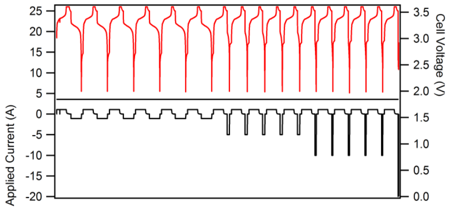
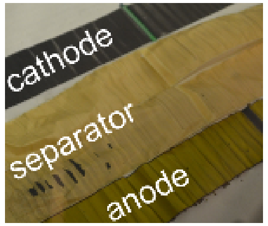
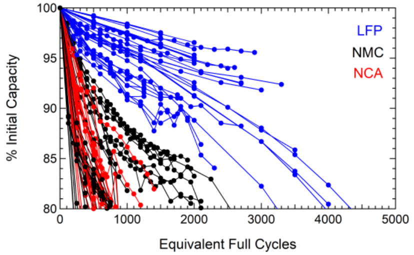
SAND2023-05701C

Sandia National Laboratories

Degradation of Li-ion Cells Beyond 80% Initial Capacity







PRESENTED BY

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Power Sources Conference

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Challenge: battery selection and operation is fraught with uncertainty

Head of rural electric cooperative, after operating a $1.4 million BESS for a year:

“Here is what we learned about BESS….Deep cycling causes rapid loss of life, shallow cycling extends life and total kWh throughput”

Insurance company representative:

“I am researching Li-ion battery reliability…would you be able to point me towards any data on Li-ion battery failure modes and rates in energy storage systems?”

Energy-storage startup (non-battery):

“I believe my technology can perform better than Li-ion batteries at XX condition. Do you know how batteries perform in that window?”

Motivation for 18650 Li-ion long-term cycling study

Problem:

Limited Li-ion battery performance and safety data is publicly available

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

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

Objective:

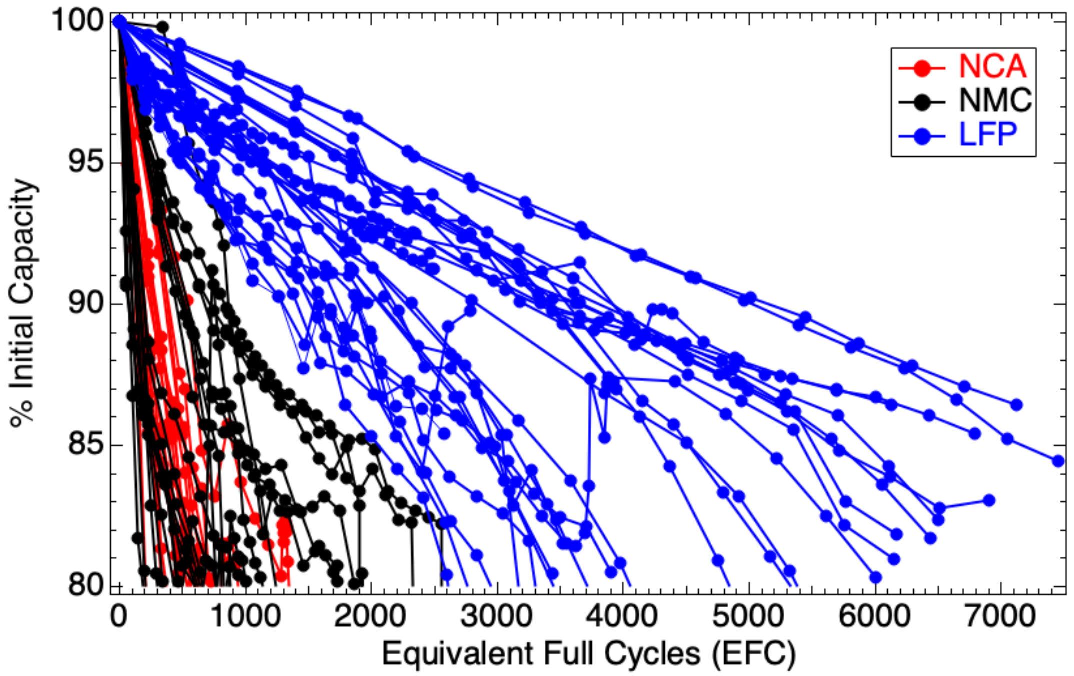
Quantify performance of popular Li-ion chemistries in ‘apples to apples’ approach and identify ‘tipping points’ in performance

Approach to long-term cycling study

Design of experiment with at least two cells at each condition, aged to 80% capacity

Variables:

- Chemistry: LFP, NCA, NMC
- Charge Rate: 0.5C
- Discharge Rate: 0.5C, 1C, 2C, 3C
- State-of-Charge Range: 40-60%, 20-80%, 0-100%
- Temperature: 15°C, 25°C, 35°C



Preger et al. *J. Electrochem. Soc.* **2020**, *167*, 120532.
(plot updated with more recent data)

