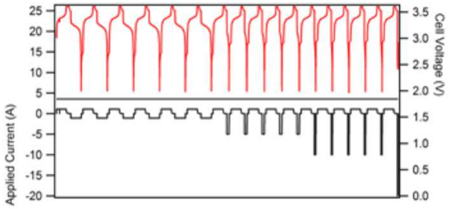
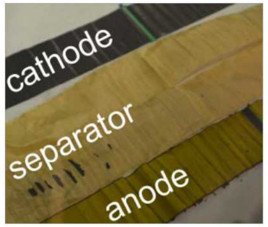
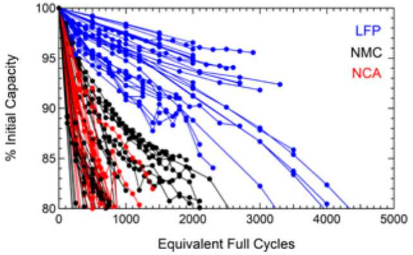
Sandia National Laboratories

SAND2020-2820C

Degradation of Commercial Li-ion Cells Beyond 80% Capacity







PRESENTED BY

Yuliya Preger

Energy Storage Systems Safety & Reliability Forum

March 5, 2020

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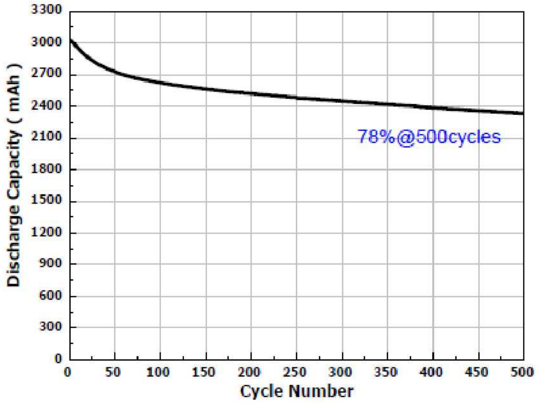
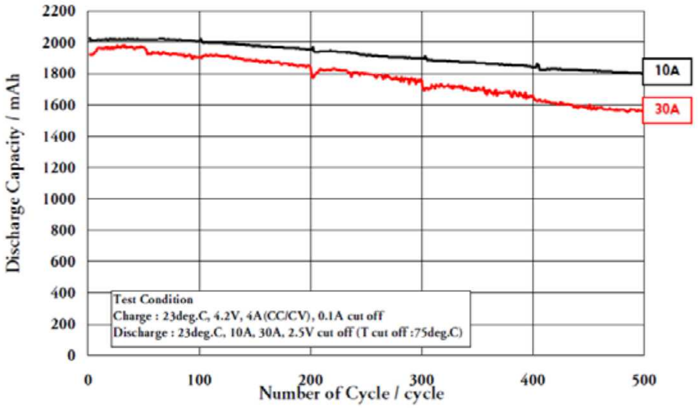
Moving Beyond 80% Capacity for Grid Applications

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

Examples:





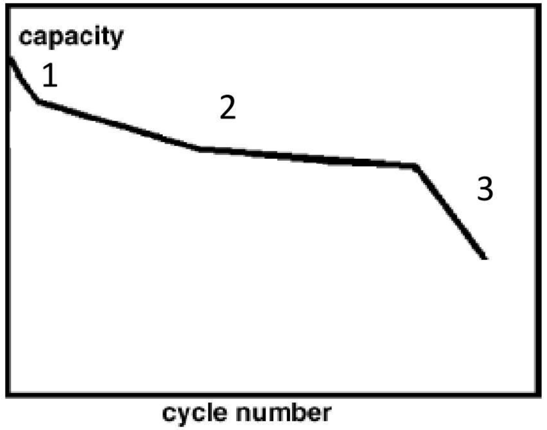
- 80% capacity is a holdover from the EV world
  - USABC 1996: "*EV batteries should be removed from automotive use when* ***current battery capacity is 80% of initial battery capacity*** *and current battery power capability is 80% of initial battery power capability*"
  - At this time, EVs were primarily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

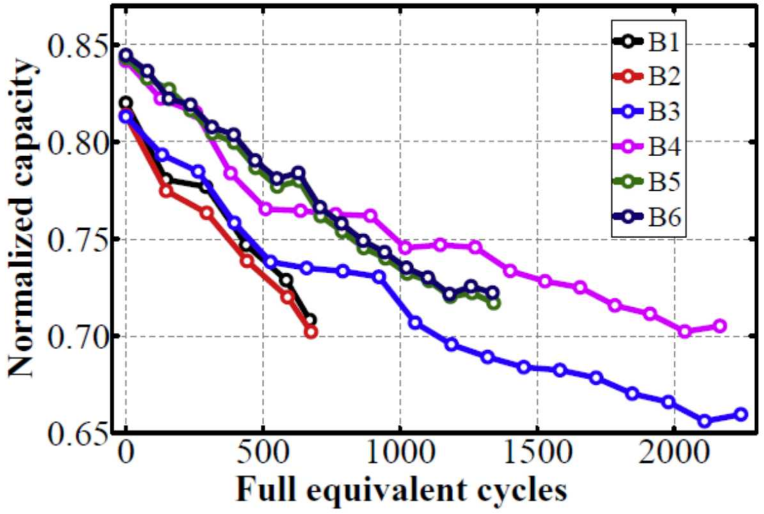


Spotnitz et al. *J. Power Sources* **2003**, *113*, 72.

