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Systematic Cycle and Calendar Aging of Commercial 18650 LFP Lithium-Ion Cells

PRESENTED BY

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Unknowns about Cell Degradation Prevent Optimal Use

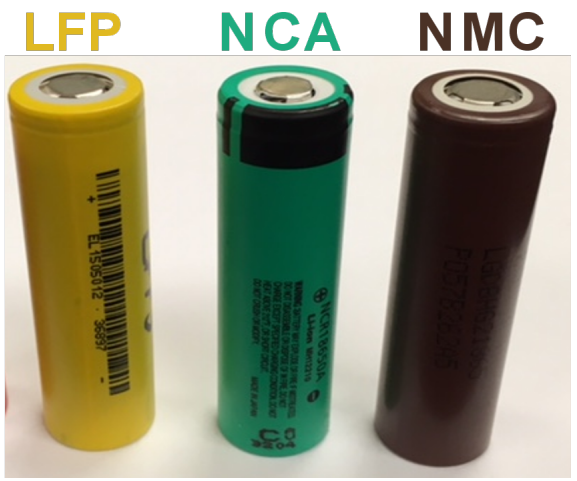
- Manufacturer spec sheets focus on safe operating limits, not performance
- Unaddressed questions:
  - What are optimal cycling conditions for each cell chemistry?
  - How do cells behave beyond 80% initial capacity?
  - What causes rapid capacity fade in cells at different conditions?
  - How does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

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) 40% initial capacity
2. Electrochemical characterization during cycling
3. Materials characterization on selected cells at 80% capacity and EOL

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



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

Cycling Conditions and Procedure

- At least 2 cells cycled at each condition
- Capacity check done at beginning and end of each round of cycling
- Electrochemical Impedance Spectroscopy (EIS) done after every 3% decrease in capacity
- Cycling done by Arbin Battery cyclers

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

Calendar Aging Study Conditions

- At least 2 cells aged at each condition
- Each round of aging was between 30 and 120 days
- Capacity check done at beginning and end of each round of aging
- EIS done every round of aging

Aging Conditions

SOC and Temperature		
25%, 15°C	25%, 25°C	25%, 35°C
50%, 15°C	50%, 25°C	50%, 35°C
90%, 15°C	90%, 25°C	90%, 35°C

Topline Conclusion: Cycling Based Capacity Fade Appears to be a Combination of the Conditions of Cycling and Calendar Aging at Different Conditions

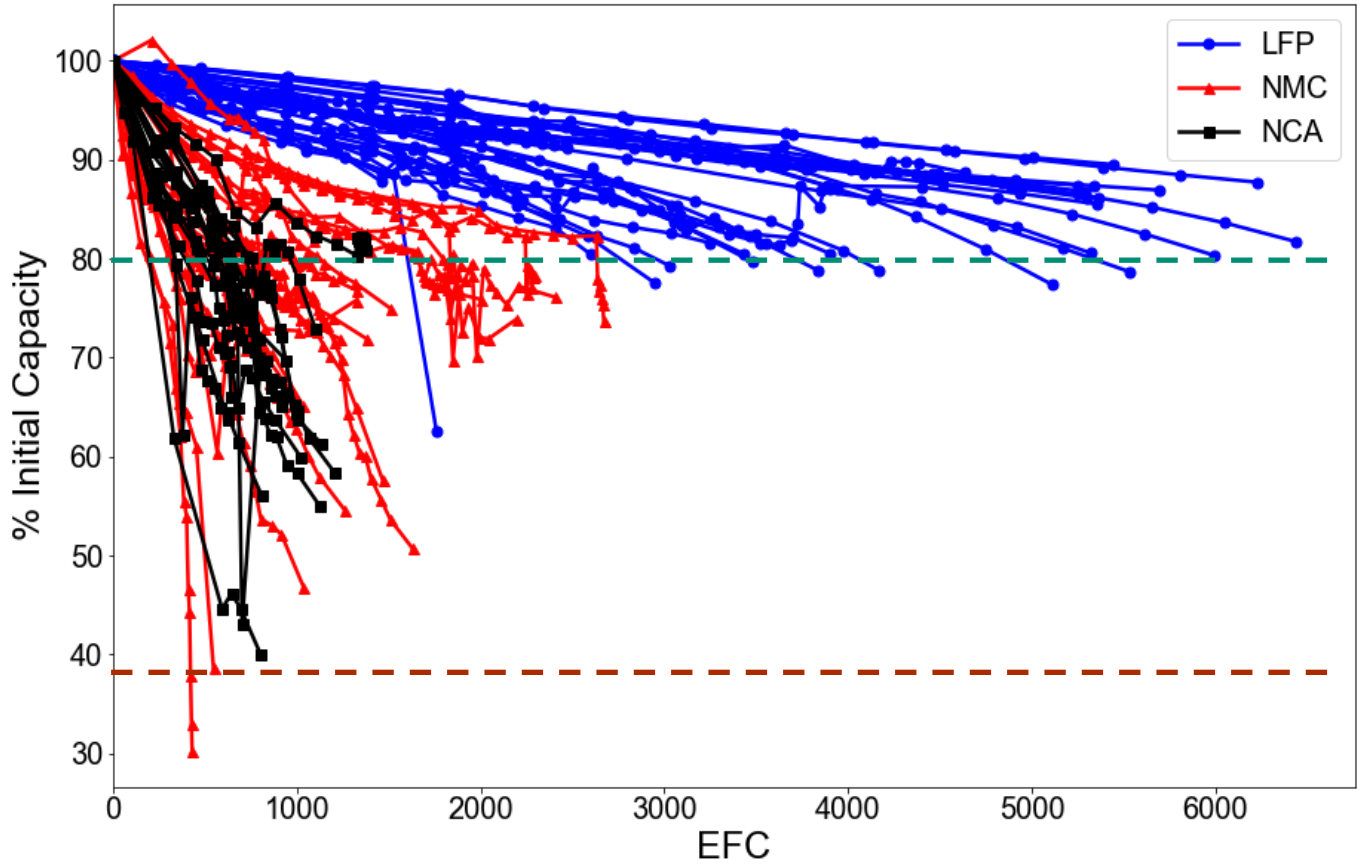
- LFP cells show increased cycle life compared to NMC and NCA cells but this advantage is reduced when looking at energy passed
- Temperature appears to be the most important factor in LFP cycling
- Calendar aging proceeds as expected where increased temperature and SOC increase rate of capacity fade
- A significant portion of capacity fade from temperature based cycling in LFP cells appears to be from time spent at a given temperature

Capacity Fade Rate of Cells Varies Significantly by Chemistry, Cycling Conditions, and Age Metric

