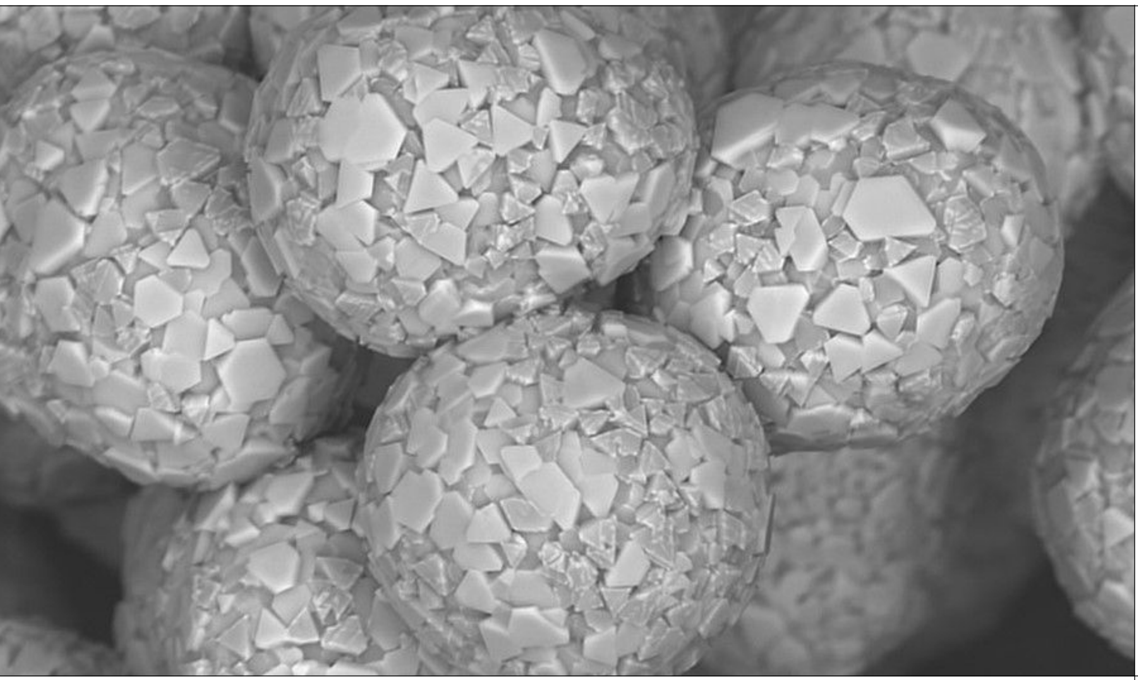
Whitepaper

A GAME-CHANGING APPROACH TO STABLE CYCLING OF LNMO-GRAPHITE CELLS



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INTRODUCTION

The need for cost-effective and high-performance energy storage solutions has been a driving force in advancing battery technology. In this context, the combination of a high-voltage cathode material, like Lithium Nickel Manganese Oxide (LNMO) with graphite as the anode, has emerged as an exceptionally promising system for automotive application.

While LNMO-graphite cells present great promise for the future, insufficient capacity retention still hinders their full commercialization. As reported in literature[1], the capacity retention is mainly limited by the interplay between the graphite anode and the LNMO cathode, often referred to as “crosstalk”. The most referred crosstalk is dissolution of Mn from the cathode that migrates to the anode and integrates into the SEI layer which increases impedance. This is one of several phenomena generalized as “chemical crosstalk” where electrolyte-soluble species produced on one electrode migrate to the other electrode and change cell resistance and/or lithium inventory, i.e., amount of active lithium.

This paper will introduce *“non-chemical crosstalk”* that relates to the interplay between state of charge at the electrodes which is largely governed by N/P ratio and voltage window. Using 3-electrode measurements, we show how optimization of these parameters drastically reduces the stress on each electrode and minimizes the chemical crosstalk, resulting in significantly improved capacity retention.