- 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

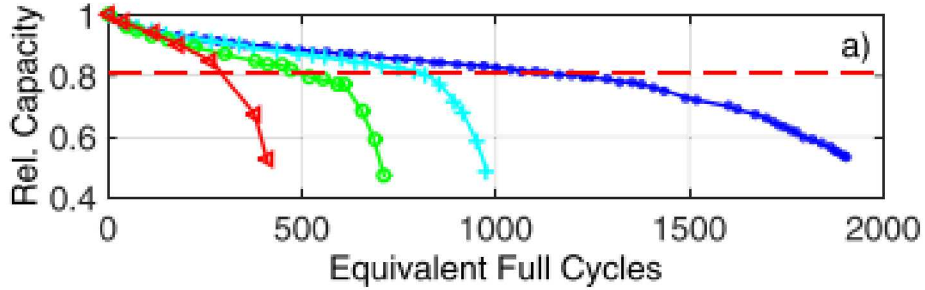
No knee down to 65% capacity

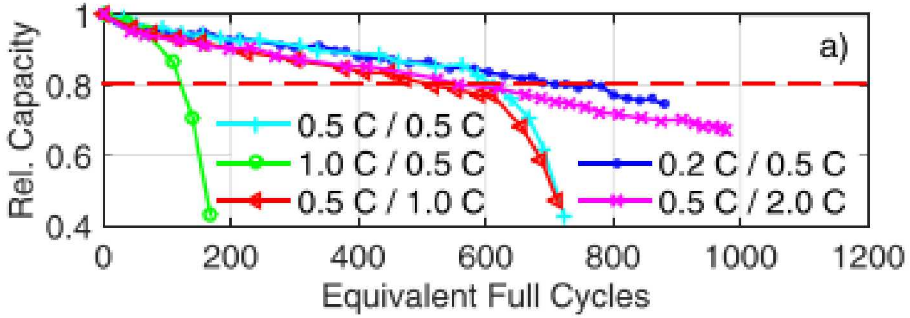


60Ah LFP cells cycled with various load profiles

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

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



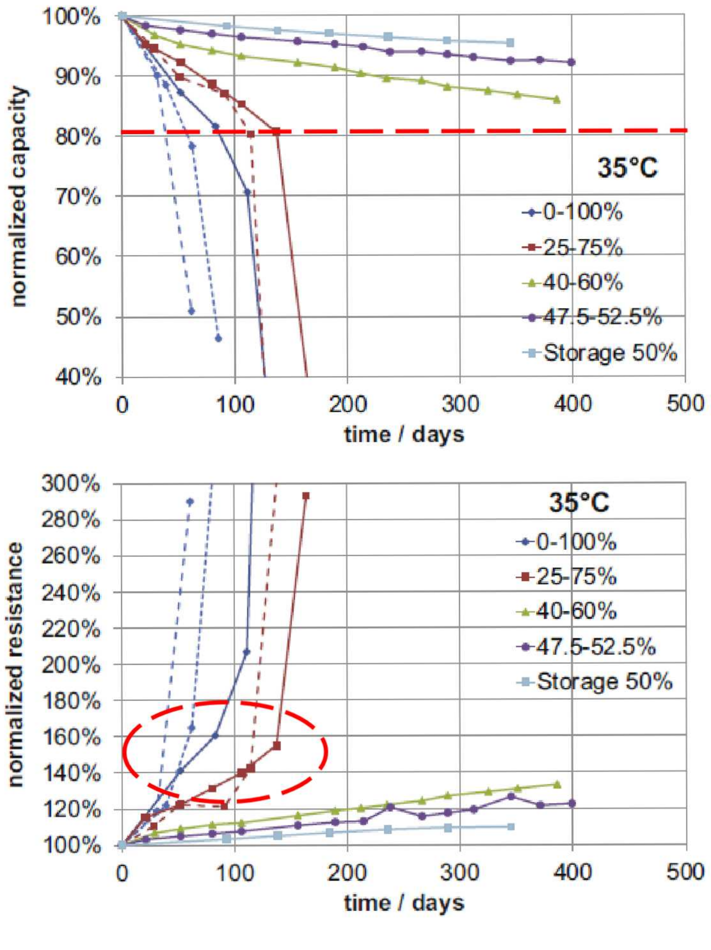


18650 1.95Ah NMC cells cycled with various temperatures, DOD, charge/discharge rate

