Exploring the Nanoscale Origin of Performance Enhancement in Li$_{1.1}$Ni$_{0.35}$Mn$_{0.55}$O$_2$ Batteries Due to Chemical Doping

Thomas Thersleff,* Jordi Jacas Biendicho, Kunkanadu Rajappa Prakasha, Elias Martinez Moreno, Leif Olav Jøsang, Jekabs Grins, Aleksander Jaworski, and Gunnar Svensson

Despite significant potential as energy storage materials for electric vehicles due to their combination of high energy density per unit cost and reduced environmental and ethical concerns, Co-free lithium ion batteries based on layered Mn oxides presently lack the longevity and stability of their Co-containing counterparts. Here, a reduction in this performance gap is demonstrated via chemical doping, with Li$_{1.1}$Ni$_{0.35}$Mn$_{0.54}$Al$_{0.01}$O$_2$ achieving an initial discharge capacity of 159 mAhg$^{-1}$ at C/3 rate and a corresponding capacity retention of 94.3% after 150 cycles. The nanoscale origins of this improvement are subsequently explored through a combination of advanced diffraction, spectroscopy, and electron microscopy techniques, finding that optimized doping profiles lead to an improved structural and chemical compatibility between the two constituent sub-phases that characterize the layered Mn oxide system, resulting in the formation of unobstructed lithium ion pathways between them. A structural stabilization effect of the host compound is also directly observed near the surface using aberration corrected scanning transmission electron microscopy and integrated differential phase contrast imaging.

1. Introduction

The increased demand on energy storage has initiated a dramatic increase in research on high performance battery materials.$^{[1,2]}$ While cathode materials with a layered structure containing Co such as LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (NMC111) can currently provide high capacities, their use for next-generation Li-ion batteries is limited by the high toxicity, cost, and ethical issues associated with cobalt mining.$^{[3,4]}$ Due to the strategic importance of Co reduction or elimination, a wide range of alternative compounds and lithium chemistries are currently being researched;$^{[5]}$ however, most of these exhibit significant drawbacks compared to NMC111. For example, olivine (LiFePO$_4$)$^{[6]}$ and spinel (LiNi$_{0.5}$Mn$_{1.5}$O$_4$)$^{[7]}$ based materials have interesting properties such as being Co-free, low cost and presenting high C-rate performance for rapid battery charging, but their capacity is limited to <200 mAhg$^{-1}$. Ni-rich layered oxides with low cobalt content, for example, LiNi$_{0.8}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC811) and LiNi$_{0.8}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NCM811) deliver high energy densities but suffer from slow kinetics and poor cycling stability requiring complex engineering at the particle level to enhance performance.$^{[8,9]}$ Additionally, these materials are prone to reactivity and instability upon exposure to ambient conditions$^{[10]}$ and their price has increased lately.

In addition to the aforementioned compounds, it is also possible to fabricate Co-free cathode materials based on the layered Li-Mn-rich oxides. These form complex nanocomposite structures due to their nanoscale integration of two structural components: a monoclinic $C2/m$ Li$_2$MnO$_3$-like phase (M-phase) and a rhombohedral $R3m$ Li$_5$Mn$_3$Ni$_2$O$_8$-like phase (R-phase).$^{[11,12]}$ The presence of both structures as a nanocomposite material is desirable, as they differ in their cation ordering and are active at different potentials up to 4.6 V versus Li$^+$/Li, thereby maximizing energy density. However, without the inclusion of Co, these nanocomposites show limited capacity retention, poor efficiencies, severe voltage fade, and a failure to deliver capacity at high C-rates.$^{[11,14]}$ Several approaches have been discussed in the literature to improve the performance of this system, and some of the most promising results have been obtained by chemical doping.$^{[11,15,16]}$ For instance, Al-doped samples showed superior cycling performance and lower voltage decay than parent compositions.$^{[17-19]}$ which was attributed to a robust R-phase stabilizing the overall structure while blocking the random growth of spinel-like phases.$^{[17]}$ The effect...
of an Al\textsuperscript{3+} stabilizing agent during electrochemical cycling was also investigated within the framework of density-functional theory with positive effects for both layered structures LiMO\textsubscript{2} and Li\textsubscript{1/2}MO\textsubscript{1/2}O\textsubscript{2}.\textsuperscript{[20]} Also, Sn\textsuperscript{4+} has been reported as an interesting dopant to enhance performance, improving cycle life and ionic conductivity for the samples due to its higher electronegativity and larger ionic radius with respect to Mn\textsuperscript{4+}.\textsuperscript{[21,22]}

In addition to chemical doping, the phase-specific particle morphology in this system can be influenced via a structural engineering approach exploiting synthesis conditions.\textsuperscript{[8,13,23]} For example, we recently demonstrated that it is possible to achieve a core–shell morphology in Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}O\textsubscript{2} with the Ni-rich R-phase preferentially segregated to particle surfaces by combining spray-pyrolysis with a post-deposition calcination at 900 °C.\textsuperscript{[24]} This microstructure correlated to an enhanced electrode performance, with the optimal parameters delivering 160 and 100 mAhg\textsuperscript{−1} at C/20 and 1C, respectively, with 80% capacity retention after 150 cycles.

