive Capability

What is the remaining useful life (RUL) of a battery?

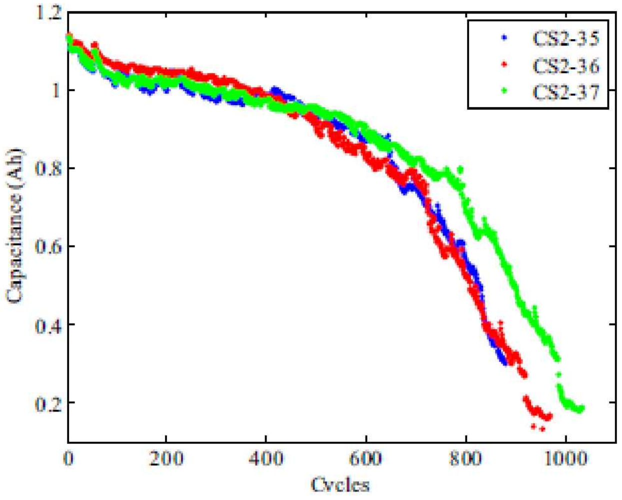
- Most studies calculate RUL with threshold of 75-85% capacity
- Most studies only model data in linear degradation region
- Of models that consider a 'knee,' most based on just one experimental data set

Typical linear data set in RUL model




Richardson et al. *J. Power Sources* **2017**, *357*, 209.

One data set with knee used by dozens of models/studies




Sun et al. *Microelectron. Reliab.* **2018**, *88-90*, 1189.

# Recent Modeling Includes More Knee Data, but is Still Empirical

**Goal of study**: Develop accelerated degradation model as a function of stress factors to predict capacity fade under normal operating conditions

## Scope

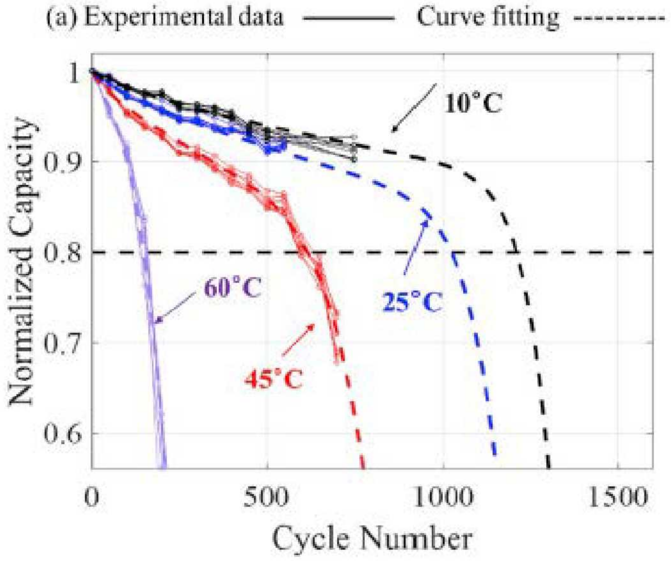
- 3.36Ah LCO/graphite pouch cells
- 24 conditions x 8 cells each

Cycling test matrix.

| Charge cut-off C-rate | Ambient temperature (°C) | | | | Discharge C-rate |
|---|---|---|---|---|---|
| | 10 | 25 | 45 | 60 | |
| C/5 | Test # 1 | # 7 | # 13 | # 19 | 0.7C |
| C/40 | # 2 | # 8 | # 14 | # 20 | |
| C/5 | # 3 | # 9 | # 15 | # 21 | 1C |
| C/40 | # 4 | # 10 | # 16 | # 22 | |
| C/5 | # 5 | # 11 | # 17 | # 23 | 2C |
| C/40 | # 6 | # 12 | # 18 | # 24 | |

## Outcome

$$NDC = f(N,\ T) = 1 - \exp(A * T + B)\ \ {}^*N^{b_1} - \exp(C * T + D){}^*N^{E^*T+F}$$




Diao et al. *J. Power Sources* **2019**, *435*, 226380.
Diao et al. *Energies* **2019**, *12*, 2910.