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

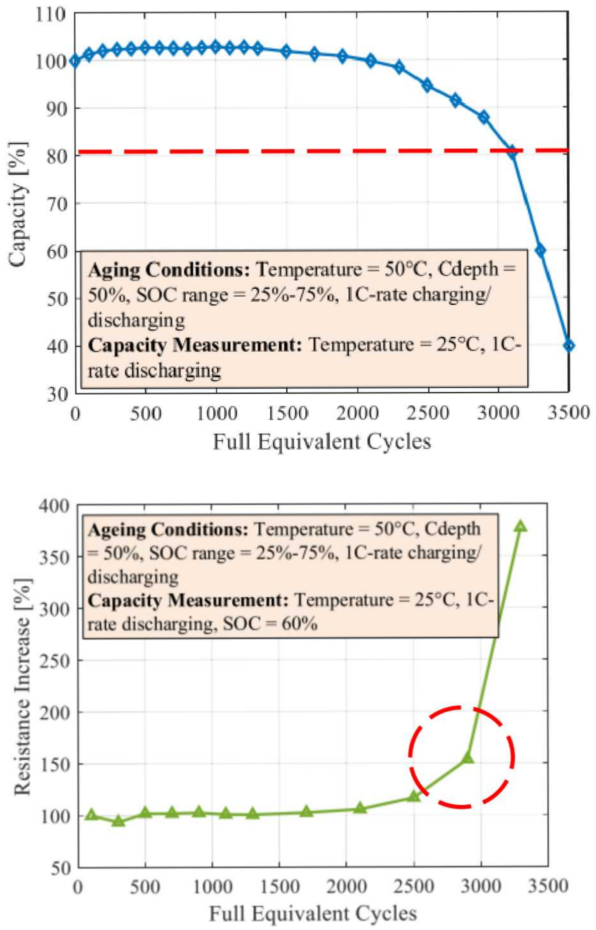
Rapid Capacity Fade Due to Resistance Increase

Tipping point coincides with resistance increase of ~150%



Sanyo 18650 2.05Ah NMC/graphite cells

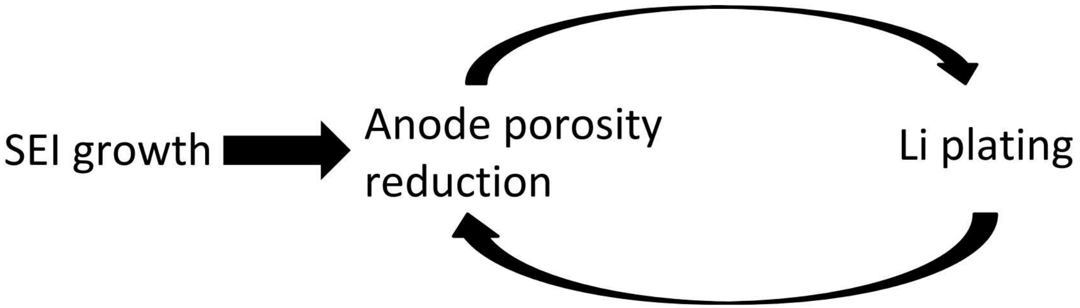
Ecker et al. *J. Power Sources* **2014**, *248*, 839.

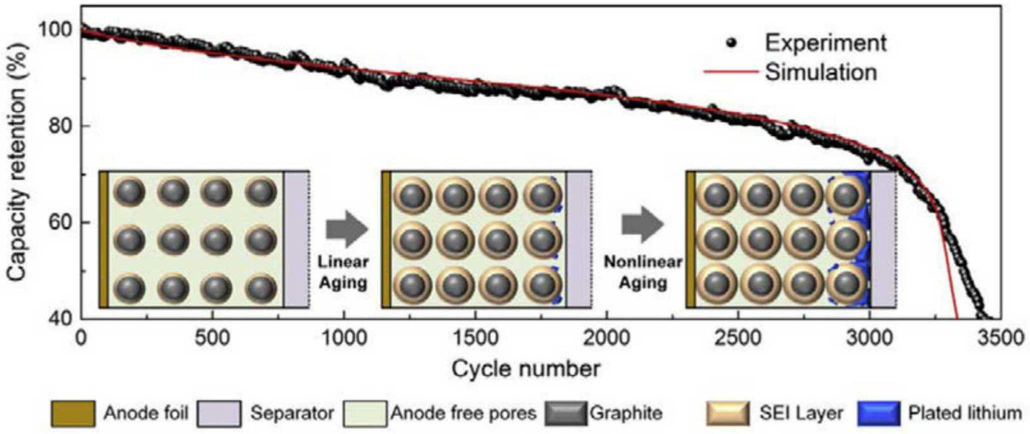


13Ah NMC/LTO cells

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

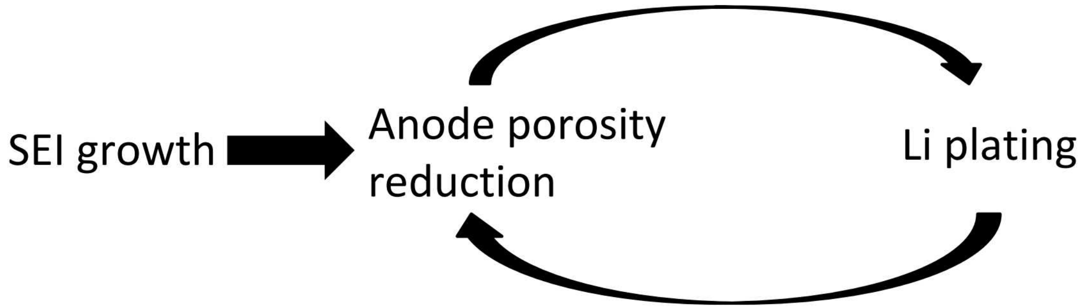
Li Plating as Cause of Rapid Resistance Increase