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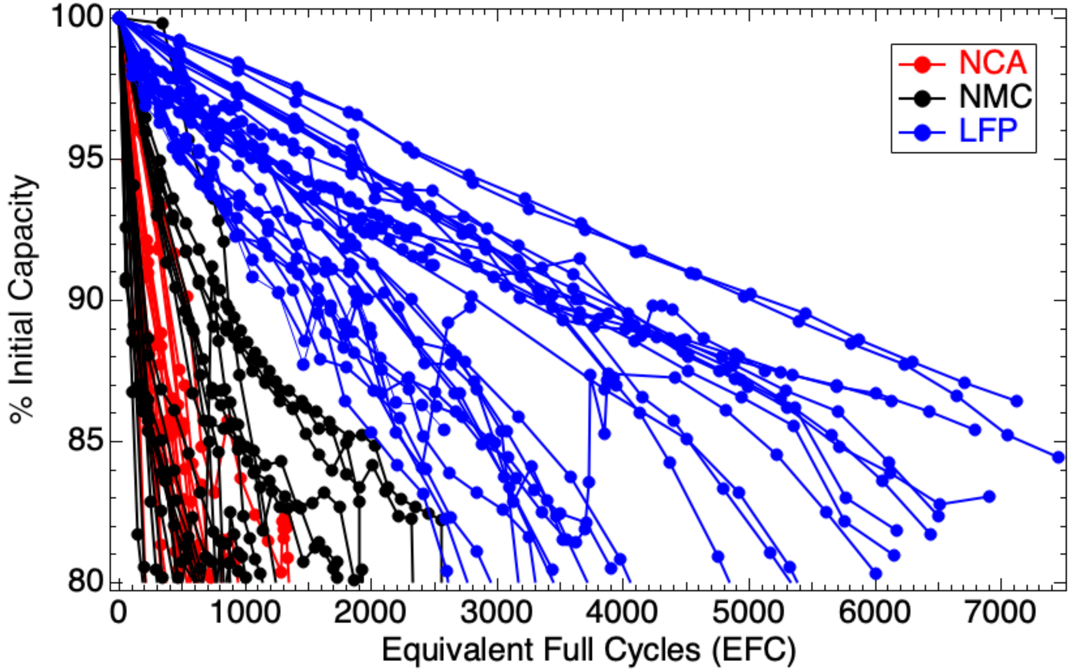

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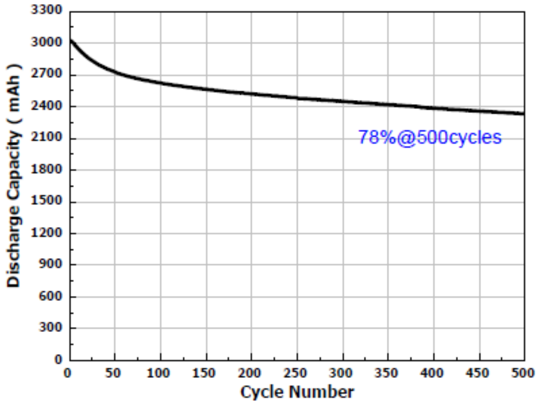
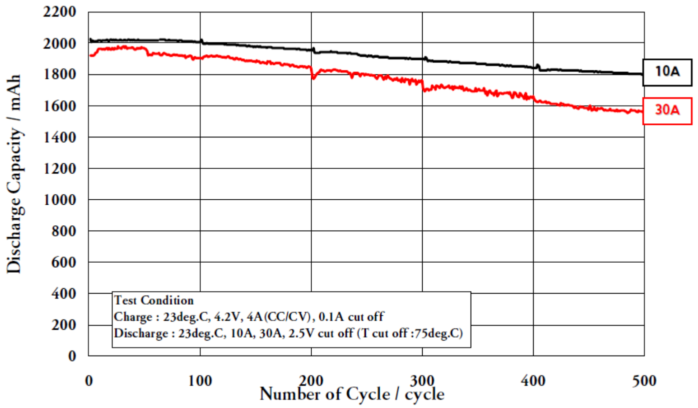
Next phase: what does degradation look like beyond 80% capacity?