# Next Steps: Expand Electrochemical and Materials Data Sets of Commercial Cells Beyond 80% Capacity

**Goal**: Complete large-scale, long-term cycling study beyond 80% capacity to understand what causes and how to delay tipping point

- Include materials characterization at various points in lifetime

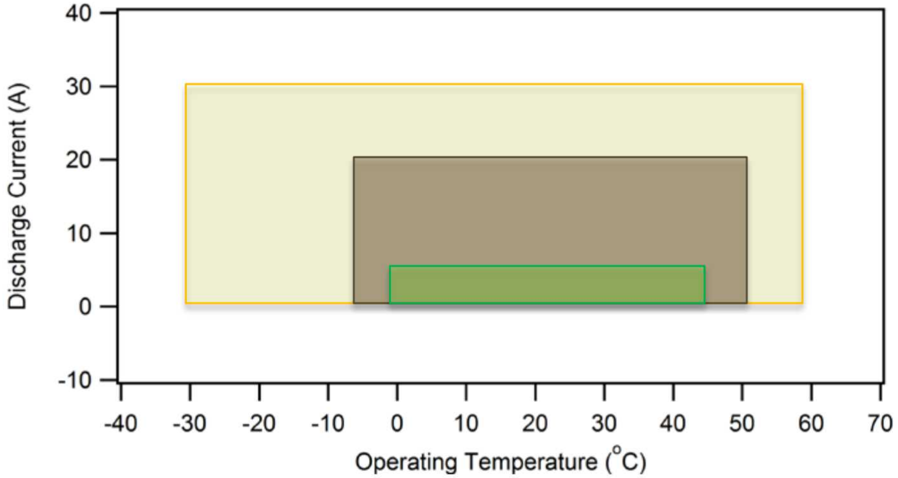
**Key Questions**

1) What materials mechanism leads to rapid fade? Are there multiple?
2) If ESS installation with fresh batteries, how to predict RUL to knee based on full cycling history?
3) If ESS installation with $2^{nd}$ life cells, how to predict RUL to knee if limited knowledge of previous capacity fade?
4) How much advance warning/buffer is needed prior to rapid degradation?

# Scope of Current Study at SNL: Cells and Manufacturer Specifications

| Cathode Chemistry | AKA | Vendor | Specific Capacity (Ah) | Max Discharge Current | Acceptable Temperature (°C) |
|---|---|---|---|---|---|
| $LiFePO_4$ | LFP | A123 | 1.1 | 30 | -30 to 60 |
| $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ | NCA | Panasonic | 3.2 | 6 | 0 to 45 |
| $LiNiMnCoO_2$ | NMC | LG Chem | 3.0 | 20 | -5 to 50 |

