SAND2021-12275C

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Systematic Long-Term Cycling of 18650 Batteries Beyond 80% Capacity

PRESENTED BY

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U.S. DEPARTMENT OF ENERGY

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Unknowns about Cell Degradation Prevent Optimal Use

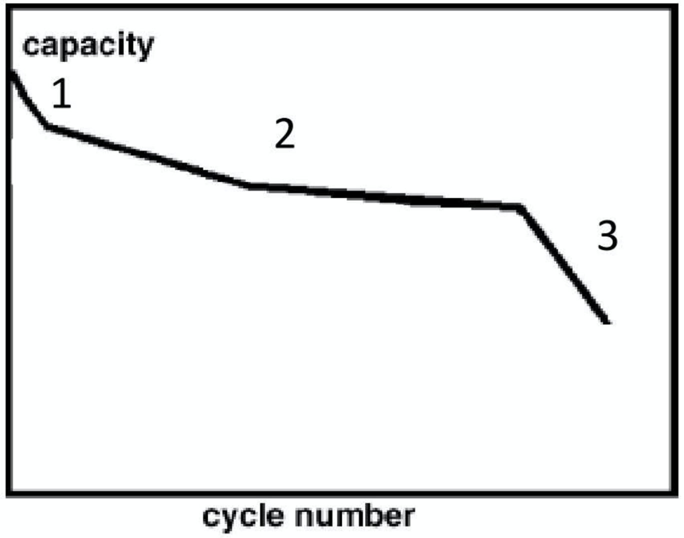
- Manufacturer spec sheets focus on safe operating limits, not performance
- Unaddressed questions:
  - What are optimal cycling conditions for each cell chemistry?
  - How do cells behave beyond 80% initial capacity?
  - What causes rapid capacity fade in cells at different conditions?
  - How does safety change with increased cycling?

Why is There a Need to Study End of Life (EOL) Cycling?

- Li-ion cycling studies and manufacturing spec sheets focus on cycling to 80%
  - A convention that was adopted out of the early applications for EVs
  - EVs at this time primarily used Ni-based batteries
- This cutoff may not be applicable to higher energy and power density Li-ion cells
  - Particularly for grid type applications which have different requirements than EVs
- Currently, cycling behavior beyond 80% capacity is not well known as most studies focus on cycling to 80% capacity
- Unknowns about useful cycle life and optimal use during long term cycling inhibit widespread adoption of Li-ion storage systems for grid use

Mapping Degradation of Cell Performance Will Enable Optimal Use

- Cells may undergo different rates of degradation depending on their cycled life
- Current model for degradation suggests that fade occurs in 3 steps
  - Step 1: Initial rapid decline due to SEI formation
  - Step 2: Linear decline dominated by LLI reactions
  - Step 3: Rapid decline after a knee point is reached
- Currently, occurrence and location of knee points is not well understood
- Need to understand this behavior to predict useful life of systems



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

Conducting Broad Study of Li-ion Cycling to Understand Performance and Degradation

Approach

1. Cycled 18650 format cells to 80% initial capacity[1] and now, to end of life (EOL) capacity of 40%
2. Electrochemical characterization during cycling
3. Materials characterization on selected cells at 80% capacity and EOL
4. Conduct abuse testing of aged cells to observe variations in safety due to cycling

[1]Preger et al. "Degradation of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions" *J. Electrochem. Soc.,* **2020***, 167,* 120532.

Conducting Broadest Public Study of Li-ion Cycling to Understand Performance and Degradation

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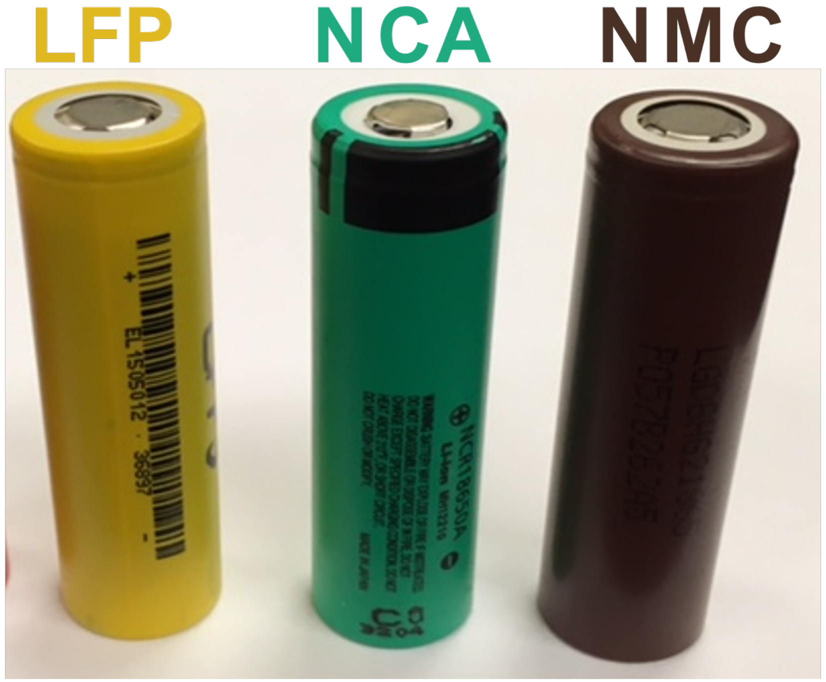
Battery	LFP* (A123)	NCA (Panasonic)	NMC (LG Chem)
Capacity	1.1 Ah	3.2 Ah	3.0 Ah
Voltage	3.3 V	3.6 V	3.6 V
Max Discharge Current	30 A	6 A	20A
Operating T	-30 to 60°C	0 to 45°C	0 to 50°C