Moving beyond 80% capacity endpoints

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

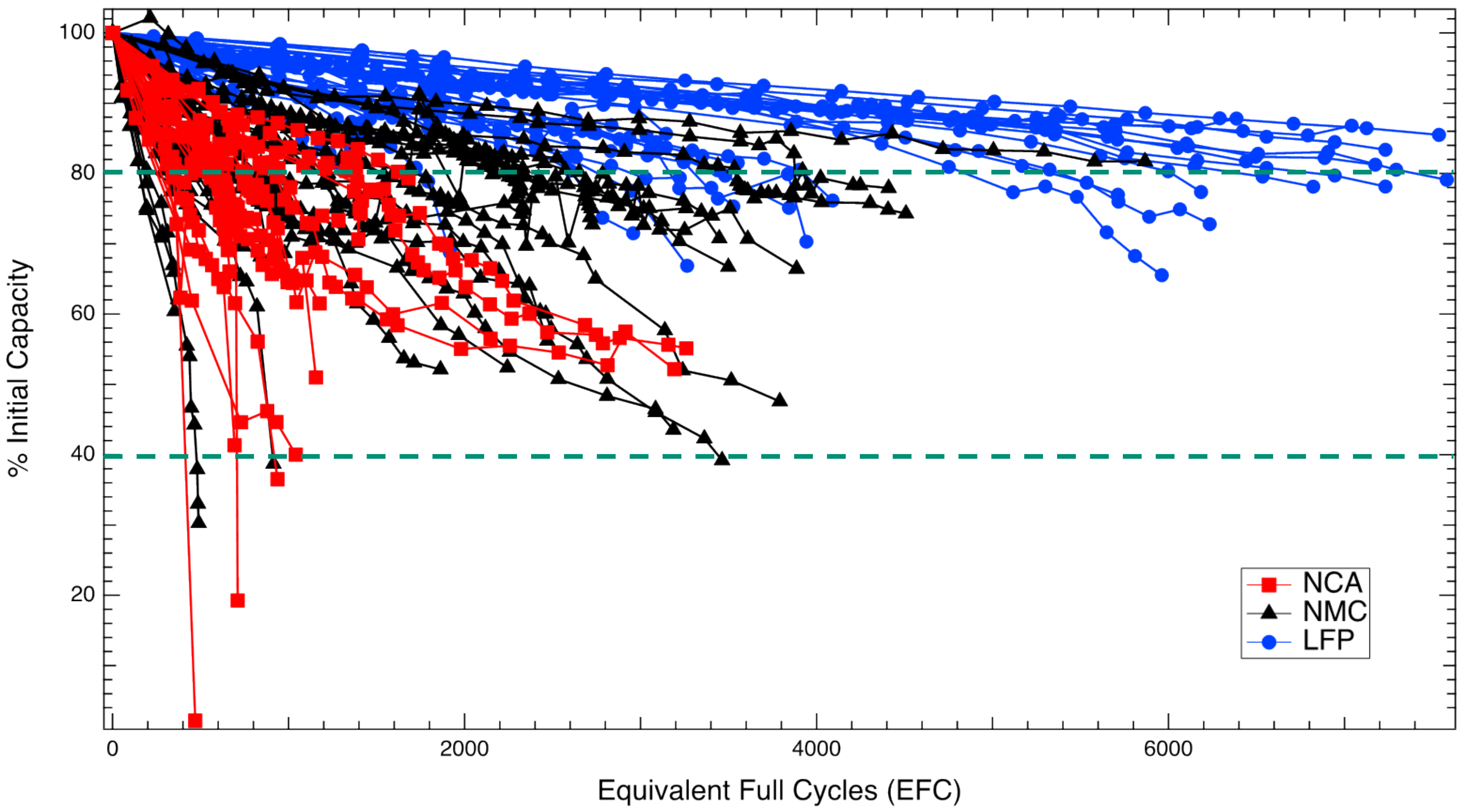




- 80% capacity is a holdover from early EV days
  - USABC 1996: “*EV batteries should be removed from automotive use when* ***current battery capacity is 80% of initial battery capacity*** *and current battery power capability is 80% of initial battery power capability*”
  - At this time, EVs were primarily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

- Understanding remaining useful life is critical for first life valuation and non-negotiable for second life applications

Cells cycled as low as 40% remaining capacity



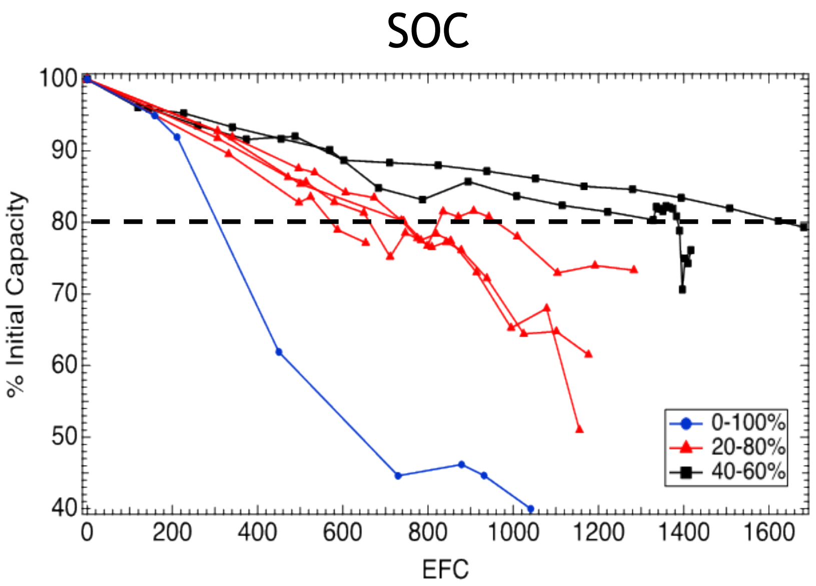
Study shows significant life possible post 80% capacity

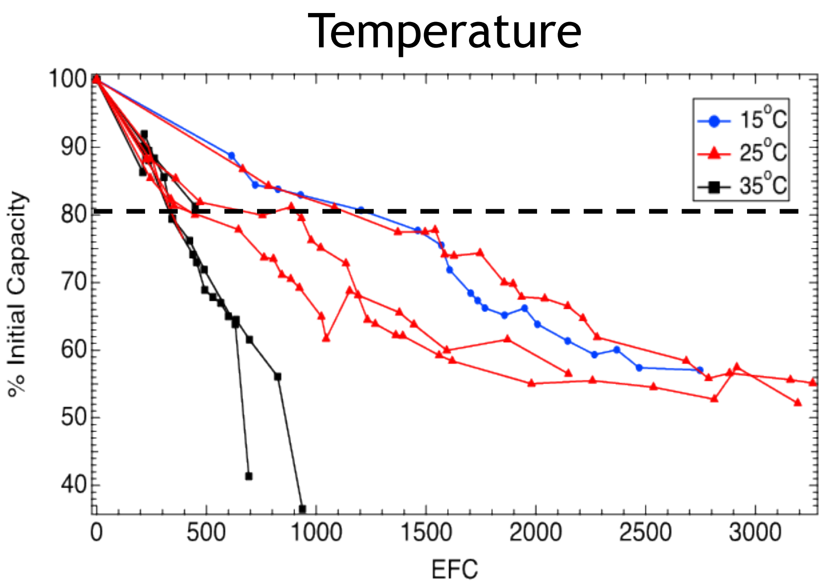
Chemistry	# of Cells Below 80%	# of Cells at 40%	Mean EFC Post 80% to date+	Mean Energy Discharge Post 80% to date+	Mean Capacity of Post 80% Cells+
NMC	19	3	685 +/- 306	6.8 +/- 3 kWh	63%
NCA	13	3	486 +/- 286	4.9 +/- 2.8 kWh	60%
LFP	15*	0	392 +/- 291	1.4 +/- 0.9 kWh	74%