LFP NCA NMC

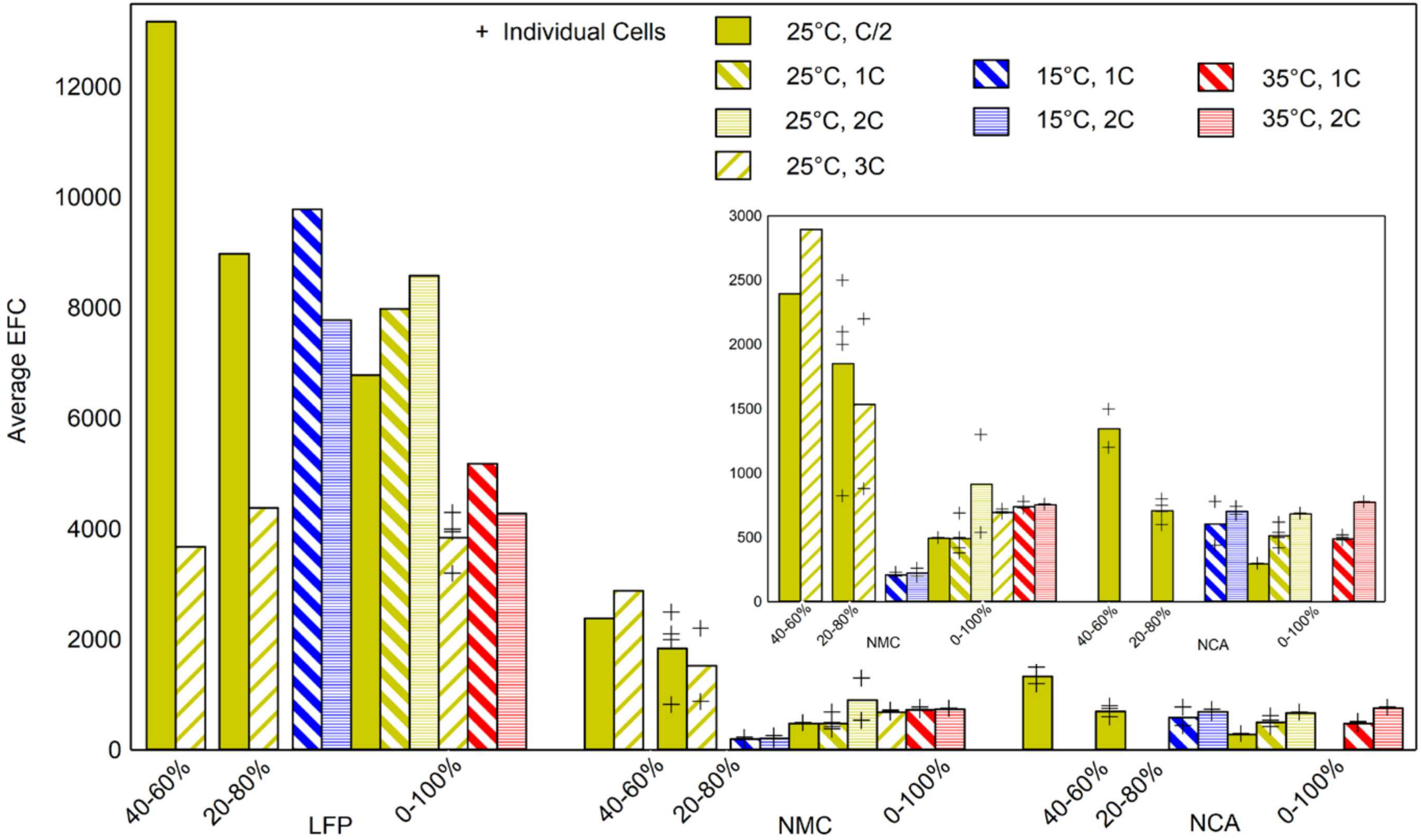



Variables:

- Charge Rate: C/2
- Discharge Rate: C/2, 1C, 2C, 3C
- SOC Range: 40-60%, 20-80%, 0-100%
- Temperature: 15°C, 25°C, 35°C