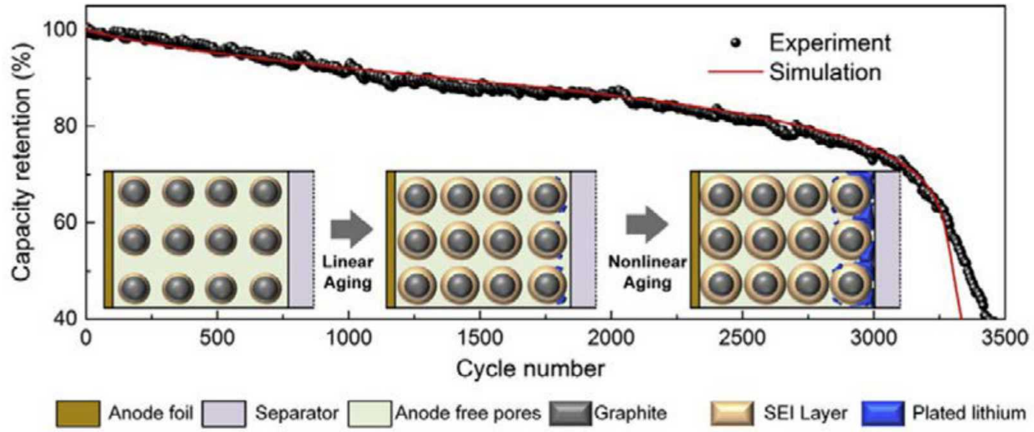




Yang et al. *J. Power Sources* **2017**, *360*, 28.

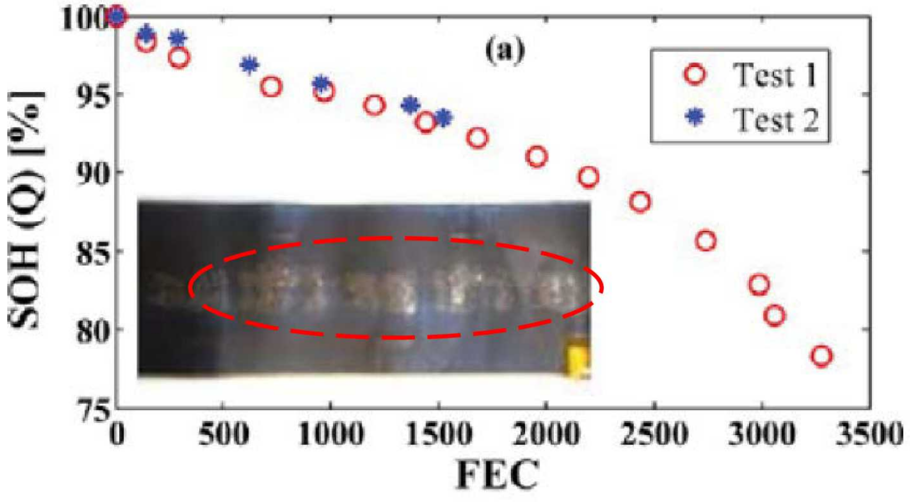
Li Plating as Cause of Rapid Resistance Increase



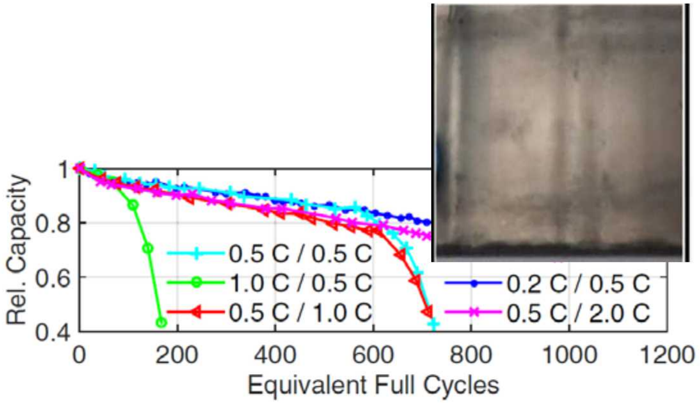


Yang et al. *J. Power Sources* **2017**, *360*, 28.

Deposits of Li observed on anode, while cathode unmodified



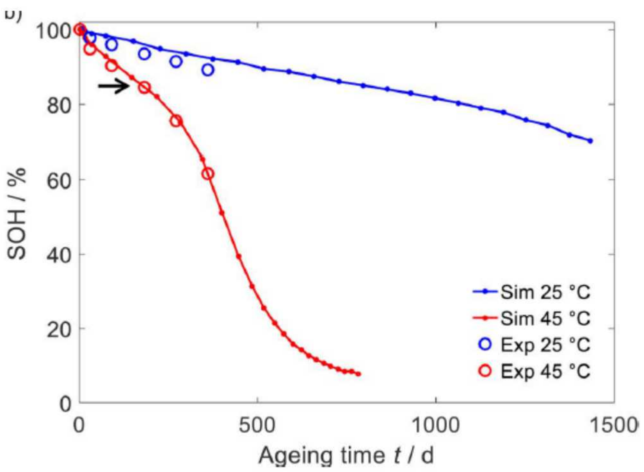
Sarasketa-Zabala et al. *J. Phys. Chem. C* **2015**, *119*, 896.