In this work, we expand our structural engineering approach to include the influence of dopants Al and Sn on the structure and local chemistry of the parent Li\textsubscript{11}Mn\textsubscript{0.55}Ni\textsubscript{0.35}O\textsubscript{2}. Macroscopic structural and chemical properties are elucidated using neutron powder diffraction (NPD), X-ray powder diffraction (XRPD), and nuclear magnetic resonance (NMR), while cathode performance is assessed with electrochemical tests subjected to galvanostatic cycling. We subsequently localize these properties to nanoscale features with aberration-corrected scanning transmission microscopy (STEM) combined with energy dispersive x-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS), and integrated differential phase contrast imaging (iDPC). Crucially, this multi-scale combination of techniques allows us to directly observe both the structural and chemical influence each dopant has on its parent Li\textsubscript{11}Mn\textsubscript{0.55}Ni\textsubscript{0.35}O\textsubscript{2} material, providing deep insight into the nanoscale origins of the improved performance for this system.

### 2. Results

#### 2.1. Cathode Fabrication and Doping Series

The effect of doping was assessed through spray pyrolysis fabrication of two sample series having nominal compositions Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}xM\textsubscript{0.05}O\textsubscript{2} where M = Sn or Al and x = 0, 0.01, 0.03, 0.05 and 0.10. Details of the fabrication process are provided in the Experimental Section. The non-doped parent compound Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}O\textsubscript{2} was additionally studied as a control. A more detailed study of the parent compound is provided by Prakash et al.\textsuperscript{[24]} In this manuscript, the individual samples are named according to Table 1.

#### 2.2. Electrochemistry Results

The overall performance for all doping concentrations was assessed using electrochemical tests. The electrodes were tested using galvanostatic cycling in the potential window of 4.8 to 2 V versus Li\textsuperscript{+}/Li. The initial three charge–discharges were performed at a low rate of C/20 to stabilize the cathode-electrolyte interface (CEI). Subsequently, the cells were cycled at C/3. The first charge–discharge profiles of the parent and Al-doped samples are presented in Figure 1a. The profiles display the characteristic sloping and plateau regions of lithium-rich layered oxides. The slope region observed for all cathodes up to ~4.4 V is associated to the oxidation of Ni\textsuperscript{2+} to Ni\textsuperscript{3+} and Ni\textsuperscript{4+}, followed by a plateau region assigned to the irreversible oxygen loss from the monoclinic phase.\textsuperscript{[25]}

Figure 1b compares the cycling performance of parent and Al-doped cathodes cycled at C/3 rate. Noticeable differences between the cathodes are found in terms of discharge capacity as a function of cycle number and capacity retention. The parent LNMO compound delivers 156 mAhg\textsuperscript{−1} (cycle 4) and retains a capacity of 121 mAhg\textsuperscript{−1} after 150 cycles corresponding to a capacity retention of 77.6%. LNMA01 delivers a discharge capacity of 159 mAhg\textsuperscript{−1} which decreases to 150 mAhg\textsuperscript{−1} after 150 cycles leading to a superior capacity retention of 94.3%. LNMA03 delivers 150 mAhg\textsuperscript{−1} with capacity retention of 83.9%, LNMA05 delivers 136 mAhg\textsuperscript{−1} with capacity retention of 80.9%, and LNMA10 delivers 102 mAhg\textsuperscript{−1} with capacity retention of 47.4%. Capacity results for the Al-doped samples are also presented in Figure 1d in the form of charge–discharge voltage profiles for selected cycles. The LNMO cathode exhibits a gradual decline in the capacity as well as voltage fading as cycling progresses. This is not the case for the LNMA01 cathode, which exhibits a stable charge–discharge capacity and lower voltage decay as cycling progresses. LNMA03 and LNMA05 cathodes show slightly better capacity retention and voltage decay than LNMO but lower than LNMA01. The extent of the voltage decay of Al-doped cathodes upon cycling was represented by plotting the average discharge voltage versus cycle number (Figure S2, Supporting Information). The average discharge voltage of the LNMA01 electrode is exceptionally stable (98.1% retention) even after 150 cycles at C/3 current rate, whereas other cathodes exhibit gradual voltage decay as cycling progresses. Finally, the LNMA10 cathode shows an abrupt decline in the discharge capacity as well as voltage fading.

| Sample label | M x | Nominal chemical formula | TEM investigation | Notes |
|--------------|-----|--------------------------|------------------|-------|
| LNMO         | –   | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}O\textsubscript{2} | Yes | Parent compound |
| LNMS01       | Sn 0.01 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Sn\textsubscript{0.01}O\textsubscript{2} | No | |
| LNMS03       | Sn 0.03 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Sn\textsubscript{0.03}O\textsubscript{2} | No | |
| LNMS05       | Sn 0.05 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Sn\textsubscript{0.05}O\textsubscript{2} | No | |
| LNMS10       | Sn 0.10 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.45}Sn\textsubscript{0.10}O\textsubscript{2} | No | |
| LNMA01       | Al 0.01 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Al\textsubscript{0.01}O\textsubscript{2} | Yes | Best electrochemical performance |
| LNMA03       | Al 0.03 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Al\textsubscript{0.03}O\textsubscript{2} | No | |
| LNMA05       | Al 0.05 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.55}Al\textsubscript{0.05}O\textsubscript{2} | No | |
| LNMA10       | Al 0.10 | Li\textsubscript{11}Ni\textsubscript{0.35}Mn\textsubscript{0.45}Al\textsubscript{0.10}O\textsubscript{2} | No | |
In Figure 1c, the cycling performance of Sn-doped cathodes cycled at C/20 for the initial 3 cycles followed by C/3 rate is presented. The Sn-doped cathodes deliver poor discharge capacity compared to both LNMO and the Al-doped cathodes. Discharge capacities of the Sn-doped cathodes are 188, 147, 110, and 89 mAhg⁻¹ for 0.01, 0.03, 0.05, and 0.1 doping levels, respectively, and with a significant capacity decay for all samples. After 100 cycles the capacity of all the Sn-doped cathodes falls down to around 50 mAhg⁻¹.

