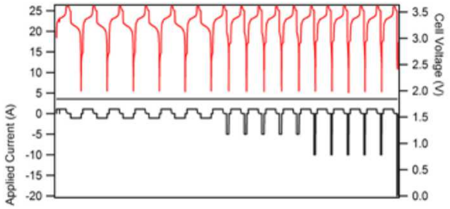
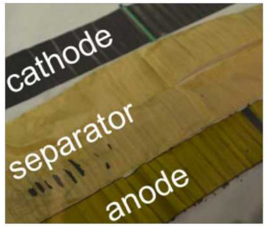
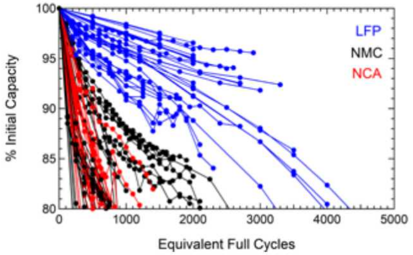
Sandia National Laboratories

SAND2019-12503C

Degradation of Commercial Li-ion Cells Beyond 80% Capacity







PRESENTED BY

Yuliya Preger

236th ECS Meeting: A05 – Batteries Session

October 17, 2019

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Challenge: System Selection Fraught with Uncertainty

Problem:

Limited LiB performance and safety data available

- Manufacturers provide range of recommended operating conditions, but limited insight into variable performance

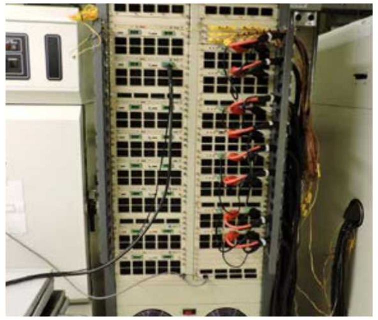
Without adequate info, potential for unintended abuse and rapid aging conditions

Objective:

Quantify performance of popular Li-ion chemistries in ‘apples to apples’ approach and identify ‘tipping points’

Project Team

Sandia Battery Test Facilities



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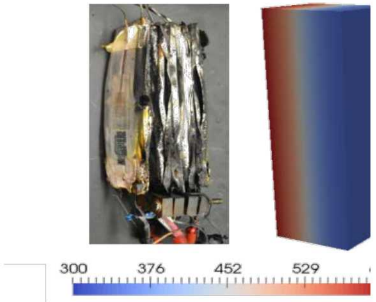

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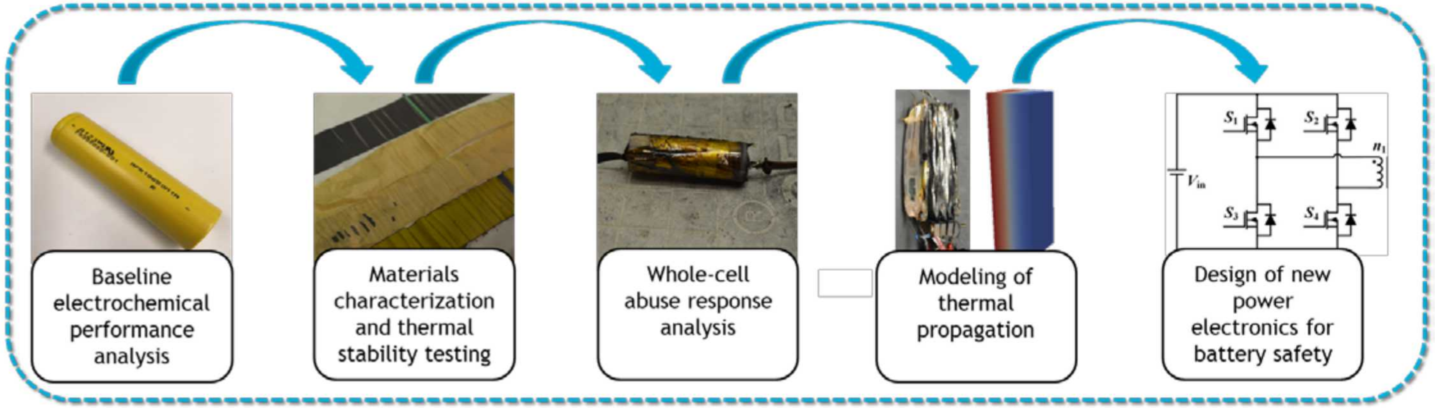
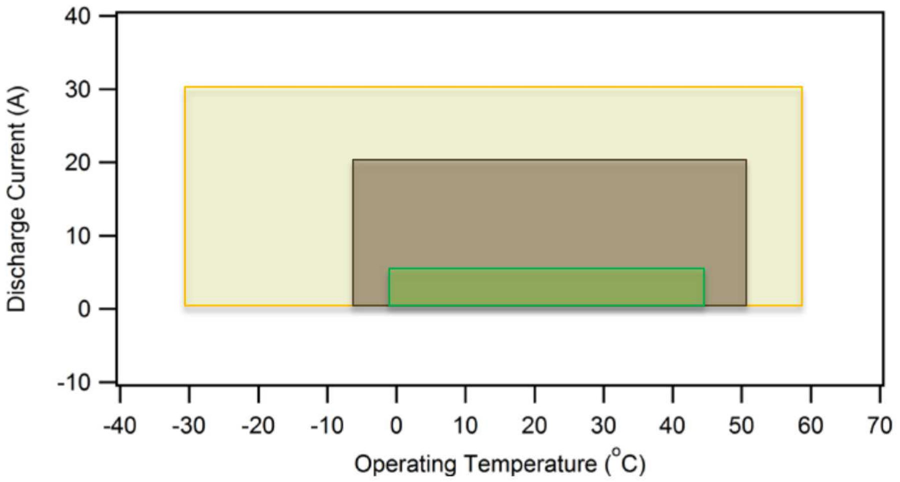


Scope of Study: Cells and Manufacturer Specifications

Cathode Chemistry	AKA	Vendor	Specific Capacity (Ah)	Max Discharge Current	Acceptable Temperature (°C)
$LiFePO_4$	LFP	A123	1.1	30	-30 to 60
$LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$	NCA	Panasonic	3.2	6	0 to 45
$LiNiMnCoO_2$	NMC	LG Chem	3.0	20	-5 to 50

LFP NCA NMC



Evaluating Cell Chemistries Uniformly: Long-Term Cycling

Two phases: 1) Short-term cycling: establish baseline and verify safety of operational window[1]
2) Long-term cycling: understand how operation at different points influence degradation

