

Systematic “Apple-to-Apple” Comparison of Single-Crystal and Polycrystalline Ni-Rich Cathode Active Materials: From Comparable Synthesis to Comparable Electrochemical Conditions

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State-of-the-art ternary layered oxide cathode active materials in Li-ion batteries (LIBs) consist of polycrystalline (PC), i.e., micron-sized secondary particles, which in turn consist of numerous nanosized primary particles. Recent approaches to develop single crystals (SCs), i.e., single and separated micron-sized primary particles, appear promising in terms of cycle life given their mechanical stability. However, a direct and systematic (“fair”) comparison of SC with PC in LIB cell application remains a challenge due to both differences on material level and state-of-charge (SoC), as SCs typically have slightly lower delithiation capacities/ Li^+ extraction ratios. In this work, PC and SC $\text{Li}[\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}]\text{O}_2$ (NMC811) are synthesized with comparable bulk and surface characteristics from identical self-synthesized precursors. Indeed, the cycle life of SCs is not only superior, when conventionally charged to equal upper cutoff voltage (UCV), as shown in NMC||Li and NMC||graphite cells, but also after adjusting UCVs to similar SoCs, where bigger SCs counterintuitively have even a better rate performance and cycle life.

cycle life strongly influence the customer experience in the form of vehicle price, driving range, and service life.^[4,5]

Increasing the Ni content of NMCs has been and is still a viable strategy to increase specific energy and reduce cost of LIBs.^[2–4,6] However, the drawback of these Ni-rich formulations ($x \geq 0.8$) is a loss of cycling stability, as an incompatible deformation along grain boundaries induced by anisotropic crystallographic deformation at high SoC ($\geq 80\%$) lead to a partial fragmentation of the particles during charging.^[7–10] This “particle breathing” phenomenon has been identified as a major failure contribution, as it repeatedly exposes reactive surfaces giving rise to surface-related degradation phenomena such as TM dissolution,^[11,12] oxygen release,^[13–16] and electrolyte decomposition,^[15,16] resulting in the continuous formation of electrochemically

inactive surface layers and permanent (intergranular) cracks.^[17–19] The accompanied increase in resistance additionally causes overvoltage-induced decrease in capacity and mean discharge voltage, both leading to lower specific energy and energy density.^[20–22]

In contrast to polycrystalline (PC) primary particle agglomerates (i.e., secondary particles), “single-crystal” (SC) particles can

1. Introduction

Mixed transition metal (TM) layered oxides like $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$ ($x + y + z = 1$, NMC_{xyz}) have established themselves as the state-of-the-art cathode active material (CAM) for lithium-ion batteries (LIBs) in battery electric vehicles.^[1–3] Key performance indicators of the CAM like cost, specific energy, and

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be comprised of a single micron-sized crystal grain as evidenced by electron backscatter diffraction (EBSD).^[23–27] The absence of grain boundaries within the particle prohibits the aforementioned failure cascade because the particle integrity is preserved and surface-related degradation reactions are suppressed.^[28–30] Additionally, the enhanced mechanical robustness of the SC particles allows for a stronger compression of electrodes enabling higher energy densities.^[31]

As proven in literature, SC-NMCs with medium nickel contents (e.g., NMC532 and NMC622) possess improved long-term cycling stability in NMC||graphite cells.^[32–35] At high upper cut-off voltage (UCV) (≥ 4.5 V) and with adjusted electrolyte formulations, these mid-Ni SC-NMCs can even compete with state-of-the-art Ni-rich PC-NMCs in terms of specific energy.^[36,37] However, higher cobalt content remains a disadvantage^[4,38,39] and Ni-rich PC-NMCs are shown to outperform mid-Ni PC-NMCs in terms of cycle life when both are forced to deliver the same specific energy.^[40] This is likely because the higher required UCVs and capacities for mid-Ni PC-NMCs aggravate irreversible side reactions.^[16,41] This motivates to apply the SC approach to Ni-rich NMCs, even though their synthesis, particularly at large scale, remains challenging and costly due to high calcination temperatures, longer calcination times, and/or additional postprocessing steps.

In general, crystal growth can be enhanced by either increasing the calcination temperature or changing the synthesis environment, e.g., to molten salt (MS) synthesis. While seemingly feasible for mid-Ni NMCs,^[42–44] the former strategy is challenging for Ni-rich NMCs as a high calcination temperature promotes unwanted oxygen release from the lattice as well as lithium–nickel ($\text{Li}^+/\text{Ni}^{2+}$) mixing, resulting in a significant worsening of electrochemical performance.^[2,31,42] Here, the MS strategy is more feasible as it allows rapid crystal growth at moderate calcination temperatures but requires an additional aqueous washing step, which can severely degrade sensitive Ni-rich materials through lithium–proton exchange.^[19,31,45]

An additional challenge lies in the separation of SC particles.^[46] Employing a dry ball-milling strategy increases surface area and potentially deteriorates particle morphology, while a separation in aqueous/protic solvents leads to the aforementioned lithium–proton exchange issues. Unfortunately, this aspect is frequently glossed over by “qualitatively estimating” the particle size from high-magnification scanning electron microscopy (SEM) images instead of appropriate methods for particle size, agglomeration analysis, and surface area quantification, i.e., laser diffraction and physisorption, respectively. These aspects are essential to systematically study morphology in LIB active materials. Furthermore, in contrast to the frequently reported cycle life benefits of Ni-rich SCNMCs in NMC||Li cells,^[47–53] the few studies in NMC||graphite cells reveal less distinct conclusions, i.e., mixed results or insignificant differences.^[30,54,55]

The present work aims to systematically validate the apparent benefit of SC-NMCs. For this purpose, a series of SC-NMC811 with varying sizes as well as PC-NMC811 reference samples are synthesized from identical home-made precursor, processed in identical manner, and finally holistically characterized to exclude differences possibly unaccounted for (e.g., undisclosed doping/coatings in commercially available materials, performance enhancement by postprocessing steps, etc.).^[56] SEM, X-

ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), particle size analysis (PSA) by laser diffraction, krypton physisorption, and X-ray photoelectron spectroscopy (XPS) are utilized to ensure comparability of bulk and surface properties before systematically evaluating the electrochemical performance in NMC||Li and NMC||graphite cells. Electrochemical testing conditions are finally adjusted to similar SoC and the practical implications for SC-NMCs discussed.

2. Results and Discussion

2.1. Synthesis and Characterization of Well-Defined “Single-Crystal” NMC811

2.1.1. Synthesis and Morphology

Ni-rich layered oxides like $\text{Li}[\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}]\text{O}_2$ (NMC811) are prone to $\text{Li}^+/\text{Ni}^{2+}$ cation mixing during synthesis at high calcination temperatures ($T_{\text{calc}} \geq 850^\circ\text{C}$) necessary for the growth of large crystals.^[2] Thus, a MS synthesis^[25] including a washing and annealing procedure^[45] is chosen for SC-NMC811 as it enables fast and controlled crystal growth at lower temperatures by realizing improved contact area and mobility of reactants as well as fast crystal growth through a dissolution–recrystallization mechanism.^[31,57]

As depicted in **Figure 1a**, the MS synthesis was employed to synthesize a series of SC-NMC811 CAMs from regular spherical hydroxide precursor (pCAM, $D_{50} \approx 8\ \mu\text{m}$). By varying the calcination temperature T_{calc} , three distinct sizes of SC-NMC811 were obtained which in the following are referred to as SC MS800, SC MS850, and SC MS900 for T_{calc} of 800, 850, and 900 $^\circ\text{C}$, respectively. As a reference, a PC-NMC811 (PC ref.) is synthesized by the ordinary solid-state reaction route at 800 $^\circ\text{C}$ from the same hydroxide precursor. To exclude the influence of the postprocessing steps used for the MS synthesis of SC, a washed and annealed PC reference sample PC wash. is additionally produced. Here, an equal amount of Li_2SO_4 is manually added before the washing step. This reference sample is essential for comparability because postprocessing steps (e.g., washing and annealing) can improve the performance of Ni-rich NMCs and can lead to misleading attributions and interpretations.^[56]

In the MS synthesis employed herein, LiOH is used as the lithiation agent while Li_2SO_4 is added as a non-participating, low-volatility flux additive (Figure S1, Supporting Information), which ensures the presence of a liquid phase at high temperatures and prolonged reaction times enabling controlled crystal growth and preventing the agglomeration of SC particles (Figure S2, Supporting Information).^[19] The choice of Li_2SO_4 can further be rationalized as Li_2SO_4 (1) forms a eutectic with LiOH (melting point $< 500^\circ\text{C}$ ^[58,59]), (2) does not introduce foreign cations and is easily removed (Table S1, Supporting Information), and (3) mitigates the water damages caused by the post-calcination washing step (Figure S3, Supporting Information), likely by forming a protective coating on NMC811.^[60] Given the dissolution of precursor (pCAM) during MS synthesis, the SCs are independent of pCAM morphology (Figure S4, Supporting Information) and can be designed more flexible, e.g., in sizes, which consequently allows identical pCAM as for synthesis of PC-NMC.