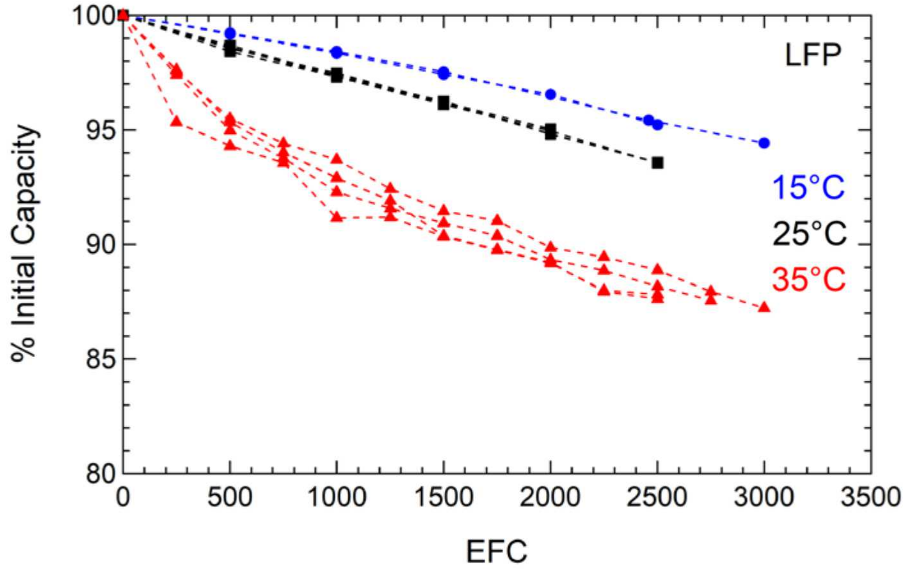
# Cycle Count to 80% Capacity

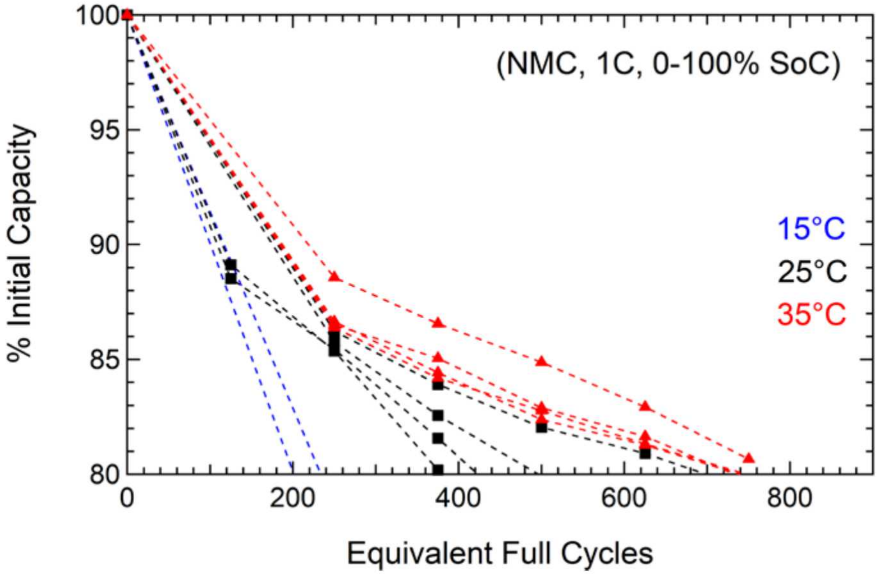
Performance highly variable even within manufacturer specs