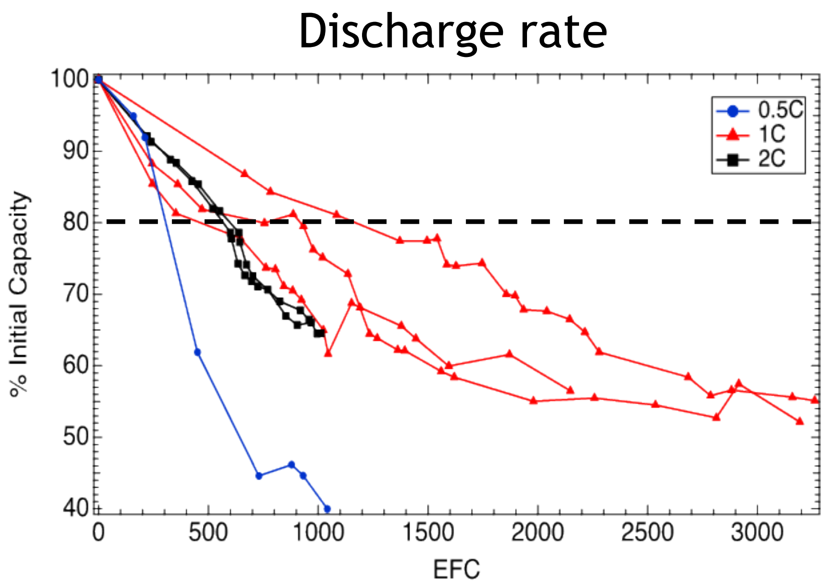
*Half of the LFP cells are still above 80% capacity

+Mean of all cells cycled, across all cycling conditions, for each chemistry

Influence of cycling conditions on NCA cell degradation







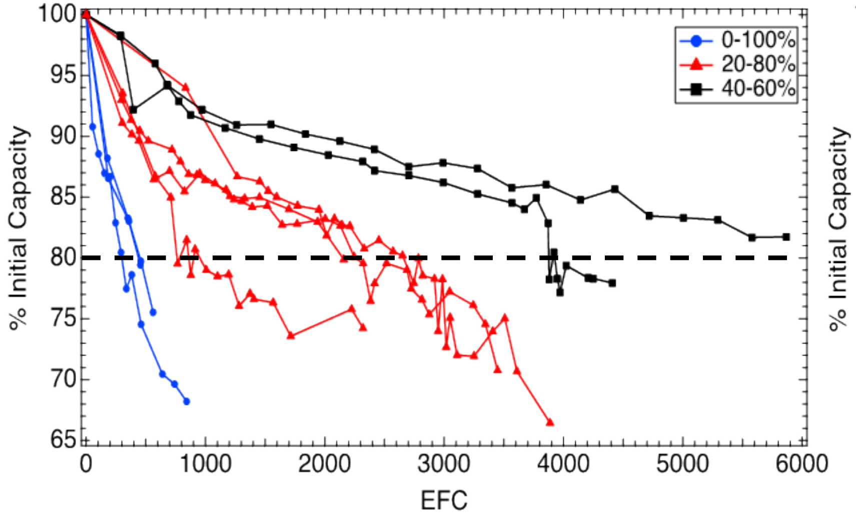
Higher SOC window accelerates degradation

Starting to see temperature dependence after 80% (higher temp. worse)

Lower discharge rates increase the rate of degradation below 80% capacity

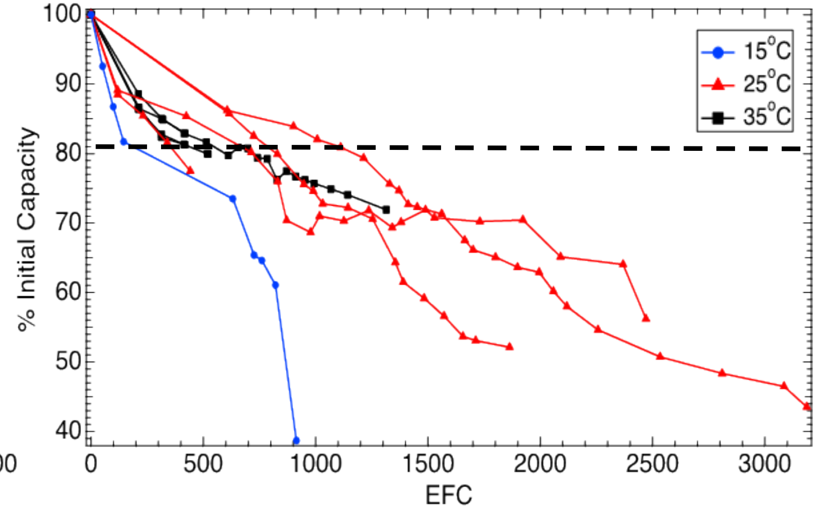
Influence of cycling conditions on NMC cell degradation