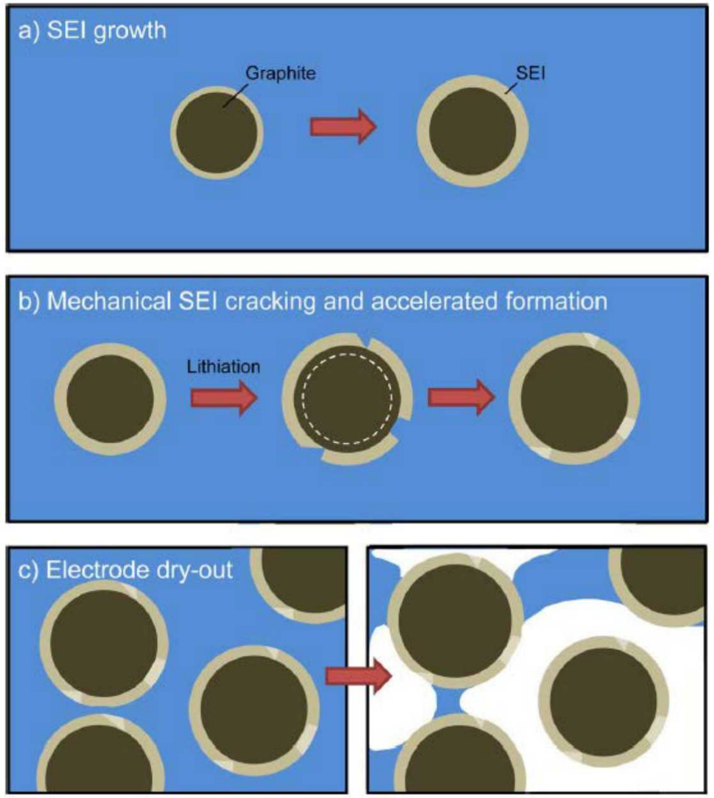


Bach et al. *J. Energy Storage* **2016**, *5*, 212.

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





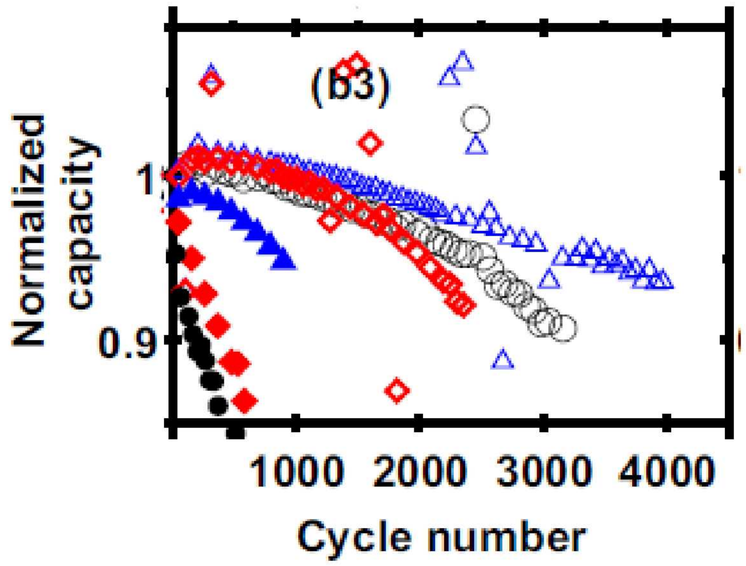
Kupper et al. *J. Electrochem. Soc.* **2018**, *165*, A3468.

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



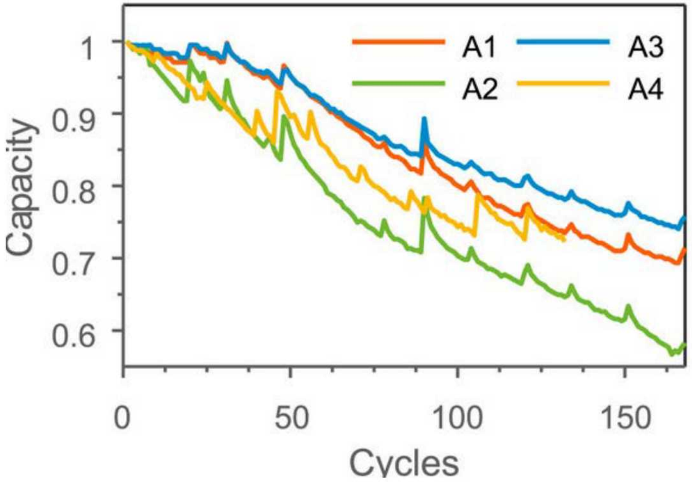
Ma et al. *J. Electrochem. Soc.* **2019**, *166*, A711.

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
- Recent modeling includes more knee data, but still empirical