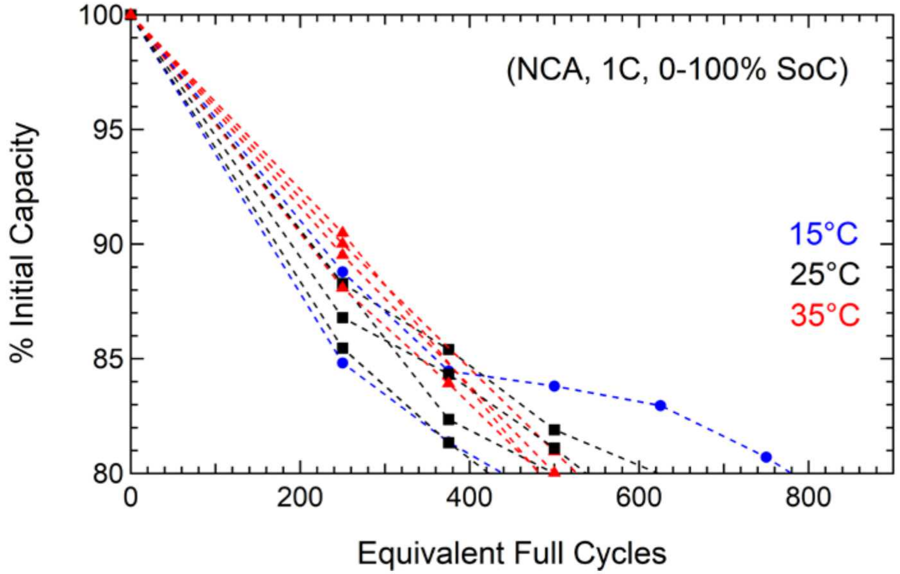



Value extrapolated for LFP cells that have not yet reached 80% capacity

# Long-Term Cycling: Temperature Dependence

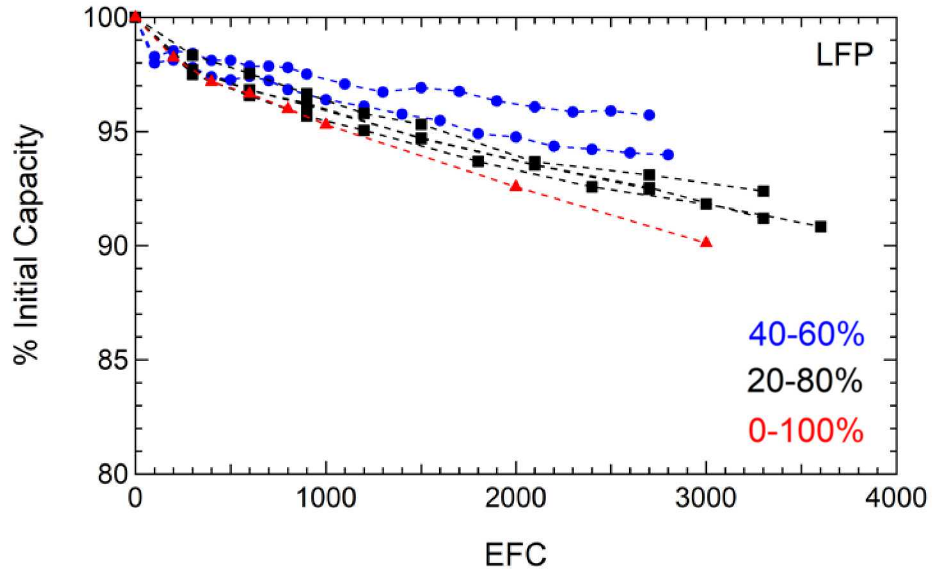