- 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)

*

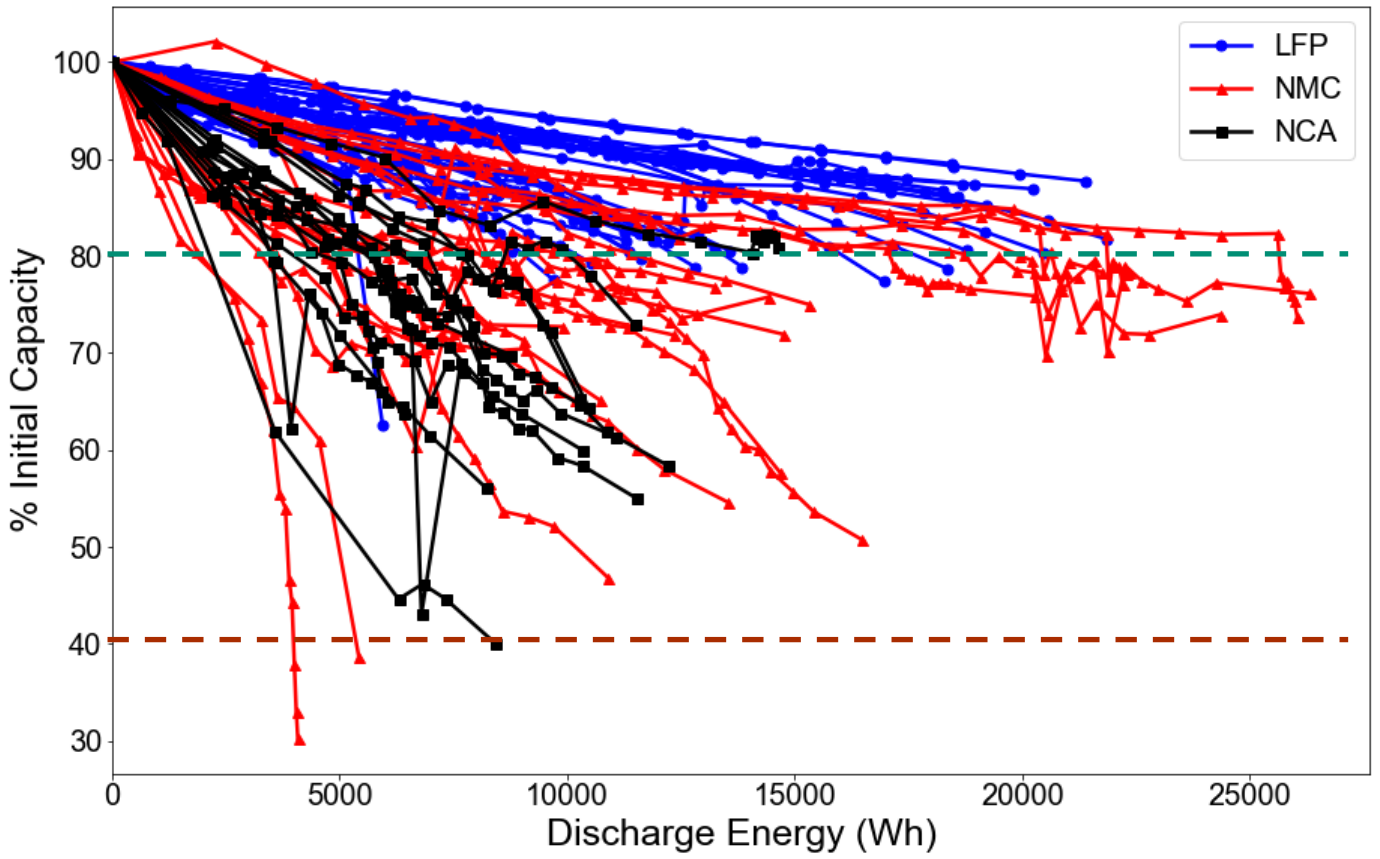
Capacity Fade of Cells at All Cycling Conditions and Chemistries (Since 2017)



*EFC is defined as equivalent full cycles

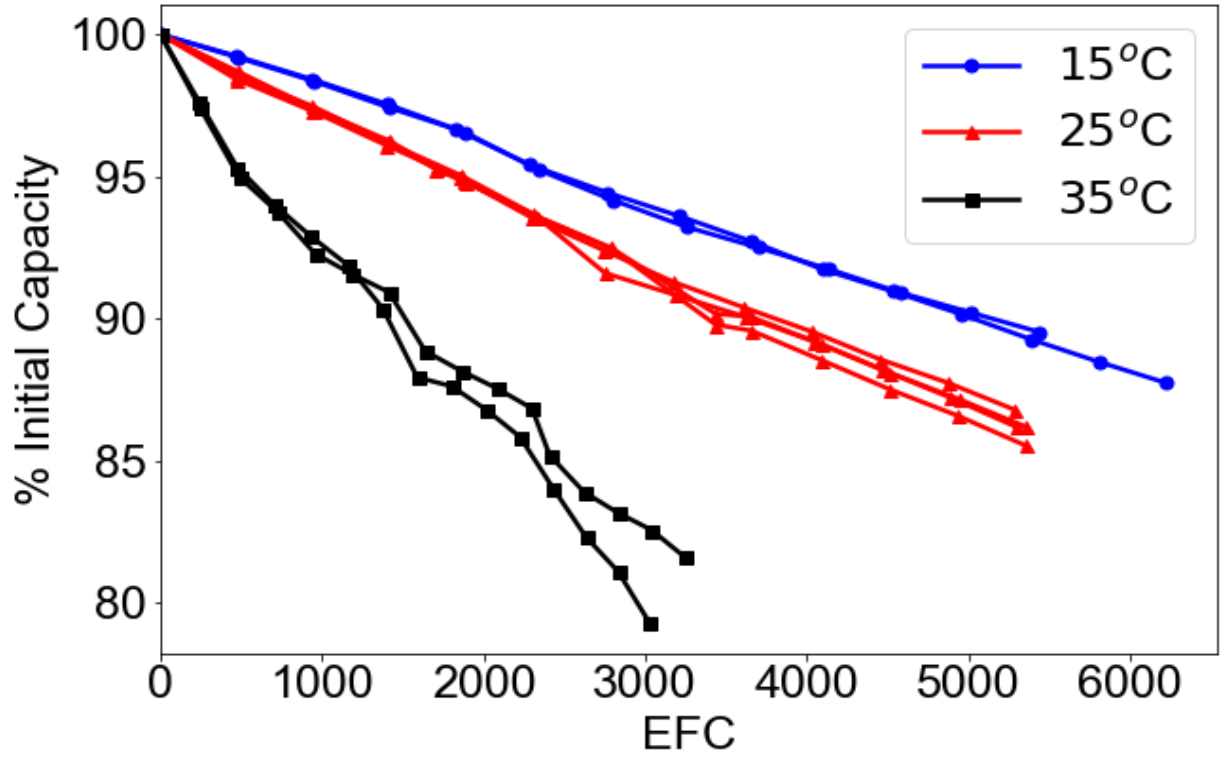
- By plotting as a function of energy discharged, chemistry variations are reduced
  - NCA and NMC cells have ~3X the capacity and higher voltage than LFP cells
- LFP's cycle life advantage is reduced and shows comparable performance to some NMC cells