Design of experiment approach with at least two cells at each condition

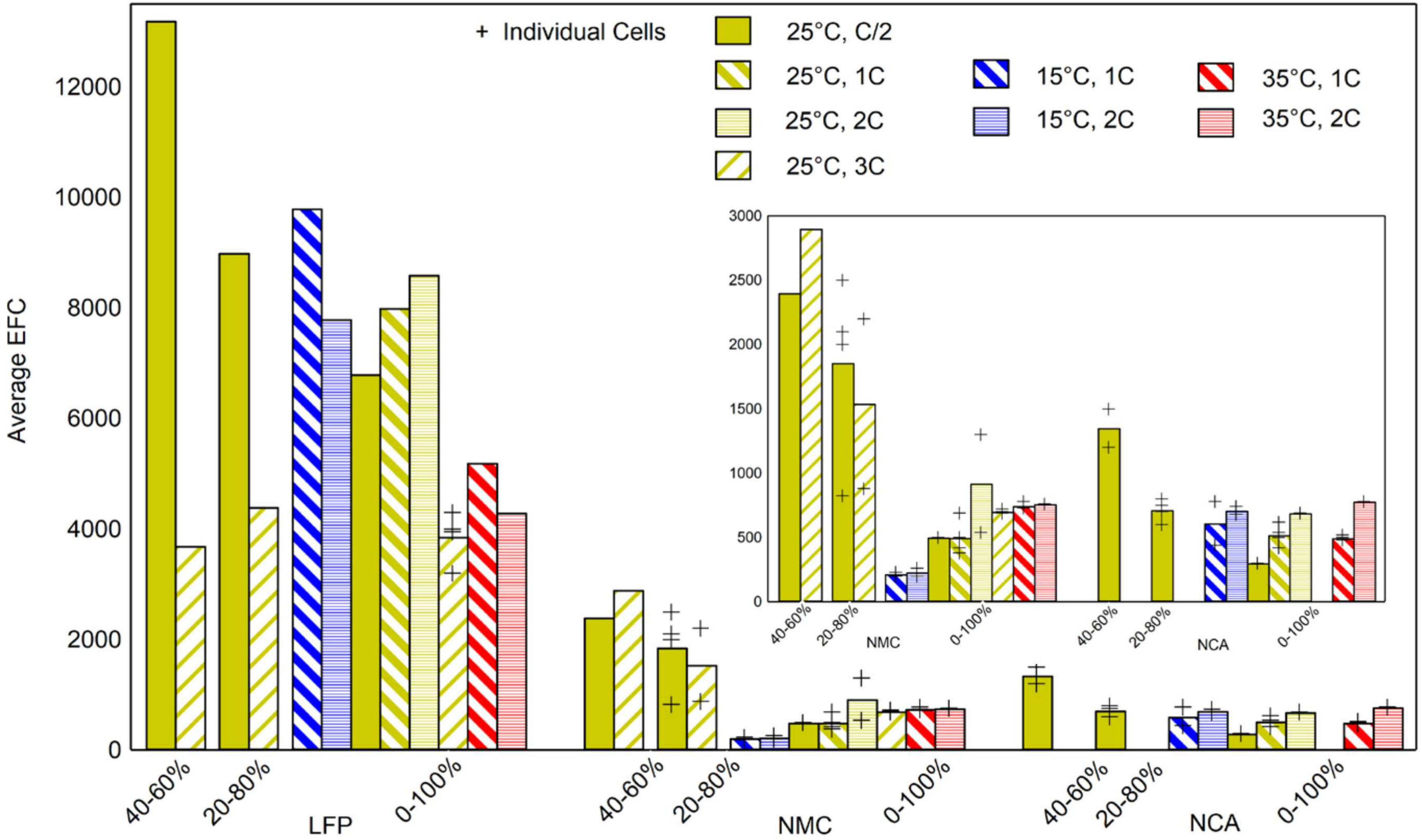
Variables:

- Chemistry: LFP, NCA, NMC
- Charge Rate: C/2
- Discharge Rate: C/2, 1C, 2C, 3C
- State-of-Charge Range: 40-60%, 20-80%, 0-100%
- Temperature: 15^{o}C, 25^{o}C, 35^{o}C

[1]Barkholtz et al. *J. Electrochem. Soc*. **2017**, *164*, A2697.

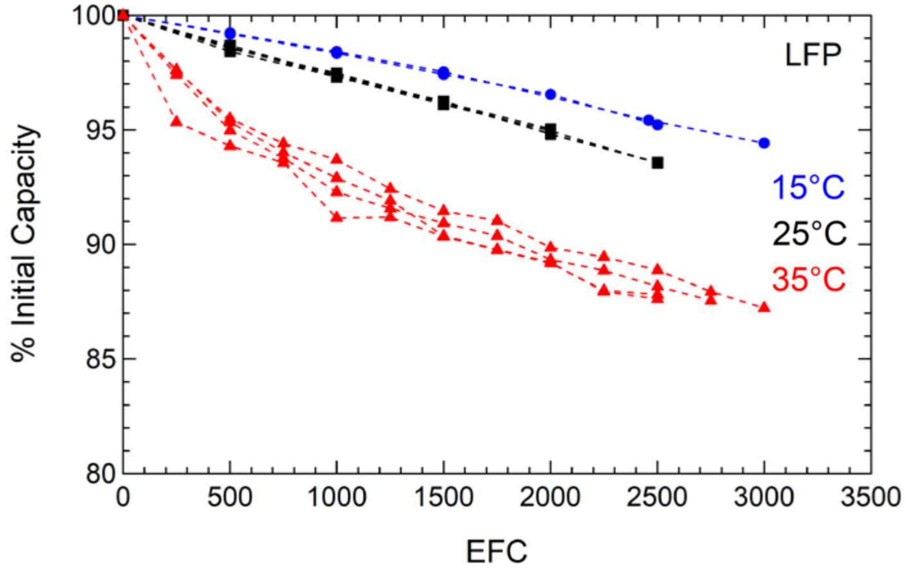
Cycle Count to 80% Capacity

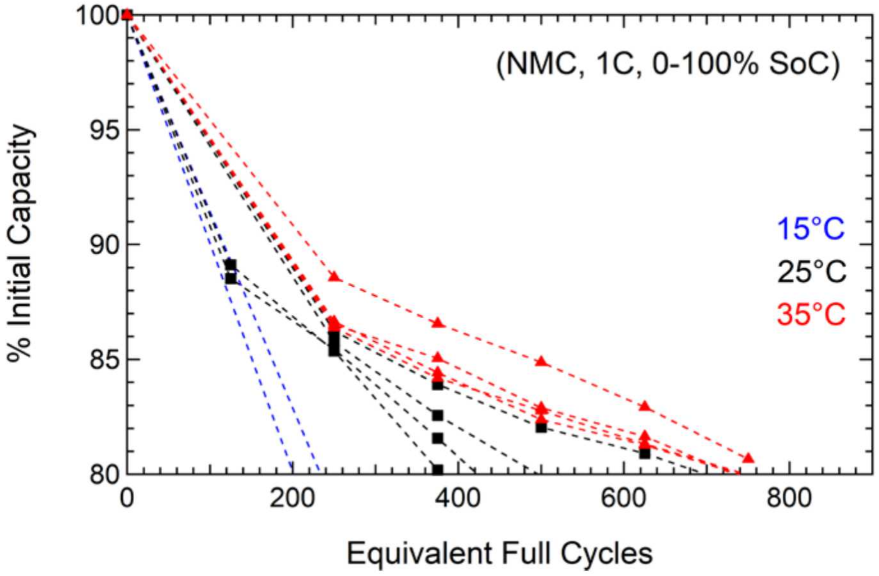
Performance highly variable even within manufacturer specs