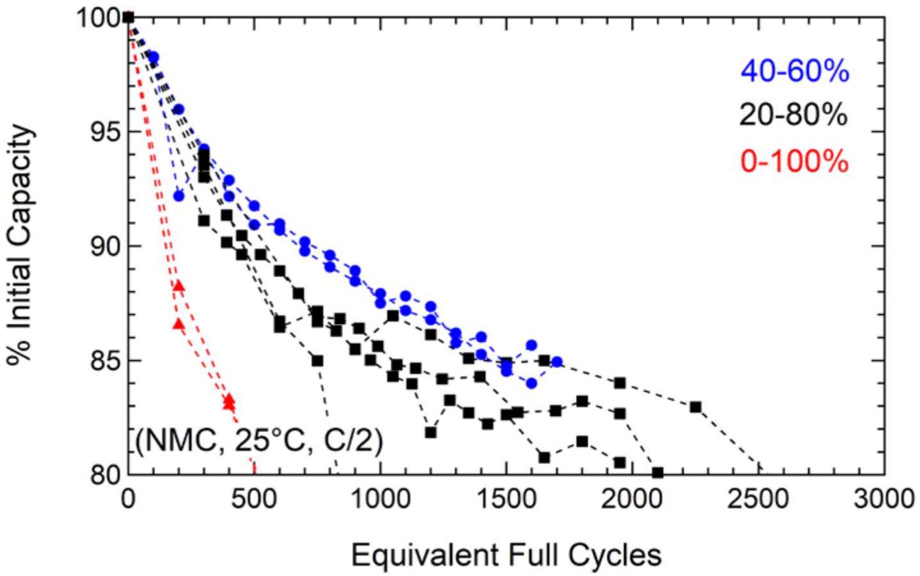



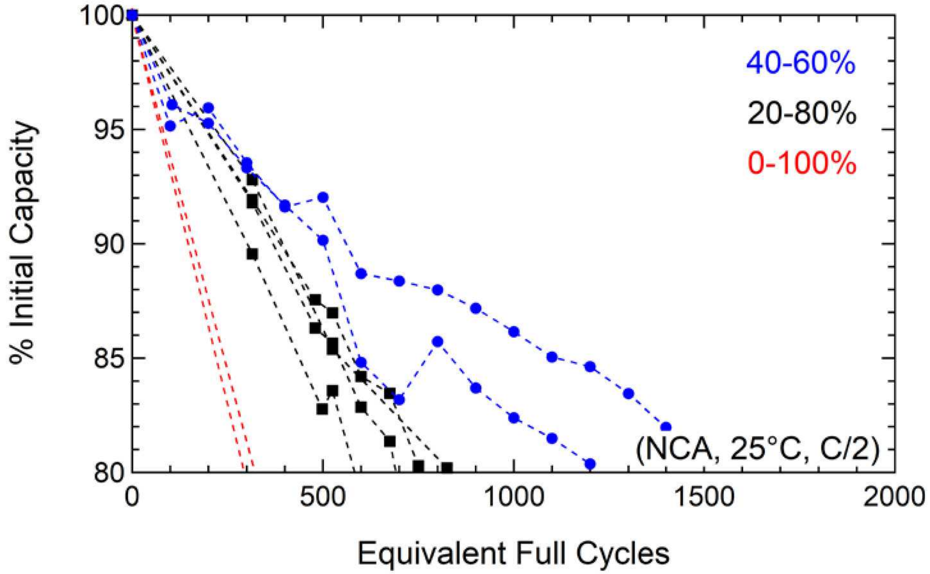




LFP and NMC exhibit inverse dependence on temperature (switch in degradation mechanism)