Energy Output of Cells at All Cycling Conditions and Chemistries



Temperature Shows an Inverse Relationship with Capacity

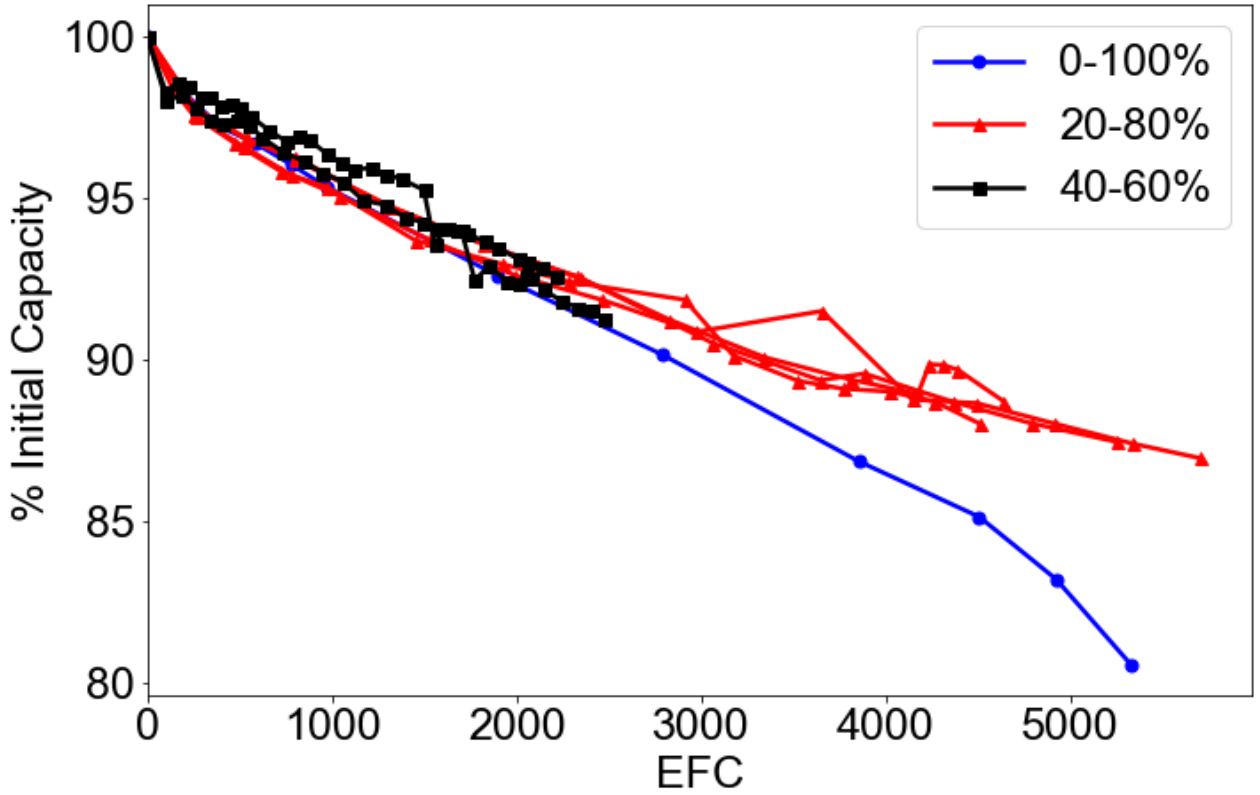
- Increased temperatures causes an increased rate of capacity fade
- Lower temperatures decreases the capacity fade rate



Note: X-axes are different for each plot

Increasing SOC Range Appears to Increase Capacity

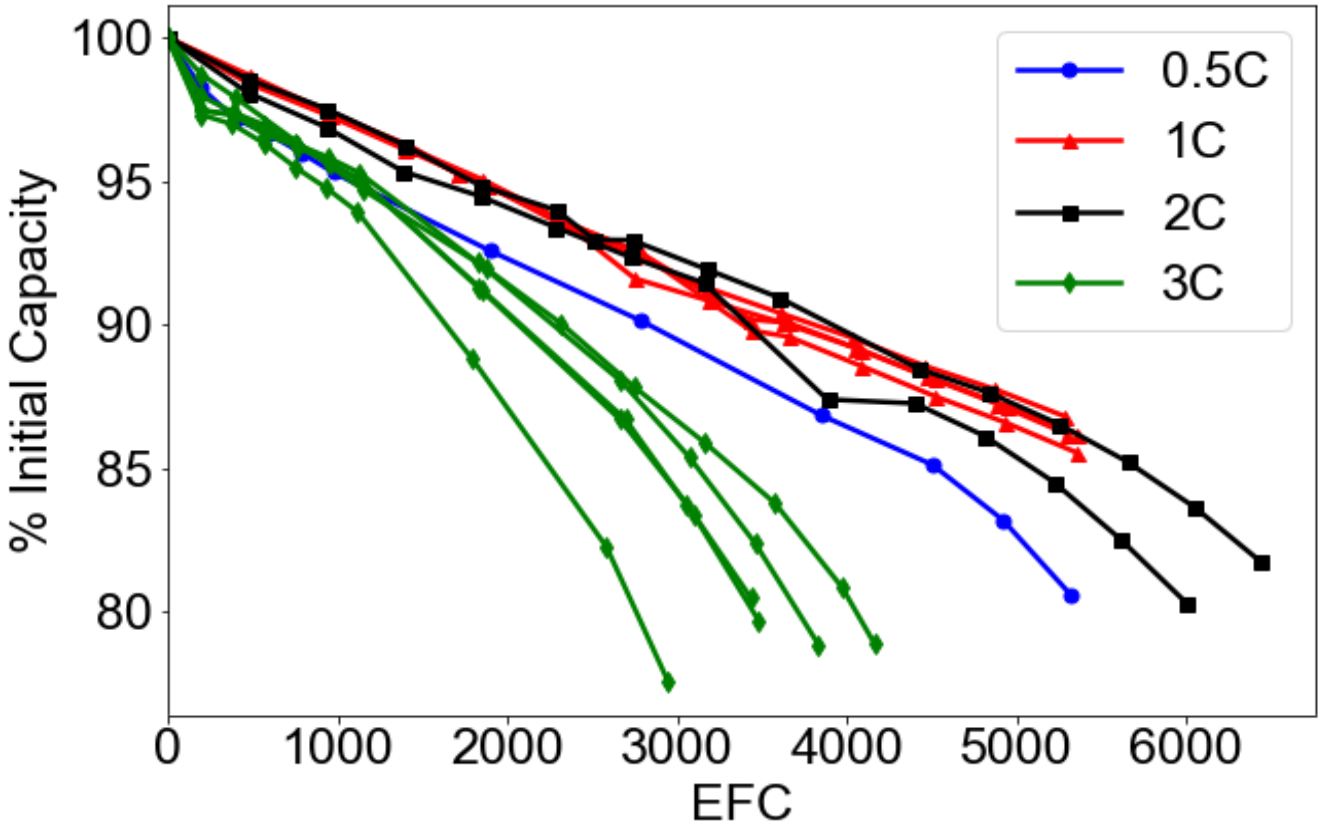
- Increase SOC range increases the rate of capacity fade
- SOC does not seem to be as much of factor until a knee point is reached in the 0-100% condition