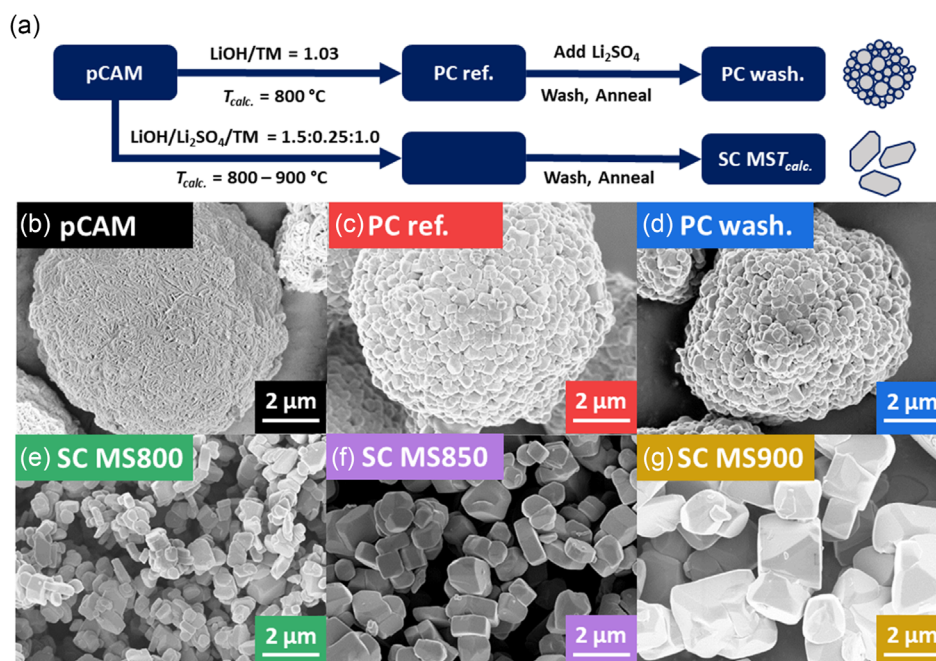


Figure 1. a) Overview of synthesis routes and conditions as well as sample definitions. pCAM = hydroxide precursor $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$, PC = polycrystalline, SC = single crystal, TM = transition metal, T_{calc} = calcination temperature and MS = molten-salt-assisted, b–g) SEM images of PC- and SC-NMC811.

The morphology of the CAMs is analyzed by SEM, PSA, and Kr physisorption. Figure 1b–g shows SEM images of the synthesized samples. While the PC-NMC811 samples show the typical spherical morphology inherited by its precursor, the SC-NMC811 present separated, monolithic, and partly faceted particles (i.e., flat faces reflecting underlying crystal symmetries). Absence of mechanical separation of the different-sized SCs implies an entire disintegration or even dissolution of pCAMs during the MS synthesis^[25] and confirms size control of SC-NMCs via synthesis conditions and independent from precursor size (Figure S4, Supporting Information).

In agreement with the SEM images, the particle size distributions (PSDs) (Figure S5, Supporting Information) of pCAM and PC-NMCs are narrow and almost identical, while the SC-NMCs show broader distributions and smaller, distinct sizes. All of the NMCs show monomodal PSDs of Gaussian shape except for the SC MS800 which has a small shoulder due to slight agglomeration during annealing. **Figure 2** shows the median particle diameter D_{50} as well as the specific surface area a_{BET} of the samples, which are inversely related. The specific surface area is 1.5 to 6 times as large for the SC-NMCs compared to the PC reference sample. This large discrepancy is further evidence for well-separated SC-NMC particles (see Table S1, Supporting Information for further data).

2.1.2. Stoichiometry and Crystal Structure

The stoichiometry and the sulfur impurity content of the samples are investigated via ICP-OES. The ratio of the three TMs corresponds to the ideal stoichiometry of $\text{Ni}:\text{Co}:\text{Mn} = 8:1:1$, and the

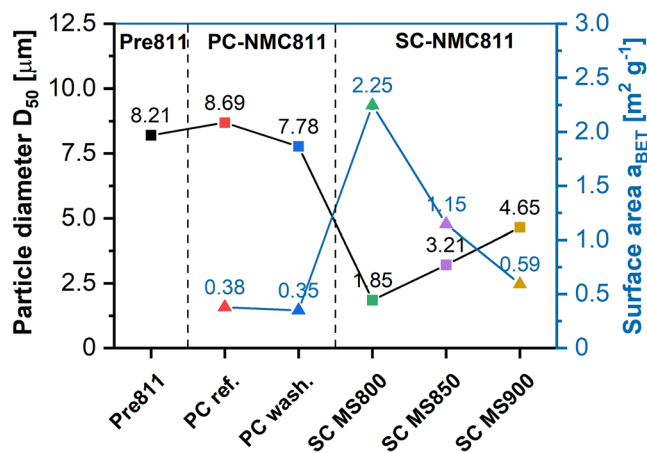


Figure 2. Median particle diameter D_{50} obtained by laser diffraction (left axis) as well as specific surface area a_{BET} obtained by Kr physisorption (right axis). Error bars are too small to be visible.

Li:TM ratios are close to unity suggesting neither Li losses nor a large excess of residual Li salts (Table S1, Supporting Information). The latter point is also supported by minimal sulfur content in all washed samples (PC and SC) proving the effectiveness of the washing procedure.

The crystal structure is investigated by powder X-Ray diffraction (PXRD) using Mo radiation and analyzed by Rietveld refinement.^[61] **Figure 3** shows the PXRD data and matched patterns from the refinement. All reflections in every pattern can be indexed according to a single-phase hexagonal $\alpha\text{-NaFeO}_2$ structure (space group $R\bar{3}m$), and a reasonable goodness of fit