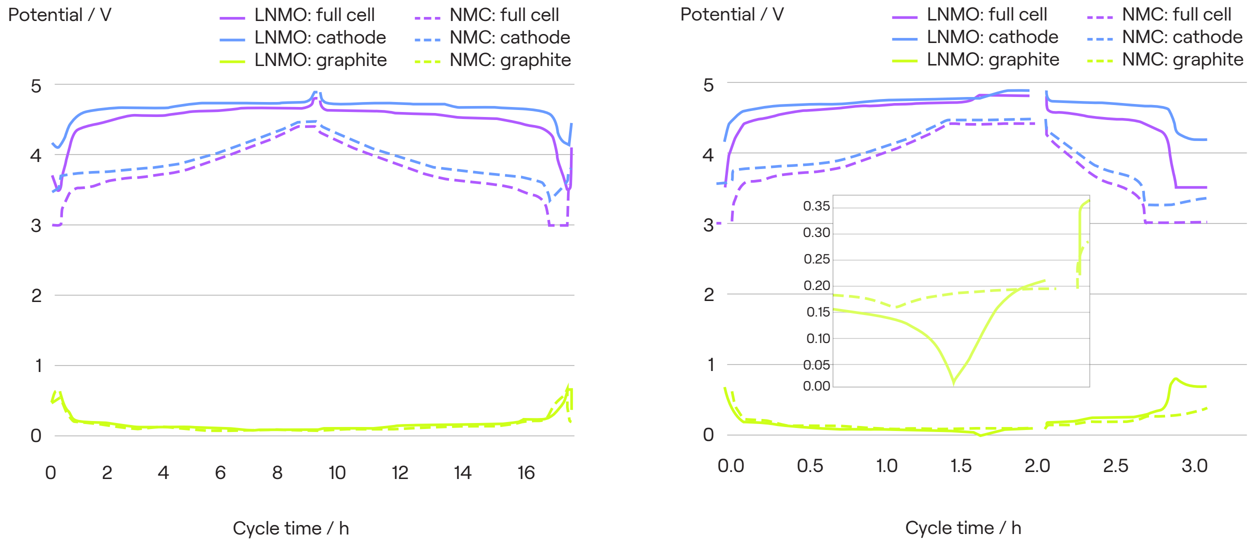
STATE OF CHARGE AND THE IMPACT OF BALANCING

To understand the origin of non-chemical crosstalk, it is important to understand how the LNMO-graphite system is different compared to other common cathode chemistries. Figure 1 shows a comparison between half- and full-cell voltage profiles of LNMO-graphite and NMC532-graphite at both slow (C/10, D/10) and fast (C/2, 1D) cycles. The three main observations when comparing the two systems are:

- Anode potential profiles are similar for both systems at low current conditions.
- The NMC cell reaches CV phase of charging earlier than the LNMO cell. It is very pronounced at fast cycling, but observable also for slow cycles.
- The maintained constant current control in the LNMO cell until a higher state of charge leads to drop of the anode voltage. At C/2 charge, this causes the potential to reach below 0 V *vs.* Li/Li^+. This is not observed for the NMC cell.

In essence, LNMO cathode with flat potential profile and easily accessible lithium cations allows to maintain the CC charging step until even 98% SOC at current rate C/2. Such conditions can easily lead to early Li-plating on the anode electrode.

FIGURE 1: Potential profile of LNMO-graphite and NMC-graphite cells



Left: Slow cycle (2nd cycle) at C/10 and D/10 and Right: Faster cycle (3rd cycle) at C/2 and 1D. Results are obtained using 3 electrode PAT-CELLs (EL-CELL) with 2 cycles C/10 and D/10 followed by cycling at C/2 and 1D. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

Figure 2 shows typical evolution of anode and cathode potentials upon cycling. Figure 2 left shows anode and cathode potential profiles of cycle 5, 25 and 45 and Figure 2 right shows maximum and minimum values of potential for both anode and cathode during cycling. The three main observations are:

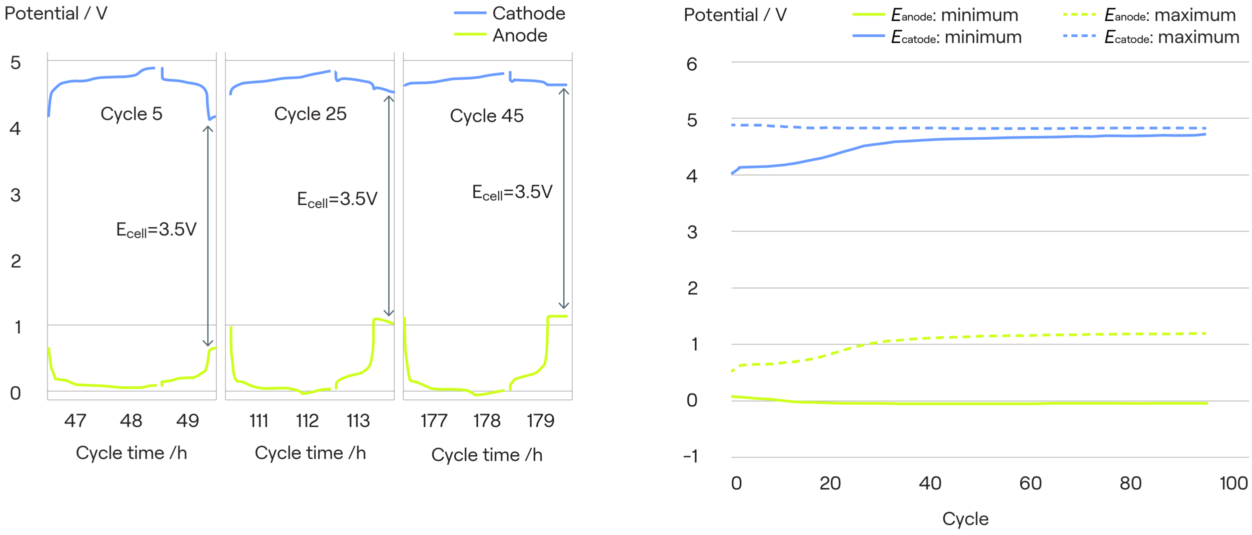
- the potential of the anode drops below 0 V *vs.* Li/Li$^+$ from cycle 12
- the lower potential limit of the cathode at the end of discharge increases with cycle numbers
- the upper potential of the anode increases to above 1 V *vs.* Li/Li$^+$ from cycle 25

With an anode potential below 0 V *vs.* Li/Li$^+$, lithium plating is thermodynamically possible and although the voltage curves are not sufficient to confirm plating, it would eventually lead to fast decrease of lithium inventory, i.e., loss of active lithium in the system.

The increased lower potential of the cathode with cycle numbers reflects a decrease in lithium inventory that prevents full lithiation of LNMO and thereby less reduction of Mn^{4+} to Mn^{3+} at around 4.3 V *vs.* Li/Li$^+$. At a certain point, lithium inventory decreases to a level where no Mn^{4+} is reduced. At this point, battery discharge ends with reduction of Ni^{3+} to Ni^{2+} at around 4.68 V *vs.* Li/Li$^+$. As the lower cut-off voltage is 3.5 V, the increased potential on the cathode leads to increasing anode potential reaching above 1 V *vs.* Li/Li$^+$. As described in literature[2] one can speculate about how such high anode potentials can change the SEI-layer by dissolution of some of its components, ultimately lowering the protection ability of the SEI-layer.

In short, cycling of LNMO-graphite cells using the same protocols as for NMC-graphite cells exposes the anode to both very high and very low potentials. That sets demanding requirements to anode material and may be the reason for limited capacity retention of LNMO-graphite cells.

