Degradation of Li-ion Cells Beyond 80% Initial Capacity

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Abstract

To better understand the true useful life of Li-ion batteries for various applications, we have been conducting a systematic cycling study of 18650 format cells. Lithium Iron Phosphate (LFP), Nickel Manganese Cobalt Oxide (NMC) and Nickel Cobalt Aluminum Oxide (NCA) cells have been systemically cycled to below 80% capacity. We find that cells have significant useful life beyond 80% and their useful life is dictated by conditions of cycling. We find that for each chemistry, state of charge range has the most impact while discharge rate and temperature show a mixed trend depending on chemistry. New trends in capacity fade of NMC and NCA cells cycled at different C-rates and NCA cells cycled at different temperatures arise post 80%. Finally knee point formation does not always occur in cells and its occurrence does not correlate to one parameter of cycling but instead is dependent on all the cycling conditions experienced by the battery.

Keywords

Li-ion Battery; Post 80%; Long Term Cycling.

Introduction

Selecting and operating Li-ion batteries currently involves significant uncertainty. Variations in positive electrode chemistry change ideal cycling conditions. Changes in ideal conditions are not well mapped. Also, the useful life of different cell chemistries for different applications is unknown. Public cycling studies traditionally stop at 80% capacity. A metric for electric vehicles may not be valid for grid applications with different energy and power requirements.

We aim to address this gap with a multi-year cycling study of 18650 commercial Li-ion cells containing three different positive electrode chemistries: Lithium Iron Phosphate (LFP), Nickel Manganese Cobalt Oxide (NMC) and Nickel Cobalt Aluminum Oxide (NCA). Cycling was conducted at varied temperatures, state of charge (SOC) range, and discharge rates.

First, cells were cycled to 80% capacity. Analysis of cell performance for this stage of cycling was conducted by Preger et al.[1] The full data sets from that part of the study can be found at battery archive.[2] Cells of interest were then disassembled and subject to materials characterization to understand the underlying causes of degradation.

The remaining cells are now cycling to 40% of initial capacity. 64 of the original 82 cells are still cycling after six years. 3 NMC and 3 NCA cells have reached the final EOL of 40%. No LFP cells have reached EOL, and half remain above 80% capacity. Each cell chemistry has shown significant ability to operate post 80% capacity. Average energy throughputs for each chemistry range from 1.4 to 6.8 kWh. Trends that existed before 80% capacity become more pronounced. New trends in capacity fade rates are observed as well. Finally, we analyze the occurrence of knee points. We find that their occurrence is dependent on chemistry and conditions of cycling.

Methods

Full experimental details can be found in Preger et al.[1]

Tested Batteries: The following commercial 18650 cells were examined: LFP from A123 Systems (Part #APR18650M1A, 1.1 Ah), NCA from Panasonic (Part #NCR18650B, 3.2 Ah), and NMC from LG Chem (Part #18650HG2, 3 Ah). The three batteries were selected because they included common electrode formulations.

Cycling Equipment: Cycle aging was done with Arbin SCTS and Arbin high-precision (Model: LBT21084) battery testing systems. Individual cells were tested in 18650 battery holders from Memory Protection Devices. The holders were connected to the Arbin with 18-gauge wire. During cycling, the cells were placed in SPX Tenney Model T10C-1.5 environmental chambers. A K- or T-type thermocouple monitored the cell skin temperature.

Cycle Aging Protocol: Each round of cycling consisted of an initial capacity check, cycling at the designated conditions, and a final capacity check. Capacity checks consisted of three charge/discharge cycles from 0%–100% SOC at protocol for all cells studied. A round of cycling for each cell varied from 125 to 1000 cycles. This value depended on the rate of degradation at the specific

Table 1: Conditions of Cycling

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

test conditions. The cycle count for a round was halved if a cell experienced over 5% capacity loss in the previous round. Study Conditions Table I shows the combinations of cycling conditions examined. The nominal capacities of the cells were used as references for calculating C-rates. All cells were charged at a rate of 0.5C, per manufacturer guidance. NCA cells were not discharged at 3C as the 9 A required for this is outside of manufacturer specifications.