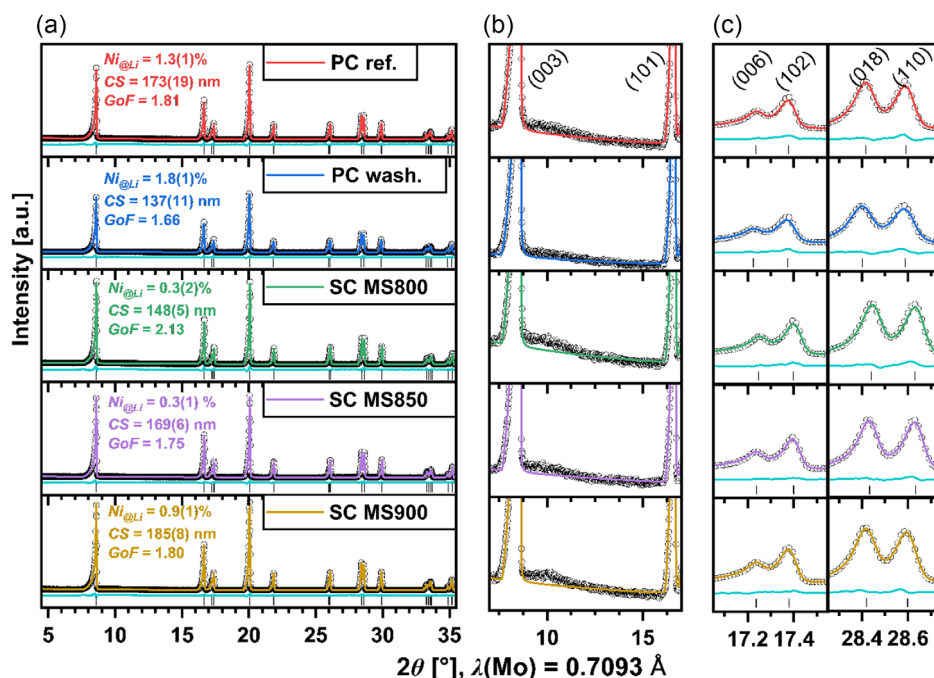


Figure 3. a) PXRD data (open circles) overlaid with respective Rietveld refinement patterns (colored lines), difference between the two (light blue lines) and reflex positions (black ticks). b,c) Different excerpts at different magnifications. $Ni_{@Li}$, CS, and GoF denote the occupancy of Ni in the Li layer (Li/Ni mixing/cation mixing), the crystallite size based on integral breadth, and the goodness of fit from the refinement. A complete list of refinement parameters and results can be found in Table S2, Supporting Information. Complete patterns are shown in greater detail in Figure S6, Supporting Information.

($1.6 < GoF < 2.1$) is achieved for all refinements indicating their reliability. The region between 8° and 16° 2θ where reflections of impurities like Li_2O , $LiOH \cdot (H_2O)$, Li_2CO_3 , and Li_2SO_4 would appear (magnified in Figure 3b) shows absence of impurities. The clear splitting of (006)/(102) and (018)/(110) reflections, shown in Figure 3c, indicates a good hexagonal ordering within the structure for all samples.^[62] Except Li^+/Ni^{2+} mixing and crystallite size, refinement results are in good agreement between samples (Table S2, Supporting Information) and with literature (Table S3, Supporting Information).

The degree of Li^+/Ni^{2+} mixing ($Ni_{@Li}$ in Figure 3a and Table S2, Supporting Information) is lower in SC- (0.3–0.9%) compared to PC-NMCs (1.3–1.8%) despite higher calcination temperatures which can be related to different synthesis methods applied. Enhanced ion mobility during MS synthesis allows for a more controlled crystallization process during the cooling phase yielding larger crystals with less defects.^[31,57] However, this effect is limited as shown by the increase in Li^+/Ni^{2+} mixing for the calcination temperature of $T_{calc} = 900^\circ C$ (SC MS900).

While the crystallite sizes determined by Rietveld refinement are unreliable for the SC-NMCs (the crystallite size-induced broadening is small compared to the instrument-induced broadening), an EBSD analysis^[23–27] confirms that in the case of the SC-NMCs most particles consist of a single crystallite (Figure S7, Supporting Information) rendering the particle size a reasonable estimate for the crystallite size as the individual particles are spatially well separated. SEM images and particle size results (Figure 1, 2) show that while the MS environment alone only

slightly increases the crystallite size, the combination with higher calcination temperatures leads to a substantial increase.^[26–30]

2.1.3. Surface Properties

The surface composition of the samples is analyzed by XPS. Survey scans reveal the presence of Ni, Co, Mn, O, C, and Li on all samples. S is additionally found on all samples except for PC wash. in alignment with ICP-OES data (Table S1, Supporting Information). The observed peaks for all samples in the core spectra can be assigned to identical species without significant peak shifts demonstrating sample comparability. A full list of peak assignments and positions can be found in the supporting information (Table S4, Supporting Information).

The overall surface composition as calculated from the fitted core spectra (Figure 4a) varies only slightly between samples. However, given sample inhomogeneities, these differences of a few atomic percent can be regarded as negligible.^[63] The surface is dominated by O, C, and Li, which can be assigned to traces of residual Li compounds (e.g., $LiOH$, Li_2CO_3 , and Li_2SO_4) from synthesis, washing, and contact to air.^[64] The presence of S in the PC ref. sample might come from some sulfate residues after the co-precipitation process of the hydroxide precursor (from transition metal sulfates).

Additional carbon is typically found due to atmospheric contamination.^[65] The presence of these surface impurities is evident in the S 2p, O 1s, C 1s, and Li 1s core spectra (Figure S8, Supporting Information). The Li 1s core spectra (Figure 4b) can quantify and distinguish intercalated Li in

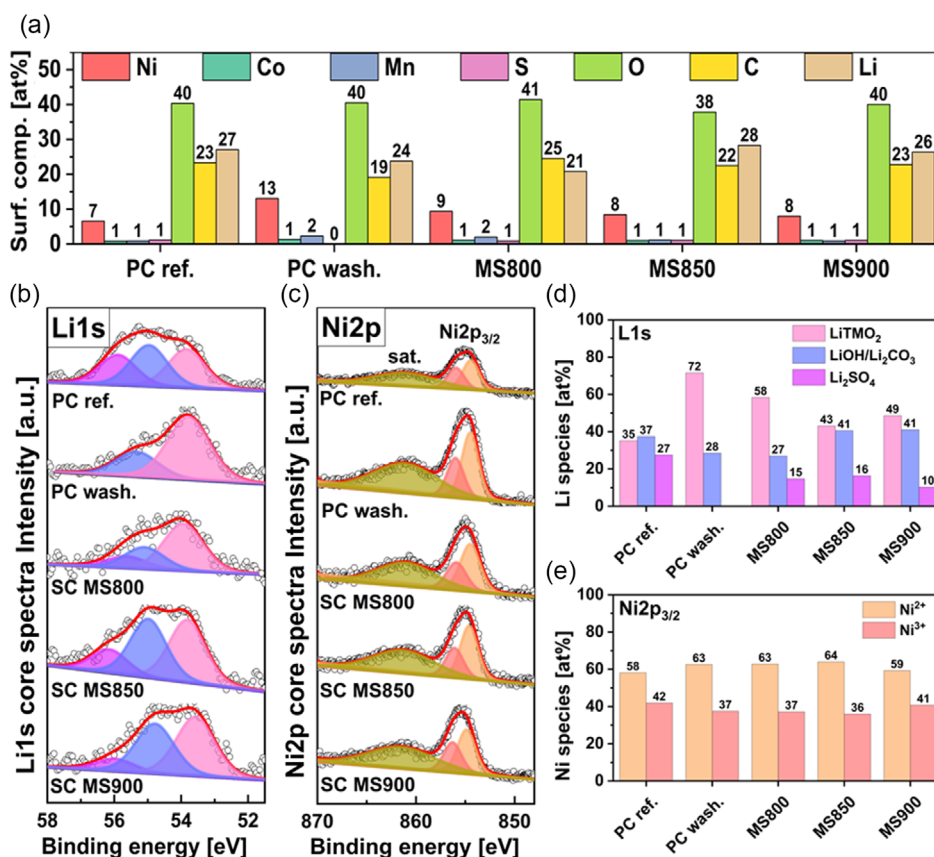


Figure 4. a) Surface composition calculated from fitted XPS core spectra b) and c) fitted core spectra Li 1s and Ni 2p, respectively. Only the Ni 2p_{3/2} region is shown for clarity. d) and e) Corresponding percentage of identified Li and Ni species, respectively.

layered oxides (53.8(1) eV) and other Li species (55.0(1) eV and 55.9(1) eV for LiOH/Li₂CO₃ and Li₂SO₄, respectively).^[66] The amount of surface impurities, given by the ratio of these Li species to intercalated Li (Figure 4d), is highest for *PC ref.* and lowest for *PC wash.*, while the degree of impurities for SC samples ranges in between. The data are reasonable, as *PC ref.* is unwashed and *PC wash.* is the only washed sample without a high excess of lithium during the synthesis. Though less pronounced, the same trend is seen by the amount of Ni in the overall surface composition (Figure 4a).