SOC



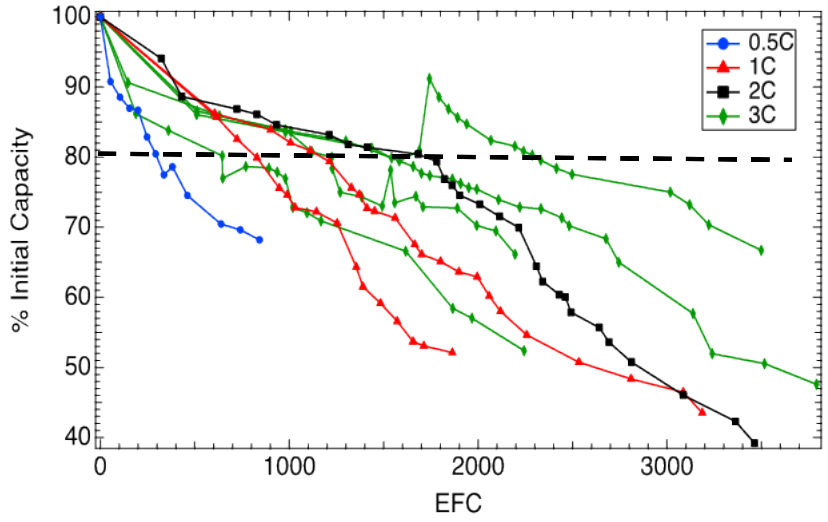
Higher SOC range continues to lead to faster capacity fade

Temperature



Pronounced temperature dependence below 80% (higher degradation at lower temp.)

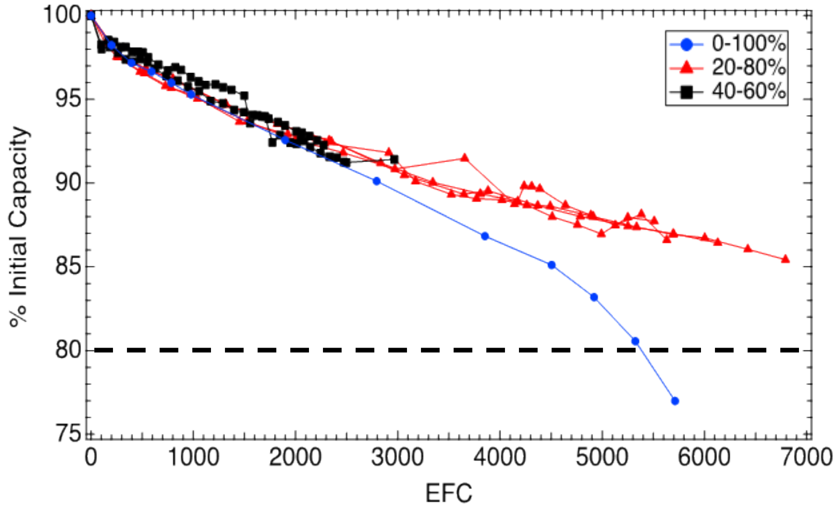
Discharge rate



Lower discharge rates show slightly higher capacity fade (calendar aging?)

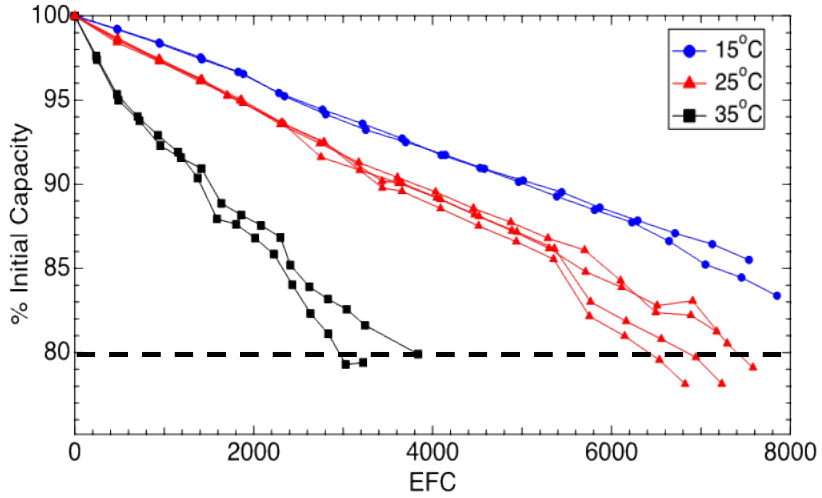
Influence of cycling conditions on LFP cell degradation