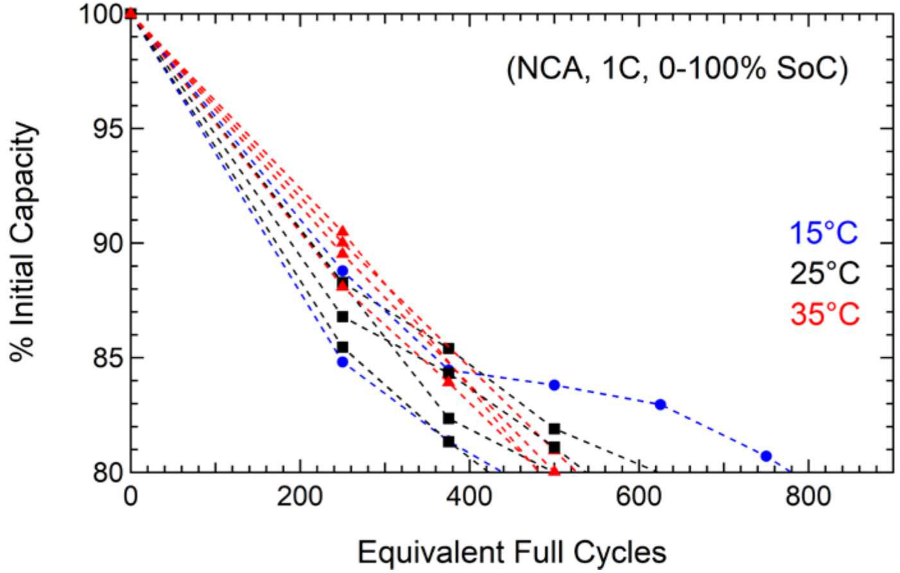


Value extrapolated for LFP cells that have not yet reached 80% capacity

Long-Term Cycling: Temperature Dependence

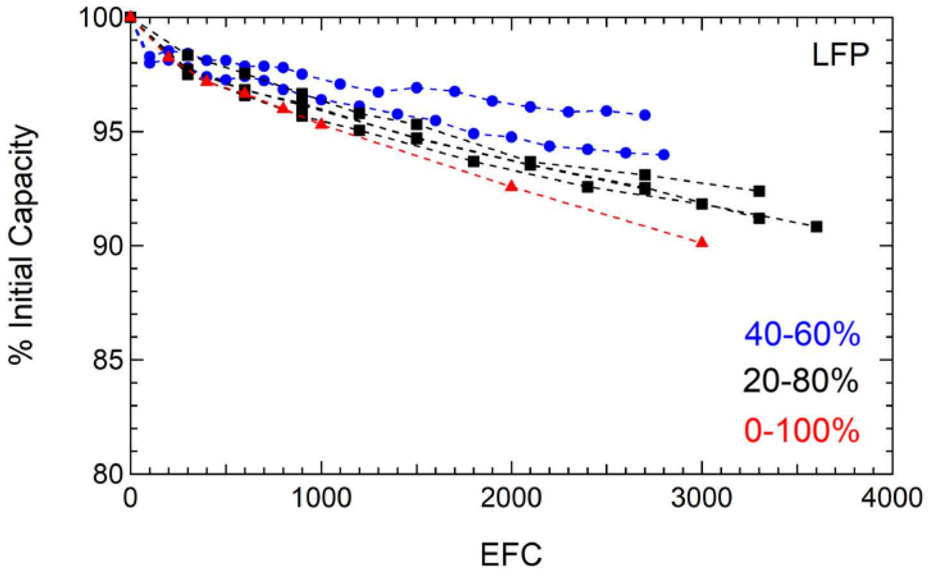


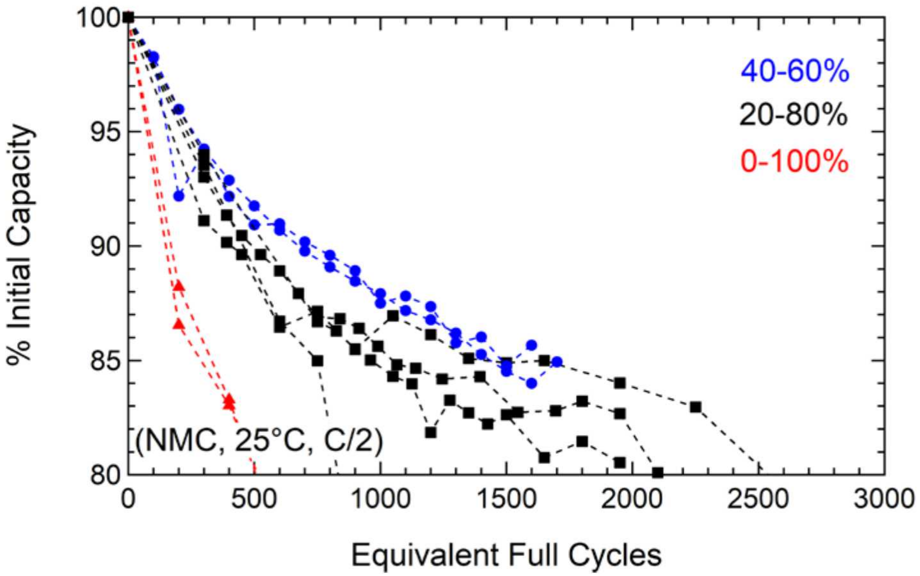


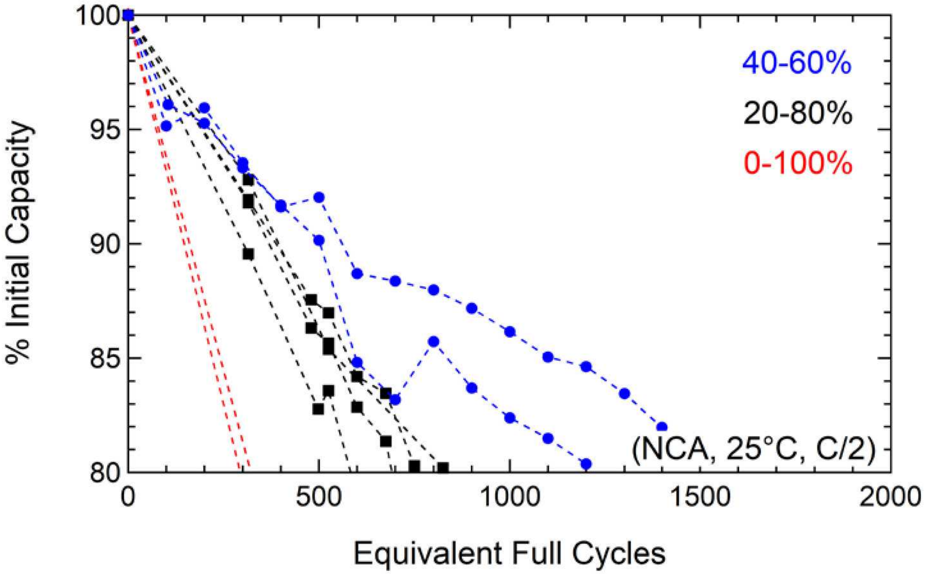


LFP and NMC exhibit inverse dependence on temperature (switch in degradation mechanism)