# Long-Term Cycling: SOC Dependence

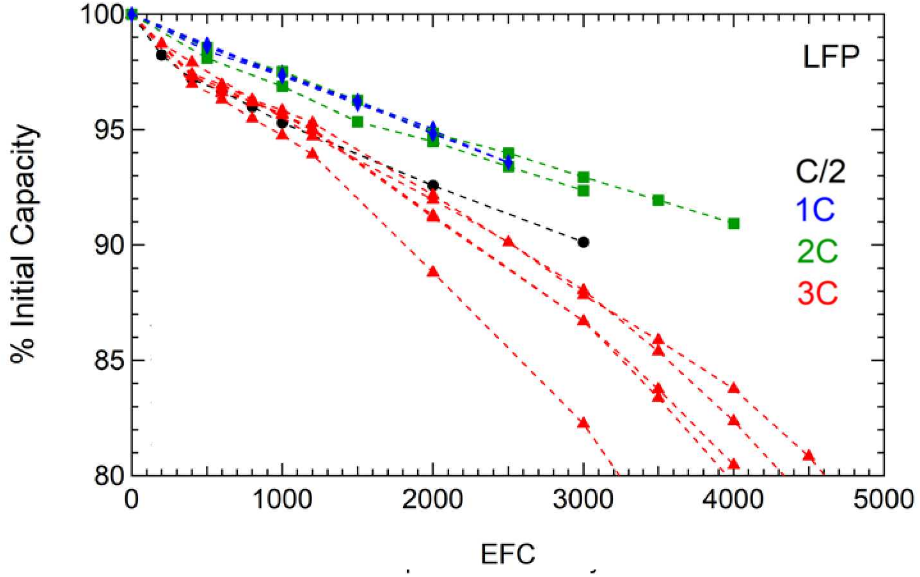


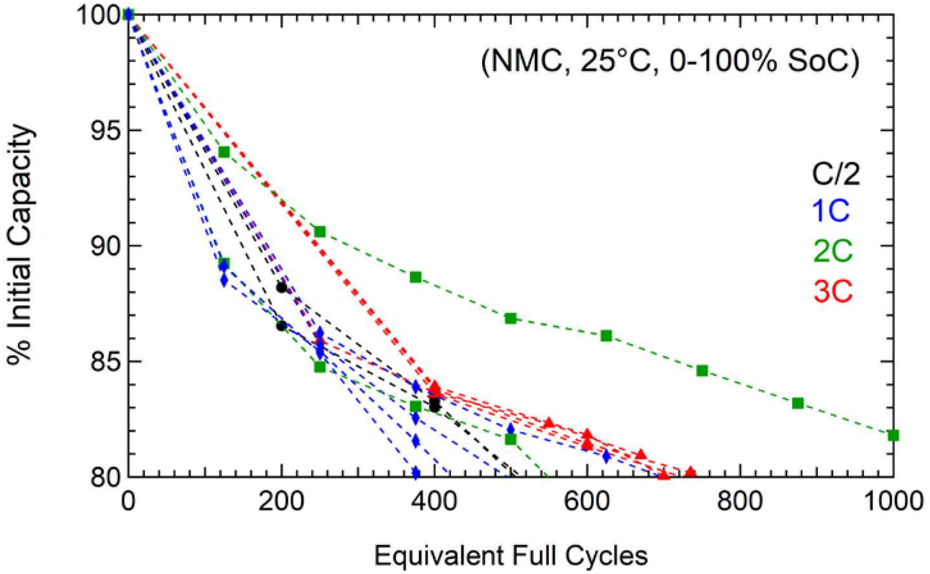



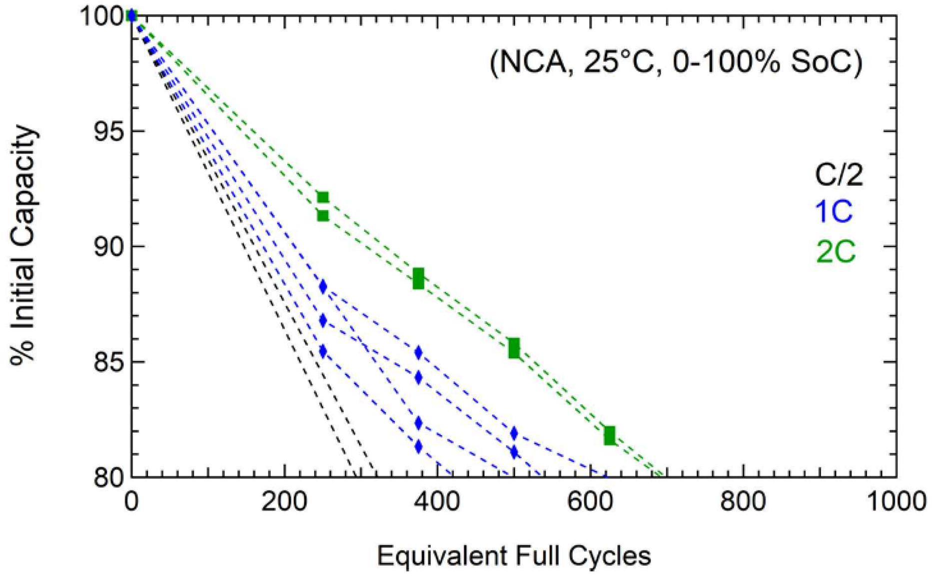




NCA and NMC more sensitive to full discharge

# Long-Term Cycling: Discharge Rate Dependence

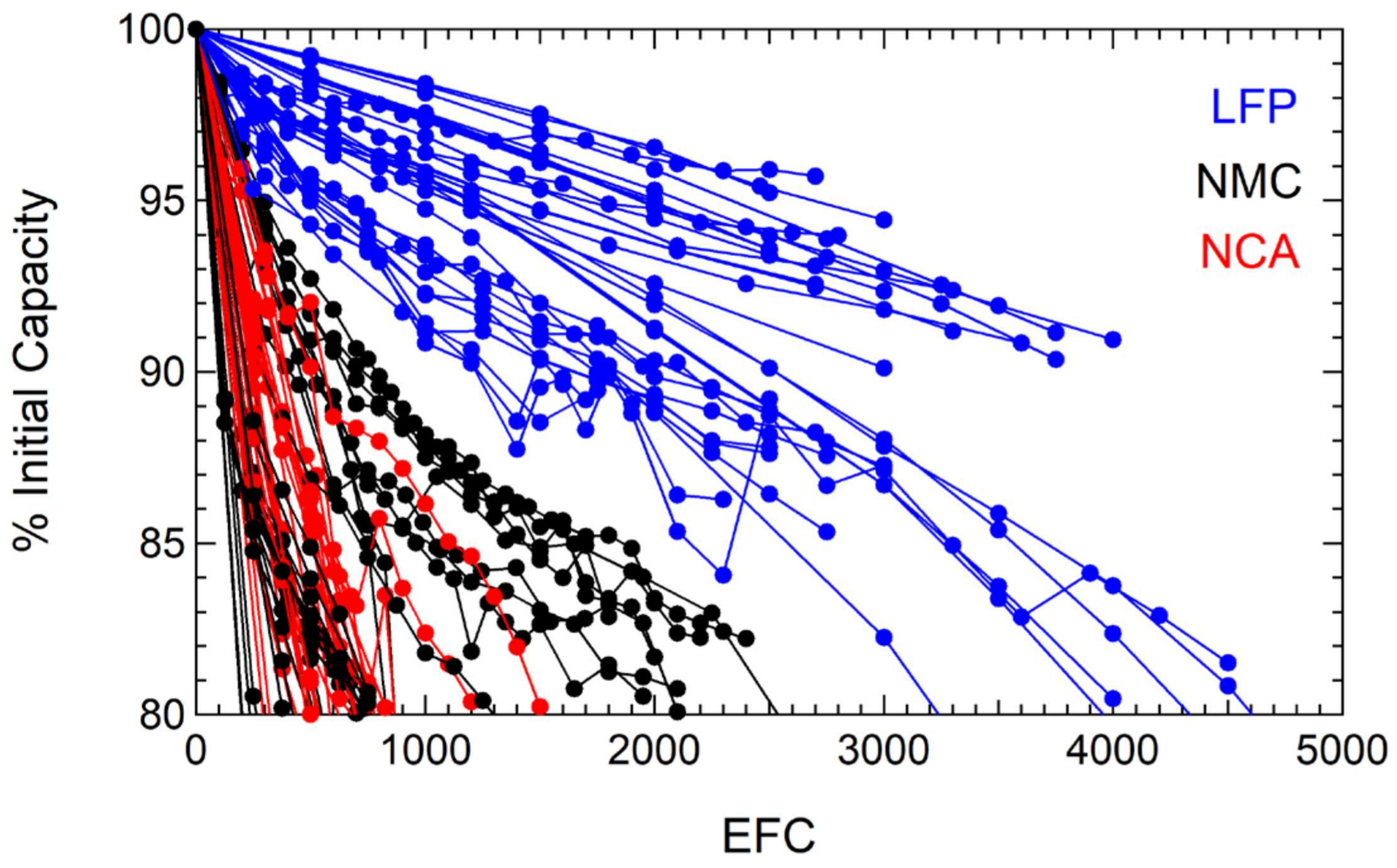



No systematic dependence on discharge rate in this range

# Cycling Past 80%: Preliminary Insights




For most conditions, degradation still linear

# Summary

**Motivation**

How much useful life does a battery have beyond 80% capacity?

**Approach**

Define end-of-life as transition to rapid capacity fade (knee/tipping point)

**Conclusions**

- In general, limited experimental data in literature showing knee point
- Knee-point capacity depends strongly on cycling conditions
- Multiple explanations for knee point: critical resistance, Li plating, electrode dry out, cathode impedance
- Substantial long-term studies needed coupling electrochemical performance with materials characterization

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For questions about this presentation: ypreger@sandia.gov