FIGURE 2: Potential profile of LNMO-graphite cell



Left potential profile for anode and cathode of LNMO-graphite cell in cycles 5, 25, and 45, and right maximum and minimum potentials experienced by anode and cathode for each cycle. Results are obtained using 3 electrode PAT-CELLs (EL-CELL) with 2 cycles C/10 and D/10 followed by cycling at C/2 and 1D. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

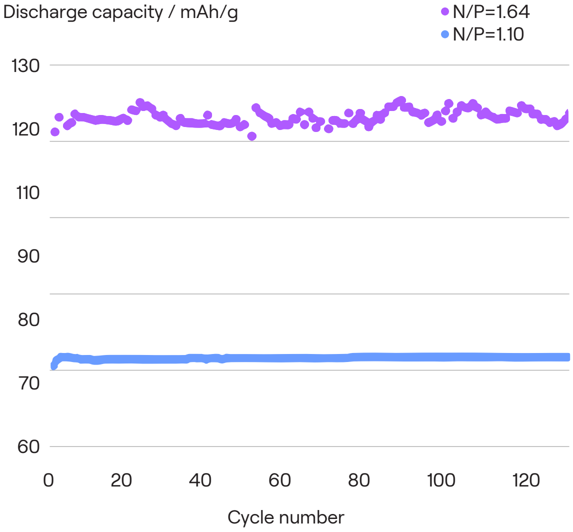
AN LNMO-GRAPHITE CELL WITHOUT FADE

To test the impact of limiting stress on the anode, a safe potential range for graphite anode was selected as 0.1-0.8 V *vs.* Li/Li+, and LNMO-graphite cells were cycled with control of anode (anode potential *vs.* lithium metal reference electrode). It is important to understand the implications of such an approach:

- current flow between anode and cathode is determined by the kinetics of the anode
- charging stops when the potential of the anode reaches 0.1 V *vs.* Li/Li$^+$
- discharging stops when the potential of the anode reaches 0.8 V *vs.* Li/Li$^+$
- the voltage and state of charge of the LNMO cathode undergoes continuous adjustments as cycling is determined by the anode

Limiting anode potential to 0.1-0.8 V *vs.* Li/Li$^+$ limits capacity of the anode with around 30%. To maintain high capacity of the cell (in mAh/g$_{LNMO}$), it is therefore necessary to increase capacity of the anode. For the graphite and LNMO used in this study, the optimal N/P ratio was 1.64. For comparison, a cell with N/P=1.10 was also tested. Figure 3 shows cycling curves of cells with the two N/P ratios. The results demonstrate that it is possible to build stable LNMO-graphite cells and maintain stability for more than 100 cycles with a capacity of 120 mAh/g$_{LNMO}$, when the conditions of the cycling are governed by the state of the anode. The stable cycling under these conditions further indicates that the origin of capacity loss in LNMO-graphite cells is linked closely to non-chemical crosstalk, where the combination of a standard CC-CV protocol and an LNMO cathode forces extreme cycling conditions on the anode, leading to the chemical crosstalk known from literature.

FIGURE 3: Cycling performance of LNMO-graphite cells with improved anode control



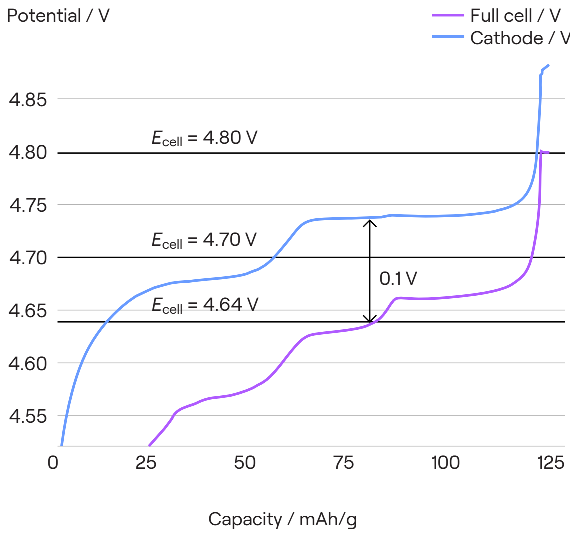
Cycling performance of LNMO-graphite cell with anode control protocol (E_{anode} = 0.1-0.8 V vs. Li/Li$^+$). Results are obtained using 3 electrode PAT-CELLs (EL-CELL). Electrolyte: 1M LiPF$_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.10 and N/P = 1.64, respectively. Temperature: 25°C.