Note: X-axes are different for each plot

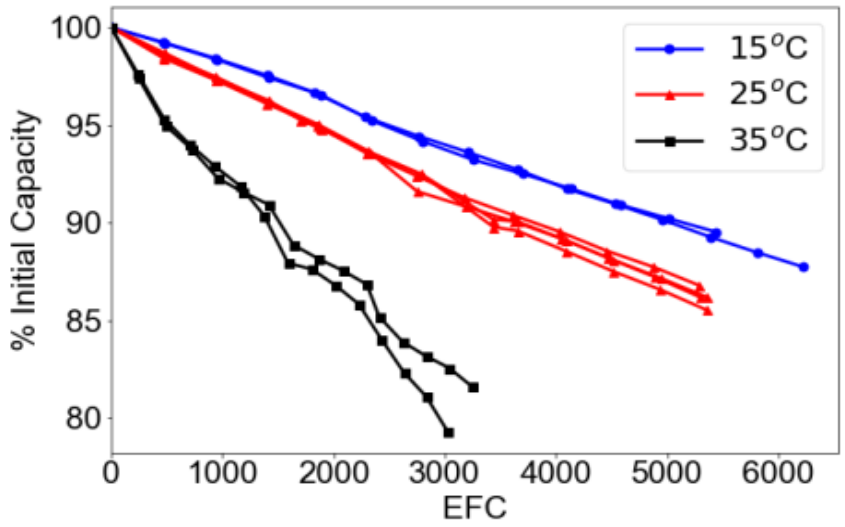
Discharge Rate Shows a Mixed Impact on Capacity Fade

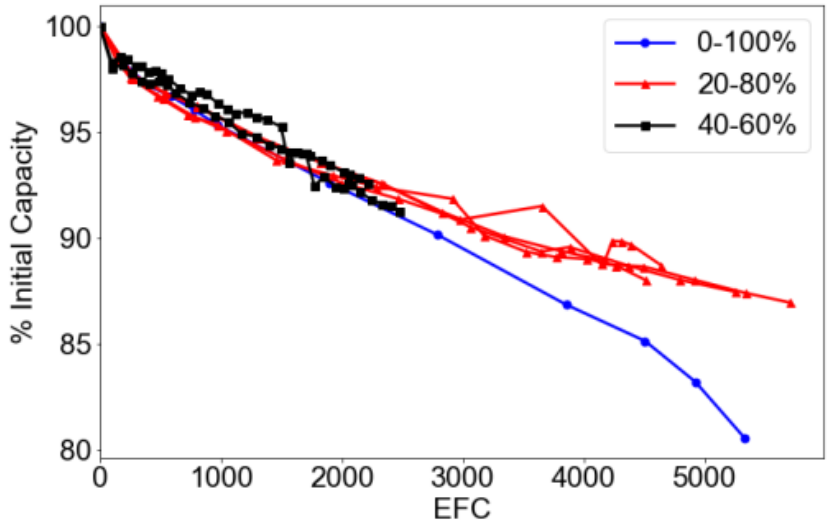
- Discharge rate shows a mixed reaction on capacity fade
- Increasing rate from 0.5C to 2C increases the cycle life
- Discharging at 3C dramatically reduces cycle life