Cycling Conditions, Procedure and Current Status

- Started at least 2 cells at each condition
  - Some conditions in EOL cycling have one cell after one was selected for materials characterization
- Capacity check done at beginning and end of each round of cycling
- Electrochemical Impedance Spectroscopy (EIS) done after every 3% decrease in capacity

Cycling Conditions

DOD, Temperature, Discharge Rate*			
40-60%, 25°C, 0.5C	0-100%, 15°C, 1C	0-100%, 15°C, 2C	40-60%, 25°C, 3C
20-80%, 25°C, 0.5C	0-100%, 25°C, 1C	0-100%, 25°C, 2C	20-80%, 25°C, 3C
0-100%, 25°C, 0.5C	0-100%, 35°C, 1C	0-100%, 35°C, 2C	0-100%, 25°C, 3C

*0.5C charge rate for all

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20-80%, 25°C, 0.5C	0-100%, 25°C, 1C	0-100%, 25°C, 2C	20-80%, 25°C, 3C
0-100%, 25°C, 0.5C	0-100%, 35°C, 1C	0-100%, 35°C, 2C	0-100%, 25°C, 3C

*0.5C charge rate for all

Summary of Long Term Cycling Project Status

Chemistry	Currently Cycling	Above 80%	Between 80 and 40%	Below 40%
LFP	32	15	17	0
NCA	15	0	14	1
NMC	21	0	19	2
Total	68	15	50	3

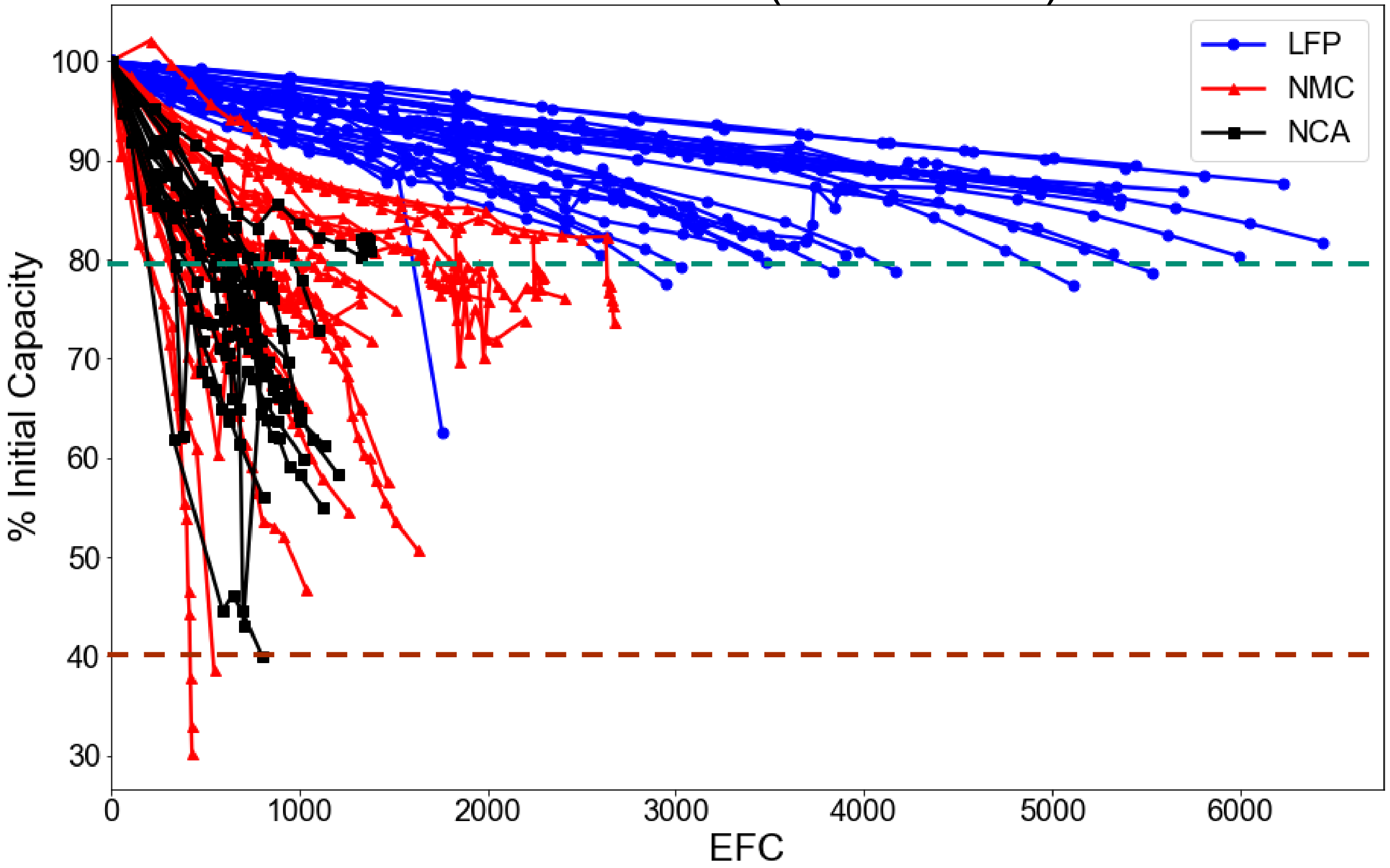
Key Result: Capacity Fade Rate Varies Significantly with Cycling Conditions and Cell Chemistry