2.3. Lithium Ion Diffusivity

Insight into the origin of the voltage hysteresis during cycling was obtained by measuring lithium ion diffusion coefficients using galvanostatic intermittent titrations (GITT). Only the Al-doped series was studied due to the poor performance of the Sn-doped cathodes. Discharge capacities of the Sn-doped cathodes are 188, 147, 110, and 89 mAhg⁻¹ for 0.01, 0.03, 0.05, and 0.1 doping levels, respectively, and with a significant capacity decay for all samples. After 100 cycles the capacity of all the Sn-doped cathodes falls down to around 50 mAhg⁻¹.

Lithium-ion diffusion coefficients $D_{Li^+}$ were calculated from the GITT measurements as outlined in the supplementary information, and the results are presented in Figure 2c. LNMA01 exhibits a noticeably higher diffusion coefficient $D_{Li^+}$ than LNMO, LNMA03, or LNMA05 cathodes between $10^{-9}$ and $10^{-14}$ cm² s⁻¹, thereby indicating a higher ionic conductivity.

2.4. Powder Diffraction

Structural variations to the cathode materials as a function of doping concentration were investigated with x-ray diffraction (XRD) and NPD. XRD results reveal that all powders were found to consist of two-phase mixtures: a monoclinic C2/m
Li$_2$MnO$_3$-type structure (M-phase) and a rhombohedral R-$3m$ LiMn$_{1/2}$Ni$_{1/2}$O$_3$-type structure (R-phase) (see supplementary information). Al-doped samples with $x \geq 0.03$ additionally contain about 1.3 wt% Li$_2$CO$_3$. XRPD peak widths of about 0.20° at 20° and 0.5–1.5° at 130° imply both size and strain sample broadening. The metrics of M and R structures are similar and many peaks of the two phases overlap, but for most compositions, the presence of both can easily be seen, especially at higher 2θ values and in particular for Sn-doped samples with high Sn contents. The characteristic reflections from M at 20°–25° are affected by the presence of stacking faults.

The NPD data were used for final structure refinements. About 25 parameters were refined. The M-phase has 9 refinable atomic positions while the R-phase only has 1. Collective thermal parameters were used in order to obtain accurate estimates of other parameters. The structure reliability indices vary between 4% and 6% for the M-phase and 2–3% for the R-phase. The derived weight percentage of the M-phase varies for the Sn samples between 46% and 53% and for the Al samples between 44% and 70%, with no clear dependence on x. For the Al samples, the overlap of peaks from M and R increases as x increases. For x = 0.1 the overlap is so severe that while M and R can both be refined and quantified by the NPD data, this is not possible to do from only the XRPD data.

For the M-phase, Ni was allowed to enter the structure, both for Sn and Al, by the substitution mechanism $3Ni^{2+} -> 2Li^{+} + Mn^{4+}$, where Mn is assumed to occupy only the 4g site. One free parameter thus determines the amount of Ni in the structure. In addition, one parameter allowed for a transference of Li and Ni between the 2b and 4g sites in the transition metal layer. The negative neutron scattering lengths for Li and Mn provide a good determination of the cation distribution and the derived average scattering lengths on the 4g and 2b sites agree well with unconstrained refined scattering lengths on these sites, both for Sn and Al, albeit significantly better for Sn.

The refinements for the Sn-doped samples, as well as derived metal-oxygen distances and the unit cell volume variation (see below), strongly indicate that Sn enters predominantly R and no Sn was assumed in M in the refinements. For the Al-doped samples, it is not possible to conclude from the NPD data with certainty into which phase Al is incorporated. In the initial refinements, Al was assumed to incorporate itself solely into R, as M appears to have a constant composition. However, as the TEM study (Figure 3) showed that Al is distributed over both phases, the final structural model was altered accordingly, with equal amounts of Al put in both phases. This resulted in slightly improved fits between observed and calculated patterns. Details on structures, refinements, and derived cat-ion distributions are given in the SI.

The compositions of the R phases cannot be determined from the NPD data alone, although some indications are obtained by refining average neutron scattering lengths on the 3a and 3b metal sites. They are estimated by assuming the nominal overall compositions and subtracting the derived M compositions using the refined phase fractions. The derived average cross sections on the 3a and 3b sites agree well with unconstrained refined scattering lengths on the sites for the Sn samples, but not for the Al samples, for which the observed scattering lengths are in general larger than the calculated lengths. One possible reason for this is that the presence of Li$_2$CO$_3$ has not been considered. This suggests that these R phases probably contain less Li than assumed, and have consequently higher average cross sections for the metal sites. Derived compositions for the M and R phases are given in

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**Figure 2.** a) Charge and GITT discharge curves during 31st cycle in the voltage range of 4.8–2 V. b) Single GITT titration at 3.8 V with schematic labeling of different parameters along with inset figure of voltage against $\tau^{1/2}$ to show the linear relationship. c) $D_L$ is calculated from the GITT data during discharge processes.
Tables 1 and 2, respectively. Errors from the refinements for the compositions are considerably less than 1 at%.

The unit cell volumes ($V_n$) of M and R, normalized to the formula unit $M\text{O}_2$, from NPD data are shown in Figure 3a as a function of $x$ in $\text{Li}_{1.1}\text{Ni}_{0.35}\text{Mn}_{0.55-x}\text{M}_x\text{O}_2$.