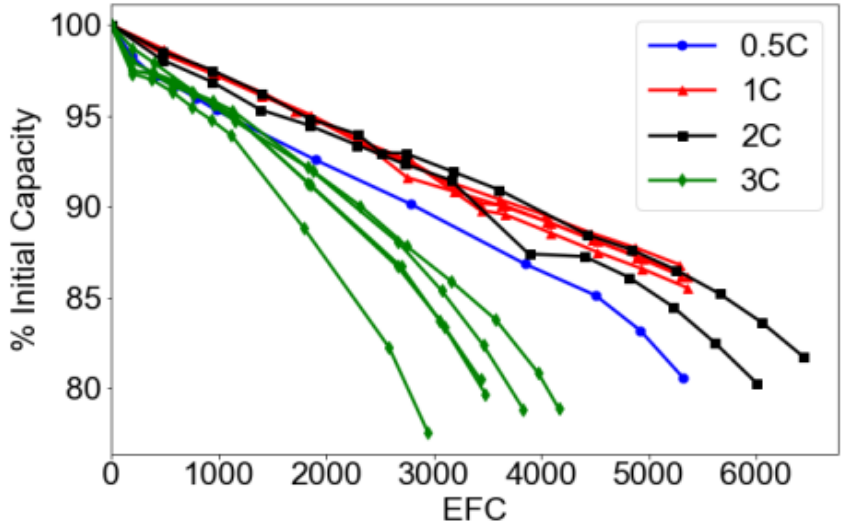


Note: X-axes are different for each plot

To Date Temperatures Appears to be the Most Important Factor in LFP Cycle Life





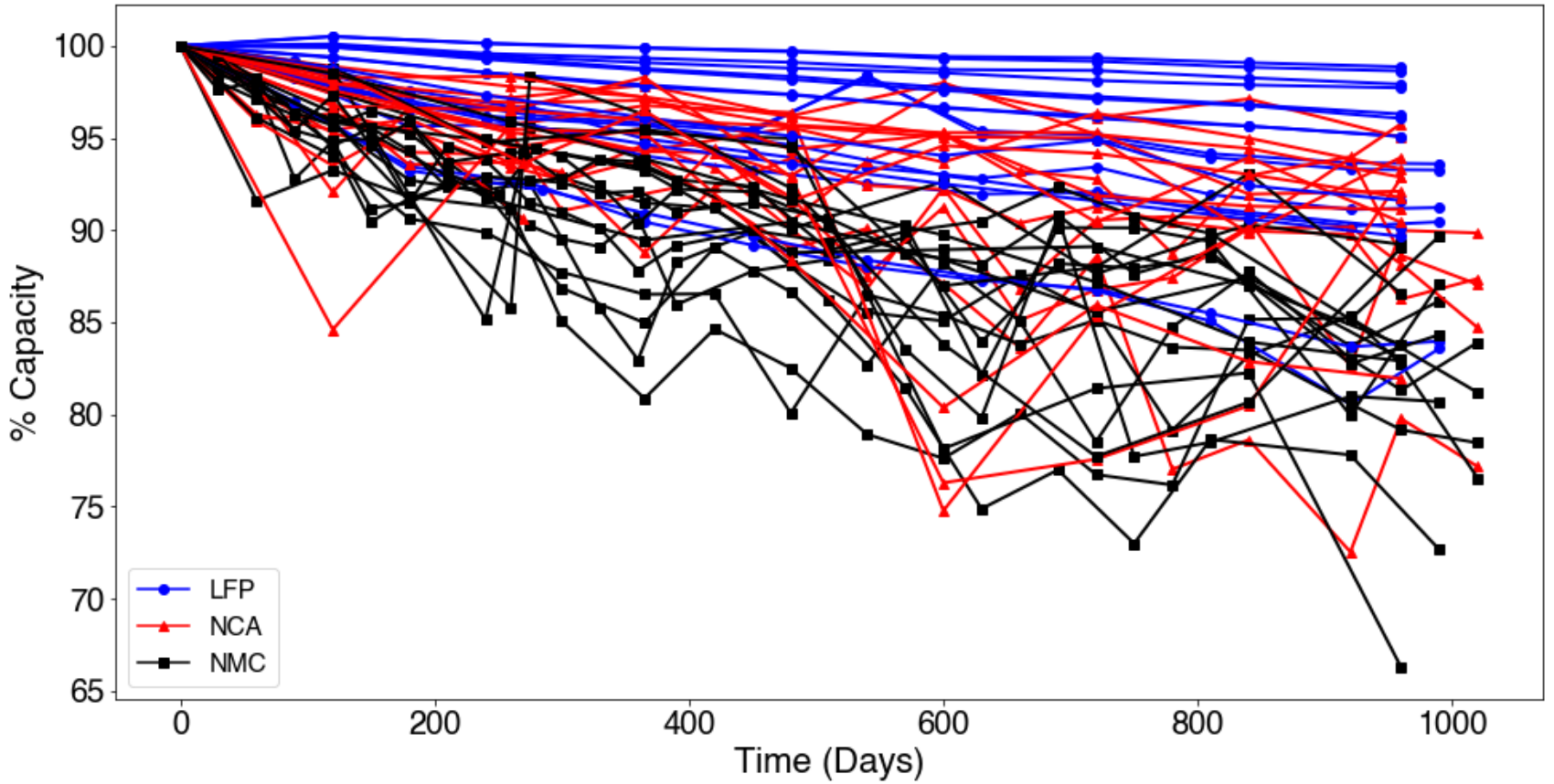


- Temperature of cycling show the most dramatic impact on LFP capacity fade rate
  - Temperature trend is also the most consistent so far
- Discharge rate appears to have the second most impact on capacity fade depending on rate applied
- SOC range trend is less clear due to lag in some data but appears to show increasing SOC rate increases fade rate

Note: X-axes are different for each plot

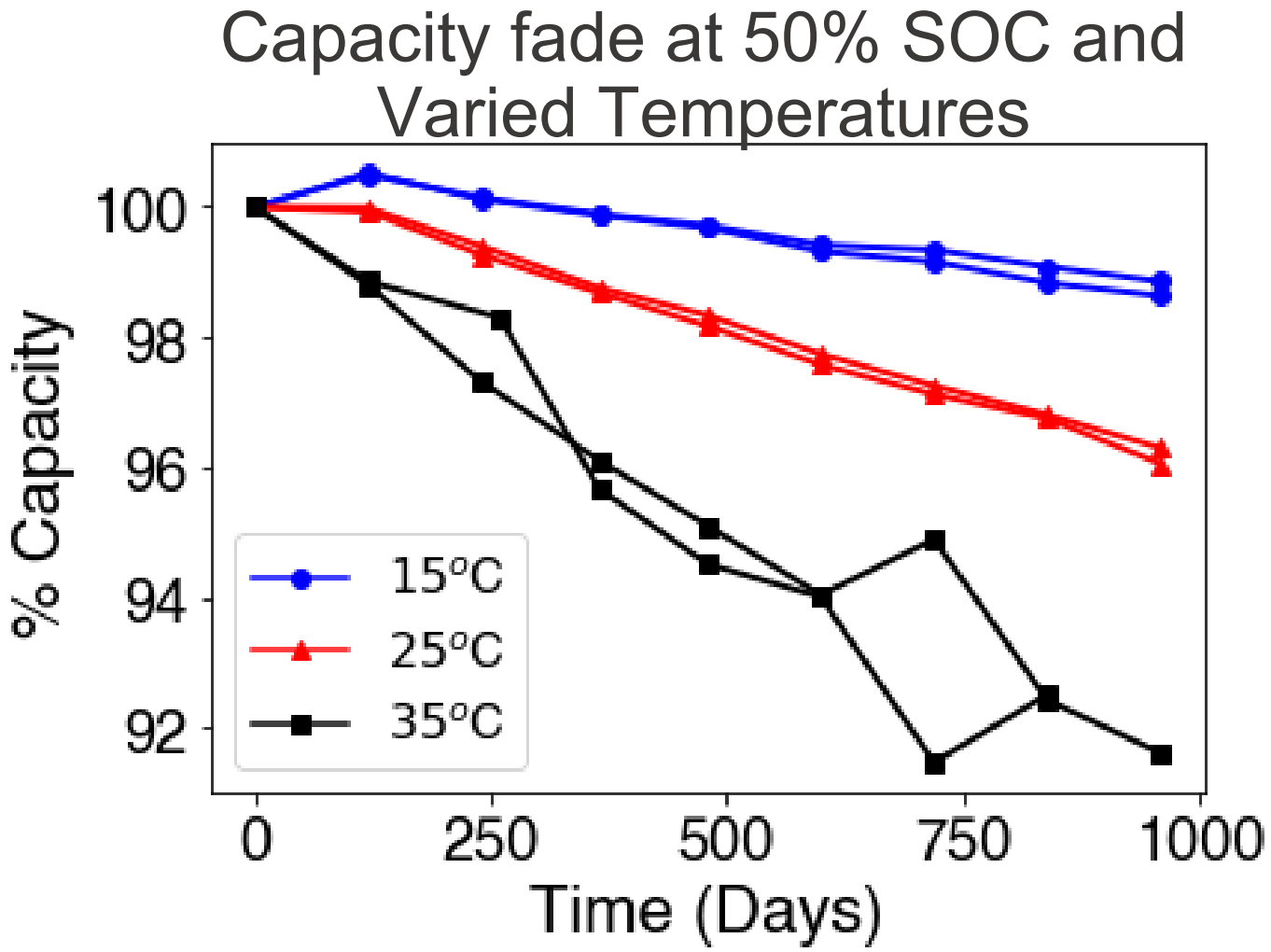
LFP Shows Generally Improved Calendar Aging Compared to NMC and NCA