- Capacity as a function of Equivalent Full Cycles (EFC) varies greatly with both condition of cycling and cell chemistry
  - State of Charge (SOC) range has the greatest impact across chemistries
  - Temperature and discharge rate show different impacts for each cell chemistry
- LFP consistently has the slowest capacity fade, while NCA generally has the most rapid
- NMC cells show the largest variation in capacity fade rate depending on condition of cycling
- Knee points are hard to pinpoint and depend on chemistry and condition of cycling.

Cycle Life of Cells Varies Significantly by Chemistry and Cycling Conditions

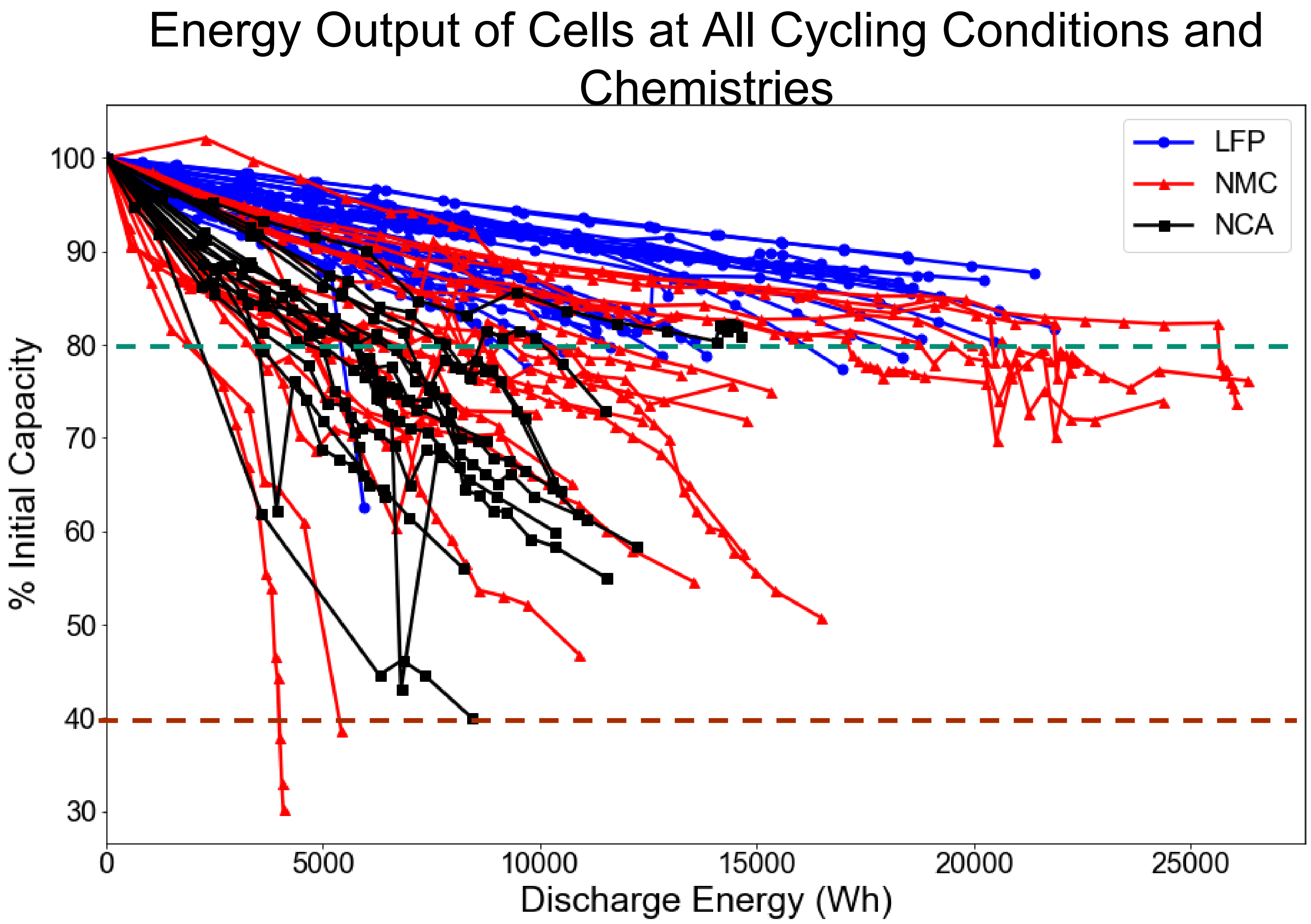
- LFP cells show dramatically longer cycle life than NMC and NCA cells
- NCA cells have generally the shortest cycle life
- NMC cells have the greatest variation in cycle life (based on conditions)