For the Sn samples, $V_n$ diverges for M and R as $x$ increases. The nearly constant $V_n$ for M indicates that the composition of M is also nearly constant, while the increasing $V_n$ for R indicates a changing composition, that is, that Sn enters R. A substitution of Mn$^{4+}$, ionic radius 0.54 Å, by Sn$^{4+}$, ionic radius 0.69 Å, is expected to increase $V_n$. In contrast, for the Al samples, the evolution of $V_n$ indicates a comparatively smaller difference in compositions of M and R. For M, $V_n$ is here also nearly constant for $x \geq 0.01$, but is larger than for the corresponding Sn samples. The structure refinements show that this is due to larger contents of Ni$^{2+}$ (ionic radius 0.70 Å). $V_n$ for M and R for the Al-doped samples converge as $x$ increases and are very similar for $x \geq 0.03$. An incorporation of Al$^{3+}$, ionic radius 0.53 Å, is expected to decrease $V_n$.

In Figure 3b, the distortion of the M and R phases in the O atom close packing direction is plotted versus the normalized unit volume. It is calculated from the ratio of the observed periodicity in this direction and a calculated periodicity for an ideal structure where all metal-O octahedra are equal and regular, as described in the SI. All structures show an elongation along the close packing direction. The distortion diverges with $x$ for the Sn-doped samples and converges with $x$ for the Al-doped samples. For the Al-doped samples, the distortion of M and R becomes essentially the same for $x = 0.10$, leading to a near to total overlap of Bragg reflections.

### 2.5. NMR Results

In Figure 4, $^7$Li MAS NMR spectra collected from the four studied samples are presented. The spectrum of the parent composition reveals an isotropic shift of 720 ppm, which

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**Table 2. Derived compositions of M phases from NPD data.**

| Sample | Composition | % Li | % Mn | % Ni | % M |
|--------|-------------|------|------|------|-----|
| LNMO   | $\text{Li}_{1.29}\text{Ni}_{0.30}\text{Mn}_{0.63}\text{O}_2$ | 63   | 32   | 5    | 1   |
| LNMS01 | $\text{Li}_{1.25}\text{Ni}_{0.30}\text{Mn}_{0.65}\text{O}_2$ | 64   | 32   | 4    | 1   |
| LNMS03 | $\text{Li}_{1.30}\text{Ni}_{0.24}\text{Mn}_{0.65}\text{O}_2$ | 65   | 33   | 2    | -   |
| LNMS05 | $\text{Li}_{1.35}\text{Ni}_{0.26}\text{Mn}_{0.65}\text{O}_2$ | 65   | 33   | 2    | -   |
| LNMA10 | $\text{Li}_{1.31}\text{Ni}_{0.15}\text{Mn}_{0.57}\text{Al}_{0.05}\text{O}_2$ | 66   | 33   | 2    | -   |
| LNMA01 | $\text{Li}_{0.29}\text{Ni}_{0.15}\text{Mn}_{0.57}\text{Al}_{0.05}\text{O}_2$ | 59   | 29   | 11   | 1   |
| LNMA03 | $\text{Li}_{0.29}\text{Ni}_{0.15}\text{Mn}_{0.57}\text{Al}_{0.05}\text{O}_2$ | 59   | 28   | 11   | 1   |
| LNMA05 | $\text{Li}_{0.29}\text{Ni}_{0.15}\text{Mn}_{0.57}\text{Al}_{0.05}\text{O}_2$ | 60   | 28   | 10   | 2   |
| LNMA10 | $\text{Li}_{0.29}\text{Ni}_{0.15}\text{Mn}_{0.57}\text{Al}_{0.05}\text{O}_2$ | 60   | 25   | 10   | 5   |
changes only marginally (within ±10 ppm) among the compositions studied herein, as well as in comparison to similar compositions in our previous work. The shape of the shift anisotropy pattern does not change as well across the samples. Hence, it can be assumed that oxidation states of the involved paramagnetic metal ions, on average, are the same in all samples. Otherwise, changes to isotropic and anisotropic shifts due to the Fermi contact shift and anisotropic paramagnetic NMR shift mechanisms would be expected to be observed in the spectra. On the other hand, the spectrum of LNMA10 exhibits severe broadening, which is only partially revealed for LNMA01, and not observed at all for LNMS10. This observed broadening can be explained from bulk magnetic susceptibility (BMS) effects that would occur if the M-phase and R-phase are present in the form of nanosized domains that mix on the sub-10 nm length scale in LNMA01 and, to a much larger extent, LNMA10. BMS induces a demagnetizing field that modifies NMR shift. In MAS NMR of paramagnetic systems, randomly distributed demagnetizing fields in a powder sample introduce broadening of resonances due to the distribution of paramagnetic shifts, even if the structure is perfectly crystalline. These are called anisotropic bulk magnetic susceptibility (ABMS) effects.

The significant spin-orbit coupling, and therefore substantial anisotropy of the magnetic susceptibility of the Ni\(^{2+}\) ion combined with the strongly anisotropic shape of nanodomains in the Al-doped (x = 0.10) samples are expected to result in a particularly pronounced ABMS effects.

2.6. STEM and Spectroscopy

While the results of XRD and NPD strongly suggest that both the Sn-doped and Al-doped materials consist of a two-phase system, advanced TEM techniques are used to visualize their spatial distribution. These studies were carried out on four selected samples: LNMO, LNMS10, LNMA01, and LNMA10 and are divided into two subsections. First, wide field-of-view (FOV) spectroscopy was performed to elucidate compositional variations on the length scales from hundreds of nanometers to a few nanometers. Second, high resolution STEM micrographs were acquired from selected samples to better understand the structural variations on the sub-nanometer length scale that pertain in particular to the distribution of nanosized domains of M-phase and R-phase and their associated Li\(^{+}\) diffusion channels.