SOC



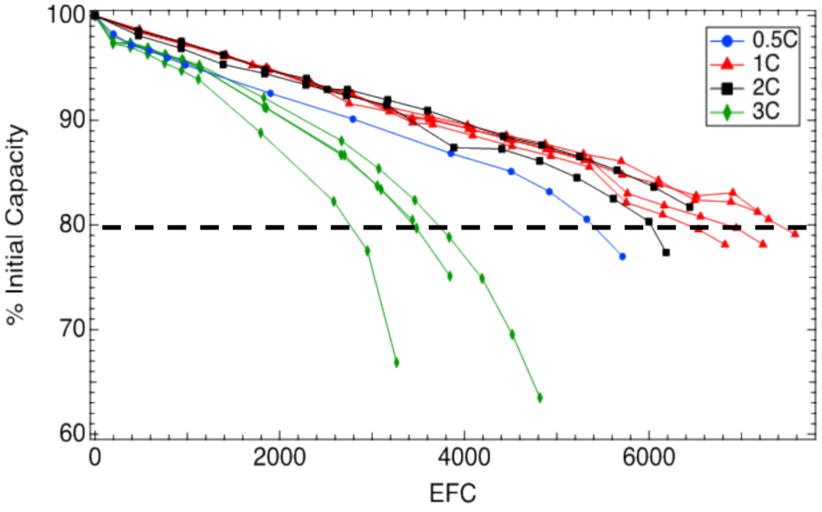
Higher SOC range again leads to faster capacity fade

Temperature



Higher degradation at higher temperatures

Discharge rate

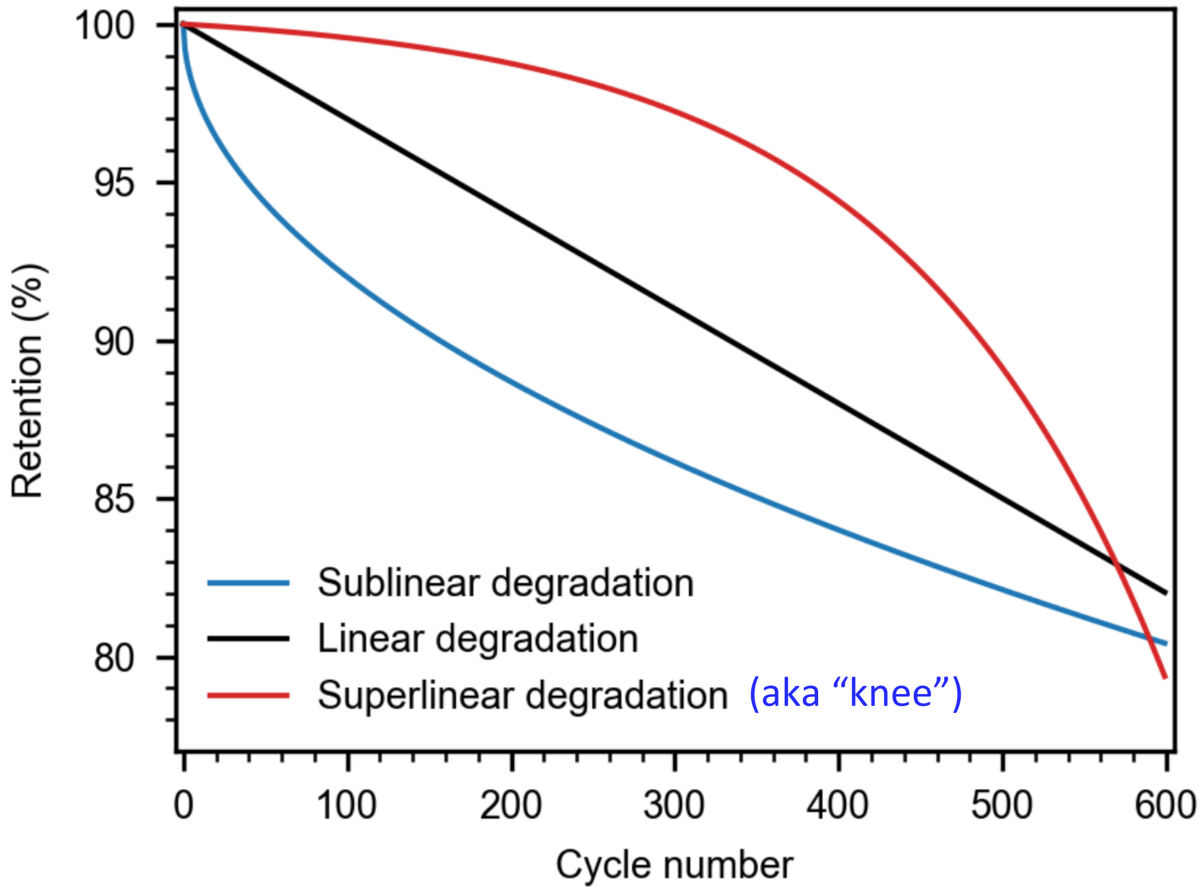


Lowest and highest discharge rates show more rapid capacity fade

Summary of pre and post 80% capacity fade trends

	SOC Range		Temperature		Discharge Rate	
	Pre 80%	Post 80%	Pre 80%	Post 80%	Pre 80%	Post 80%
NCA	Fade rate increases with increased SOC range	Pre 80% trend becomes more pronounced	No discernable trend	Increased fade rate at higher temp	No discernable trend	Increased fade rate at lower discharge rates
NMC	Fade rate increases with increased SOC range	Pre 80% trend becomes more pronounced	Increased fade rate at lower temp	Pre 80% trend becomes more pronounced	No discernable trend	Increased fade rate at lower discharge rates
LFP	Fade rate increases with increased SOC range	Pre 80% trend becomes more pronounced	Increased fade rate at higher temp	Has not reached 80%	High and low rates cause increased fade rate	Has not reached 80%

What is the shape of the aging trajectory?



Attia et al. *J. Electrochem. Soc*. **2022**, *169*, 060517.

