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Fast Charging of Lithium-Ion Pouch Cells at Elevated Temperature

by ViChi Tran and Jeffrey A Read

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14. ABSTRACT Lithium (Li)-ion batteries demonstrate high energy density and good cycle life under low- to moderate-charge-rate conditions but tend to suffer rapid capacity fade and safety problems under fast charge. Fast charging of Li-ion batteries provides promising capabilities for Army applications and for the electric vehicles market. To understand some of the limitations of Li-ion cell charging, two types of Li-ion pouch cells of similar size and construction were tested under different fast charging rates (full charge in 6 to 30 min) over a range of temperatures (20 to 60 °C). The collected data is evaluated as a function of discharge capacity and energy.					
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Contents

List of Figures	iv
List of Tables	iv
1. Introduction	1
2. Procedures and Experiment	1
3. Results	3
4. Summary and Conclusions	12
5. References	13
List of Symbols, Abbreviations, and Acronyms	14
Distribution List	15

List of Figures

Fig. 1	Typical formation capacities for NMC811 cells.....	3
Fig. 2	Typical formation capacities for NCA cells	4
Fig. 3	Capacity power curves for NMC811 cells at beginning of life	5
Fig. 4	Capacity power curves for NCA cells at beginning of life.....	5
Fig. 5	Energy power curves for NMC811 cells at beginning of life.....	6
Fig. 6	Energy power curves for NCA cells at beginning of life.....	6
Fig. 7	Capacity power curves for NMC811 cells at 20 °C.....	7
Fig. 8	Capacity power curves for NMC811 cells at 60 °C.....	8
Fig. 9	Capacity power curves for NCA cells at 20 °C	8
Fig. 10	Capacity fade during power curve testing in NCA cells at 60 °C	9
Fig. 11	Capacity power curves for NCA cells at 60 °C	9
Fig. 12	Long-term NMC811 and NCA cycling at 4C and 40 °C.....	11
Fig. 13	Long-term NMC811 and NCA cycling at 4C and 60 °C.....	11

List of Tables

Table 1	Commercial cell design parameters	2
Table 2	Cell test matrix.....	2

1. Introduction

Lithium (Li)-ion cells are used extensively in Army batteries today, including the BB2590, 6T vehicle battery, and the Conformal Wearable Battery (CWB). Because Li-ion batteries have the ability to perform in environments requiring high specific energy, high energy density, and high power densities, the Army is exploring their use for hybrid or all-electric vehicles as well as distributed energy systems on the battlefield.¹

Li-ion cells have demonstrated power densities on discharge exceeding 10 kW/kg, but limitations surface when attempting fast charge at specific power in the range of 1–2 kW/kg. These limitations are often attributed to the graphite anode, where insertion of Li-ions into the graphite layers on charge is considered a rate-limiting step.² This limitation arises from some combination of the energy barrier associated with Li-ion de-solvation, transport limitations of Li-ions in the electrolyte, the diffusion limitation of intercalated lithium in graphite, and impedance from a solid electrolyte interphase (SEI).³ Issues that arise when cells undergo fast charge include reduced cycle life, increased SEI impedance growth, and importantly, reduced safety of the battery.⁴ Li-ion pouch cells perform well under low to moderate charging rates, but there is uncertainty about the extent to which can they perform under more extreme sets of charging conditions.⁵

The purpose of this work is to understand the limitations of Li-ion cell charging in conventional Li-ion pouch cells and how fast charging behavior affects cell performance at elevated temperature. Two different types of 190-milliamp-hour (mAh) Li-ion pouch cells were used to investigate the performance under a range of temperatures (20 to 60 °C) and charging rates (6 to 30 min). Data on both discharge capacities and energy as a function of these different temperatures and charging rates is collected and compared in order to assess the extent of the different cell's fast charge capabilities as well as the effect of fast charge on capacity fade.

2. Procedures and Experiment

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811) Li-ion cells purchased from Li-Fun Technology Company were evaluated in this project. Cell design parameters are shown in Table 1. Both cells use an artificial graphite anode and have a nominal capacity of 190 mAh. The NCA cells were designed to be cycled from 3.0 to 4.2 V while the NMC811 cells were designed for a 3.0- to 4.7-V cycling range. Both cell types have similar cathode thicknesses while the NMC811 cells have a thicker anode coating to accommodate a higher charge capacity expected at 4.7 V. The batteries arrived as sealed dry cells, so the pouches were

opened in a vacuum atmospheres dry box (<20 ppm H₂O, < 20 ppm O₂), dried under antechamber vacuum at 70°C overnight, then filled with 1 g of 1M LiPF₆ in 3:7 ethylene carbonate:ethyl methyl carbonate (LP57) electrolyte, and then temporarily sealed. The cells were then taken out of the dry box and vacuum sealed in a dry room before being weighed. Four NCA cells and four NMC811 cells were activated for each test condition.

Table 1 Commercial cell design parameters

Cell type	Electrode area (cm ²)	Coated thickness (μm)	Cycling capacity (mAh/cm ²)	Anode/cathode area ratio
NMC811	94	37	2.1	...
Graphite	106	75	3.3	1.13
NCA	87	43	2.3	...
Graphite	100	65	2.9	1.15

Formation Cycling. After electrolyte fill and vacuum sealing, all pouch cells underwent formation cycling to prepare for long-term testing and to determine baseline performance at ambient temperature (20 °C) conditions. Utilizing MACCOR 4000 testers, the cells were cycled once at C/20, and then three times at C/5. Between cycles the cells were allowed to rest for 10 min.