Results and Discussion

Overview of Results: Overview of Results: To date our study indicates that NMC, NCA and LFP cells have significant useful life post 80% capacity. Table 2 shows the status of cells cycling below 80% capacity for each chemistry. While 3 NMC and NCA cells have reached an EOL of 40% capacity, no LFP cells have reached EOL. Currently only half the LFP cells are below 80% capacity. Figure 1 shows the capacity retention of cells as a function of equivalent full cycles (EFC). Post 80% NMC, NCA and LFP cells have averaged 685, 486 and 392 EFCs respectively. NMC, NCA and LFP cells currently have a respective mean capacity retention of 63%, 60% and 74%. This has allowed the cells to discharge 6.8, 4.9 and 1.4 kWhr of energy after passing 80% capacity.

Table 2: Summary of cell performance post 80% capacity by cell chemistry. *Half of the LFP cells are still above 80%

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

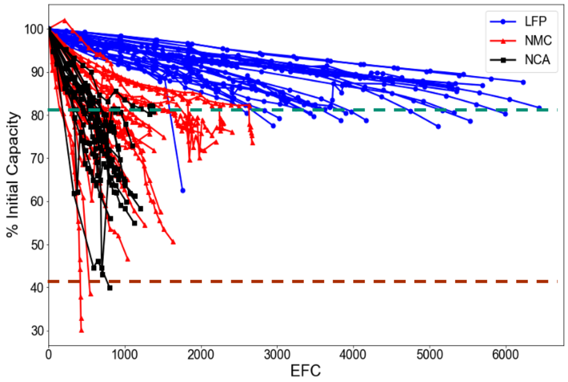

Figure 1: Cycling data for all cells in the study since the start of the study.

The cell capacity fade shows significant dependence on the conditions of cycling. We observe this in Figure 1, where there is significant variance in capacity fade rates within each chemistry studied. This is better quantified when looking at Table II which shows the standard deviation for the mean EFC and discharged energy post 80% capacity. This large standard deviation is most pronounced in the NMC cells, which have a standard deviation of approximately 50% of the mean totals for both EFC and energy discharge data.

Developing Trends in Capacity Fade: Figure 2 shows capacity fade for each chemistry as a function of State of Charge (SOC) range, ambient temperature, and discharge rate. The most significant factor in degradation rate for each chemistry pre-80% capacity was the SOC range it was cycled at. As the SOC range increased, the capacity fade rate increased for all the cells studied. Temperature showed a mixed trend based on the cell chemistry. Only the LFP cells showed a significant trend associated with discharge rate.

For all cells the impact of SOC range becomes more significant post 80% capacity. NCA cells appear particularly affected by SOC range. The 0-100% cell reached EOL by 800 EFC, while by 1,000 EFCs the 20-80% cells are near 65% capacity. The 40-60% cells remain in a linear degradation regime near 80% capacity at ~1300 EFCs. NCA cells reached 80% capacity within ~400EFC of each other, however currently there is ~600EFC separating the lowest and highest capacity cell. NMC and LFP cells follow a similar trend but in a less dramatic fashion.

NMC cell's preference towards higher temperature cycling is more pronounced below 80% capacity. The cells reached 80% capacity with approximately 500EFC between the low and high temperature cells. The 15oC cell reached EOL at ~550 EFC, while the 25oC cells are all below 70% in a range of 1100 to 1300 EFC and the 35oC cell is at ~75% capacity at around 1400 EFC. This data suggests that the higher temperature cells may achieve an order of magnitude higher through put by EOL.

New Trends in Capacity Fade: Post 80% capacity, new trends have emerged in the data for the cycling of NMC