APPLICATION IN COMMERCIAL BATTERY CELLS

Monitoring anode potential during cycling is not feasible for commercial applications, and it is therefore necessary to translate the learnings from the 3-electrode system to normal cells without a reference electrode.

Options to improve anode control could be advanced cycling protocols, such as e.g., multistage constant current, pulse, or current modulated charging, to replicate potential and current profiles obtained in anode-control mode in standard LNMO-graphite cells.

FIGURE 4 : Charge potential profiles of LNMO and full cell in LNMO-graphite cell

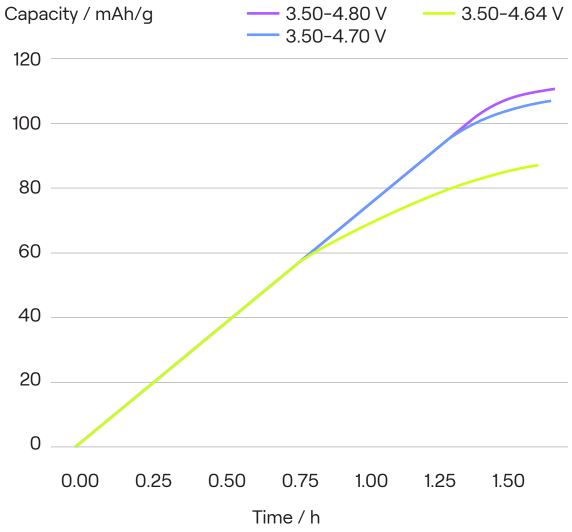


Results are obtained using 3 electrode PAT-CELLs (EL-CELL) at C/10 charge. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

Herein we would like to demonstrate the first step in that direction, obtained by reducing the upper voltage cut-off potential and using an N/P ratio of 1.20. Figure 4 shows how the decrease in cut-off potential will eventually compromise the available capacity. The three selected upper cut-off potentials are 4.80 V, 4.70 V, and 4.64 V. 4.80 V is selected as a reference often used in literature. 4.70 V is selected to decrease current towards end of charge by entering CV step earlier and without significantly compromise in capacity. 4.64 V is selected as the best way to mimic results in the 3-electrode cell, where the charge is terminated exactly as the anode reaches 0.1 V *vs.* Li/Li^+. As marked in Figure 4, a cut-off voltage of 4.64 V in a cell with N/P ratio 1.2 will be reached when the anode potential (difference between cathode potential and full cell potential) changes from slightly above 0.12 V *vs.* Li/Li^+ to around 0.08 V *vs.* Li/Li^+ as the cathode potential is 4.74 V *vs.* Li/Li^+ in this region.

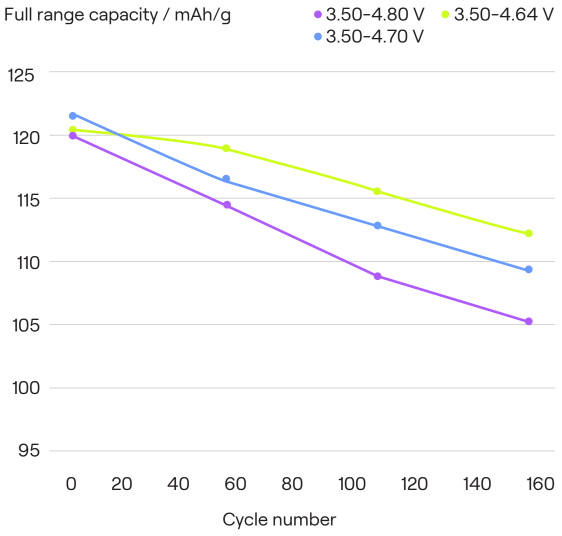
An important effect of changing the upper voltage cut-off is that the current profile towards end of charge is modified significantly. Figure 5 shows capacity vs. time for the three conditions. The slope corresponds to the current, and the CV step is initiated when the slope decreases from the initial straight line. As further substantiated in Table 1, the CC charging step is reduced from 93% down to 63%. This means that lowering the upper cutoff voltage decreases the available capacity and increases time at CV from 16% to 53%. The total charging time is almost unchanged as the capacity is 20% less for the upper cut-off voltage of 4.64 V compared to 4.80 V.