Long-Term Cycling: SOC Dependence

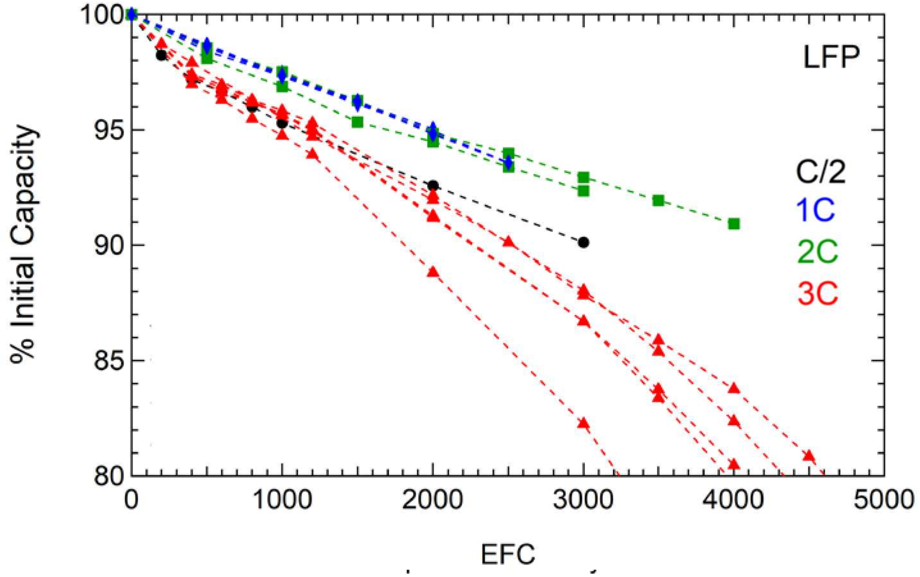


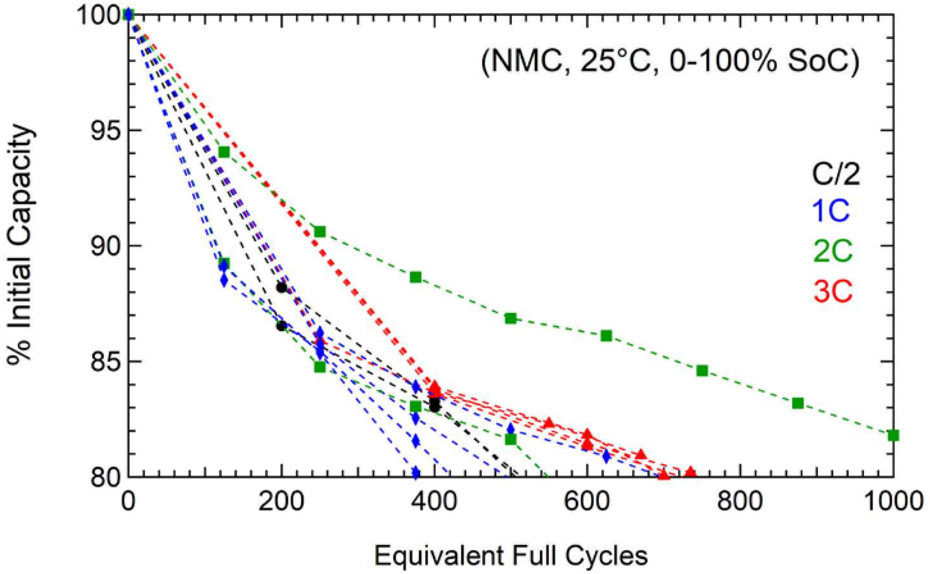


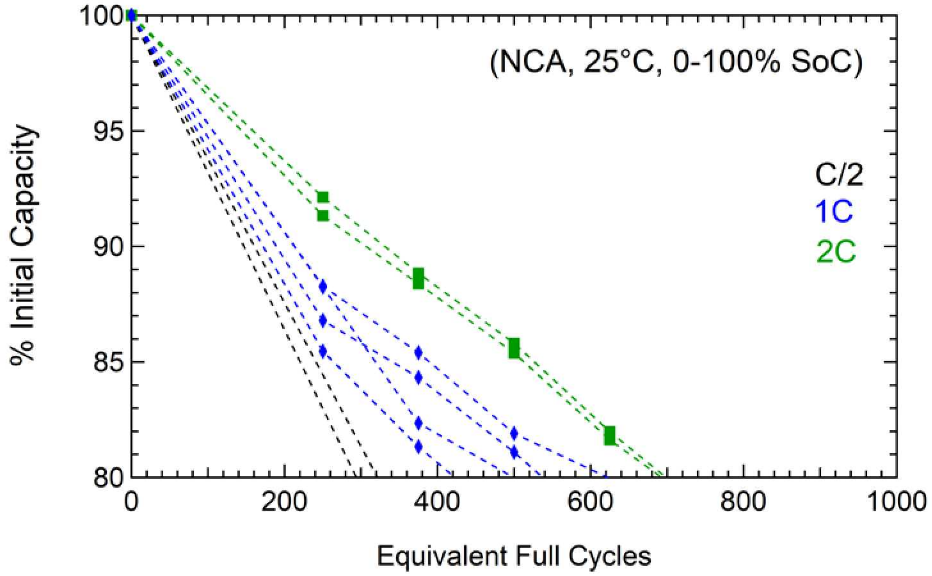


NCA and NMC more sensitive to full discharge

Long-Term Cycling: Discharge Rate Dependence





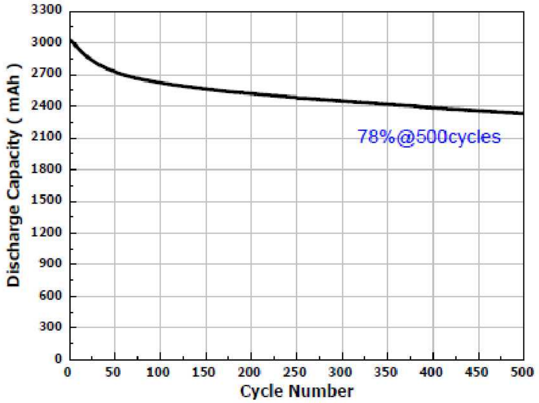


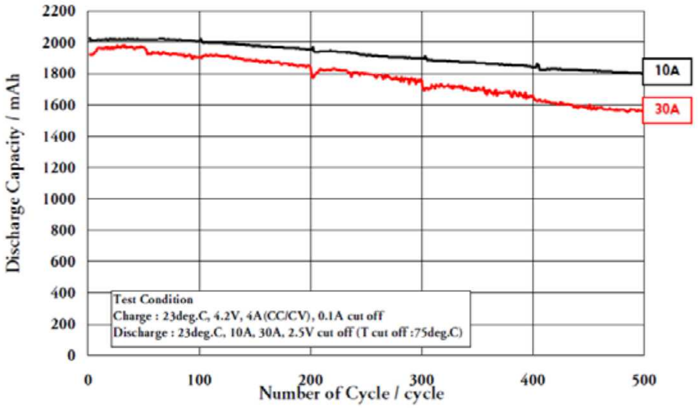
No systematic dependence on discharge rate in this range

Moving Beyond 80% Capacity for Grid Applications

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

Examples:



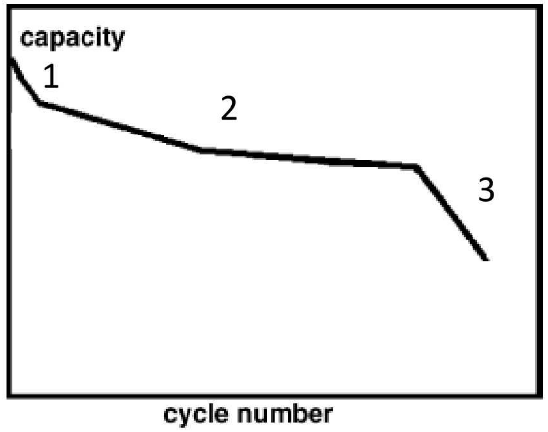


- 80% capacity is a holdover from the EV world
  - o USABC 1996: "*EV batteries should be removed from automotive use when* ***current battery capacity is 80% of initial battery capacity*** *and current battery power capability is 80% of initial battery power capability*"