Generally, the low amount of TMs in the overall surface composition complicates their quantification. This is especially evident for Co and Mn as the signal-to-noise ratio is only barely above the limit of quantification. In addition, the Mn signal is hard to deconvolute because it is overshadowed by a Ni LMM auger transmission peak (Figure S8, Supporting Information). Hence, the ratio of TMs differs from the bulk composition and in between samples. The high intensity of the Ni 2p core spectra, on the other hand, allow for further interpretation. The Ni 2p_{3/2} (≈855 eV) peaks within the Ni 2p core spectra (Figure 4c) were deconvoluted using two peaks representing Ni²⁺ (854.4(2) eV) and Ni³⁺ species (855.8(2) eV), respectively, so that the Ni³⁺ fraction could be quantified.^[67] In NMCs, Ni is typically present in a mixed oxidation state as the higher energy of the Mn³⁺/Mn⁴⁺ redox couple facilitates the partial reduction

of Ni³⁺.^[68,69] In this case, the Ni³⁺ fraction was determined to be ≈40% for all samples (Figure 4e) which agrees well recent literature on NMC811.^[67] Hence, neither synthesis conditions nor postprocessing fundamentally changed the nature of the surface (e.g., in the form of a reductive coating) and additionally proves the similarity of the samples.

In conclusion, the results of the material characterization show that while presenting in a distinctly different morphology, all samples synthesized in this work show comparable bulk and surface properties. Thus, morphology is the only remaining parameter on the material level that can be attributed to electrochemical performance. This perfectly qualifies the presented model materials for an apple-to-apple performance comparison between Ni-rich PC- and SC-NMCs.

2.2. Electrochemical Performance Comparison between PC- and SC-NMC811

2.2.1. Electrochemical properties in NMC||Li cells

Initially, the CAMs are tested in NMC||Li cells. **Figure 5a** shows data from rate capability test with discharge rates from 0.1 to 3.0 C. Compared to the PC-NMC, the specific discharge capacities of SC NMCs are slightly lowered at 0.1 C and the difference roughly remains up to 3.0 C, except for SC MS800, which fades

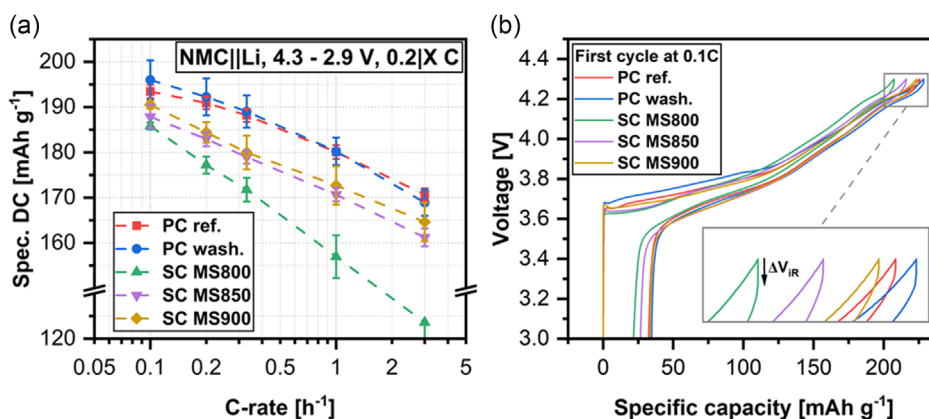


Figure 5. a) Specific discharge capacities of PC- and SC-NMC in NMC||Li coin cells at varying discharge rates (0.1–3.0 C with 1 C $\triangleq$ 190 mA g⁻¹) in a voltage window of 4.3–2.9 V. The charge rate is kept at 0.2 and 0.1 C, respectively to avoid Li dendrite formation. Error bars represent the standard deviation of at least three cells. Corresponding cycling data is shown in Figure S8, Supporting Information. b) Representative voltage vs. specific capacity curves for the first cycles at 0.1 C. Inset shows enlarged view of the iR drop (ΔV_{IR}) appearing after the switch from charge to discharge. Averaged data of specific charge capacities, specific discharge capacities, and Coulombic efficiencies as well as iR drops (ΔV_{IR}) can be found in Table S5 and Figure S9, Supporting Information.

more. While the decreased specific capacity of SC-NMCs is ascribed to kinetic hindrances caused by their larger crystallite size and resulting longer diffusion pathways for Li⁺ ions,^[35,70] it is counterintuitive here, where higher SC particle sizes perform even better at higher rates. Similar to NMC||Li cells, this trend is also observed for symmetric charge–discharge cycles in NMC||graphite cells in NMC 0.1C and 1.0C, respectively (Figure 6b).

The voltage vs. specific capacity curves (Figure 5b) show higher overvoltages for SC-NMCs compared to the PC and reach the UCV at lower states-of-charge (SoC) (Table S5, Supporting Information). Higher Ohmic cell resistance, estimated from the iR drops (ΔV_{IR}) at the switch from charge to discharge,^[71] is observed for decreasing particle size and increasing specific surface area a_{BET} of the SC-NMCs (Figure S10, Supporting Information). The same trend cannot be observed for the PC-NMC samples presumably because their surface area changes drastically upon charging.^[28] Therefore, the reduced discharge capacity of SC-NMCs compared to PC-NMCs might be the result of an interplay between surface-to-volume ratio and its change during charging. While a more rigid investigation of the supposed kinetic limitations of SC-NMCs is necessary, it is beyond the scope of this work.

2.2.2. Cycle Life in NMC||Graphite Cells

Figure 6a shows the results of a long-term cycling experiment for an UCV of 4.2 V. In Figure 6b, the specific discharge capacities reached at 0.1C (last cycle of formation) and 1.0C (cycle which determines 100% state-of-health (SoH)) are separately indicated for clarity. Mostly, the CAMs achieve similar (yet slightly reduced) specific discharge capacities as observed in NMC||Li cells, while SC MS800 fades severely and is therefore excluded in this comparison. The data are only shown in Figure S11, Supporting Information for the sake of completeness. Though SC NMCs begin with lower capacities (≈ 10 mAh g⁻¹ lower), the average cycle life until 80% SoH is prolonged by 36% and

47% for SC MS900 and SC MS850, respectively, compared to PC ref. The average cycle life of PC wash, on the other hand, is lowered by 22%, which excludes a beneficial impact of post-processing (washing and annealing step).

The benefit of SC- vs. PC-NMCs in terms of cycle life can be reasonably questioned because SoC differences have a relevant impact on cycle life of layered oxide cathodes. For same UCV, the SoC is lower, which in fact might be beneficial for structural stability and cycle life.^[8,16,40] At higher SoCs, the low amount of remaining lithium can no longer support the layered structure so that the interlayer distance of TM oxide layers shrinks drastically causing the build-up of anisotropic lattice strain which is released as inter- or even intragranular cracking.^[9,72,73] The critical SoC for this crystallographic phenomenon to affect cycling stability is found to be at $\approx 80\%$ for ternary layered oxides.^[7] While the particle fragmentation is only partly irreversible, the enhanced surface reactivity in the charged state is the cause of related irreversible phenomena such as the build-up of densified lithium-poor surface layers, concurrent oxygen release, and other intertwined degradation phenomena such as electrolyte decomposition.^[16,19,41,73] Estimated from the first cycle specific charge capacity in the NMC||Li cells, the materials in this study reach an SoC of $\approx 80\%$ (Table S5, Supporting Information) when cycled to 4.3 V (vs. Li|Li⁺) corresponding to ≈ 4.2 V in NMC||graphite full cells. In a practical two-electrode cell, individual electrode overpotentials can decrease SoCs.^[21,72] Synthesis modifications that can change the overpotential of a material (e.g., coating, doping, and change in morphology) will thus also affect the SoC window.^[62] Consequently, to enable a fair comparison between PC- and SC-NMCs, the SoC is controlled by the delivered capacity in a cycling experiment, where the SC-NMCs are forced to deliver the similar capacity as PC ref. by adjusting the UCV.