2.6.1. Wide FOV Spectroscopy

Figure 5 summarizes the wide FOV STEM spectroscopy experiments. For each specimen, a high-angle annular dark field (HAADF) overview image provides a survey of the region of interest (ROI) using Z-contrast, with co-registered EDX compositional density maps presented in false colors (grey—oxygen, blue—manganese, red—nickel, green—dopant Sn/Al if present).

The results from LNMO are presented in Figure 5a. Despite the lack of a dopant, the parent compound displays a clear compositional inhomogeneity, with Ni-rich regions frequently appearing close to particle edges and facets. This finding is discussed in more detail in Prakash et al.[24] Figure 5b summarizes variations to the relative nickel concentration (defined as Ni/(Ni + Mn)) from these maps in the form of a histogram. We observe that, while the histogram is roughly centered on the nominal value of 0.39, it exhibits trimodal behavior and a large spread. Much of this variation can be accounted for with additional normally-distributed phases having compositions close to the M- and R-phases, respectively. The appropriate distributions are overlaid in Figure 5b in color and demonstrate that the observed compositional maps can thus be reasonably well described as a linear combination of these two phases. While the Ni-rich phase commonly appears close to particle surfaces, at least one single-phase particle is observed in this FOV, suggesting that these compositional domains mix on length scales of tens to hundreds of nanometers.

Figure 5c,d presents the results from LNMS10. In this sample, a very strong chemical segregation is immediately obvious, with the presence of Sn being strongly correlated to Ni and anticorrelated to Mn, heavily implying that the Ni-rich phases accumulate most or all of the dopant. These variations also manifest themselves on the length scale of tens to hundreds of nanometers and are clearly resolved over the wide FOV presented here. The correlation between the relative nickel content and the dopant concentration can be further studied through the use of the bivariate histogram presented in Figure 5d, which reveals a strong positive correlation between the relative nickel content and Sn. Critically, the nominal composition sits directly along the distribution of compositions in the middle, suggesting that it derives from measuring a sufficiently large and mixed assortment of nanoparticles.

In contrast to the Sn-doped sample, the composition distribution for the Al-doped samples is considerably more nuanced. Elemental maps for LNMA01 are presented in Figure 5e,f. The relative nickel concentration in this sample appears to vary, but not as strongly as in the parent compound, and considerably less so than in the Sn-doped sample. The bivariate histogram analysis presented in Figure 5f shows a weak bimodal behavior, with compositional clusters showing a phase with low relative Ni-content and one with high relative Ni content with slightly higher Al for the former. The nominal composition falls roughly between these two clusters suggesting that a low resolution average measurement of the composition would struggle to establish the presence of two distinct phases. This distribution is more similar to the parent compound in those strong variations in the relative Ni content are visible on the 10–100 nm scale.

For LNMA10, the chemical maps presented in Figure 5g show no evidence for a variation of the relative Ni content over a wide FOV, and the Al distribution appears to be similarly homogenized. The bivariate histogram presented in Figure 5h reveals that the bimodal distribution observed in LNMA01 has largely been replaced by an elongated ellipsoid whose center matches the nominal composition. These EDX maps do not show clear evidence for different compositions in the monoclinic and rhombohedral phases at the sampling resolution of these measurements.

These results indicate that the LMNO, LNMS10 and, to some extent, LNMA01 materials manifest themselves as two-phase
Figure 5. STEM spectroscopy experiments on agglomerates from LNMO a,b) LNMS10 c,d) LNMA01 e,f) and LNMA10 g,h) For each specimen, a HAADF overview image provides a survey of the ROI using Z-contrast. Their compositional EDX maps are presented as false color density maps, gray—oxygen, blue—manganese, red—nickel, and green—dopant (Sn/Al if present). Color composite images for the doped samples are also presented, providing a sense of the materials’ chemical segregation. For each sample, a histogram showing the relative Ni content for all samples is presented. For doped samples, bivariate histograms are used to relate the relative Ni content to the dopant. The point marked “N” represents the nominal composition for each sample.
systems on the 10–100 nm length scale. The Ni-rich R-phase either forms primarily at particle surfaces or, particularly in the case of Sn-doping, even segregates out as phase-specific particles. In contrast, LNMA10 appears to be more complex; Figure 5 indicates that it must either be a single-phase system, thereby contradicting the XRD, NPD, and NMR results, or that the individual phases intermix on the nanoscale in the form of nanodomains, and that the resolution at this FOV is insufficient to resolve them. Such nanodomain systems have been described in previous works, although it was noted that isolating these individual phases is very challenging in thick particles due to overlap in the beam projection direction.

2.6.2. Thickness Dependent Nickel Content

An alternative way to test for the presence of multiple phases with differing compositions at this wide FOV is to check how the relative Ni content varies as a function of the particle thickness. Each of the datasets in Figure 5 samples a wide range of thicknesses, which are calculated from the simultaneously acquired low-loss EELS datasets. As the thinnest regions correspond to the particle surfaces, if these surfaces are Ni-rich, one would expect to see an increase in the relative nickel content at the lowest thicknesses. Additionally, presenting the data in this manner also indirectly tests the domain size of the M- and R-phases, as each individual EDX spectrum is averaged over the particle thickness at that probe position. If a single particle consists of very small M- and R-phase domains, and if these domains are homogeneously distributed throughout the particles, thicker regions will converge on the average (nominal) composition, while thinner regions will diverge toward the composition of the individual phases as they are less likely to sample a random mixture of the two phases.