  - o at this time, EVs were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

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

Theories of Capacity Fade During 'Normal' Operation

- Classical 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.

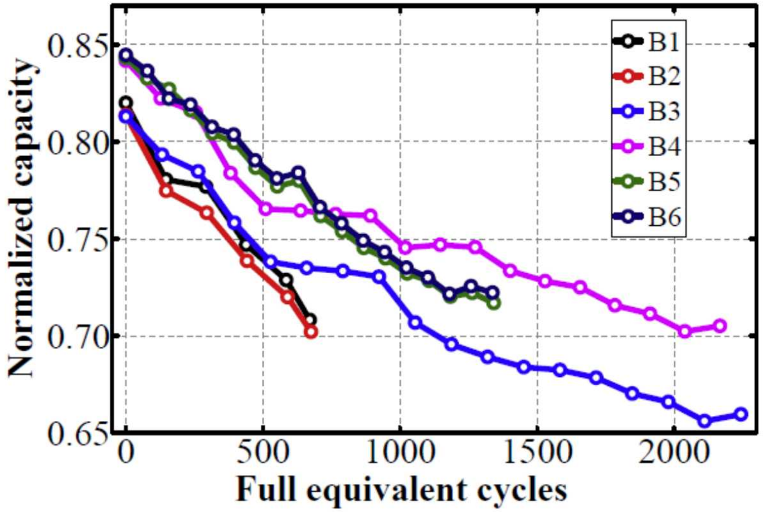
- Transition to rapid capacity fade has many names
  - Transition point, tipping point, knee, rollover

- 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

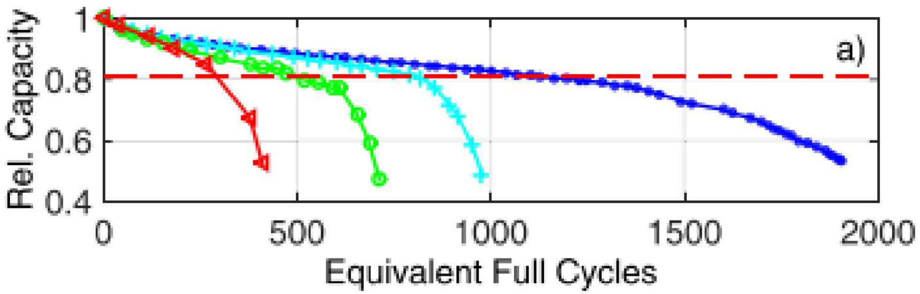
No knee down to 65% capacity

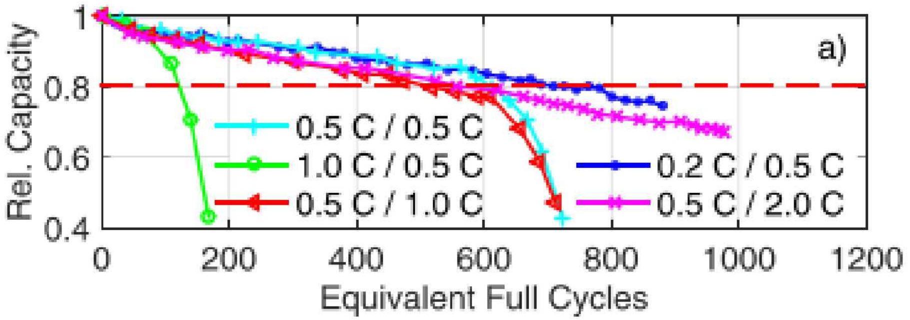
Knee at ~80% capacity, but also earlier or later