Aging trajectory impacts the remaining useful life of the battery

Assessment of previous experimental studies of “knees”

Knees are complex and occur under many conditions

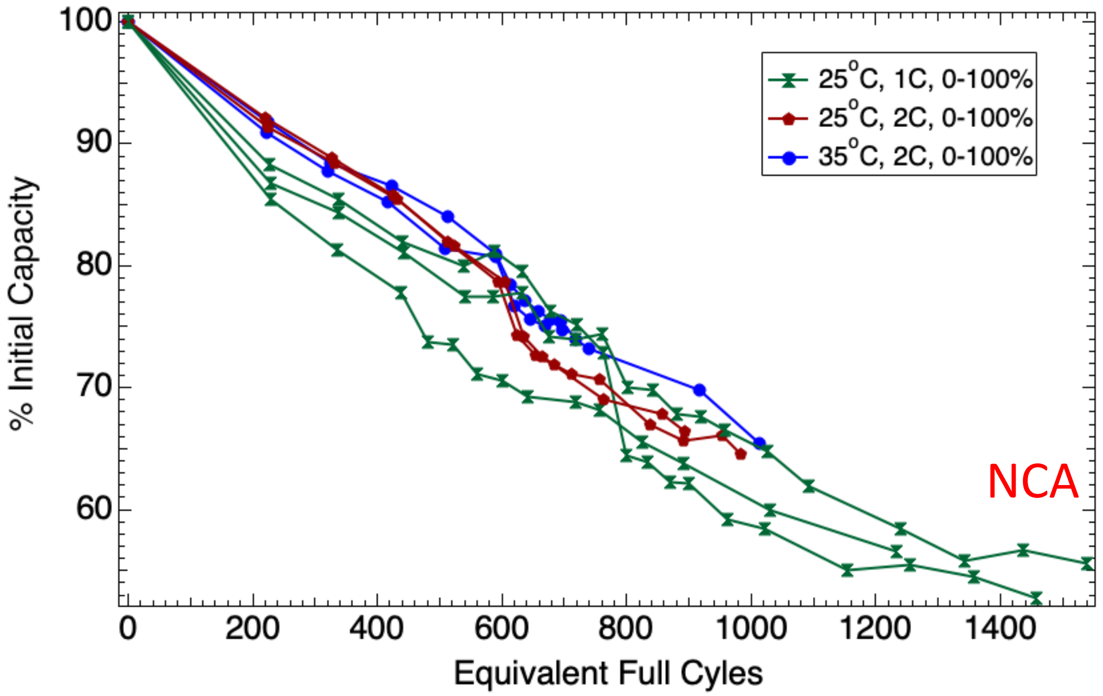
- Higher charging rate and wider DOD consistently accelerate knees
- Temperature/pressure have a ‘sweet spot’ outside of which knee is accelerated
- Discharge rate/rest time – it varies

- Knees can occur during cycling within manufacturer specifications
- Knees observed as high as 90% remaining capacity and as low as 40%

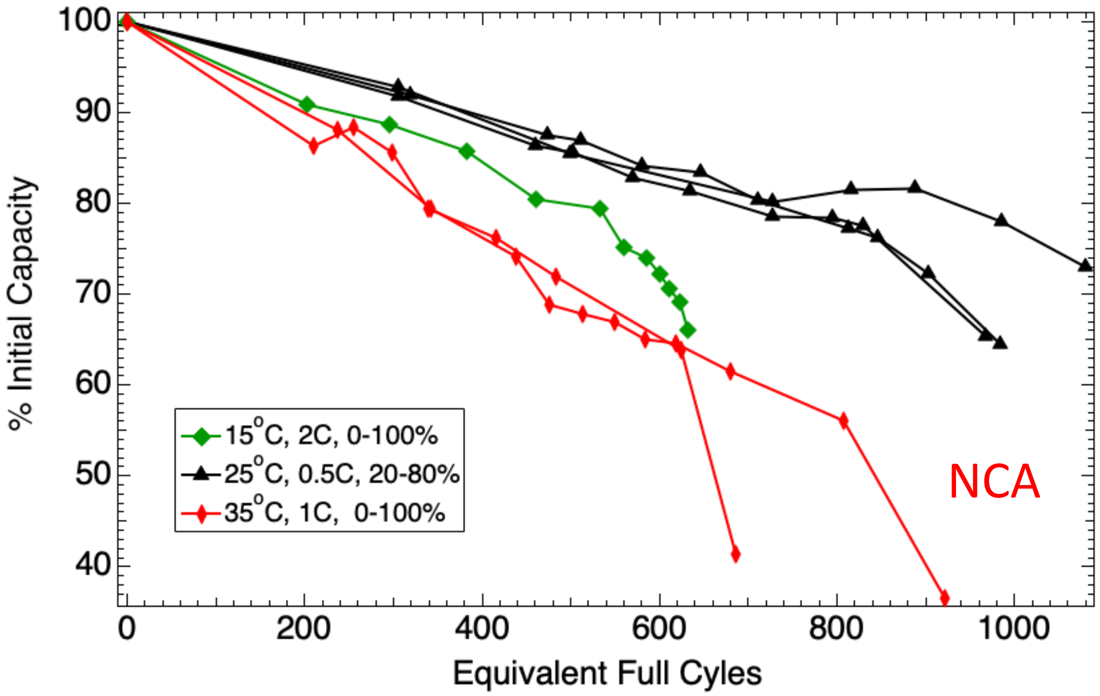
Attia et al. *J. Electrochem. Soc*. **2022**, *169*, 060517.