Power Curve Cycling. Tenney chambers were used for the various temperature testing conditions, with cells being allowed to equilibrate for 2 h before initiating cycling. The formed cells were charged and discharged in a repeated sequence of five different rates: 2C, 4C, 6C, 8C, and 10C. The total charge time at each rate was time limited to correspond to the appropriate C rate, for example 2C charge corresponded to a 380-mA constant current charge to 4.2 V followed by a constant voltage hold at 4.2 V for a total charge time of 30 min. This was followed by a constant current discharge of 380 mA to 2.5 V. At each rate, five cycles were performed before moving to the next rate. Between each cycle, cells were allowed to rest for 10 min. The series of cycling rates was repeated 10 times for a total of 50 cycles per rate and 250 cycles overall. Table 2 shows the cell conditions and the batteries that underwent each cell condition.

Table 2 Cell test matrix

C-Rates	Temperature					
	20 °C		40 °C		60 °C	
	NMC811	NCA	NMC811	NCA	NMC811	NCA
2, 4, 6, 8, 10	4 cells	4 cells	4 cells	4 cells	4 cells	4 cells

The cycling data for each temperature was averaged over the four cells and then graphed as discharge capacity and energy versus rate over the life of the test. Power curves were generated from this data by averaging capacity over the five cycles. The power curves were generated at both beginning of life and end of life for the pouch cells.

Long-Term Cycling. NCA and NMC811 cells underwent formation cycling in preparation for long-term cycling (1000 cycles) at 4C. Higher cycling rates were investigated for this long-term testing, but initial data indicated that performance deteriorated quickly under these conditions. Two cells of each type were tested at 40 and 60 °C under these fast charge conditions.

3. Results

The formation cycling of both types of Li-ion pouch cells showed similar behavior with the NCA cells having slightly greater discharge capacities (199 mAh) compared with the NMC811 cells (186 mAh). Figures 1 and 2 display the formation cycle capacities for representative NMC811 and NCA cells.

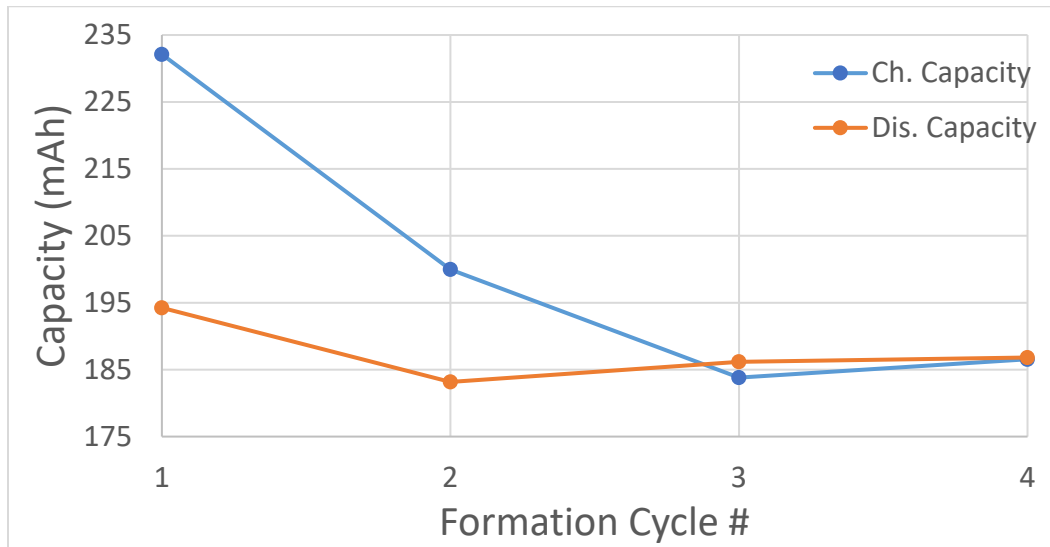


Fig. 1 Typical formation capacities for NMC811 cells

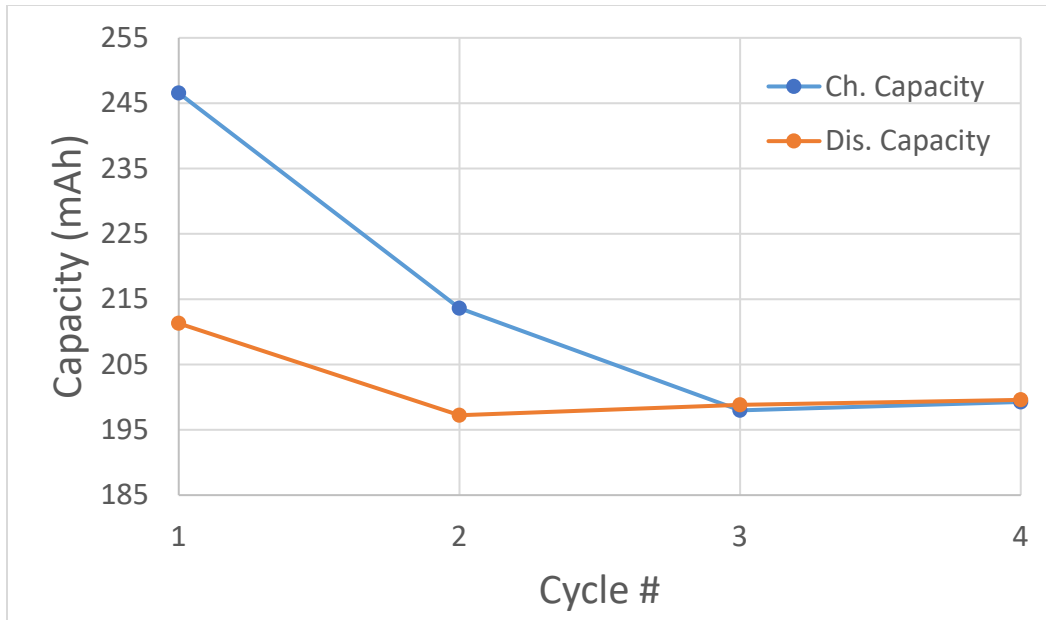


Fig. 2 Typical formation capacities for NCA cells

Figures 3 and 4 demonstrate the discharge capacity power curves at the beginning of life for the two types of cells. The power curves show a significant drop in discharge capacity as the charge rate increases above 2C. This is somewhat mitigated as the test temperature increases, although since these cells were designed for energy, they cannot sustain greater than 50% capacity above 6C charge rates. The discharge energy power curves are shown in Figs. 5 and 6.