60Ah LFP cells cycled with various load profiles

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



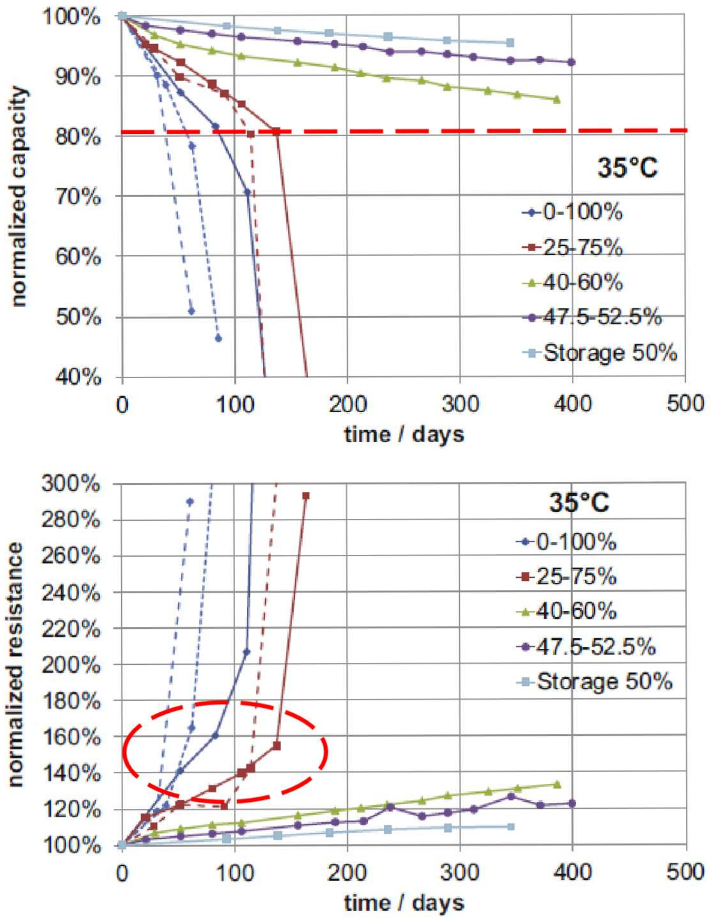


18650 1.95Ah NMC cells cycled with various temperatures, DOD, charge/discharge rate

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

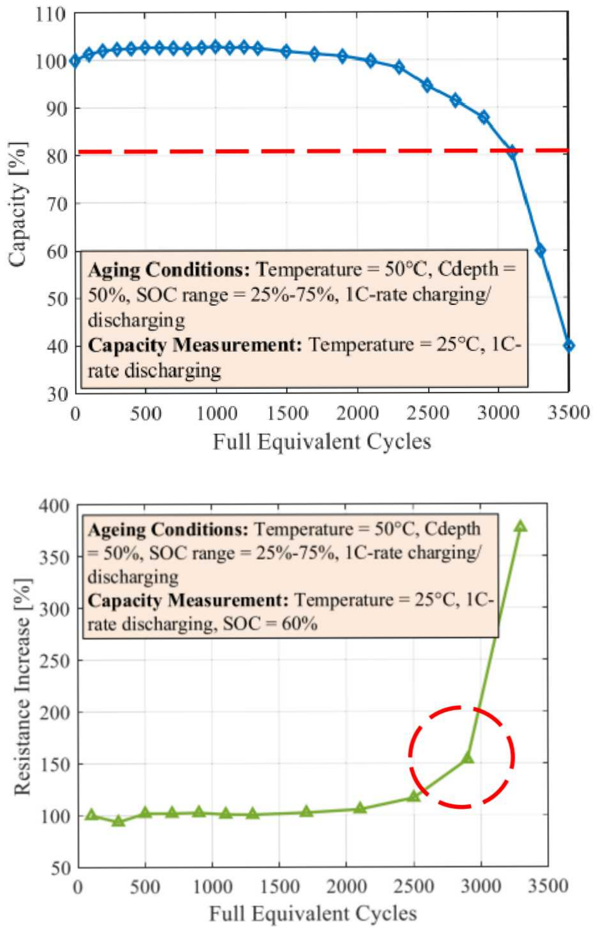
Rapid Capacity Fade Due to Resistance Increase

Tipping point coincides with resistance increase of ~150%



Sanyo 18650 2.05Ah NMC/graphite cells

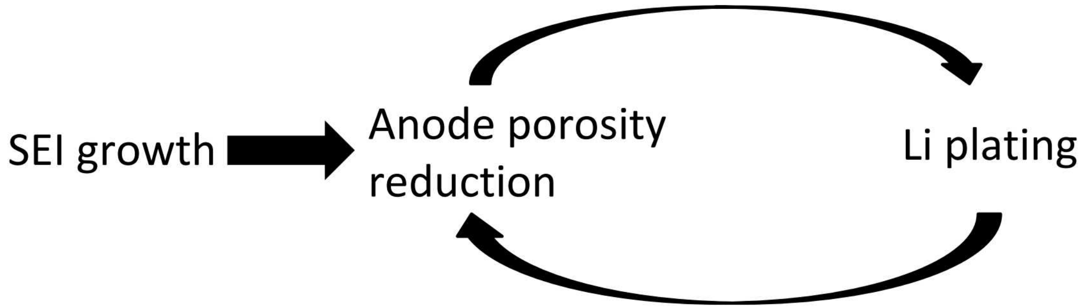
Ecker et al. *J. Power Sources* **2014**, *248*, 839.

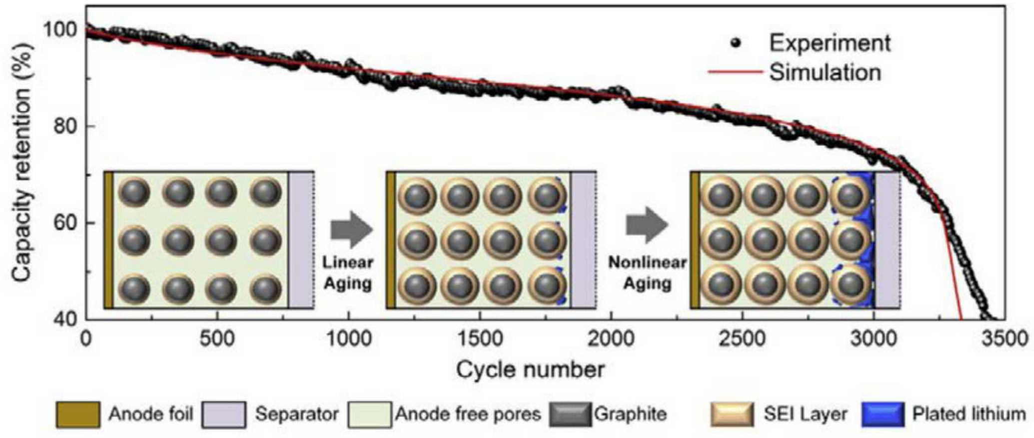


13Ah NMC/LTO cells

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

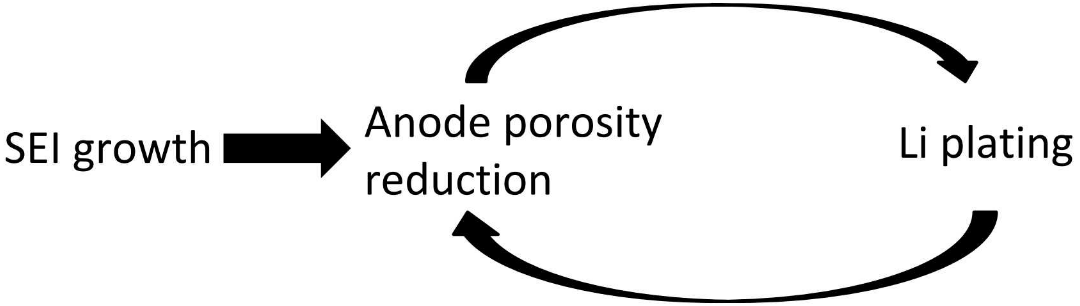
Li Plating as Cause of Rapid Resistance Increase