A test of different UCVs in NMC||Li cells revealed that SC MS800 was not able to deliver the required capacity even at an UCV of 5.0 V, so it is omitted from further investigations (Figure S12, Supporting Information). Figure 6c shows the results of long-term cycling experiments where all of the

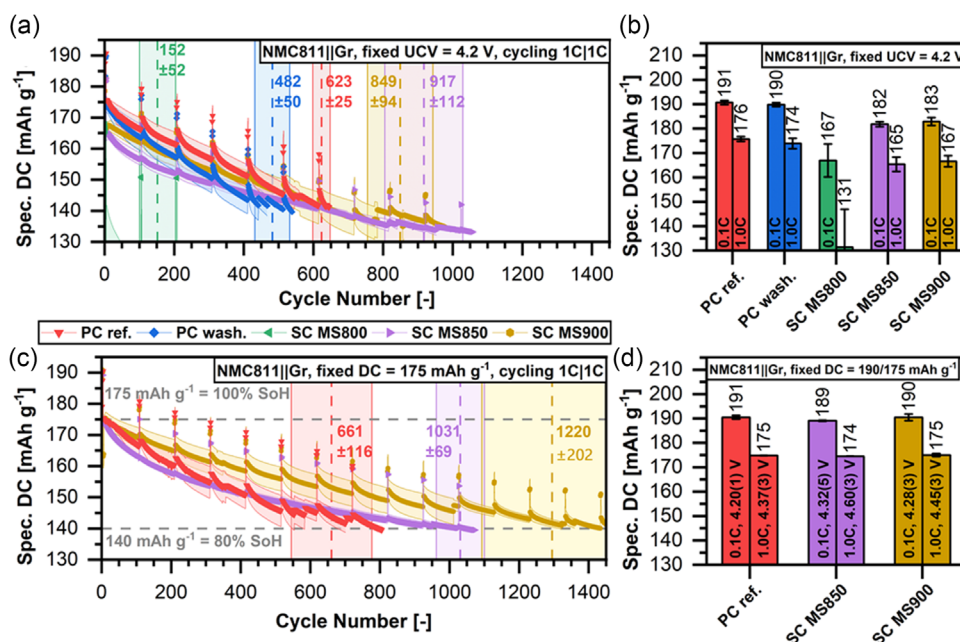


Figure 6. Charge–discharge cycling plots (specific discharge capacity vs. cycle number) in NMC811||graphite cells for 1C|1C (1C = 190 mA g⁻¹) until 80% SoH. a) With the same UCV of 4.2 V and c) with varying UCVs to reach similar SoCs via similar initial specific capacities of 190 and 175 mAh g⁻¹ (=100% SoH) at 0.1C and 1.0C, respectively. Dashed vertical lines denote the average cycle life until 80% SoH (including error bars) based on the first cycle at 1.0C, respectively. b) and d) show obtained specific discharge capacities at 0.1C (last cycle of formation) and 1.0C (cycle to determine 100% SoH), respectively. UCVs and C-rates are indicated in columns. All given errors represent the standard deviation of at least three cells. Additional data can be found in Table S6, Supporting Information.

CAMs start out at the same initial specific discharge capacity of 175 mAh g⁻¹ (=100% SoH) and their end-of-life is defined at 140 mAh g⁻¹ (=80% SoH). Again, the specific discharge capacities reached at 0.1C (last cycle of formation) and 1.0C (cycle which determines 100% SoH) are separately indicated for clarity in Figure 6d complemented by the required UCVs which are kept constant after the initial cycles. Despite higher UCVs, the average cycle life of SC MS850 and SC MS900 is still higher and is enhanced by 56% and 84%, respectively, compared to PC ref. Additional data from these cycling experiments can be found in Table S6, Supporting Information.

Insights into mechanism of capacity fading can be derived from the development of the average charge and discharge voltages V_C and V_{DC} , respectively, as well as their difference $\Delta V = V_C - V_{DC}$ (Figure S13, Supporting Information). A loss of lithium inventory would increase both V_C and V_{DC} ($\Delta V \approx \text{const.}$), whereas an increase in internal resistance would only increase V_C while decreasing V_{DC} , i.e., leading to higher ΔV .^[73] Apart from SC MS800 (see discussion in Supporting Information), when cycled to the same UCV (Figure S13a,c, Supporting Information), all samples begin with a similar ΔV but increase more for PC afterward, indicating an increase in internal resistance. This could be due to the continuous build-up of resistive surface layers caused by the exposure of fresh, reactive surfaces due to “particle breathing” in the charged state which besides increasing the internal resistance will also decrease capacity via loss of active material.^[19] When the SC samples are cycled to higher UCVs, the advantage of lower increase in internal resistance disappears for SC MS850 (Figure S13b,d,

Supporting Information), suggesting that the longer cycle life can be explained by higher lithium inventory and/or lower active material losses.^[74] For SC MS900, on the other hand, practically no increase in internal resistance is observed, which likely leads to the superior cycle life.

To further understand the cycling results, cells were disassembled in the discharged state for *postmortem* investigations. SEM images of cathode cross sections (Figure S14, S15, Supporting Information) show that over the course of cycling PC ref. suffers from irreversible particle cracking along grain boundaries, while the SC-NMCs do not show any signs of morphological change. One would assume that this particle cracking would promote surface-related degradation mechanisms such as TM dissolution and subsequent cross-talk. However, when the TM content on the anode is determined by ICP-OES, no significant difference can be observed as the standard deviation between cells is too high (Figure S16, Supporting Information). The similarity of the cycled anodes as seen by ICP-OES supports the conclusion that the cathode is the limiting factor for the cycle life.

2.2.3. Practical Implications of Using “Single-Crystal” NMCs

With similar specific capacity, the cell voltage is necessary to obtain specific energy. In Figure 7a and Figure 7c, the mean discharge voltage V_{DC} and resulting specific discharge energy, respectively, are plotted vs. the cycle number. Despite the difference in UCVs, all materials initially deliver similar mean

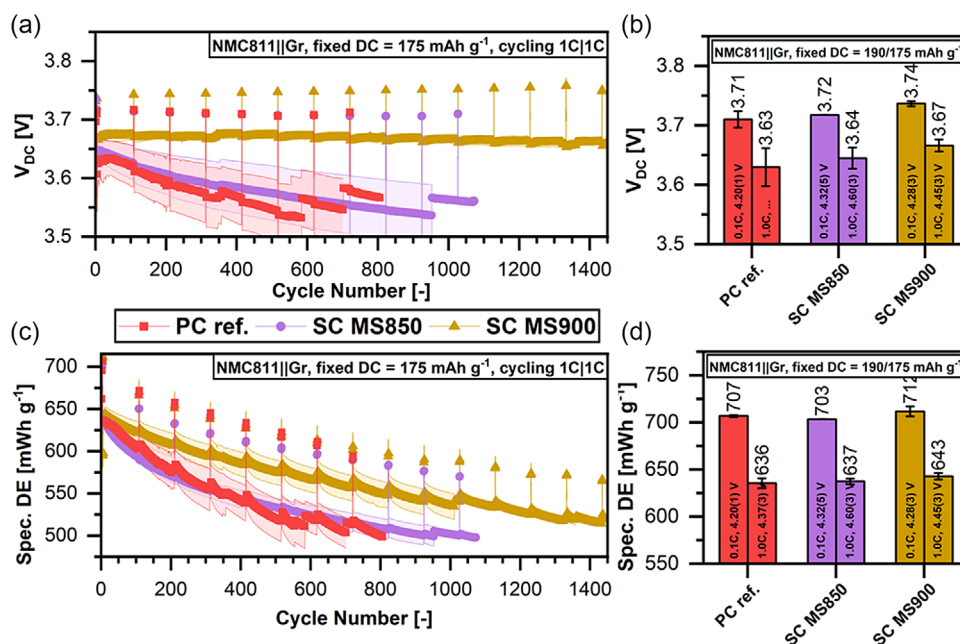


Figure 7. Long-term cycling results in NMC811||graphite cells in constant current–constant voltage mode at 1C|1C (1C = 190 mA g⁻¹) until 80% SoH with varying UCVs to reach 175 mAh g⁻¹ (=100% SoH) at 1.0C. a) Mean discharge voltage V_{DC} vs. cycle number. b) Mean discharge voltage at 0.1C (last cycle of formation) and 1.0C (cycle to determine 100% SoH), respectively. c) Specific discharge energy vs. cycle number. d) Specific discharge energy at 0.1C (last cycle of formation) and 1.0C (cycle to determine 100% SoH), respectively. UCVs and C-rates are indicated in columns. All given errors represent the standard deviation of at least three cells.