Knee points arose under unexpected conditions in present study

No Knee



Knee



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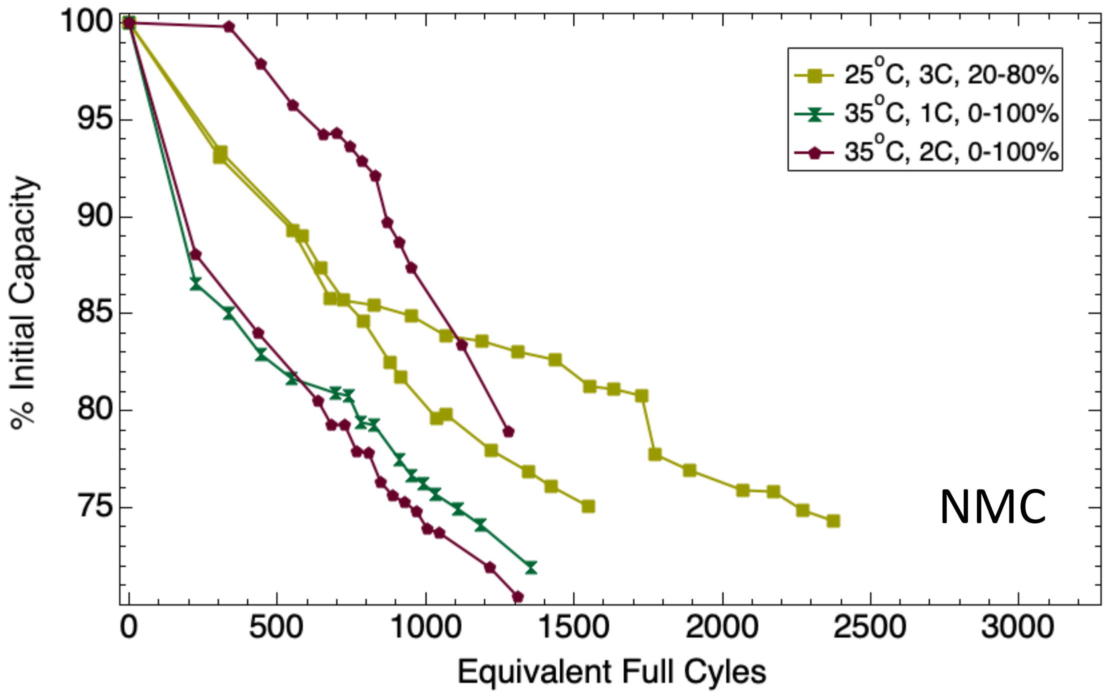
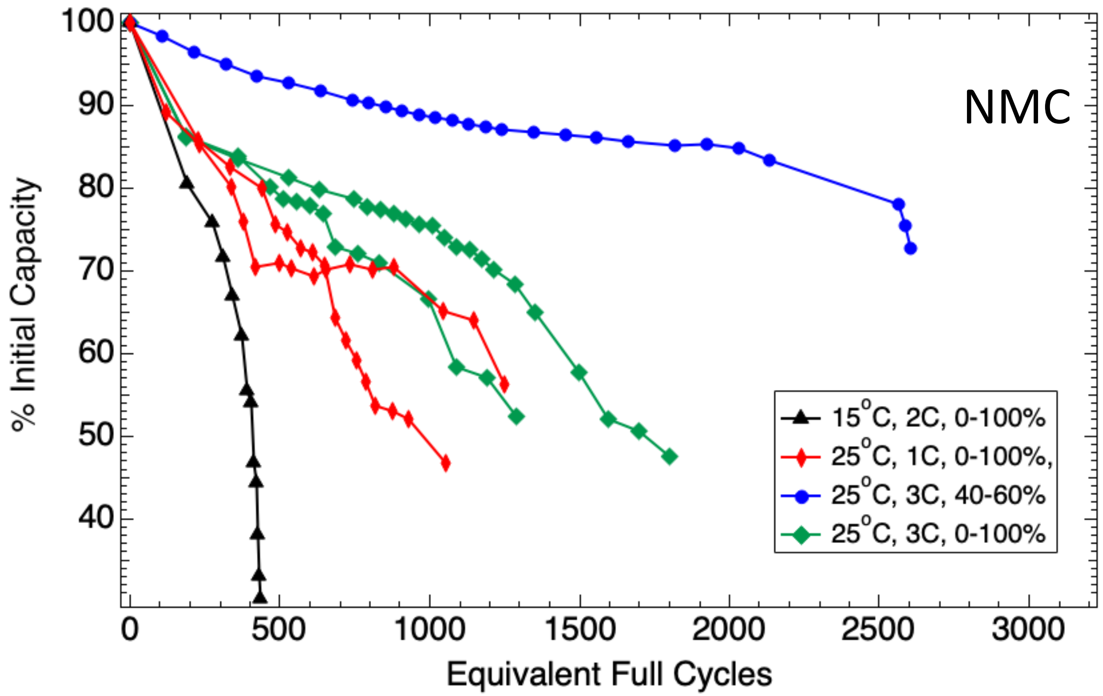


Knee



Summary

- Cells can have long cycle life beyond 80% capacity (as low as 40%)
- Degradation is dependent on the cycling conditions and the cell chemistry
  - Some degradation trends become more pronounced after 80%, but new trends can arise
- Relationship between cycling conditions and ‘knee’ not always straightforward

Acknowledgments

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