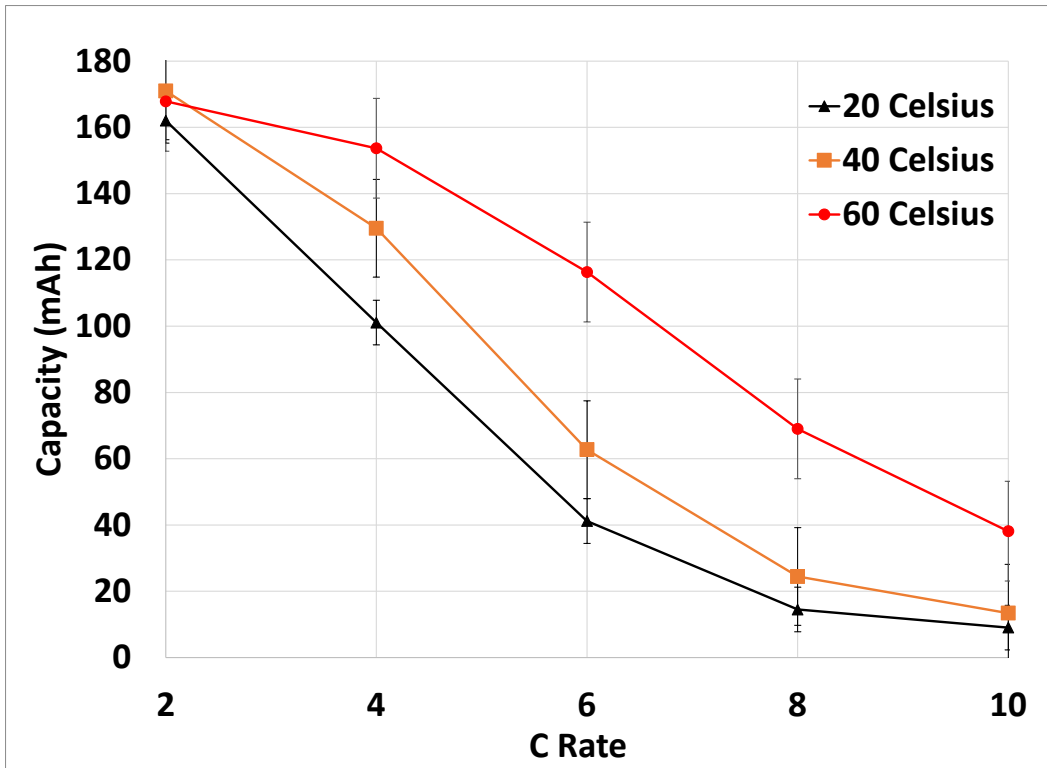


Fig. 3 Capacity power curves for NMC811 cells at beginning of life

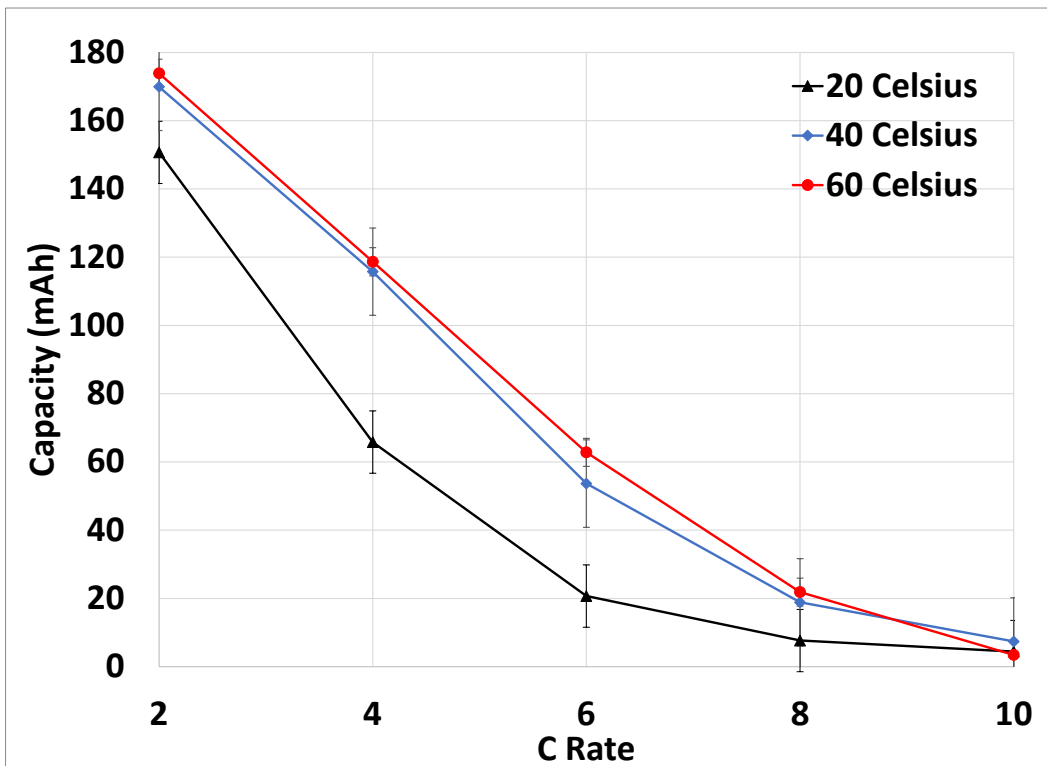


Fig. 4 Capacity power curves for NCA cells at beginning of life

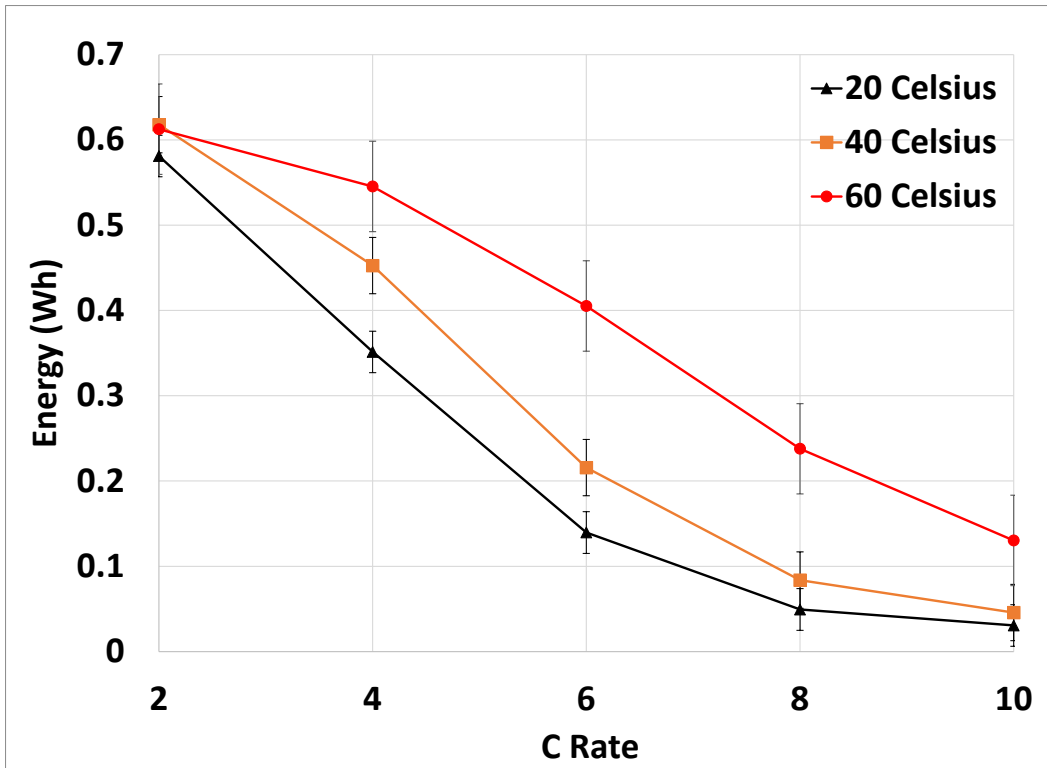


Fig. 5 Energy power curves for NMC811 cells at beginning of life

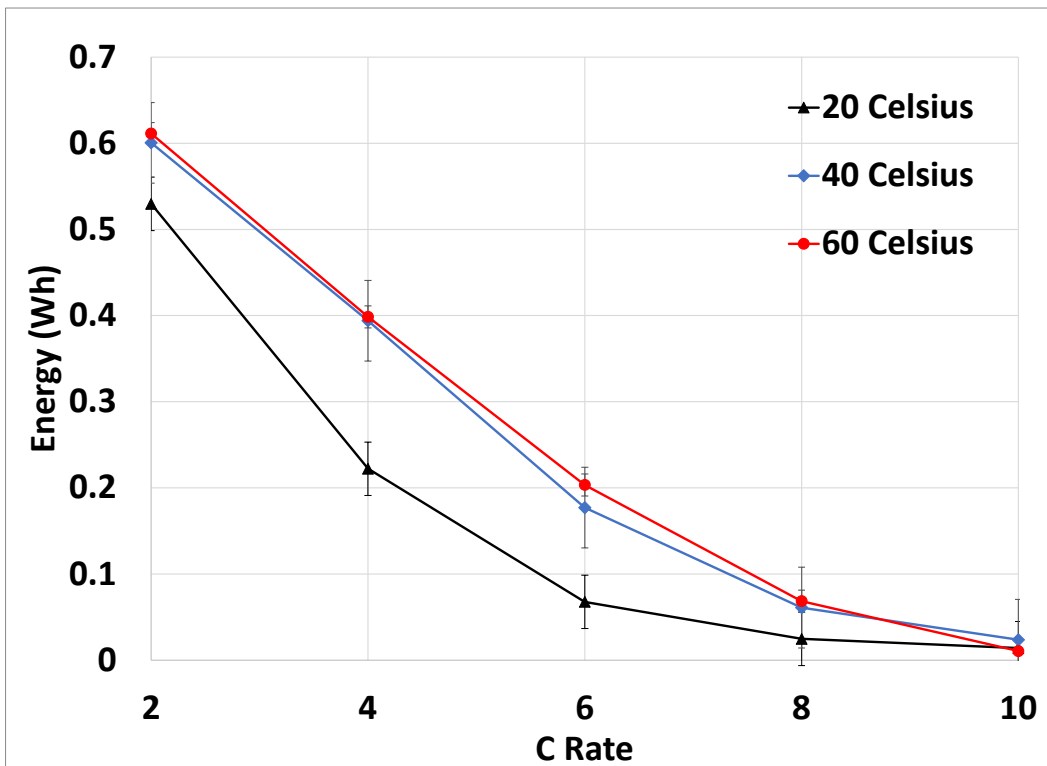


Fig. 6 Energy power curves for NCA cells at beginning of life

During the power curve testing, consisting of 250 total cycles, the NMC811 cells showed little capacity or power fade at either 20 or 40 °C as shown in Fig. 7 for 20 °C. There was, however, significant capacity fade in NMC811 cells at 60 °C, as shown in Fig. 8. In contrast, the NCA cells showed significant capacity and power fade at each rate and every temperature condition, as shown in Fig. 9 for 20 °C. NCA cells cycled at 60 °C demonstrated rapid capacity fade within the first 50 cycles as shown in Fig. 10 for an individual cell and in Fig. 11 for the group of cells tested, where the power curves at beginning and end of life are shown.