FIGURE 5: Impact of upper cut-off voltage on current and capacity



Charge at C/2 with varying upper cut-off voltage of 4.80 V, 4.70 V and 4.64 V, respectively. Results are obtained in 2 electrode coin cells. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

FIGURE 6: Cycling performance based on full range capacity



Results are obtained in 2 electrode coin cells cycled at C/2 and 1D with varying upper cut-off voltage of 4.80 V, 4.70 V and 4.64 V, respectively. Full range capacity is measured every 50th cycle between 3.50 V and 4.80 V at C/10 and D/10. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

TABEL 1: Key values for charge at C/2 with different upper cut-off voltages

Potential range [V]	Q_{total} [mAh/g]	Q_{CC}/Q_{total}	t_{total} [h]	t_{CV}/t_{total}
3.50-4.80	110.9	93%	1.66	16%
3.50-4.70	107.0	85%	1.64	25%
3.50-4.64	87.0	63%	1.61	53%

Results are obtained in 2 electrode coin cells at C/2 (5th cycle) with varying upper cut-off voltage of 4.80 V, 4.70 V and 4.64 V, respectively. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

To provide periodical ‘check’ of the available capacity, the cells were cycled slowly (C/10, D/10) in the full voltage range of 3.5 V–4.8 V every 50 cycles. Figure 6 shows capacities at slow cycles of the three conditions and comparing these, it is clear that milder cycling significantly improves capacity retention. This result is further substantiated in Table 2 that shows capacities and capacity retention corresponding to the three conditions. On one hand, the available capacity is lower when the upper cut-off is decreased, while at the same time the capacity retention is much better, decreasing the capacity fade at slow cycles and full voltage range from 5.6 mAh/g to 1.5 mAh/g in the first 50 cycles. Loss of capacity speeds up in subsequent cycle ranges, but is always the slowest when lower cut-off voltage is applied.

TABEL 2: Key values for cycling with different upper cut-off voltages

Potential range [V]	Q_{full} (cycle 1) [mAh/g]	$Q_{limited}$ (cycle 5) [mAh/g]	Capacity loss cycles 2-52 [mAh/g]	Capacity loss cycles 52-102 [mAh/g]	Capacity loss cycles 102-152 [mAh/g]
3.50-4.80	120	110	5.6	5.7	3.6
3.50-4.70	121	106	5.0	3.7	3.5
3.50-4.64	120	87	1.5	3.5	3.3

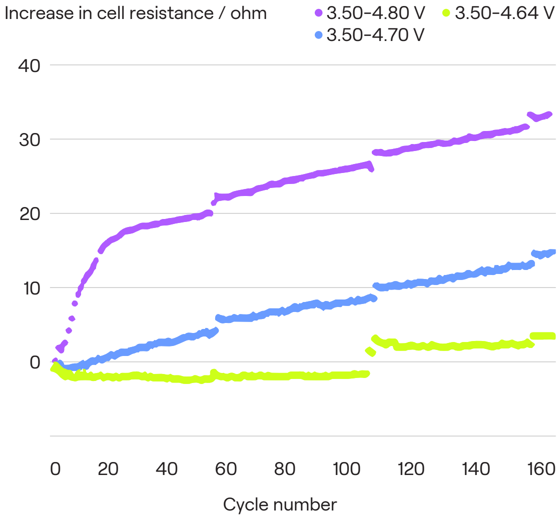
Results are obtained in 2 electrode coin cells with varying upper cut-off voltage of 4.80 V, 4.70 V and 4.64 V, respectively. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

To better understand how the voltage window impact the cell, intermittent current interruption (ICI) method was used to monitor cell resistance.