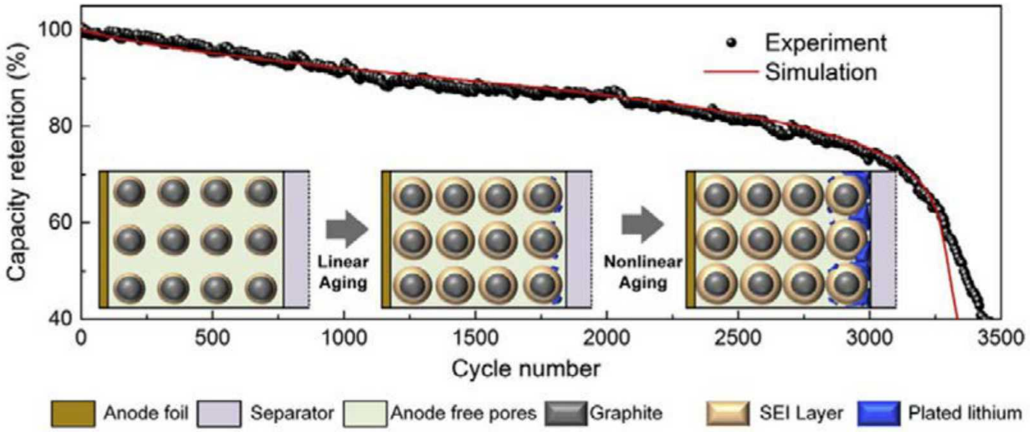




Yang et al. *J. Power Sources* **2017**, *360*, 28.

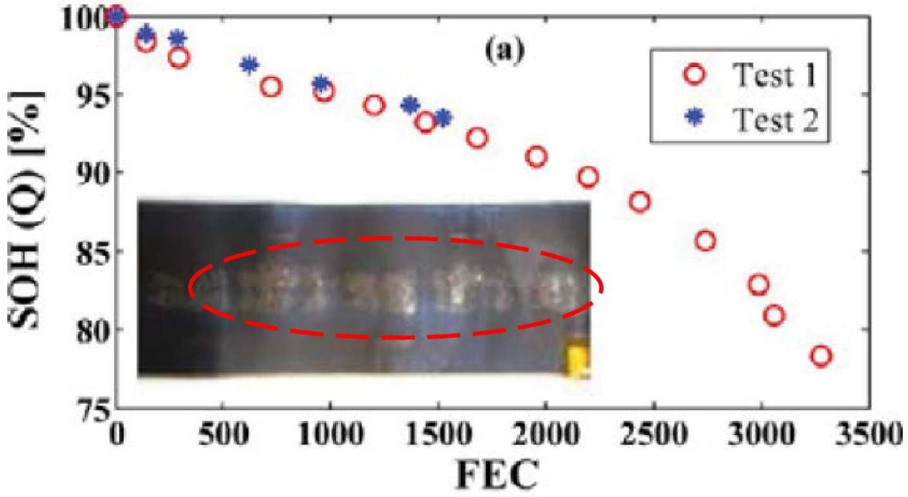
Li Plating as Cause of Rapid Resistance Increase



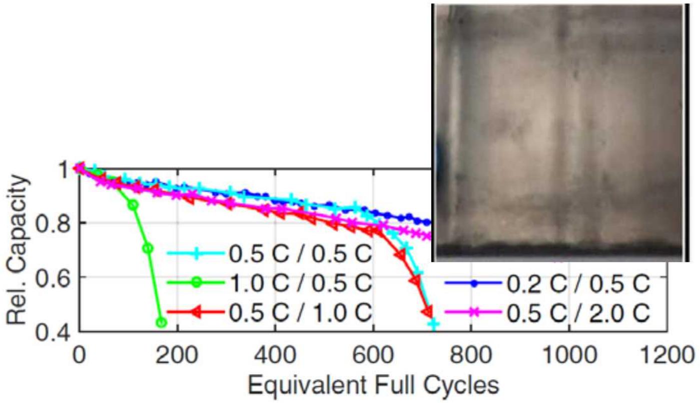


Yang et al. *J. Power Sources* **2017**, *360*, 28.

Deposits of Li observed on anode, while cathode unmodified



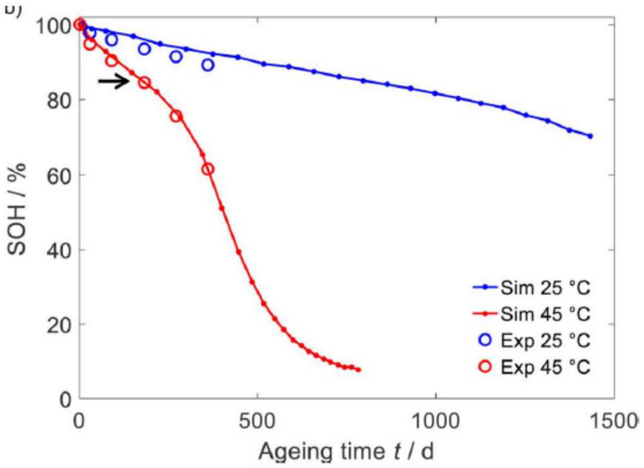
Sarasketa-Zabala et al. *J. Phys. Chem. C* **2015**, *119*, 896.

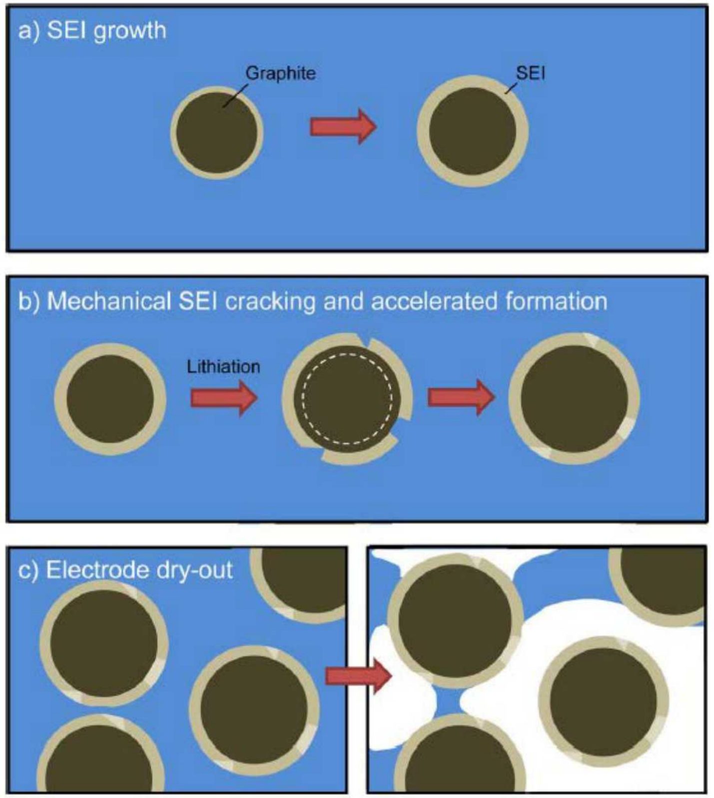


Bach et al. *J. Energy Storage* **2016**, *5*, 212.