Figure 6 presents this analysis for the datasets shown in Figure 5 in the form of bivariate histograms revealing the relationship between the relative Ni content and the relative thickness as mean free paths (t/λ). LNMO (Figure 6a) shows a clear trend toward a Ni-rich phase at the thinnest regions, consistent with the observation that the edges are Ni-rich. LNMS10 (Figure 6b) shows a clear separation between the phases in the thinnest regions, with few data points between the two clusters. Only at medium thicknesses around 0.6 t/λ is significant mixing observed, representing areas where two individual particles with different compositions spatially overlap. This behavior is expected for a two-phase system with relatively large domain sizes. LNMA01 (Figure 6c) also shows a divergence from the nominal composition at lower thicknesses, with a slight preference for a Ni-rich phase at lower thicknesses, although this is more subtle than for LNMO. Finally, LNMA10 (Figure 6d) shows a relatively even divergence at lower thicknesses that would be consistent with the presence of very small nanodomains with no strict preference for accumulation of either phase at the particle surfaces.

2.6.3. High Resolution STEM

While the wide FOV results presented in Figures 5 and 6 probe the chemical and morphological distribution of the M-phase and R-phase on the length scales of 10–1000 nm, higher resolution methods are needed to investigate the 0.1–10 nm length scales. Figure 7 summarizes the findings from LNMA10. In Figure 7a, a high resolution HAADF STEM from a thin region of the sample tilted is presented. The crystal was tilted to the R-phase [2 1 0] zone axis (equivalent to the M-phase [1 0 0]/[0 1 0]/[1 0 1] zone axes) to resolve the stacking of the 2D lithium-rich planes. Within this single image, two crystallographically distinct domains can be unambiguously identified, and these are marked and enlarged in Figure 7b (magenta) and Figure 7c (yellow). Since these are Z-contrast images, the heavier transition metal elements reveal the positions of the atomic columns and allow these individual domains to be indexed as the M-phase (Figure 7b) and R-phase (Figure 7c), respectively. Atomic models are provided next to the enlargements, and the stacking fault configuration characteristic of the M-phase is denoted. Thus, not only are both crystallographic domains in the composite LNMO structure identified, but it is also immediately evident that their individual domain size is approximately a few nanometers.

However, the existence of nanodomains is not the only feature observed in this sample, rather it is also evident that the 2D ordering of the transition metal and lithium-rich layers is inconsistent in multiple regions. This effect is best visualized by viewing parallel to the layers at a low elevation angle, and these conditions are simulated as a 3D relief, which is presented in Figure 7d. The black arrows in Figure 7a,d denote equivalent viewing directions. At present, our favoured...
explanation for this alternating stacking sequence is the presence of antiphase boundaries (APBs) having displacement vectors $\begin{bmatrix} 0 & b & c \end{bmatrix}$ in the M-phase and $\begin{bmatrix} a & b & c \end{bmatrix}$ in the R-phase.

Similar defect structures have been observed in Co-containing Li(Ni$_{1-x-y}$Co$_x$Mn$_y$)O$_2$,[30] pure Li$_2$MnO$_3$,[31] as well as in an all-solid-state spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$.[32] There, it was argued on theoretical grounds that the addition of dopants such as Al should reduce the number of APBs, although concentrations as high as LNMA10 were not investigated. Atomic models for the proposed defect structure in our system are provided in Figure 7e. While these models are restricted to M-phase [1 1 0] and R-phase [2 1 0] domains, it is apparent that the equivalency extends to M-phase [1 1 0] and [1 1 0] orientations as well as M-phase/R-phase boundaries.

This observation suggests that such APBs can form provided that the atomic positions of cations in the 2D transition metal and lithium-rich layers can be nearly exactly matched, which appears to be the case for this dopant concentration. However, the congruency of the cation sublattice does not extend to the oxygen sublattice, which instead exhibits a slight mismatch. This results in local strain, which is also best visualized in Figure 7d. This perspective allows us to easily identify a slight buckling of the TM-rich layers as they extend away from the area of APB overlap, as well as a rotation to the TM layers, which are both likely strain-induced effects. Thus, we observe that the nanoscale microstructure of LNMA10 exhibits a relatively large number of complex phase boundaries and local strain fields that arise from the formation of nanodomains.

Similar high resolution STEM investigations were carried out on LNMA1, and these are summarized in Figure 8. As in Figure 7, a thin crystal was tilted to the same zone axis and the edge of this crystal was studied. Figure 8a,b presents both HAADF and iDPC overviews of this region. iDPC is a technique that maps the center-of-mass (COM) of the transmitted electron probe[33] and as such, is a linear contrast mechanism that can be used to simultaneously image both light and heavy elements in well-oriented crystals, including Li in layered Mn oxide batteries.[34] Similar to LNMA10, both the M-phase and R-phase are readily identifiable in this image. However, in contrast, these phases are not present as nanodomains but, rather, are morphologically confined to the surface (R-phase) and bulk (M-phase). Additionally, a thin spinel phase is observed at the very surface. These conclusions are drawn via inspection of three distinct local Fourier transforms taken from three ROIs denoted in Figure 8b, with the transforms themselves appearing in Figure 8c–e along with the crystal structure and orientation that most closely matches the observed spatial frequencies. Figure 8c indexes most closely to a spinel-like phase (S-phase) in the [1 1 0] orientation, and this is observed closest to the edge of this crystal. Such spinels have been observed many times before at crystal surfaces, and are noted to be very thin and, thus, difficult to resolve using XRD. The cyan
box located a few nanometers away from the surface returns the Fourier transform observed in Figure 8d. This indexes very closely to the R-phase in the [2 1 0] orientation and is estimated to extend from ≈1 nm away from the surface to 6 nm into the bulk. Finally, the Fourier transform from magenta box presented in Figure 8e closely matches the M-phase in the [1 0 0]/[1 1 0]/[1 1 0] orientation, with the characteristic stacking fault streaks. Crucially, unlike LNMA10, this crystal reveals a largely unobstructed Li-ion diffusion pathway from the surface into the bulk with little to no stress or buckling observed.