Capacity Fade of Cells at All Cycling Conditions and Chemistries (Since 2017)



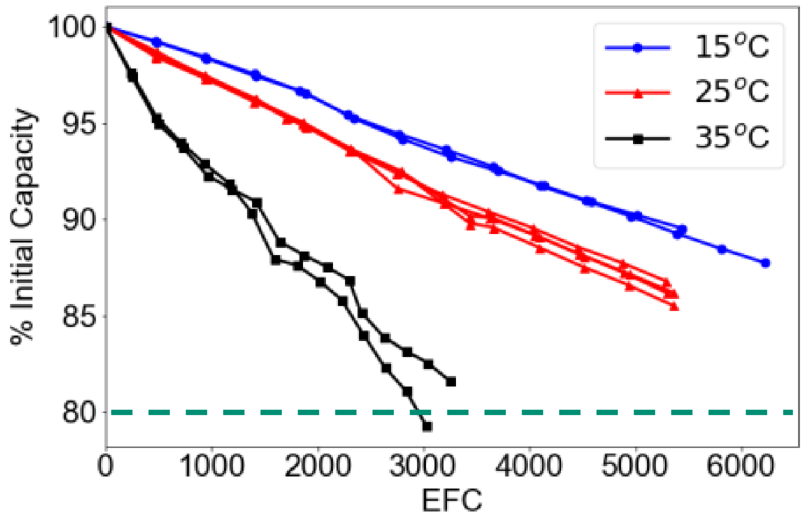
Graphing Capacity Fade as a Function of Energy Output Normalizes Cell Performance

- By plotting as a function of energy discharged, chemistry variations are reduced
  - NCA and NMC cells have ~3X the capacity and higher voltage than LFP cells
- LFP's cycle life advantage is reduced and shows comparable performance to some NMC cells
- LFP cells generally have experienced much less capacity fade for the same amount of energy output as most of the NCA and NMC cells



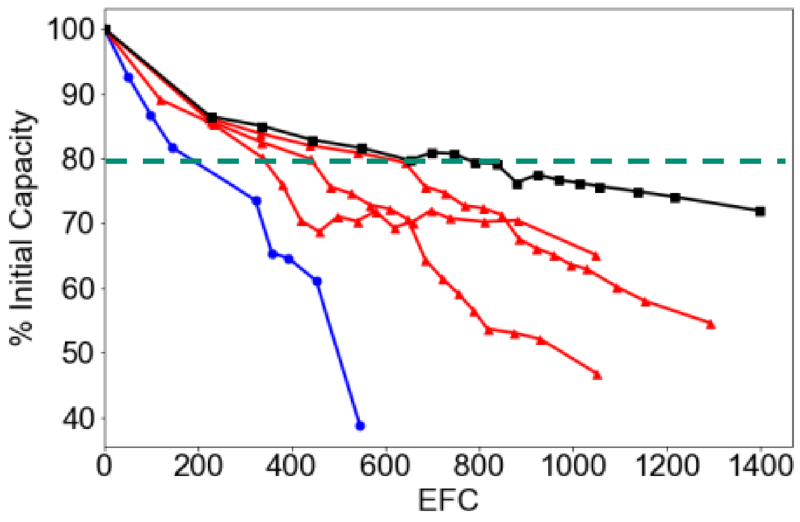
Capacity Fade by Temperature Shows Dependence Changes with both Chemistry and Age