- LFP cells generally experience the least fade under calendar aging
- NCA cells appear to show the most variability
- NMC cells generally experience the least capacity fade



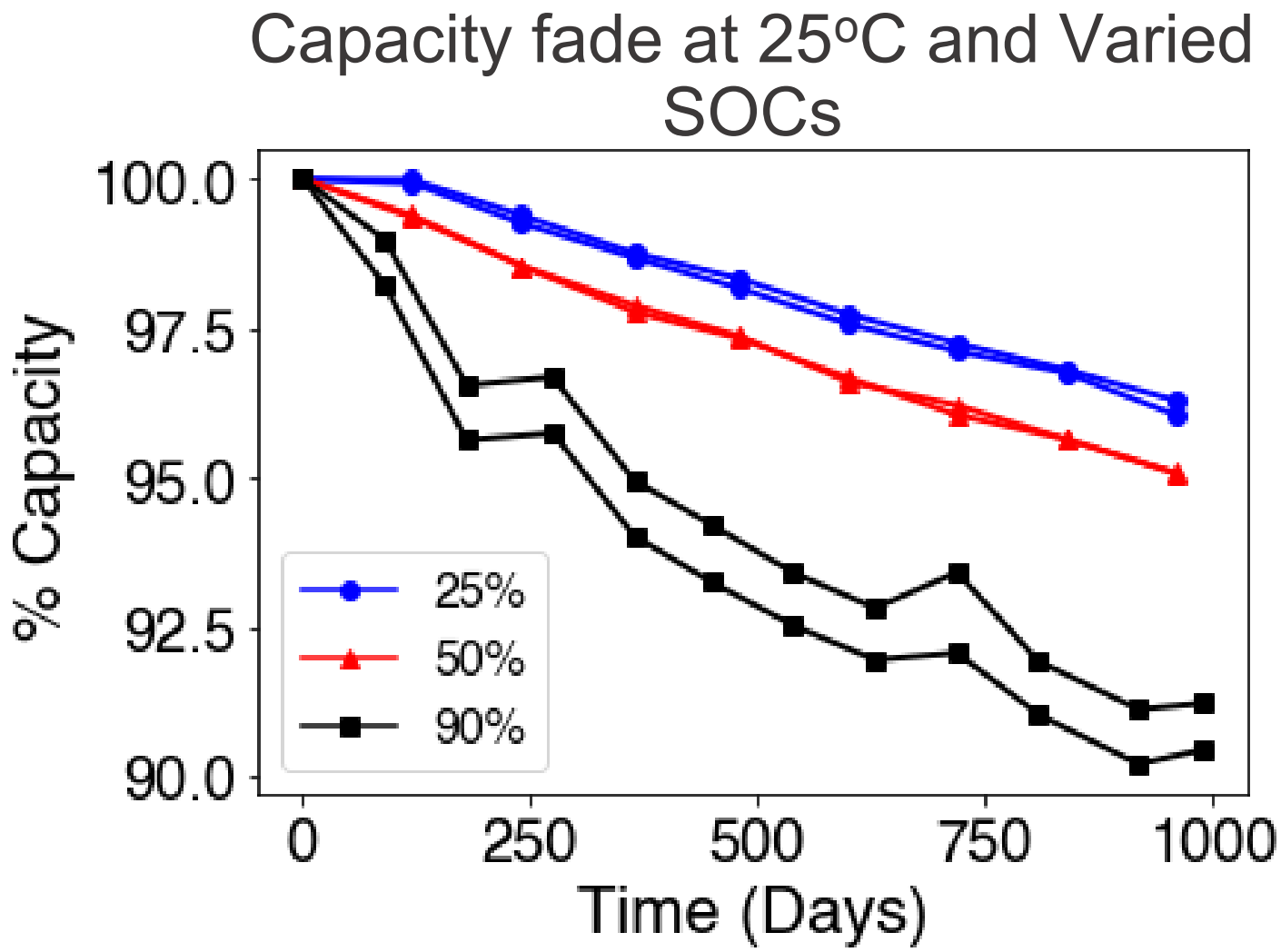
Increased Temperatures Increases Rate of Fade

- Increasing the temperature of aging increase the rate of capacity fade
  - 35°C cells show about 8% loss of capacity over 3 years
  - 15°C significantly reduces capacity fade with ~1% loss over 3 years
- This matches well with the cycling data