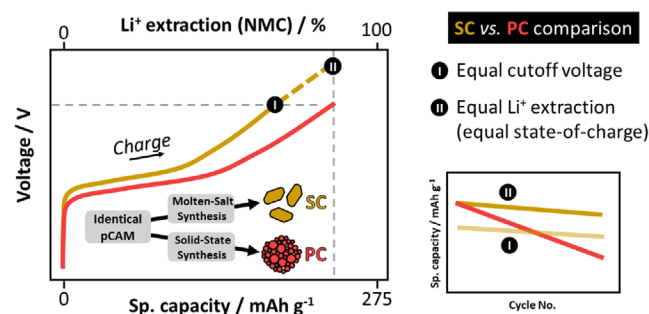


Figure 8. Schematic summary of the "fair" SC- vs. PC-NMC comparison, where the both NMC types are synthesized from identical pCAM and electrochemically compared also with respect to equal SoC (i.e., Li⁺ extraction ratio).

discharge voltages (Figure 7b), resulting in similar initial specific discharge energies (Figure 7d). However, while *PC ref.* and *SC MS850* show a similar voltage fade, the mean discharge voltage, thus specific energy of *SC MS900* remains constant during charge–discharge cycling. For this reason, the superior cycling performance of *SC MS900* appears even more pronounced in this comparison. As a result, the delivered energy overall compared to *PC ref.* can be increased by 35% and 84% for *SC MS850* and *SC MS900*, respectively (Figure S17, Supporting Information).

Another relevant practical metric is the energy density (Wh/L), which is more important for applications where space is severely limited like portable electronics. In this regard, the lower tap

density of SCs is frequently correlated with lower energy density. However, given the absence of internal voids (Figure S18, Supporting Information), SC-NMCs have a higher material density (Table S7, Supporting Information). Thus, when electrodes are compressed to comparable porosity, SC-NMCs can slightly improve energy density (Table S7, Supporting Information). When the variability of MS synthesis conditions and higher mechanical stability of SCs are fully taken advantage of to maximize the electrode density, SC-NMC811 is even able to beat LiCoO₂ electrodes in terms of energy density.^[48,75]

3. Conclusion

State-of-the-art cathodes in LIBs and Li[Ni_xMn_yCo_z]O₂ ($x + y + z = 1$, NMC_{xyz}) are based on PC secondary particles, being agglomerates of numerous nanosized primary particles. Given their limited cycle life in course of particle cracks due to mechanical stress alongside grain boundaries, separated SC primary particle NMC appears to be a promising modification.

In this work, PC and SC for Ni-rich NMC, i.e., with $x > 0.8$, is systematically compared by synthesizing a series of SC-NMC811 with varying sizes as well as PC-NMC811 reference materials from identical self-synthesized CAM precursor (pCAM), enabled by MS and conventional solid-state synthesis, respectively. Thorough characterization by SEM, PSA, Kr physisorption, XRD, and XPS ensures that while having distinctly different, well-defined morphologies, the materials are comparable in terms of bulk and surface properties enabling purely morphology-based comparison.

Charge–discharge cycling in NMC||graphite cells with the conventional UCV of 4.2 V demonstrates an increased capacity retention for SC-NMCs but with lower initial specific discharge capacities. The latter is the well-known result of resistance reasoned overvoltages. Interestingly, when adjusting UCVs to identical SoC, i.e., similar delithiation capacities/Li⁺ extraction ratios (Figure 8), the SC indeed remains superior in terms of cycle life, voltage retention, and overall specific energy, proving the benefit of this morphology. Interestingly, within different SCs, it is counterintuitively shown that the bigger SCs are even superior in performance.

4. Experimental Section

Material Synthesis: Synthesis of Hydroxide Precursor. The hydroxide precursor (pCAM) Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ was synthesized by co-precipitation in a continuous Couette–Taylor flow reactor (CTFR) (LCTR-Tera 3300, Laminar, Rep. of Korea). NiSO₄·6H₂O (>98%, Alfa Aesar), CoSO₄·7H₂O (>98%, Alfa Aesar), and MnSO₄·H₂O (>99%, Alfa Aesar) were dissolved in deionized water in a molar ratio of 8:1:1 to yield a 1.5M solution. Additionally, a 4.875M NaOH solution and a 12wt% (≈6.7M) ammonia solution were prepared. All solutions were filtered prior to use.^[76]

For the co-precipitation, the solutions were pumped into the reactor simultaneously using peristaltic pumps coupled to the reactor. Reactant flow rates were adjusted so that the molar ratio of NaOH and ammonia to TM sulfates were 2:1 and 1:1, respectively, and the mean retention time, calculated by the quotient of reactor volume and total flow rate of reactants, was equal to ≈3.5 h. Using the signal of a pH electrode at the end of the reactor, the flow rate of the NaOH solution was automatically varied over the course of the reaction to maintain a pH of 11. After an equilibration time of 14 h (=4 times the mean retention time), the reaction mixture was collected in the form of a muddy green dispersion over the course of several hours. The dark green product was separated by centrifugation (1.5 min at 2000 RCF) and washed with deionized water until a pH of below 8 was reached. The product was first dried over night at 90 °C and then at 120 °C under reduced pressure which caused a color change to dark brown.^[76]

Synthesis of “Single-Crystal” Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂. The hydroxide precursor was mixed with LiOH and Li₂SO₄ in a molar ratio of $n(\text{LiOH})/n(\text{TM}) = 1.5$ and $n(\text{Li}_2\text{SO}_4)/n(\text{TM}) = 0.25$, respectively, and ground in a hand mortar until homogeneous. Contained in alumina crucibles the mixtures were calcined in a large tube furnace in an atmosphere of pure oxygen with a flow rate of 10 L h^{−1}. The tube furnace was first held at 500 °C for 3 h and then at the respective calcination temperature (800 °C, 850 °C or 900 °C) for 12 h using heating rates of 2 °C min^{−1}. After cooling down to below 200 °C (at ≈2 °C min^{−1}), brick-like samples were taken out of the oven, crushed to a coarse powder using a small grinding mill (IKA A11 basic) for ≈30 s, and then finely ground using a hand mortar.

To wash away remaining lithium salts, the finely powdered samples were dispersed in deionized water (≈20 mL g^{−1}) using an ultrasonic bath for 5 min and then immediately separated by centrifugation (1.5 min at 2000 RCF). This process was repeated once. Then the samples were shortly dispersed in and separated from isopropanol and acetone (≈10 mL g^{−1}), respectively, to be dried at 90 °C for at least 2 h. Dried powders were recovered from the centrifuge tubes, hand-ground, and placed in a large tube furnace again to be annealed for 3 h at 750 °C otherwise using the same settings as before. Finally, the powders were hand-ground again and immediately placed in a dryroom atmosphere. The samples were named SC-NMC811 MS800, MS850, and MS900, respectively.