LFP



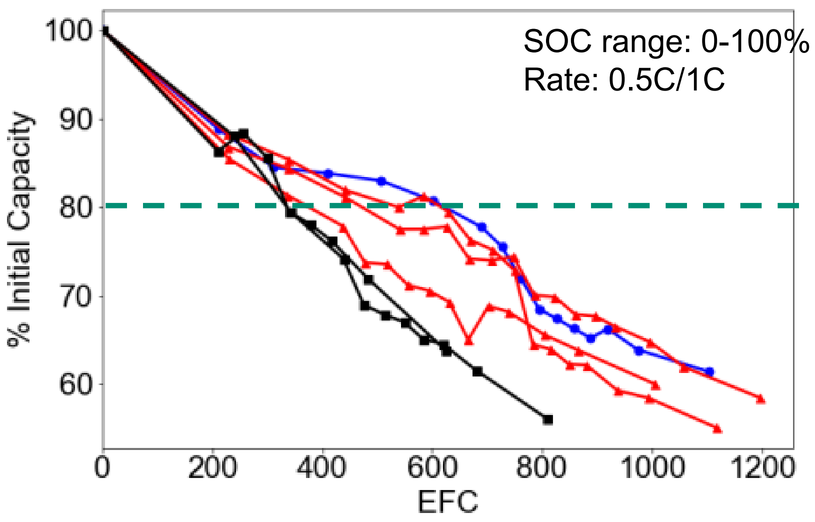
Increased degradation at higher temperature

NMC



Increased degradation at lower temperature

NCA

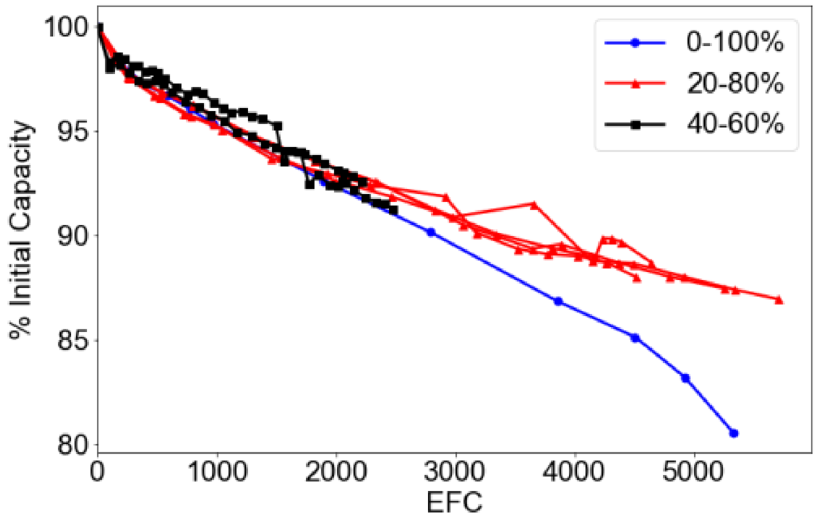


Increased degradation at higher temperature after 80% capacity

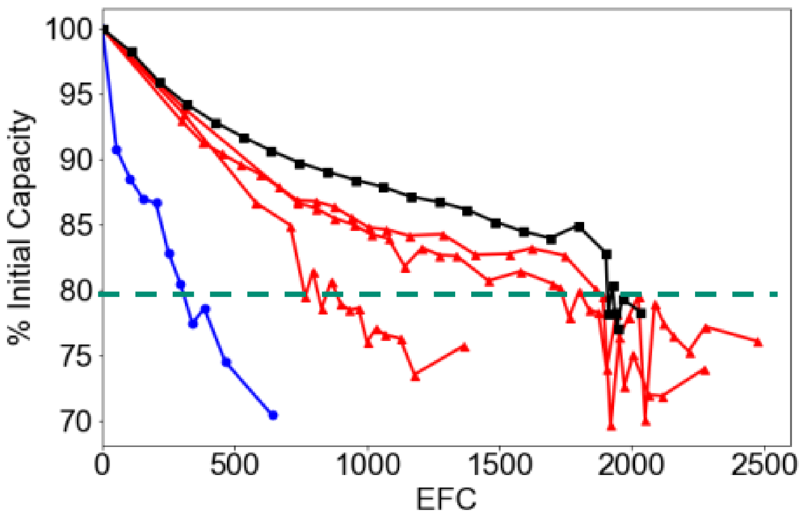
In all chemistries temperature dependence increases with cycle life