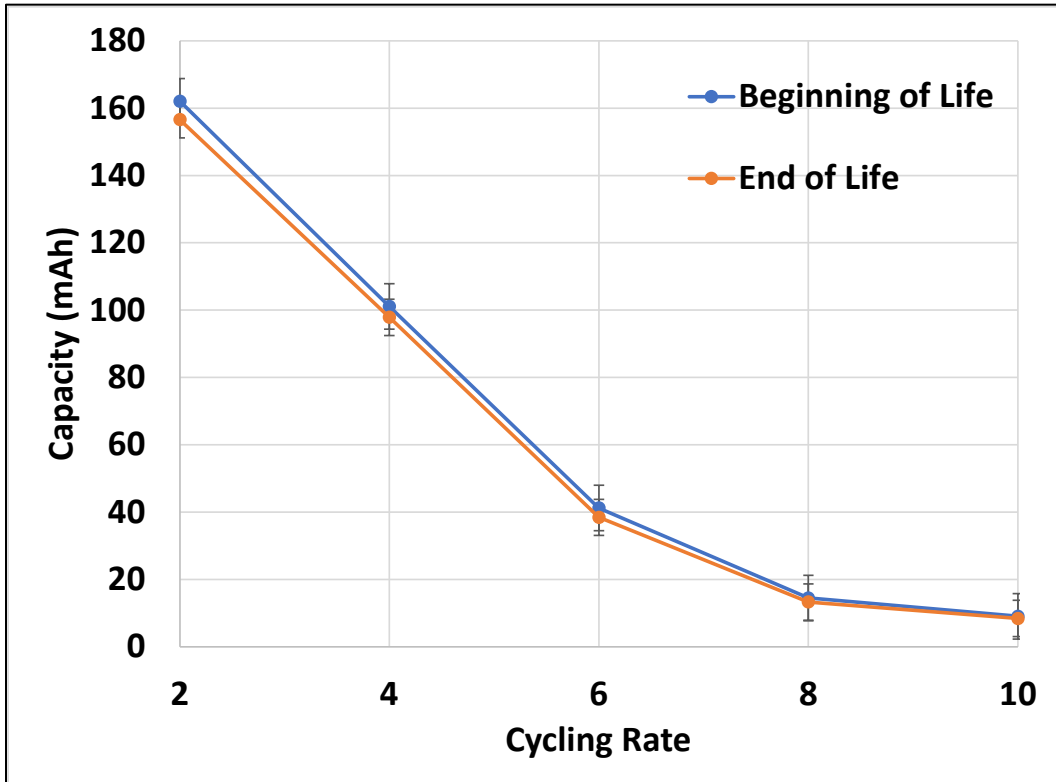


Fig. 7 Capacity power curves for NMC811 cells at 20 °C

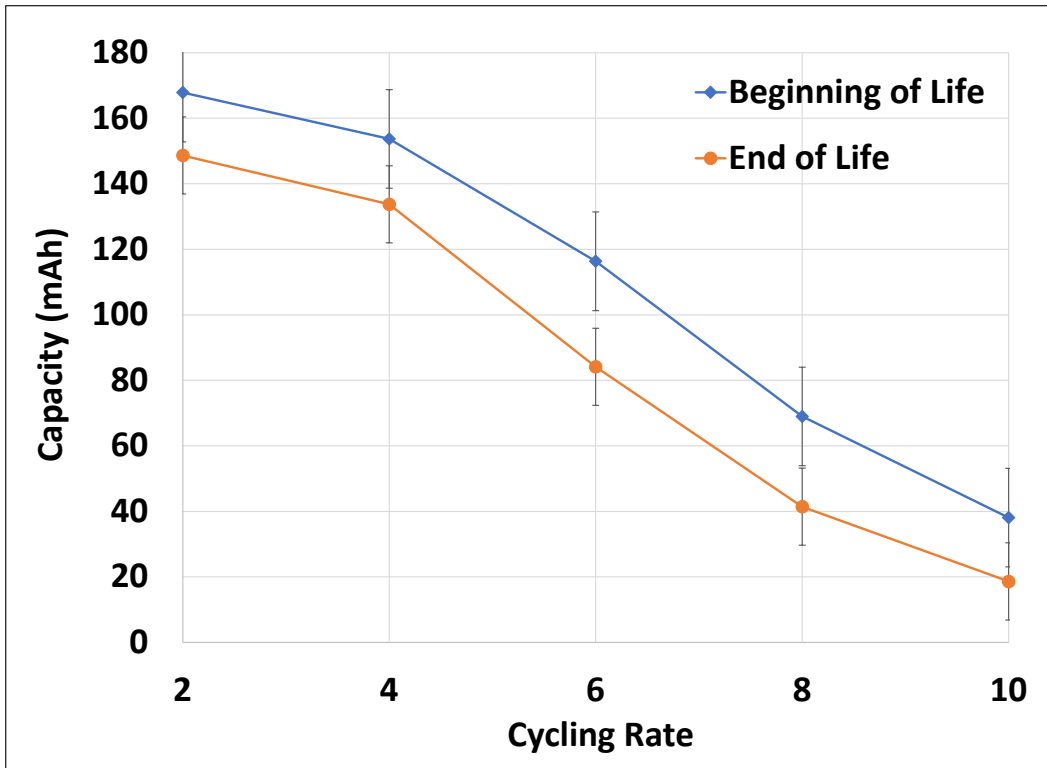


Fig. 8 Capacity power curves for NMC811 cells at 60 °C

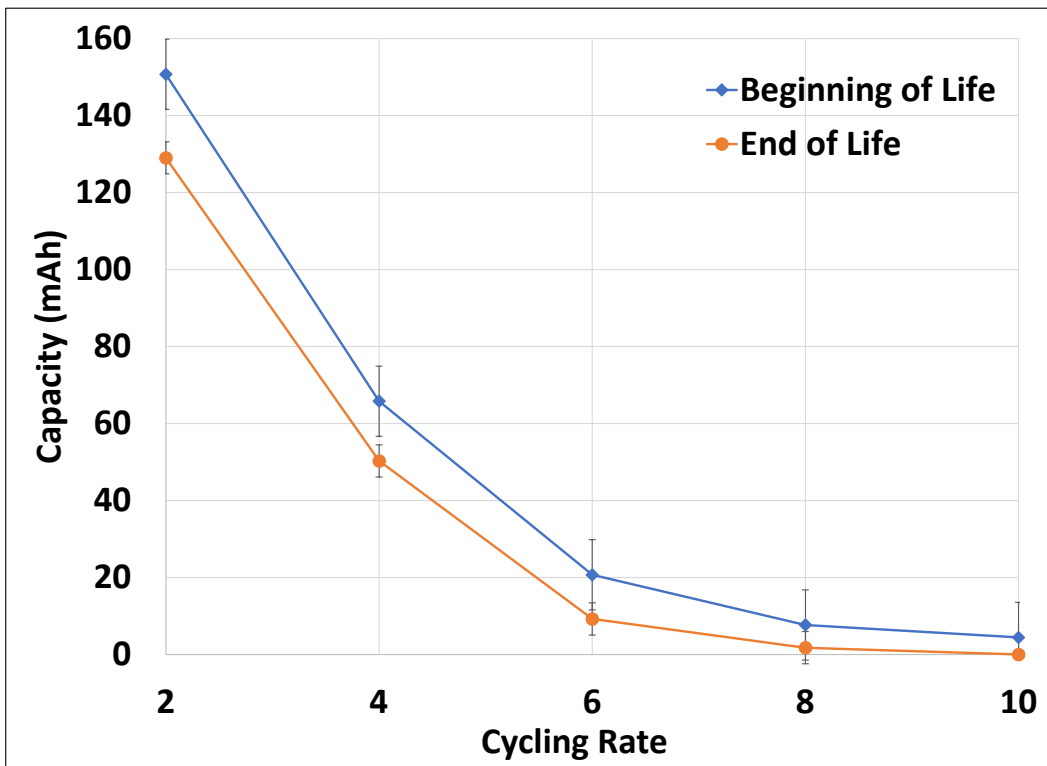


Fig. 9 Capacity power curves for NCA cells at 20 °C

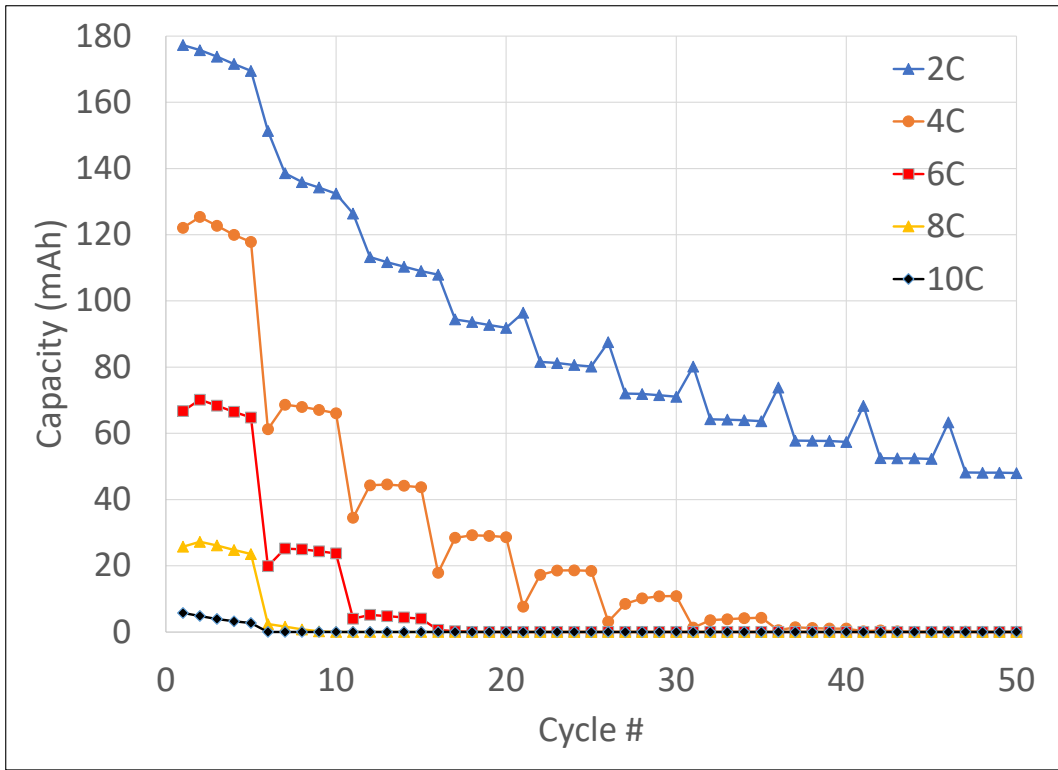


Fig. 10 Capacity fade during power curve testing in NCA cells at 60 °C

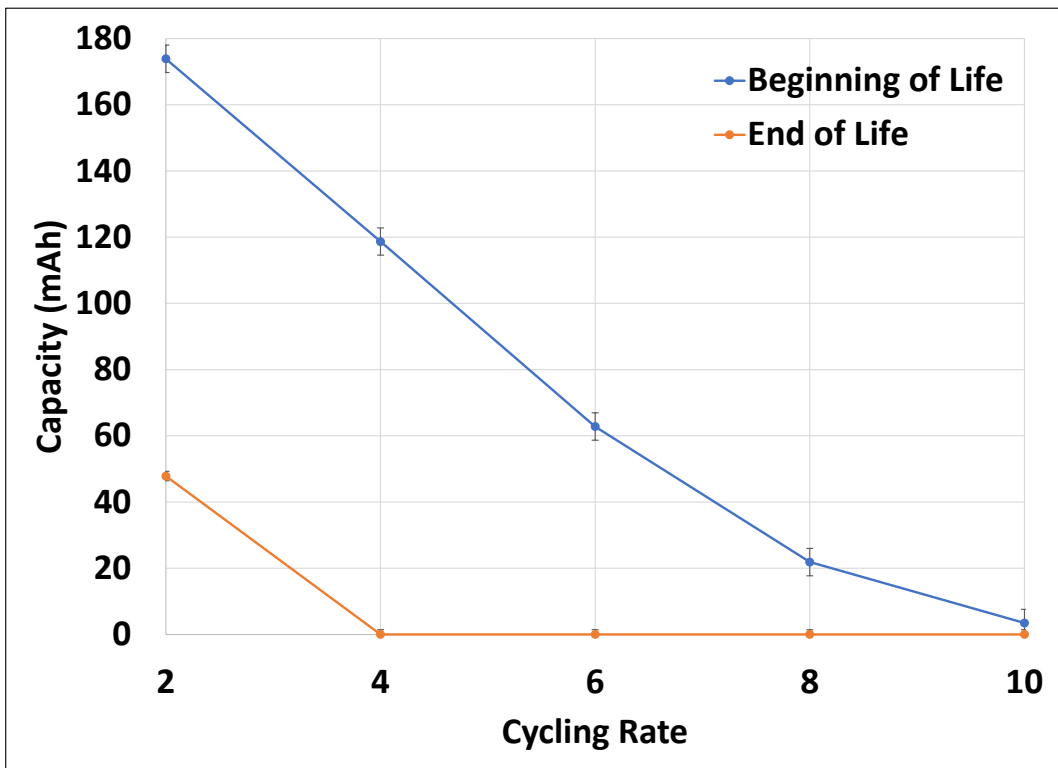


Fig. 11 Capacity power curves for NCA cells at 60 °C

The difference in performance between the NCA and NMC811 cells appears to relate to both the cathode chemistry and cell balance. The negative-to-positive ratio (N/P) in the two cell types are different and this can have an effect on fast charging and capacity fade.