Synthesis of Polycrystalline Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂. The hydroxide precursor was mixed with LiOH in a molar ratio of $n(\text{LiOH})/n(\text{TM}) = 1.03$ and ground in a hand mortar until homogeneous. Contained in alumina crucibles the mixtures were calcined in a large tube furnace in an

atmosphere of pure oxygen with a flow rate of 10 L h^{−1}. The tube furnace was first held at 500 °C for 3 h and then at 800 °C for 12 h using heating rates of 2 °C min^{−1}. After cooling down to below 200 °C (at ≈2 °C min^{−1}), samples were taken out of the oven, finely ground using a hand mortar, and immediately placed in a dryroom atmosphere. This sample was named PC ref.

To obtain the washed and annealed reference sample PC wash., PC ref. was mixed with Li₂SO₄ in a molar ratio $n(\text{Li}_2\text{SO}_4)/n(\text{TM}) = 0.25$ and ground in a hand mortar until homogeneous before going through the same washing and annealing procedure as the SC-NMC samples. The sample was then dispersed in deionized water (≈20 mL g^{−1}) using an ultrasonic bath for 5 min and then immediately separated by centrifugation (1.5 min at 2000 RCF). This process was repeated once. Then the sample was shortly dispersed in and separated from isopropanol and acetone (≈10 mL g^{−1}), respectively, to be dried at 90 °C for at least 2 h. Dried powders were recovered from the centrifuge tubes, hand-ground, and placed in a large tube furnace again to be annealed for 3 h at 750 °C otherwise using the same settings as before. Finally, the powder was hand-ground again and immediately placed in a dryroom atmosphere.

Material Characterization: Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES): The electrode material was dissolved in reversed aqua regia using a Multiwave 7000 (AntonPaar, Graz, Austria) microwave digestions system prior to analysis. The stoichiometry and chemical composition of the samples were determined by ICP-OES using an ARCOS (Spectro Analytical Instruments GmbH, Kleve, Germany) equipped with a Scott spray chamber, a cross-flow nebulizer, and an axial positioned plasma torch. The following emission lines were observed during analysis: Al (396.152), Co (238.892), Li (670.780), Mn (257.611, 259.373), Ni (221.648, 231.604), and S (180.731 nm). The method and further parameters were adapted from Vortmann–Westhoven et al.^[77] and Evertz et al.^[78]

PXRD Refinement: PXRD data was collected in a 2θ range of 4–55° with a step size of 0.015° s^{−1} using a STOE StadiP diffractometer in Debye–Scherrer geometry with a Dectris MYTHEN2 1 K detector and Mo-K_α radiation (λ = 0.7093 Å) in PSD continuous scan mode with a measuring time of 60 s per step at fixed omega. All samples were measured in sealed borosilicate glass capillaries (Hilgenberg, outer diameter of 0.5 mm), prepared at ambient conditions. The PXRD data was refined based on a hexagonal α-NaFeO₂ structure (space group R3m) implemented in Topas Academic V4 (Bruker AXS GmbH).^[79] Instrument contributions were accounted for by refining a LaB₆ NIST standard pattern and subsequently modeling broadening effects with the TOPAS macro “User_Defined_Dependence_Convolution.” For the sample refinements, Li, TMs (Ni, Co, and Mn), and O were assumed to occupy 3a, 3b, and 6c positions, respectively. To account for Li/Ni mixing, Ni was allowed to move from the 3b to the 3a site with the constraint that the ideal stoichiometry of Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ was maintained. Microstructure was refined using the TOPAS macros “LVOL_FWHM_CS_G_L” and “eO_from_Strain.” The crystallite size was determined based on integral breadth. The Lorentzian contribution to crystallite size was disregarded when the parameter CS_L exceeded its maximum value of 1000. Isotropic atomic displacement factors were refined without constraints.

SEM, Cross-Section Preparation, and EBSD Analysis: The morphology of the particles was investigated in powder form by SEM using a Carl Zeiss AURIGA field emission microscope with a Schottky field emitter as electron source and an InLens detector (Carl Zeiss Microscopy GmbH) at an acceleration voltage of 3 kV. Cross sections were prepared by cutting electrodes with a razorblade and then using a JEOL IB-1952° CCP Cryo Cross Section Polisher to polish the cutting surface at 5 kV for 2.5 h and then 2 kV for 0.5 h at a width of 1 mm. Cross sections were subsequently used for EBSD analysis using a FEI (ThermoFisher) NovaNanoSEM 230 (FEG-SEM) equipped with an EDAX (AMETEK) TSL OIM EBSD system. Data were collected at an angle of 20° to the sample surface with a working distance of 16 mm and an acceleration voltage of 18 kV.

Particle Size Analysis (PSA): PSA was performed by laser diffraction (CILAS 1064, 3 P Instruments) of a water-based dispersion which had been sonicated for 5 min. Errors are the standard deviation of three measurements of the same dispersion.

Physisorption: The specific surface area of the samples was determined by the Brunauer-Emmett-Teller (BET) method^[80] according to IUPAC guidelines^[81] using krypton physisorption data obtained on the 3Flex adsorption analyzer (Micromeritics) at liquid nitrogen temperature equipped with a 0.1 mTorr pressure sensor. The relative errors of the measurements $\Delta a_{\text{BET}}[\%]$ were calculated according to

$$\Delta a_{\text{BET}}[\%] = 1.5517 \times (m \times a_{\text{BET}})^{-0.997} \quad (1)$$

where m and a_{BET} are the measured mass and BET surface area of the sample. This equation was derived from fitting standard error data for single-point surface area measurements with krypton provided by Micromeritics.^[82] Thus, the real error is likely even smaller.

X-ray Photoelectron Spectroscopy (XPS): The surface chemistry of the samples was analyzed by XPS. The XPS was measured using the PHI5000 VersaProbe III at the National Taiwan University Science and Technology (NTUST), Taipei, Taiwan. All energies of the spectra were calibrated with a gold foil before measurement, and the Electron Neutralization Gun had been applied to avoid the charge accumulation during measuring. The spectra data were collected at 20 ms per step with step interval 0.05 eV and scanned 3 to 50 times. The pass energy for survey and each element were 224 and 55 KeV, respectively. The orientation angle was 45°. For the XPS fitting, the Co 2p XPS fitting was conducted following the spin-orbit splitting effect with the energy difference of 14.99 eV between Co 2p_{3/2} and Co 2p_{1/2} and a peak area ratio of 2:1 (Co 2p_{3/2}: Co 2p_{1/2}). Ni 2p XPS fitting was conducted following the spin-orbit splitting effect with the energy difference of 17.3 eV between Ni 2p_{3/2} and Ni 2p_{1/2} and a peak area ratio of 2:1 (Ni 2p_{3/2}: Ni 2p_{1/2}). Mn 2p XPS fitting was conducted following the spin-orbit splitting effect with the energy difference of 11.2 eV between Mn 2p_{3/2} and Mn 2p_{1/2} and a peak area ratio of 2:1 (Mn 2p_{3/2}: Mn 2p_{1/2}). S 2p XPS fitting was conducted following the spin-orbit splitting effect with the energy difference of 1.16 eV between S 2p_{3/2} and S 2p_{1/2} and a peak area ratio of 2:1 (S 2p_{3/2}: S 2p_{1/2}). The Li 1s, O 1s, C 1s, Co 2p, Ni 2p, Mn 2p, and S 2p XPS fitting were done with deconvoluting using a 20% Lorentzian-Gaussian shaped line.