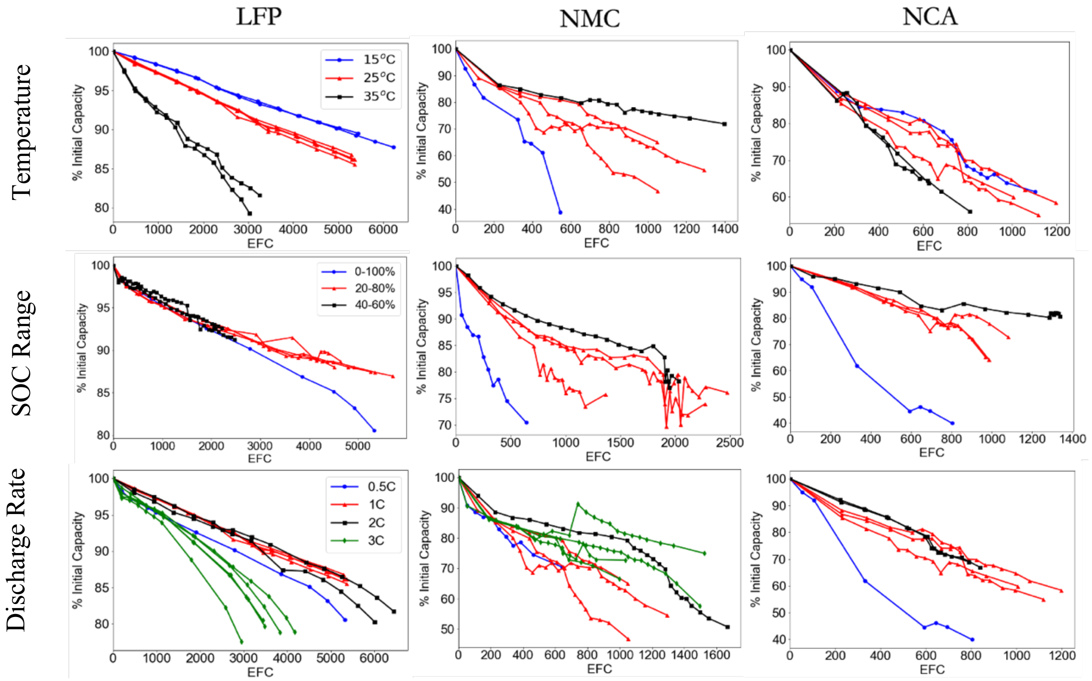

Figure 2: LFP, NMC and NCA cells cycled by temperature (0.5C and 0-100% SOC), SOC range (25C and 0.5C) and C-rate (25C and 0-100% SOC). Data is shown from start of cycling and continues most recent cycling update. Note both x and y axis vary based on number of cycles conducted and capacity retention of the cells.

and NCA cells with different discharge rates and NCA cells at different temperatures.

The NCA cells showed the new discharge rate trend most prominently, with the 0.5C cell at EOL around 600EFC and the rest of the NCA cells exhibiting a varied capacity above 60% at 1200EFC. For the NMC and NCA cells, increased degradation at lower discharge rates may correlate to time spent at high SOCs. We may be seeing both calendar and cycling aging acting on the cell. Further study is needed to understand how degradation occurs.

Below 80% capacity, NCA cells show slower capacity fade at lower temperatures than NCA cells cycled at higher temperatures. Currently the 35oC NCA cells are below 60% capacity near 800EFC. The 25 and 15oC cells do not reach 60% capacity until at least 1100EFC. This shows that high temperature degradation needs to build before it impacts an NCA cell's external performance.

Knee Points: A notable conclusion of our study is that so called knee points do not always occur. Knee points are where batteries transition from a linear degradation rate to an exponential degradation rate. Figure 3 shows examples of different degradation trends in Li-ion batteries. The superlinear degradation curve shows linear degradation until ~400 cycles, after which the degradation rate becomes increasingly rapid. This is an example of a knee in battery degradation. Knees have long been a topic of concern as they can cause the rapid loss of functionality in batteries [3, 4].

We find that the occurrence of knee points is dependent on the conditions of cycling and the cell chemistry. Figure 4 shows selected NMC cells that have not displayed a knee and cells that have shown a knee. The behavior of these cells to form or not form knees does not appear to have a clear trend. The cells that clearly experienced knees operate at a variety of temperatures, discharge rates and SOC ranges, without a clear common factor in their cycling performance. Likewise, the cells that have not experienced a knee operate at similarly varied temperatures of cycling, discharge rates and SOC ranges.

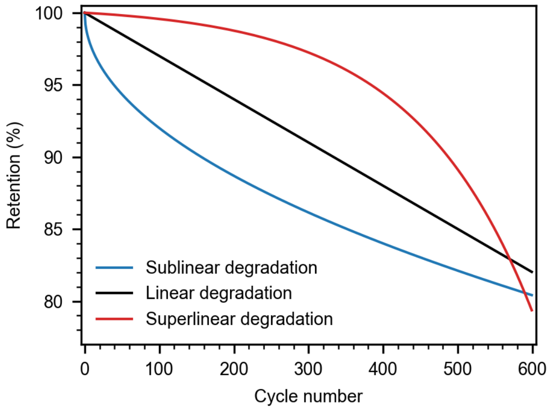

Figure 3: Schematic of three Li-ion battery aging trajectories, sublinear, linear, and superlinear ("knees"). Reprinted from Attia et al. JECS 2022

Typically knee points occur later in a battery's operational life as accumulated degradation impacts cell performance[3]. This has been correlated to cells