Close inspection of the R-phase region in Figure 8a reveals additional information about the site-specific cation population in this crystal. Since the contrast mechanism is primarily sensitive to the atomic mass, this image is particularly sensitive to the location of the transition metals. Nearly all of the 3a sites observed in this crystal return similar intensities, thus suggesting that they are uniformly populated with transition metals. However, the observed intensities on the 3b sites vary considerably in a seemingly random manner. The white box in Figure 8a,b picks out a region from the HAADF and iDPC images that illustrates this effect. This selection is rotated and enlarged in Figure 8f. Additionally, line profiles that were vertically integrated over one of the R-phase (0 0 6) planes that capture the 3b sites (denoted by the dotted yellow lines) are presented below each image. This particular plane was chosen to highlight the contrast difference between the two imaging modes.

The line profile from the HAADF image in Figure 8f shows a clear loss of contrast in the dark region of this atomic plane. This would be expected if these particular atomic sites were to be primarily populated with lithium atoms, as their low scattering power renders them largely invisible in HAADF imaging. However, the same region in the iDPC image reveals a clear contrast that can be directly ascribed to the 3b sites, albeit with a much lower intensity than the neighboring sites in this plane. As iDPC is more sensitive to lighter elements, this contrast is therefore best explained by the presence of atomically-localized weak scattering centers in the form of columns of lithium atoms on this site. Consequently, by combining the information from both the HAADF and iDPC images, we argue that these images directly show that the Li-rich 3b site in the R-phase is randomly populated with transition metals and/or Al, which has been hypothesized to stabilize the host system during delithiation.[17,19]

3. Discussion

The electrochemistry results clearly show that the performance of these Co-free LIB cathodes is strongly influenced by chemical doping with Al and Sn. Sn^{4+} doping reduces the discharge capacity in LNMS01 and LNMS10 from 140 to 60 mAh g⁻¹, respectively (Figure 1), in agreement with reported results.[21,22] In contrast, small amounts of Al increase the discharge capacity and cycling stability, even when compared to the undoped parent compound. These effects are difficult to explain by assuming a solid solution of dopant material, requiring a more rigorous structural, chemical, and nanoscale investigation to understand, as outlined in this manuscript.

The XRD results summarized in Tables 2 and 3 as well as in Figure 3 reveal that all of the samples investigated...
here, regardless of dopant type or level, are structurally best described as a two-phase system consisting of both the R-phase and M-phase. Sn doping leads to a strong divergence in unit cell parameters for the two phases (Figure 3), while phase-specific compositions derived from NPD refinement (Tables 2 and 3) support the interpretation that Sn and Ni both preferentially migrate into the R-phase, leading to a Mn-rich M-phase. We interpret this to mean that the introduction of Sn leads to decreasing structural and chemical compatibility between the two phases, forcing them to separate into individual phase-pure nanoparticles with minimal mixing.

In contrast, the introduction of Al to the parent structure causes a convergence of the unit cell parameters for both crystallographic phases (Figure 3), while the Ni to Mn ratio remains closer to the parent compound. The origin of this convergence appears to be that Al is observed to enter both phases, resulting in a preferential migration of Ni from the R-phase to the M-phase. Consequently, the unit cell volumes of both phases converge to similar values, increasing their structural and chemical compatibility. This manifests itself as an increasingly intimate domain mixture on the nanoscale as the amount of Al doping increases.

Upon introduction of Al to the system, charge balance can be maintained via the mechanism $\text{Al}^{3+} + \text{Ni}^{2+} \leftrightarrow \text{Mn}^{4+} + \text{Ni}^{3+}$ (oxidation from $\text{Ni}^{2+}$ to $\text{Ni}^{3+}$) or by expelling lithium oxide from the system, resulting in a nominal composition of $\text{Li}_{1+x} \text{Mn}_{0.55} \text{Ni}_{0.45} \text{Al}_{0.05} \text{O}_{2-x}$. The NPD results presented in the supplementary information along with the NMR results from Figure 4 provide evidence for Li expulsion through the formation of $\text{Li}_2\text{CO}_3$. However, EELS (Figure S12, Supporting Information) and XPS (Figure S13, Supporting Information) results also suggest that nickel oxidation at least partially contributes. Our current interpretation is that the charge compensation mechanism for this substitution is likely a balance of these two and possibly even more mechanisms. A comprehensive mechanism explaining the driving force behind the migration of Ni into the M-phase as a function of Al doping can only be partially elucidated at this stage, and will require a phase-specific chemical and compositional analysis.

This interpretation of a decrease in the domain size of the M- and R-phases is first provided by the NMR study (Figure 4). The lack of significant broadening due to BMS effects in LNMS10 strongly suggests that, even for the highest dopant concentration, both the R- and M-phases are structurally and chemically distinct and have large domain sizes. Contrarily, the severe broadening observed for the LNMA10 sample is best explained by assuming that both phases are intimately mixed and present in the form of nano-sized domains. Crucially, this broadening is also observed for the LNMA01 sample, suggesting that some degree of mixing has taken place already at these low dopant concentrations.