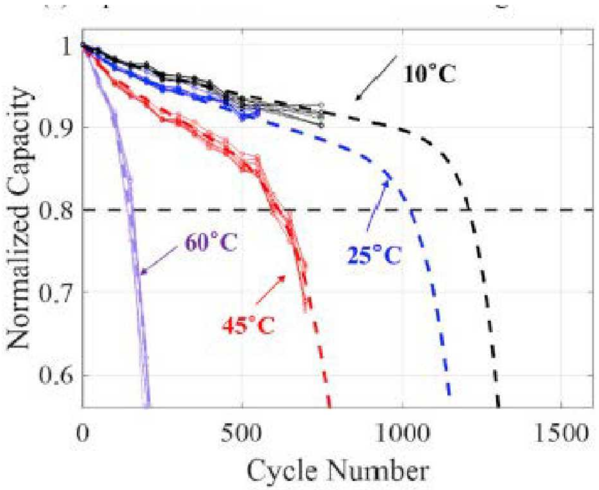
Typical linear data set in RUL model



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

Data set with knee – empirical modeling

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



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

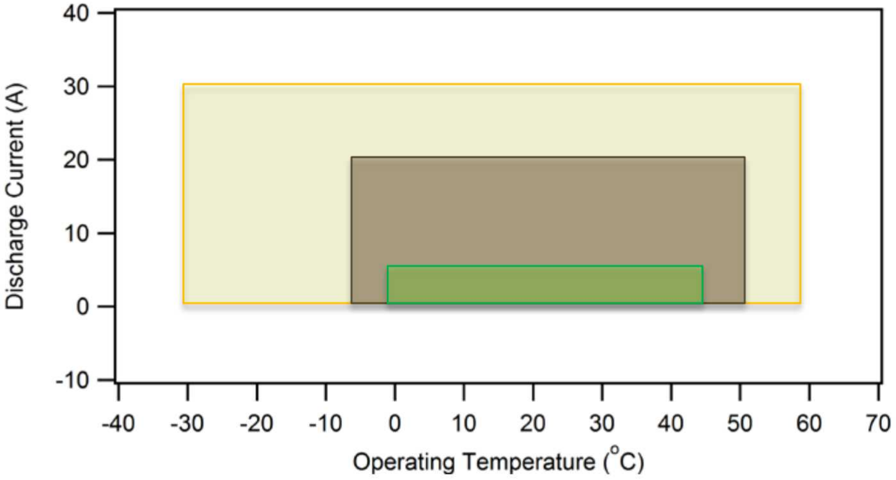
Key Questions

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 2nd life cells, how to predict RUL to knee if limited knowledge of previous capacity fade?
    - Is the economic case factoring in this transition?
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 (^oC)
$LiFePO_4$	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

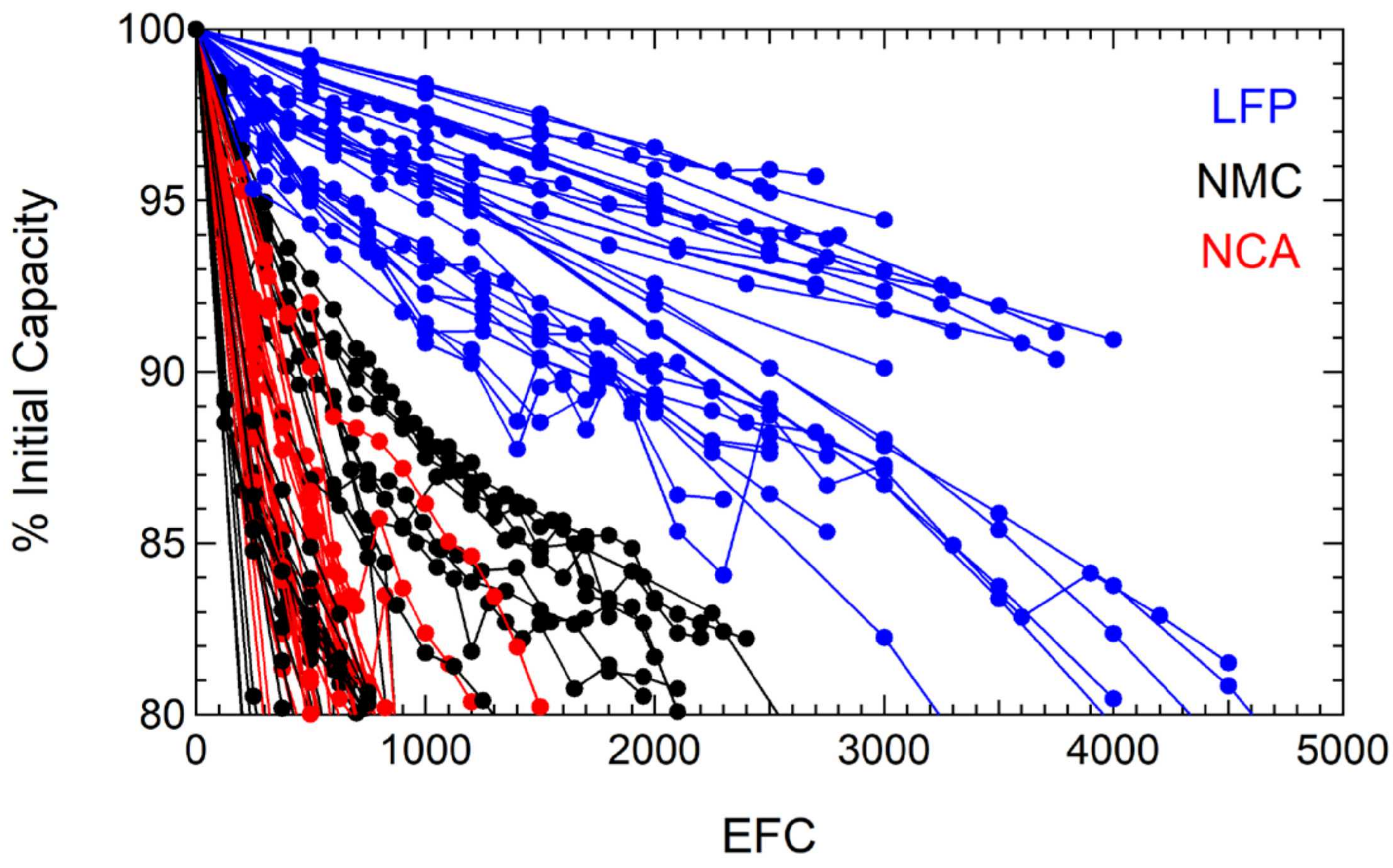
LFP NCA NMC



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

Cycling Past 80%: Preliminary Insights



For most conditions, degradation still linear

Another Critical Topic: Influence of Cell Age on Safety

Standard abuse testing is reported only for fresh cells

Influence of cell age on safety is unclear:

- More safe (due to capacity loss)?
- Less safe (due to materials instability)?
- Little difference?