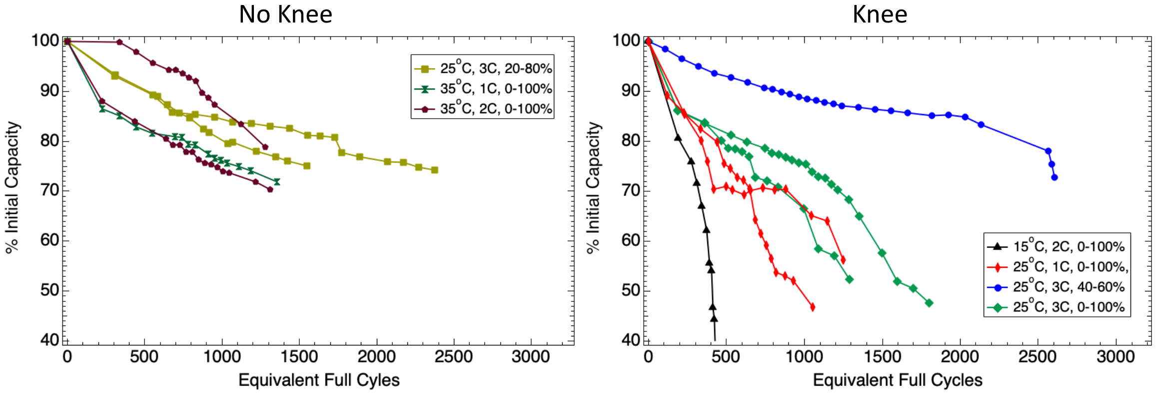

Figure 4: Example of NMC cells that have not experienced a knee (left) and cells that have experienced a knee transition (right). Cells do not show a consistent trend in which form knees or not. This is representative of LFP and NCA cells.

approaching 80% capacity[4, 5]. In NMC cells the knees have been correlated to Li-plating, electrolyte oxidation and SEI formation. It has been suggested that higher upper SOC limits, lower discharge rates and temperatures below of 35°C can accelerate NMC knee point formation[3].

We see in Figure 4 all the no knee cells are below 80% capacity and continue to cycle, which is true for both LFP and NCA cells as well. Knee occurrence in NMC cells only correlates with the literature in cycling below 35°C. The selected knee point cells have ambient temperatures at 15 and 25°C. However, this trend is not universal, as shown by two NMC no-knee cells cycling at 25°C below 80% capacity, suggesting that there is not just one parameter that causes or prevents knee growth. This is true for the NCA and LFP cells as well, where knee formation appears to be condition dependent without a discernible trend. Further work will be done to study knee point formation as our study progresses.

Conclusions:

Our study has shown that Li-ion batteries have significant useful life post 80% capacity. Each of the cell chemistries have discharged over 1kWh of energy and averaged an EFC of 400 or greater. LFP cell capacity fade appears to be slower at all conditions than for the NCA and NMC cells. The NCA cells appear to have a fast capacity fade rate and NMC cells showed the most range in fade rates. Currently 3 NMC and NCA cells have reached 40% capacity. For the LFP cells, none have reached 40% capacity, and half are still above 80% capacity.

Knee points occur inconsistently so far in the study. Cells do not universally form knees at or near 80% as suggested in literature. The formation of knees appears to be condition dependent and can occur at any capacity. There is currently no observable trend in our data to predict knee point formation. Further work is needed to better clarify this occurrence.

Post 80% use of Li-ion batteries is feasible but requires careful consideration of their use before and after 80% capacity. Better state of health diagnostics is needed to monitor cells, which will insure optimal use of batteries throughout their entire operational life.

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References

1. Y. Preger, H. M. Barkholtz, A. Fresquez, D. L. Campbell, B. W. Juba, J. Romàn-Kustas, S. R. Ferreira, and B. Chalamala, *J. Electrochem. Soc.,* **167**, 120532 (2020).
2. *Battery Archive*, www.batteryarchive.org
3. Peter M. Attia, A. Bills, F. B. Planella, P. Dechent, G. d. Reis, M. Dubarry, P. Gasper, S. Greenbank, D. Howey, O. Liu, Y. Preger, A. Soni, S. Sripad, Richard Gilchrist, E. Khoo, A. G. Stefanopoulou, and V. Sulzer, *J. Electrochem. Soc.,* **169** (2022).
4. M. Johnen, S. Pitzen, U. Kamps, M. Kateri, P. Dechent, and D. U. Sauer, *J. Energy Storage,* **34** (2021).
5. N. Kirkaldy, M. A. Samieian, G. J. Offer, M. Marinescu, and Y. Patel, *ACS Appl Energy Mater,* **5** (2022).