The spatial distribution of these two phases along with their composition is explored through the TEM results at two different length scales: tens to hundreds of nanometers (Figures 5 and 6) and sub-nanometer (Figures 7 and 8). The wide FOV EDX maps and bivariate histograms from Figure 5 reveal that the interparticle phase segregation observed in the parent compound becomes exacerbated to full individual particles when doping with Sn. Combined with the other results, this indicates that Sn doping leads to two distinct phases that fail to intermix on the nanoscale. As phase intermixing is known to be a prerequisite for higher voltage retention, we conclude that this is the proximate cause for the degraded electrochemical performance of these samples observed in Figure 1. Conversely, the introduction of Al causes a much more intimate phase mixture, such that it is no longer even possible to confirm the presence of two chemically-distinct phases in the LNMA10 sample at the resolution presented in Figure 5. However, the thickness-dependent relative nickel content presented in Figure 6 does suggest that some sort of domain mixing is occurring, albeit at length scales that are shorter than the particle thickness, which we refer to as nanodomains.

Direct visualization of these nanodomains as well as their influence on the lithium diffusion pathways requires both a sufficiently thin sample as well as sub-nanometer spatial resolution imaging, which we present in Figure 7 and Figure 8 for LNMA10 and LNMA01, respectively. High resolution HAADF imaging of the LNMA10 sample (Figure 7) provides structural evidence for the presence of not only M-phase and R-phase nanodomains with lateral dimensions on the order of a few nanometers, but also antiphase boundaries. The presence of nanodomains along with antiphase boundaries disrupts the coherency of the oxygen sublattice, resulting in localized strain fields and disordering which we believe conspire with the larger number of interfaces to hinder ionic transport in this system, consistent with the degraded electrochemical properties from Figure 1 as well as the reduced lithium diffusivity from Figure 2. For the LNMA01 sample, these nanodomains appear to be morphologically segregated to the particle surface (R-phase) and particle bulk (M-phase), with an additional thin S-phase observed at the vacuum/particle boundary. In contrast to LNMA10, the M-phase and R-phase boundary is highly coherent with no disruption of either the oxygen sublattice or the lithium ion pathways (save for at the thin S-phase surface). High resolution STEM imaging combined with iDPC (Figure 8) moreover confirms that the 3b-site in the R-phase is randomly populated with a small percentage of transition metal and/or Al atoms. This thus constitutes a direct atomic-scale observation of structural stabilization in this system, consistent with the inferred findings from previous studies in Co-containing compounds\cite{Wang2013, Wang2014} as well as theoretical works on Co-free systems.\cite{Chen2015}
4. Conclusions

In this manuscript, we outline how doping Li_{1+δ}Ni_{0.35}Mn_{0.65}O_2 with small amounts of Al or Sn influences the size, composition, and distribution of the M- and R-phases on the nanoscale. Through combined use of XRD, NPD, aberration-corrected STEM, EDX, EELS, and NMR measurements, we are able to deduce that the composition, lateral dimensions, and spatial distribution of these domains vary considerably depending on the type and amount of dopant used. Doping with Sn results in a strong phase segregation, while doping with Al homogenizes the system both compositionally and structurally. A small amount of Al leads to a structural improvement in the lithium diffusion pathways, while too much Al results in overmixing characterized by the formation of nanodomains and the subsequent disruption of these pathways. We therefore conclude that this study provides researchers with unique insight into how chemical doping can be parameterized to control the spatial distribution and local chemistry of the M-phase and R-phase in this system, yielding a tool with which the electrochemical performance can be optimized in this and other layered manganese oxide systems.

5. Experimental Section

Sample Series Fabrication: All samples were fabricated using the spray pyrolysis process. An aqueous solution was prepared by dissolving stoichiometric amounts of metal nitrates in distilled water mixing individual precursor solutions under stirring. The homogeneous solution was atomized by a two-phase nozzle (pressurized air + solution) into a pre-heated rotating (≈2 rpm) furnace (Entech Energiteknik AB) under constant air flow, yielding an approximate average residence time of about 2 s at 900 °C. This caused instant water vaporization, and onset of nitrate decomposition, as mixed metal oxide began to form. The collected powders were calcined using a Nabertherm NW300 chamber furnace at 900 °C for 6 h in air with heating and cooling rates of 200 °C h⁻¹, as this was determined to be the optimal temperature for phase segregation in a previous study.

Electrochemistry Tests: The electrodes for electrochemical testing were prepared by mixing 85 wt% active material with 10 wt% conductive carbon Super-P (Alfa Aesar) and 5 wt% polyvinylidene fluoride (Sigma Aldrich) dissolved N-methyl pyrrolidinone by ball milling (Retsch MM400) for 45 min at 15 Hz with 16.67 g of stainless steel balls so the active material/balls weight ratio was 0.12. The obtained slurry was coated on an Al current collector using a laboratory doctor blade, then using a double aberration-corrected Themis Z instrument (Thermo Fisher) operated at 300 kV. Three samples were chosen for TEM investigation: Sn x = 0.10, Al x = 0.01, and Al x = 0.10. These samples were prepared for TEM analysis by diluting a small amount of powder in isopropanol alcohol, ultrasonicating it for ~30 min, and dispersing a few drops onto a thin carbon grid. STEM experiments were performed by correcting pre-specimen aberrations up to fifth order with a CEOS DCOR corrector and then scanning a finely focused electron probe across the thin specimen. EELS and EDX experiments were performed simultaneously using a probe current varying between 100 and 250 pA for each experiment, depending on the FOV. EELS was collected using a post-column Gatan Image Filter (GIF, Gatan Inc.) using a convergence angle of 21.4 mrad and a collection angle of 23 mrad. IDPC images were acquired on a 4-quadrant annular dark field detector (Thermo Fisher) using a probe current of 50 pA.

X-Ray Photoelectron Spectroscopy: XPS measurements were performed using a Thermo Scientific multilab-2000 spectrometer. The binding energy scale for all the spectra was calibrated from the C 1s core peak at 284.6 eV.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords
cobalt-free layered cathodes, lithium ion batteries, nanostructures, structural stabilization, transmission electron microscopy

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