Safety Testing Example Data

TEST REPORT
IEC 62133, Second Edition
Secondary cells and batteries containing alkaline or other non-acid electrolytes – Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications

Test Report issued under the responsibility of:

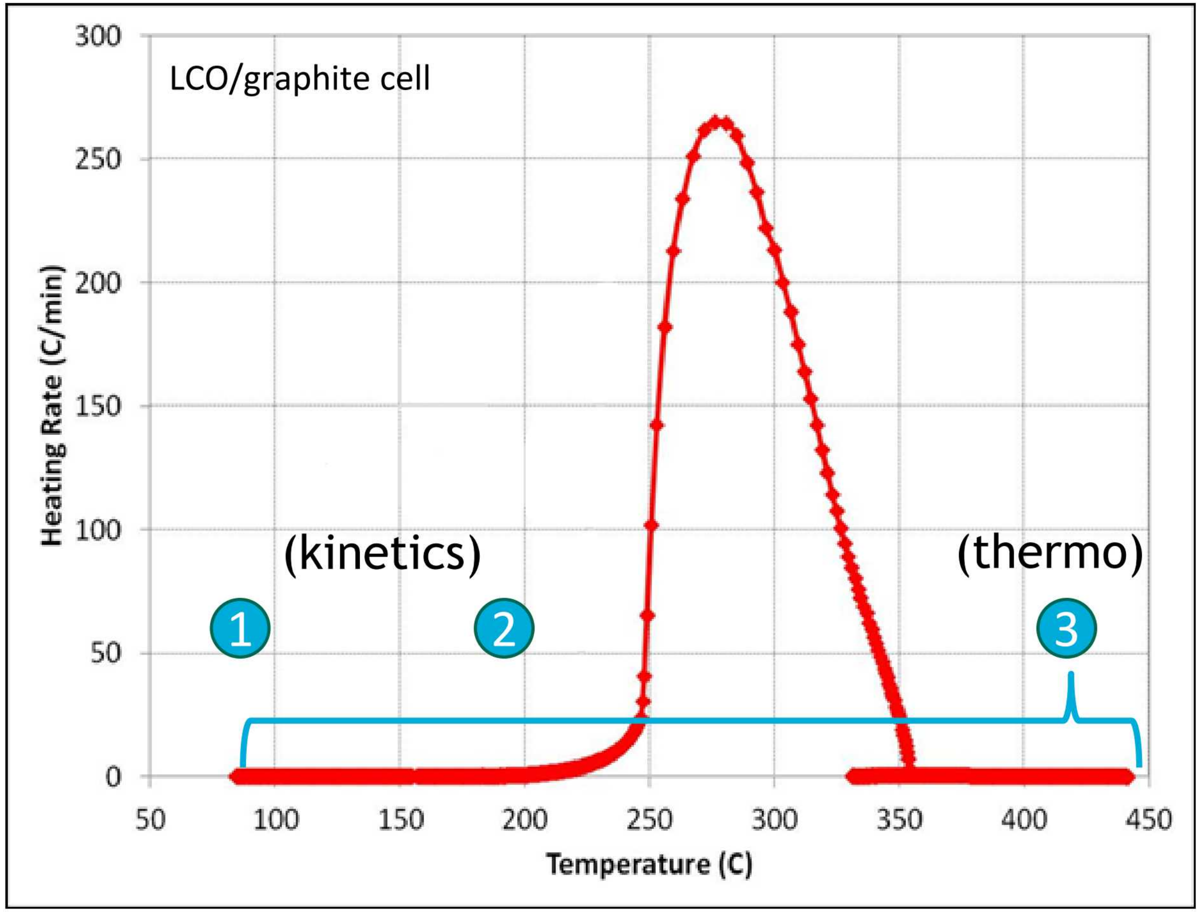
Summary of testing:

Tests performed (name of test and test clause):

8.2.1 – Continuous charging at constant voltage (cells)
8.3.1 – External short circuit (cells)
8.3.3 – Free fall
8.3.4 – Thermal abuse (cells)
8.3.5 – Crush (cells)
8.3.7 – Forced Discharge
8.3.9 – Forced internal short circuit (cells)

Source: LG Chem, IEC Test Report issued under UL

How to Compare Safety of Fresh and Aged Cells



Thermal runaway measured via accelerated rate calorimetry (ARC)

1. Self-heating onset temperature
2. Thermal runaway onset temperature
3. Total heat release (ΔT)

Summary of Calorimetry on Aged Cells

No comprehensive studies, but broader conclusions possible from many individual studies

- Aged cell less safe (red)
- Little difference (grey)
- Aged cell more safe (blue)