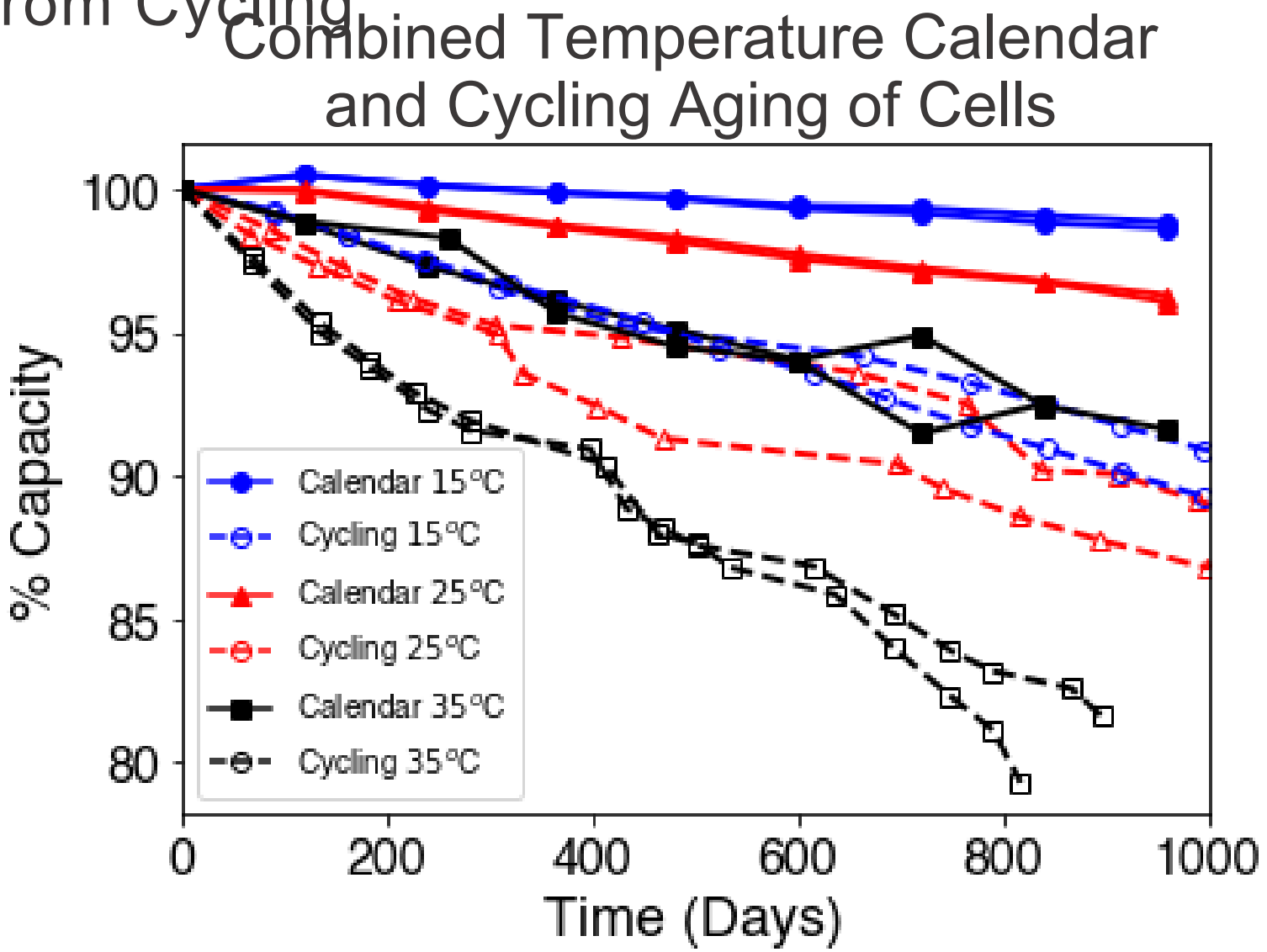
Increased SOC of Aging Increases Capacity Fade Rate

- SOC of aging increases the rate of capacity fade
  - 90% SOC cells experience ~9% loss of capacity
  - 25% SOC cells experience ~2.5% loss of capacity
- This matches well with the cycling data



Can Parse out How Much Capacity Fade is from Calendar Aging and How Much is from Cycling

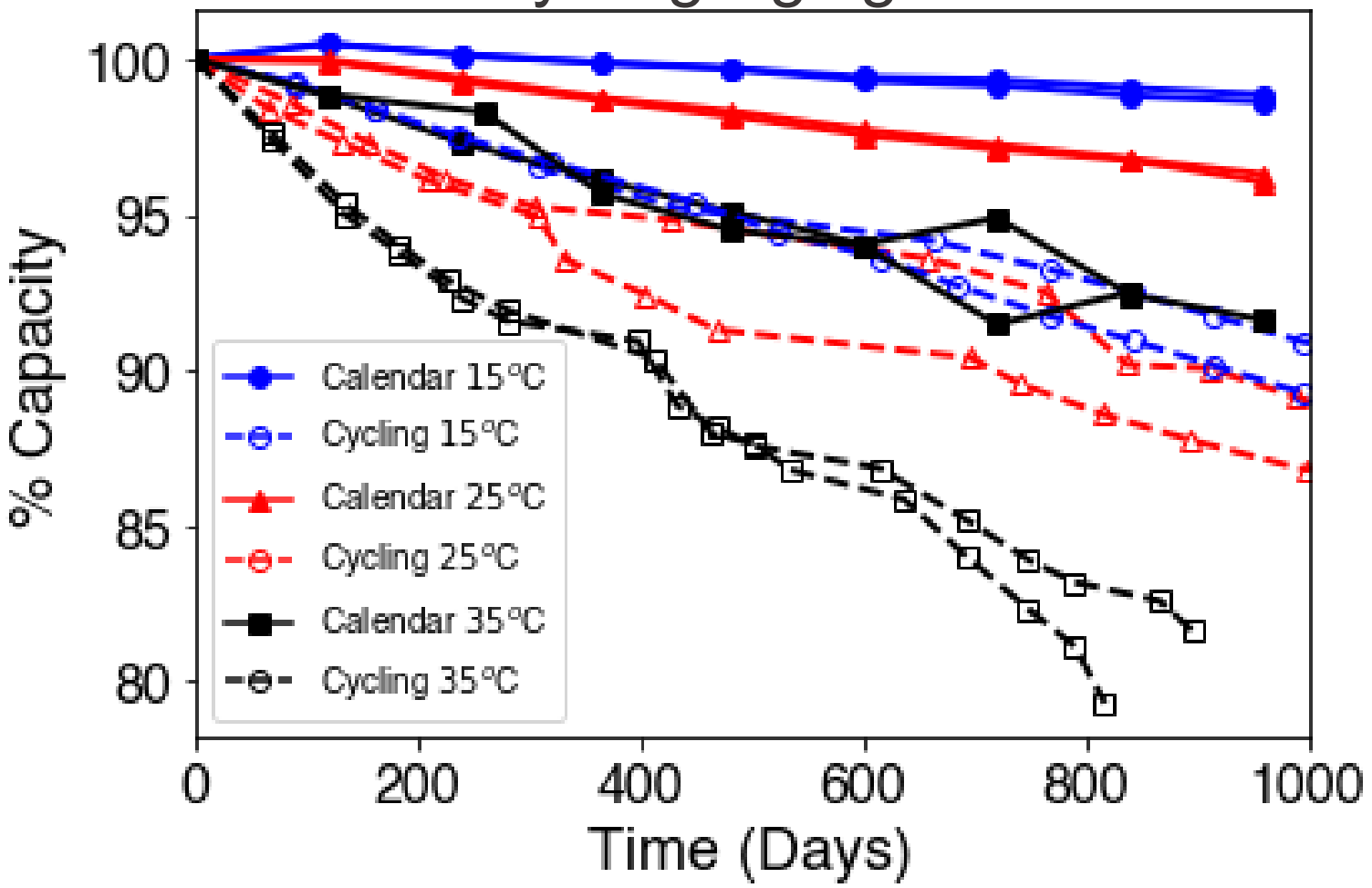
- Because the same cells were used for both cycling and calendar aging we can compare the fade rates
- Plotting both by days gives a measure of much of capacity fade came from the calendar age vs the cycling
- Assume that at similar ages similar amounts of calendar aging would occur in the cycled cells
- In temperature condition shown