² The NMC811 cells have an effective cell balance N/P of 1.57 as compared to the NCA cells with an N/P ratio of 1.26. This balance means that effectively, there are more graphite particles to accept lithium during fast charge in the NMC811 cells but since the anode is thicker, Li-ion transport limitations in the anode should reduce some of that benefit. For this particular design, the cell balance appears to have benefitted the fast charge capability.

For longer-term cycling under fast charge, two cells of each type were tested at 40 and 60 °C under 4C charge/discharge. Figure 12 shows the 40 °C performance of both cell types through 1000 cycles. The NMC 811 shows better overall rate capability with the capacity dropping at a steady rate throughout but maintains 65% of the initial 4C capacity at end of life. The NCA cells show more rapid capacity fade at 4C maintaining only 33% capacity at end of life. This correlates with the power curve cycling showing similar capacity fade after 250 cycles. The 60 °C cycling shown in Fig. 13 is even more dramatic with again the NMC811 outperforming the NCA cells at 4C cycling. The performance of the NMC811 is reasonable given the rate and electrode thicknesses and compares well with other commercial cells. The NCA cell performance throughout appears to be worse than expected. The NCA cells have difficulty cycling even at 2C rates without significant fade indicating that the NCA cathode may not be capable of fast charge. The N/P ratio being effectively lower in the NCA cells also may contribute to fast charge cycling degradation in this cell design.