Cell Type	Aging Approach	SOH (State-of-Health)	Self-Heating Onset	Thermal Runaway Onset	Total Heat Release (ΔT)
NMC-LMO	-10°C (cyc)	81%	Lower by 50-70°C	Lower by 150°C	--
NMC-LMO	-10°C (cyc)	78%	Lower by 10-30°C	Lower by 20°C	Little difference
NMC	-5°C (cyc)	80-95%	Lower by 10-20°C	Lower by 20°C	Little difference
NMC532	0°C (cyc)	70%	Lower by 60°C	Lower by 90°C	--
LCO	0°C (cyc)	70%	Little difference	Little difference	--
NCA	0/5°C (cyc)	65%	Lower by 95°C	Lower by 100°C	Lower by 130°C
NMC532	20°C (cyc)	70-90%	Lower by 10°C	Little difference	--
NMC442	20°C (cyc)	80%	Little difference	Little difference	--
LCO	21°C (cyc)	89-94%	--	Little difference	--
NMC-LMO	25°C (cyc)	78%	Lower by 20°C	Little difference	--
NMC	25°C (cyc)	80-95%	Lower by 10°C	Lower by 5-20°C	Lower by 20-290°C
NCA	25/45°C (cyc)	70-85%	Little difference	Little difference	Lower by 50°C
NMC532	45°C (cyc)	70-90%	Higher by 10-20°C	Little difference	--
LCO	25/60/70°C(cal)	--	Higher by 25-40°C	--	--
NMC	55°C (cyc)	80-95%	Little difference	Little difference	Little difference
NMC	55°C (cal)	80-95%	Higher by 15-25°C	Little difference	Little difference
NMC-LMO	60°C (cal)	55%	Lower by 20°C	Little difference	--
LFP	60°C (cal)	70-90%	Higher by 10°C	Lower by 20°C	--
NCA	60°C (cal)	80%	Little difference	Little difference	Lower by 150°C
LCO	80°C (cal)	56%	Higher by 10-15°C	Little difference	--
NMC-LMO	80/90/100°C (brief ARC)	73-95%	Higher by 15-35°C	Higher by 15°C	Lower by 45-80°C

Lower Self-Heating Onset at Lower Aging Temperatures

Likely due to Li plating at lower temperatures

Aged cell less safe
Little difference
Aged cell more safe

Cell Type	Aging Approach	SOH (State-of-Health)	Self-Heating Onset	Thermal Runaway Onset	Total Heat Release (ΔT)
NMC-LMO	-10°C (cyc)	81%	Lower by 50-70°C	Lower by 150°C	--
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NMC532	20°C (cyc)	70-90%	Lower by 10°C	Little difference	--
NMC442	20°C (cyc)	80%	Little difference	Little difference	--
LCO	21°C (cyc)	89-94%	--	Little difference	--
NMC-LMO	25°C (cyc)	78%	Lower by 20°C	Little difference	--
NMC	25°C (cyc)	80-95%	Lower by 10°C	Lower by 5-20°C	Lower by 20-290°C
NCA	25/45°C (cyc)	70-85%	Little difference	Little difference	Lower by 50°C
NMC532	45°C (cyc)	70-90%	Higher by 10-20°C	Little difference	--
LCO	25/60/70°C(cal)	--	Higher by 25-40°C	--	--
NMC	55°C (cyc)	80-95%	Little difference	Little difference	Little difference
NMC	55°C (cal)	80-95%	Higher by 15-25°C	Little difference	Little difference
NMC-LMO	60°C (cal)	55%	Lower by 20°C	Little difference	--
LFP	60°C (cal)	70-90%	Higher by 10°C	Lower by 20°C	--
NCA	60°C (cal)	80%	Little difference	Little difference	Lower by 150°C
LCO	80°C (cal)	56%	Higher by 10-15°C	Little difference	--
NMC-LMO	80/90/100°C (brief ARC)	73-95%	Higher by 15-35°C	Higher by 15°C	Lower by 45-80°C

Heat Release Not Always Lower at Lower Capacity

Total energy available for thermal runaway may be unchanged due to role of inactive materials like electrolyte

- Aged cell less safe (red)
- Little difference (grey)
- Aged cell more safe (blue)

Cell Type	Aging Approach	SOH (State-of-Health)	Self-Heating Onset	Thermal Runaway Onset	Total Heat Release (ΔT)
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NMC	55°C (cyc)	80-95%	Little difference	Little difference	Little difference
NMC	55°C (cal)	80-95%	Higher by 15-25°C	Little difference	Little difference
NMC-LMO	60°C (cal)	55%	Lower by 20°C	Little difference	--
LFP	60°C (cal)	70-90%	Higher by 10°C	Lower by 20°C	--
NCA	60°C (cal)	80%	Little difference	Little difference	Lower by 150°C
LCO	80°C (cal)	56%	Higher by 10-15°C	Little difference	--
NMC-LMO	80/90/100°C (brief ARC)	73-95%	Higher by 15-35°C	Higher by 15°C	Lower by 45-80°C

Summary

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

- limited literature on cycling cells to knee point
- knee-point capacity depends strongly on cycling conditions
- need studies coupling electrochemical performance with materials characterization to understand knee point

2) How does safety of battery change as it ages?

- kinetics: lower self-heating onset temperature if battery aged at low temperatures
- thermodynamics: total energy available for thermal runaway not always reduced for aged cells
- gap: need non-thermal abuse tests to understand impact of aging on overcharge/short circuit protective devices

Acknowledgments

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