Temperature of Cycling Contributes Significantly to the Portion of Capacity Fade comes from Calendar Aging

- Data sets match with the 15 and 25°C relatively grouped together and the 35°C show significantly increased fade from both
- Calendar aging may contribute ~33% of the fade experienced by the 35°C cycled cell
- As temperature decreases this fraction decreases to ~25% and 10%
- This suggests that the temperature of cycling contributes significantly to aging through both processes happening during cycling and processes just due to time spent at a given temperature

Combined Temperature Calendar and Cycling Aging of Cells

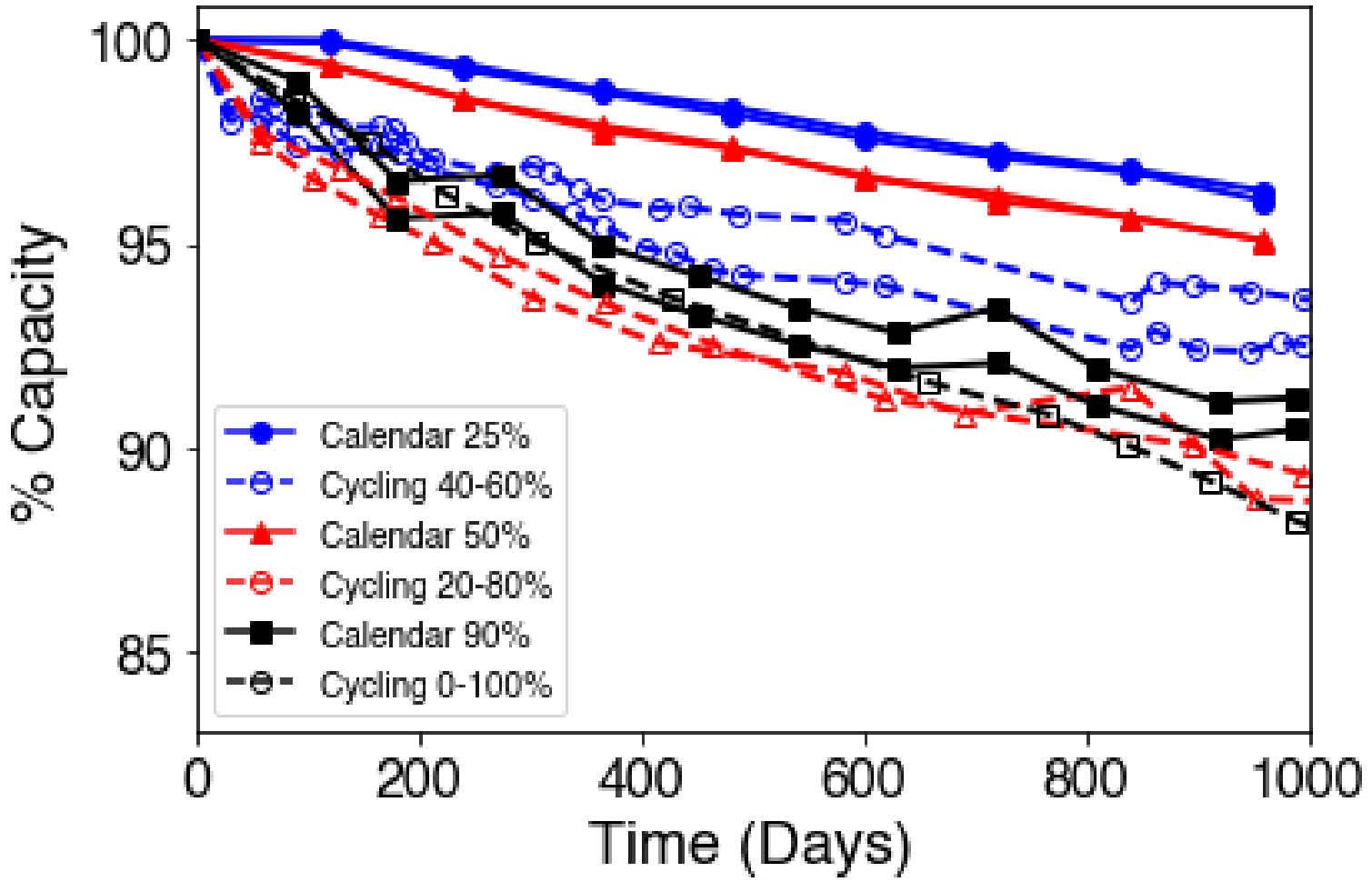


Note: Cycled cells cycled from 0-100% SOC and at a 1C discharge, Calendar Aged cells held at

SOC of Cycling and Calendar Aging show a more Complicated Relationship that is not easy to Parse

- SOC range of Cycling and SOC of Calendar Aging do appear to directly correlate
- This is partially due to the lack of distinction between the the 20-80% and 0-100% SOC cycled cells
- The 90% SOC calendar cell appears to line up with the 20-80% and 0-100% SOC cycled cells
- The 40-60% SOC cycled cells is between the 90% SOC and the 25 and 50% SOC aged cell
- What may be observed here is the average SOCs of the cycled cells lining up with the 50 and 90% SOC cells

Combined SOC Based Calendar and Cycling Aging of Cells



Note: Cycled cells cycled at 25°C and at a 0.5C discharge, calendar aged

Main Conclusions:

- LFP cells show increased cycle life compared to NMC and NCA cells but this advantage is reduced when looking at energy passed
- Temperature appears to be the most important factor in LFP cycling in the study so far
- This is followed by discharge rate and then SOC range
- Calendar aging proceeds as expected where increased temperature and SOC increase rate of capacity fade
- A significant portion of capacity fade from temperature based cycling in LFP cells appears to be from time spent at a given temperature

Next steps:

- Better quantify the contribution of calendar aging in different cycling conditions
- Age and cycle cells to 80% capacity
- Conduct a comparative materials analysis

Acknowledgements

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  - Yuliya Preger
  - Armando Fresquez
  - Babu Chalamala

If you have questions reach out at: rwittm@sandia.gov

We are hiring for several postdoc positions reach out if you are looking for a position or know someone who is

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