Figure 7 shows ICI measurements conducted during test of the three conditions and reveals that resistance build-up is much more significant at high upper voltage cut-off, while the cell cycled to 4.64 V did not show any noticeable increase in resistance for 100 cycles. After cycle 102 performed in full range 3.50–4.80 V, the build-up in resistance speeds up.

Thus, we can only assume that, even a single slow cycling in full range causes some irreversible changes in the cell, and the overall performance of the cell would be better if these cycles were skipped.

FIGURE 7: Cell resistance during cycling



Resistance is determined using ICI methodology. Results are obtained in 2 electrode coin cells with varying upper cut-off voltage of 4.80 V, 4.70 V and 4.64 V, respectively. Electrolyte: 1M $LiPF_6$ EC:DEC (1:1 vol.) + 1% LiBOB. Balancing: N/P = 1.20. Temperature: 25°C.

CONCLUSION

In conclusions, our research has demonstrated that it is possible to create a stable LNMO-graphite cell configuration with essentially no degradation. The key to achieving this is controlling the potential range of the anode during cell cycling. Comparison between NMC and LNMO cathodes shows that potentials below 0 V *vs.* Li/Li^+ on the anode is much more likely with LNMO due to specific intrinsic properties of LNMO and that optimization of the cycling protocol is key to avoid this. While the approach presented here aims to provide proof-of-concept, it is important to acknowledge that it is not perfect and requires further development to maintain the observed low initial capacity degradation. Our initial trials have shown that reducing capacity fading is possible, which is a promising step towards developing high-performance energy storage solutions based on LNMO-graphite cells.

METHODS

LNMO electrodes with loading of around 1 mAh/cm^2 were prepared from TOPSOE LNMO material, using procedures described in previous publications[3].

3-electrode measurements were performed using PAT-CELL provided by EL-CELL®, using Freudenberg Viledon FS 2226E + Lydall Solupor 5P09B separator and 100 µL electrolyte: 1M $LiPF_6$ in EC:DEC (vol. 1:1) + 1% LiBOB. Cycling was performed at stable 25 °C:

- First two cycles C/10 (+ CV until current below C/20), D/10 (+ CV until current below D/20); deep stabilization of current was done to perform Electrochemical Impedance Spectroscopy at both charged and discharged state
- Subsequent cycles were performed using C/2 (+ CV until current below C/20), 1D (+ CV until current below D/20)
- Potential range was set to 3.50–4.80 V for LNMO-graphite (cell control), 3.00–4.40 V for NMC532-graphite (cell control), 0.80–0.10 V for LNMO-graphite (anode control)

2-electrode measurements were performed in coin-cell geometry, using Celgard H2010 separator and 20 µL electrolyte: 1M $LiPF_6$ in EC:DEC (vol. 1:1) + 1% LiBOB. Cycling was performed at stable 25 °C:

- First two cycles C/10, D/10
- Subsequent cycles were performed using C/2 (+ CV until current below C/10), 1D
- Every 50 cycle, the slow cycle was performed: C/10, D/10
  Potential range for slow cycles was set to 3.50–4.80 V for all cells, and fast cycles were performed in range 3.50–4.80 V, 3.50–4.70 V or 3.50–4.64 V
- The cell resistances were monitored during discharge of each cycle using ICI procedure[4]

REFERENCES

[1] https://doi.org/10.1016/j.electacta.2012.12.069
[2] https://doi.org/10.1002/aenm.201801427
[3] https://www.topsoe.com/hubfs/Topsoe_status_LNMO.pdf
[4] https://doi.org/10.1016/j.electacta.2022.140888

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