Increased SOC Range Consistently Increases Rate of Capacity Fade

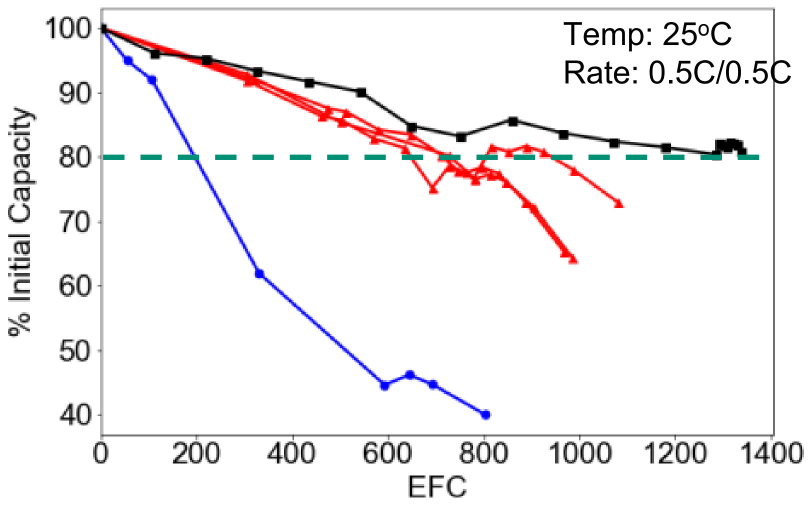
LFP



NMC



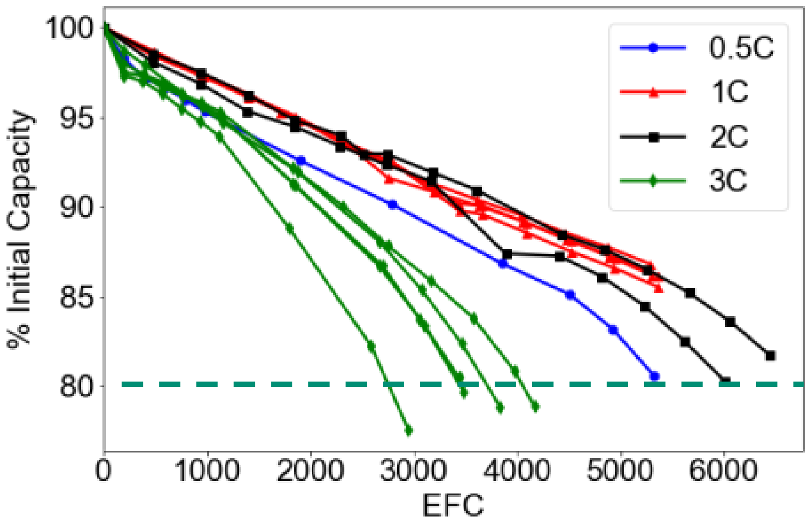
NCA



- All cells show increased SOC range increases rate of capacity fade
- LFP has the slowest fade rate while NCA has the largest
- SOC dependence increases with cycle life
  - 0-100% LFP and 20-80% NCA cells show increases in degradation rate

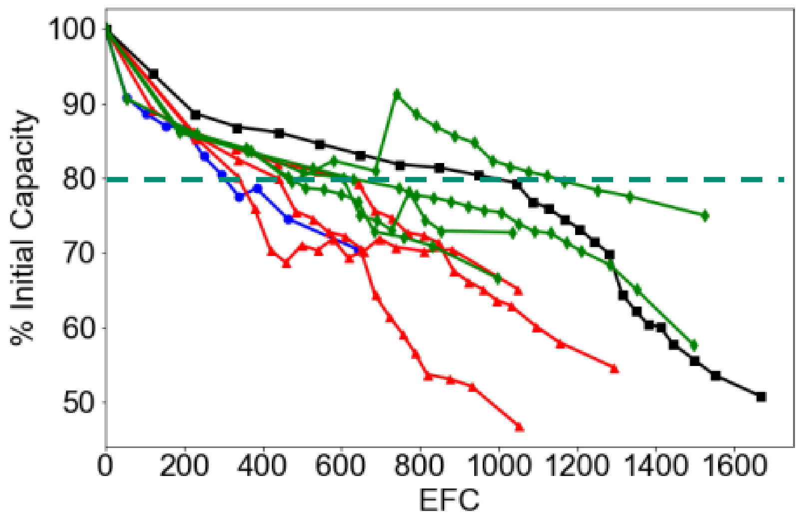
Capacity Fade Shows a Mixed Dependence on Discharge Rate

LFP



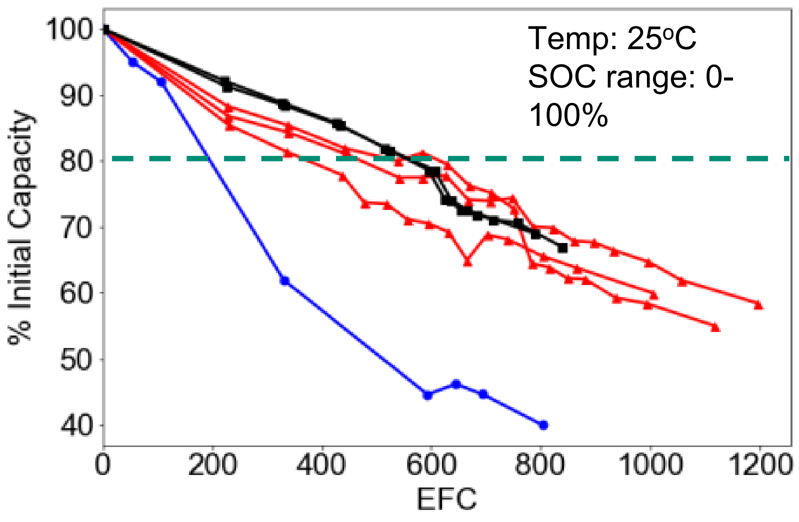
Highest and lowest discharge rate increased degradation