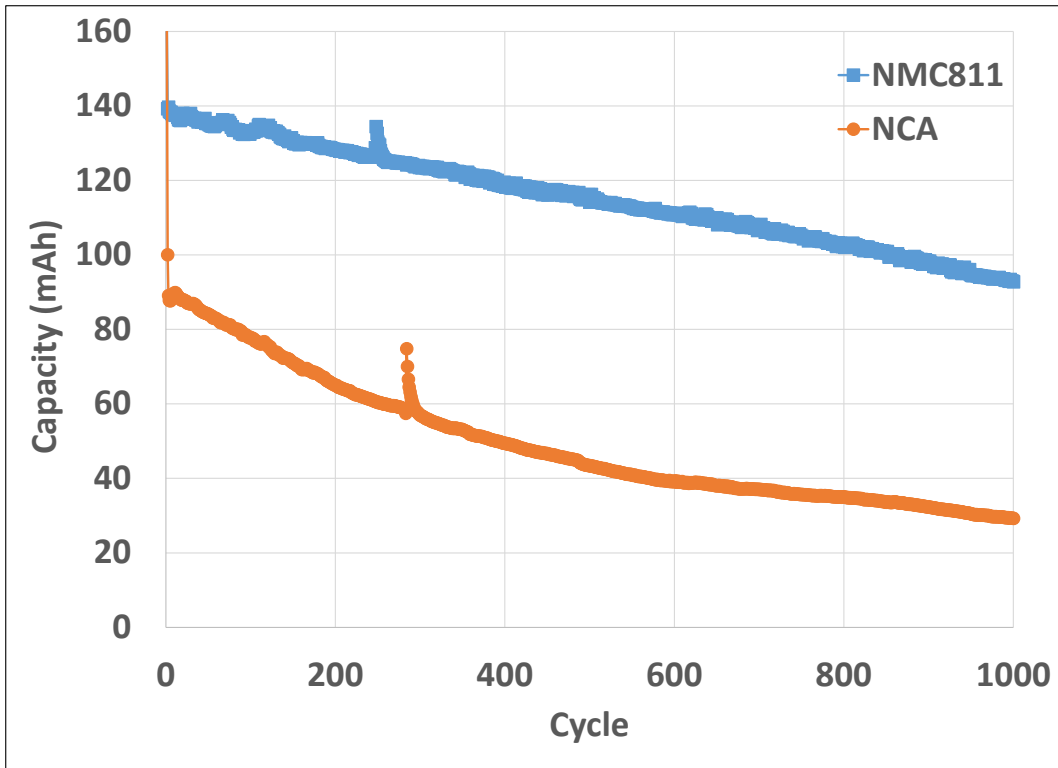


Fig. 12 Long-term NMC811 and NCA cycling at 4C and 40 °C

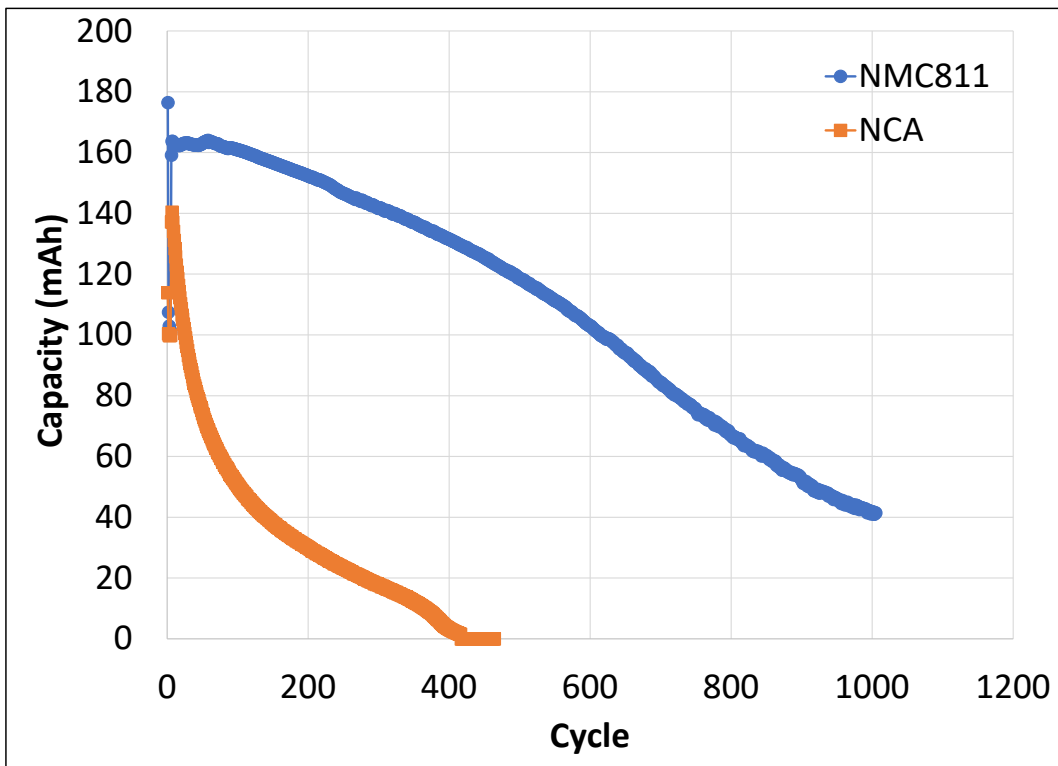


Fig. 13 Long-term NMC811 and NCA cycling at 4C and 60 °C

4. Summary and Conclusions

The performance of two types of Li-ion pouch cells were evaluated over a range of elevated temperatures and charging rates to determine their fast charge capabilities. It was found that NCA cells cannot withstand higher temperatures without rapidly decreasing in capacity. NMC811 cells generally perform well at elevated temperatures, although cycling at 60 °C leads to measurable capacity fade. Elevated temperature cycling improves rate performance, especially at 4C and 6C rates, but also leads to increased capacity fade. Overall, although the performance is not optimal, NMC811 Li-ion cells have better performance than NCA cells under fast charge rates at 20 to 60 °C.

5. References

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List of Symbols, Abbreviations, and Acronyms

CWB	Conformal Wearable Battery
mAh	milliamp-hour
NCA	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
NMC81	$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$
SEI	solid electrolyte interphase

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