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





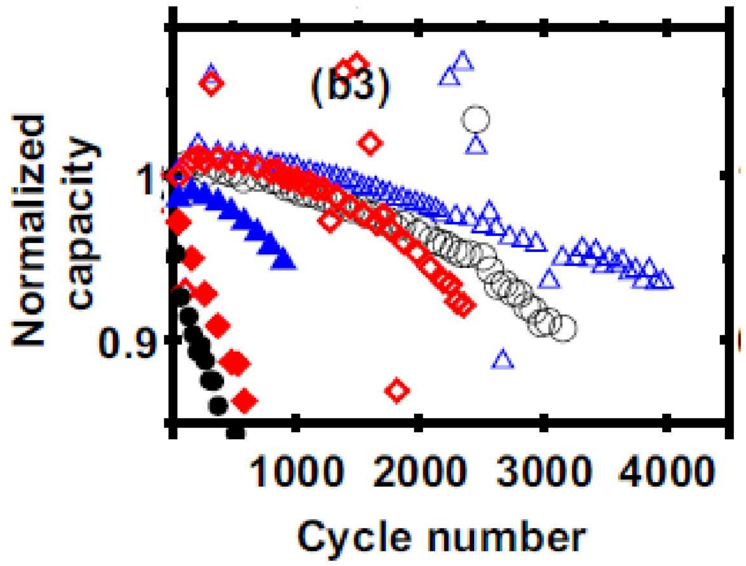
Kupper et al. *J. Electrochem. Soc.* **2018**, *165*, A3468.

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.

Expanding Data Sets of Commercial Cells Beyond 80% Capacity

Our approach: 1) Short-term cycling: establish baseline and verify safety of operational window
2) Long-term cycling to 80%: understand how operation at different points influence degradation
3) Long-term cycling beyond 80%: understand what causes and how to delay tipping point

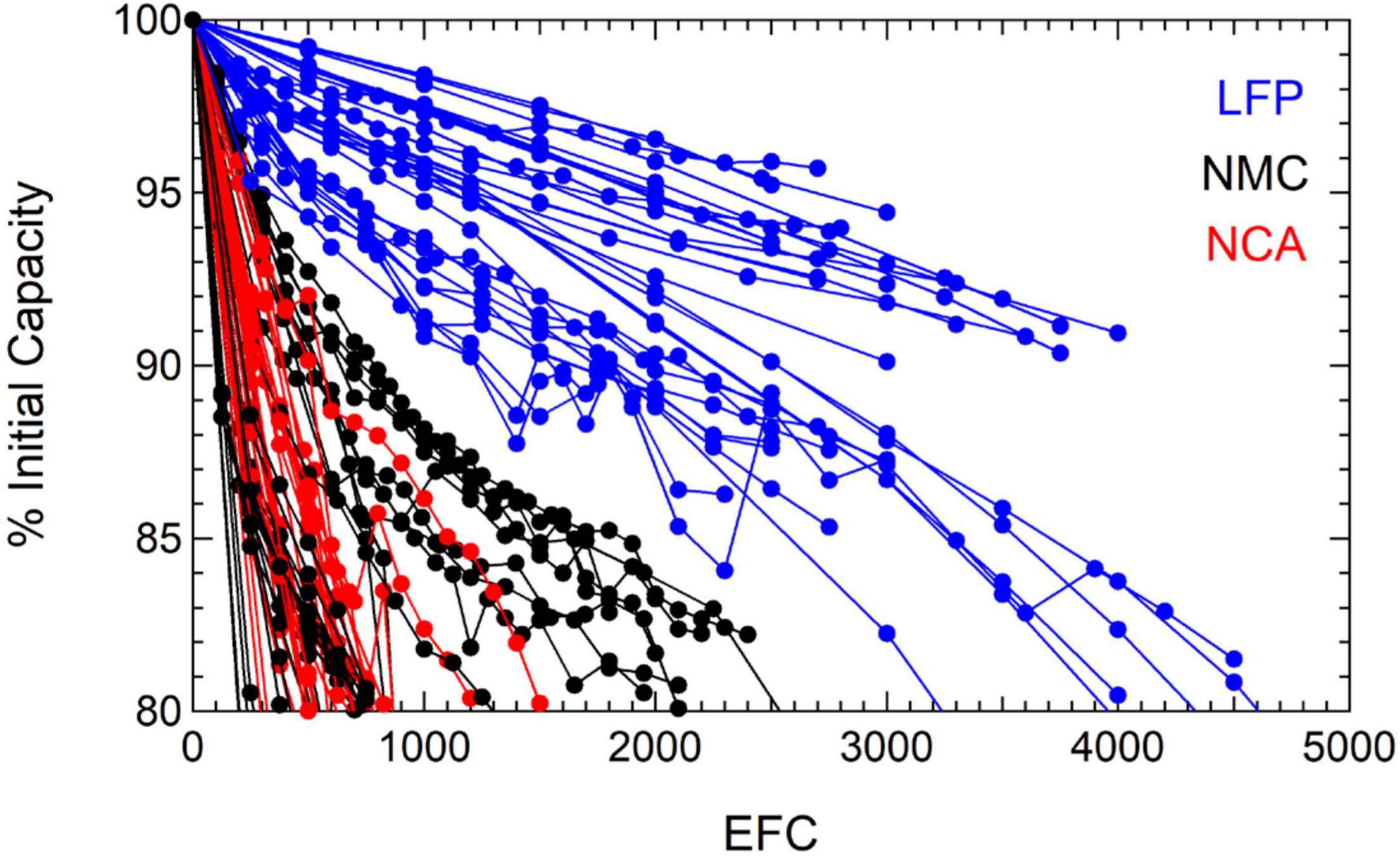
- most studies limited to a couple of cells past the knee
- need more experimental data to enable generalizable conclusions

New study: design of experiment approach with at least two cells at each condition

Variables:

- Chemistry: NCA, NMC (LFP later)
- Charge Rate: 0.25C, 0.5C, 1C
- Discharge Rate: 1C
- State-of-Charge Range: 20-80%
- Temperature: 15^{o}C, 25^{o}C, 35^{o}C

Cycling Past 80%: Preliminary Insights



For most conditions, degradation still linear

Summary

Motivation

Minimize uncertainty (and identify knowledge gaps) in LiB cell selection for energy storage installations

Approach

Quantify cell performance with uniform methodology in short and long-term cycling studies

Conclusions

- Cells' degradation can vary up to thousands of cycles, even within the manufacturer specified range of conditions
- 80% capacity is not a reasonable lifetime end point, should be based on transition to rapid fade
- In general, still limited experimental data for rapid capacity fade; more long-term studies needed

Acknowledgments

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