Electrode Preparation -Positive Electrodes: All NMC-based electrodes consisted of 94 wt% active material (PC- or SC-NMC811), 3 wt% carbon black as conductive agent (Super C65, Imerys Graphite & Carbon), and 3 wt% poly(vinylidene difluoride) (PVDF) as binder (Solef 5130, Solvay). Electrode pastes were prepared by first dissolving PVDF in anhydrous N-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich), then adding the rest of the solid materials so that the solid content reached 50 wt%, and finally homogenizing in a high-energy disperser (Dissolver Dispermat LC30, VMAGetzmann GmbH) at a speed of 10,000 rpm for 1 h. 20 µm-thick Al foil (Nippon foil) was cleaned with ethanol and coated with 90–230 µm of electrode paste using an adjustable doctor blade (Zehnter GmbH) and an automatic film applicator (Sheen Instruments). The obtained electrode sheets were dried at 80 °C for at least 1.5 h and calendared with a gap size of 5–20 µm (depending on the mass loading) to reach a porosity ϵ of $\approx 38\%$ –47%. The porosity was estimated according to

$$\epsilon = 1 - \frac{V_{\text{c,theo}}}{V_{\text{c}}} = 1 - \frac{\sum m_i \times \rho_{\text{theo},i}}{A_{\text{c}} \times h_{\text{c}}} \quad (2)$$

with V_{c} , m_{c} , A_{c} , and h_{c} being the volume, mass, area, and thickness of the electrode coating, respectively, and $V_{\text{c,theo}}$ being the theoretical volume of the coating at 0% porosity as calculated by the sum of the products of mass and density of its components $\sum m_i \cdot \rho_{\text{theo},i}$. The densities of NMC, carbon black, and binder were taken as 4,78, 1,60, and 1,77 g cm⁻³.

Electrodes ($\varnothing = 14$ mm) were punched out of the sheets and dried under reduced pressure ($< 2.10^{-5}$ mbar, Büchi glass oven B-585) for at least 12 h. Each electrode was weighted with an analytical balance (readability 0.01 mg, Mettler-Toledo) to determine the active mass loading precisely. Positive electrodes used in NMC||Li metal cells had active mass loadings ranging from 5.7(8) mg cm⁻² to 7.4(1.3) mg cm⁻² corresponding to areal capacities ranging from 1.0(1) mAh cm⁻² to 1.5(3) mAh cm⁻². Positive electrodes used in NMC||graphite cells had active mass loadings ranging from 12.3(5) mg cm⁻² to 13.0(0) mg cm⁻² corresponding to areal

capacities ranging from 2.25(9) to 2.46(9) mAh cm⁻². Areal capacities are based on practical specific discharge capacities obtained in NMC||Li cells in the second cycle at 0.1 C (≈ 19 mA g⁻¹).

Electrode Preparation - Negative Electrodes: All graphite-based electrode sheets were prepared at an in-house pilot scale production facility to ensure good reproducibility. The electrodes consisted of 95 wt% of commercial synthetic graphite (SMG-A5, Hitachi, Japan) as active material, 1.5 wt% styrene-butadiene rubber (SBR, SB5521, LIPATON; Polymer Latex GmbH), and 3.0 wt% sodium carboxymethyl cellulose (Na-CMC, Walocel CRT 2000 PPA12, Dow Wolff Cellulosics) as binders as well as 0.5 wt% carbon black as conductive agent (Super C65, Imerys Graphite & Carbon) and were processed with DI water. The electrode paste was cast onto 10 µm-thick Cu foil (Nippon foil), dried, and calendared to reach a porosity of $\approx 30\%$. Electrodes (≈ 15 mm) were punched out of the sheets and dried under reduced pressure ($< 2.10^{-5}$ mbar, Büchi glass oven B-585) for at least 12 h. Each electrode was weighted with an analytical balance (readability 0.01 mg, Mettler-Toledo) to determine the active mass loading precisely. Graphite-based negative electrodes used in NMC||graphite cells had mass loadings ranging from 7.4(3) to 7.7(2) mg cm⁻² corresponding to areal capacities ranging from 2.60(5) to 2.70(5) mAh cm⁻². Areal capacities are based on a practical specific discharge capacity of 350 mAh g⁻¹ obtained in graphite||Li cells.

All Li metal electrodes ($\varnothing = 15$ mm) were punched out of fresh Li metal foil (Albermale Germany GmbH) which had been stored in an argon-filled glovebox before use.

Cell Assembly and Electrochemical Investigations: Electrochemical investigations were carried out in two-electrode coin cells (CR2032, Hohsen Corp.). All cells were assembled in a dryroom atmosphere (dew point < -50 °C) and sealed with coin cell crimper (Hohsen Corp.). One layer of polymer membrane ($\varnothing = 15$ mm, Celgard 2500, Celgard) was used as the separator and soaked with 35 µL of 1M LiPF₆ in a 3:7 volume by volume mixture of ethylene carbonate and ethyl methyl carbonate. The extractable specific capacity of CAMs at different C-rates (0.1–3.0 C) and UCVs (4.3–5.0 V) was probed in NMC||Li cells in constant current mode with a lower cutoff voltage of 2.8 V and a specific current of 1 C defined as 190 mA g⁻¹. To avoid inhomogeneous Li deposition, the C-rate for charging was capped at 0.2 C. The long-term cycling stability of CAMs was investigated in NMC||graphite cells. To avoid lithium plating, the anode was overbalanced by $\approx 15\%$ (N/P ≈ 1.15 based on areal capacity). The voltage limits were shifted 0.1 V downward to keep the cathode potential roughly at the respective cell voltage vs. Li metal. The cycling protocol loosely followed to recommendations made by Long, Rinaldo et al.^[83] After a short tap charge at 1.5 V, cells rested for 12 h and went through four formation cycles at 0.1 C|0.1 C before cycling at 1.0 C|1.0 C until 80% SoH was reached. Hundred percent SoH was defined by the specific discharge capacity in the first cycle at 1.0 C. Every 100th cycle, there were two diagnostic/recovery cycles at 0.1 C|0.1 C. At the end of every charge step, a constant voltage step was done until either the current dropped below 0.05 C or a time limit of 30 min was reached. For the long-term cycling tests at a fixed UCV, all materials were cycled between 4.2 and 2.8 V. For the long-term cycling tests at fixed SoC, materials were cycled to variable UCVs so that specific capacities of 190 and 175 mAh g⁻¹ were reached at 0.1 and 1.0 C, respectively. For this purpose, the required UCV was estimated from the NMC||Li cell results for the first two cycles at a respective current and then the specific charge capacity was limited to the required value for two cycles. The UCV achieved in the last cycle was then used for subsequent cycles throughout cycling. At least three identical cells were assembled for each data point. Error bars in the respective graphs represent the standard deviation of this set of identical cells.

Postmortem Investigations: After cycling to 80% SoH, coin cells were disassembled in an argon-filled glovebox. Anodes and cathodes were recovered, rinsed with 1 mL of dry DMC (per side), and dried at room temperature. The TM content on the anodes was determined by ICP-OES. The TM contents were normalized to the anode mass which was calculated by subtracting the mass of the copper current collector (also determined by ICP-OES) from the mass of the electrode.

Cross sections were prepared from cycled and pristine cathodes by cutting them with a razorblade and then using a JEOL IB-1952°CCP Cryo Cross

Section Polisher to polish the cutting surface at 5 kV for 2.5 h and then 2 kV for 0.5 h at a width of 1 mm. The cross sections were subsequently investigated by SEM using a *Carl Zeiss AURIGA* field emission microscope with a Schottky field emitter as electron source and an *InLens* detector (*Carl Zeiss Microscopy GmbH*) at an acceleration voltage of 3 kV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Marco Joes Lüther: Conceptualization; Methodology; Formal Analysis; and Investigation; Writing—Original Draft; Writing—Review and Editing and Visualization. **Shi-Kai Jiang:** Formal analysis; Investigation; and Visualization (XPS). **Martin Alexander Lange:** Investigation (XRD). **Julius Buchmann:** Formal analysis and Investigation (ICP-OES). **Aurora Gómez Martín:** Writing—Review and Editing; and Supervision. **Richard Schmich:** Writing—Review and Editing; and Supervision. **Tobias Placke:** Writing—Review and Editing; Supervision. **Bing Joe Hwang:** Resources; Supervision. **Martin Winter:** Writing—Review & Editing and Resources; Supervision; Project administration; Funding acquisition. **Johannes Kasnatscheew:** Writing—Review & Editing; Visualization; Supervision; and Project administration.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

layered oxide cathodes, lithium-ion batteries, molten salt, NCM, nickel-rich, NMC, particle morphology, single-crystal, synthesis

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