NMC



Lower rates increased degradation occurs after 80% capacity

NCA

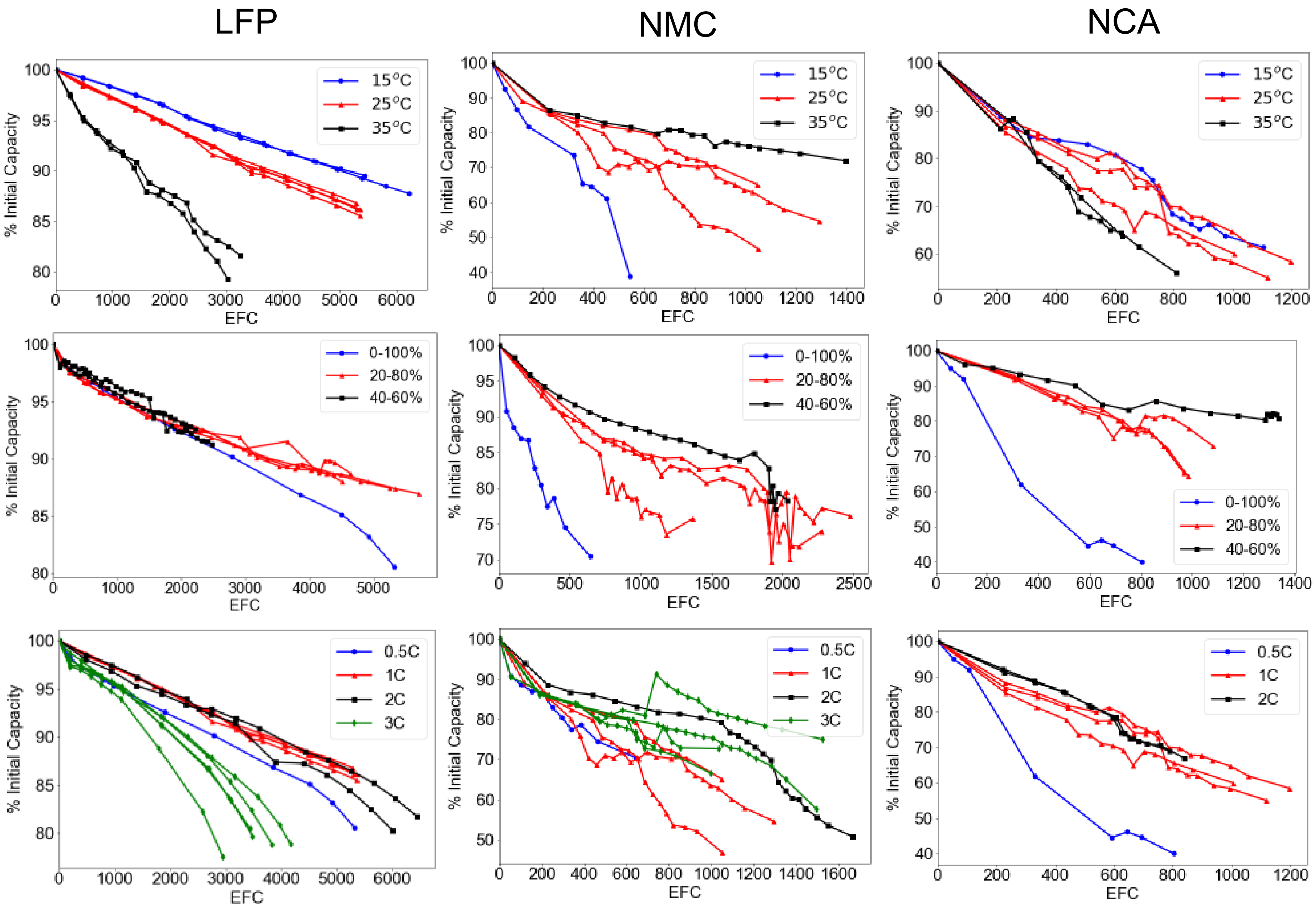


Decreased rate increases degradation

Mixed dependence on discharge rate may result from increased calendar aging at low rates vs increased stress from heating and mechanical at high rates. These appear to impact chemistries differently

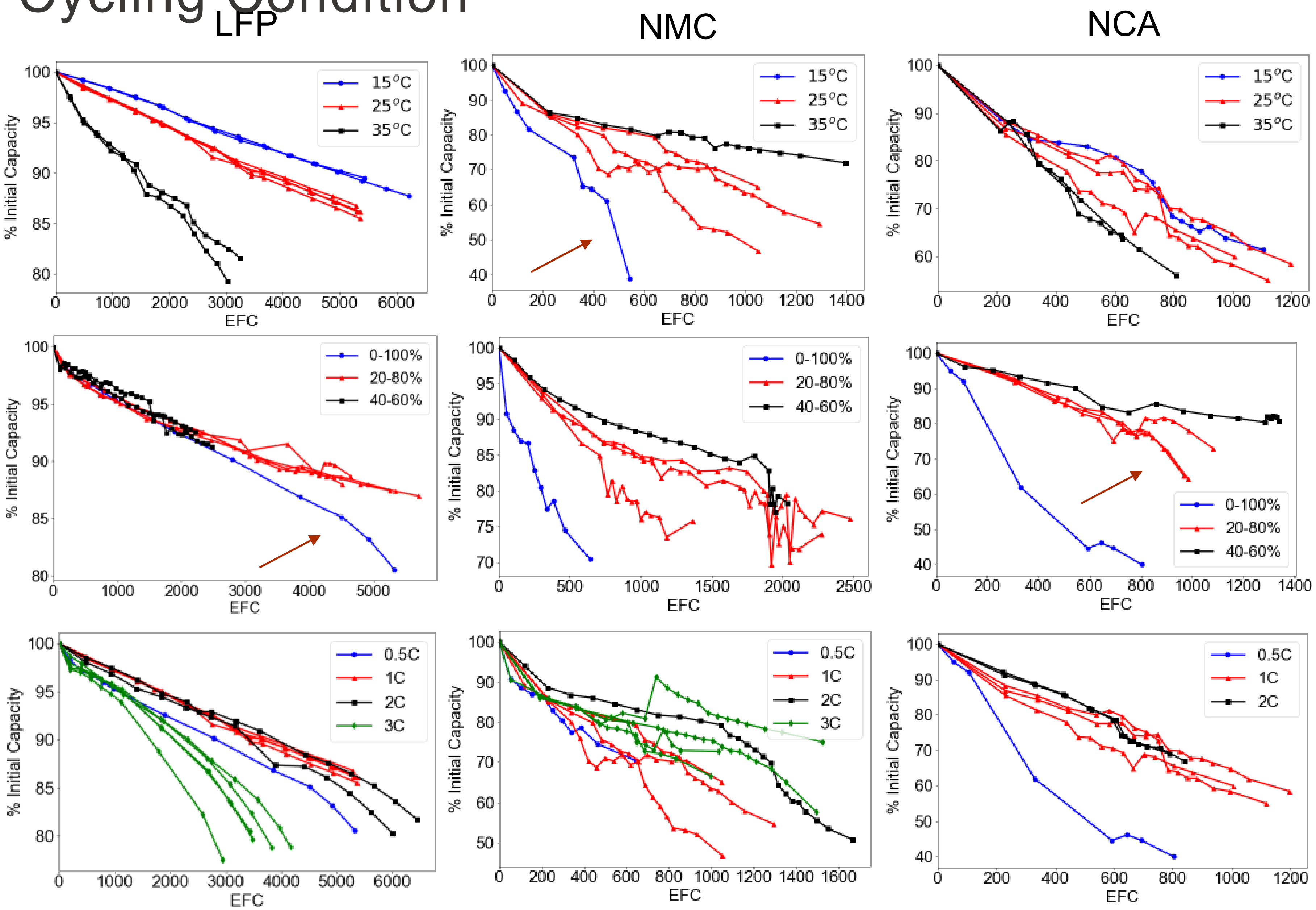
SOC Range of Cycling the Most Important Predictor of Capacity Fade Rate

- Overall SOC range is generally the best predictor of capacity fade rate
- Temperature next best predicts capacity fade, particularly at increased cycle life
- Discharge rate is least predictive of capacity fade rate
- Some factors only appear to become significant at longer cycle life



Knee Point Occurrence and Location is Dependent on Chemistry and Cycling Condition

- Knee point is chemistry and cycling condition dependent
- Knee location varies by chemistry and condition
- Some cells appear to be in rapid degradation from the start of cycling
    - 0-100% SOC NCA and NMC



Conclusions

- Cycle life of cells varies widely between chemistries and conditions of cycling
  - Energy throughput does not vary as much between cell chemistries
- Capacity fade rate most dependent on SOC range with temperature and discharge rate chemistry dependent
- Some variables only cause significant variation at longer cycle life
  - NMC at different discharge rates
  - NCA at different temperatures
- Knee points occurrence and location appear to be dependent on chemistry and condition of cycling

Acknowledgements

- Co-Authors:
  - Yuliya Preger
  - Armando Fresquez
  - Babu Chalamala

- Funded by the U.S. Department of Energy, Office of Electricity, Energy Storage program. Dr. Imre Gyuk, Program Director.

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