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Structural underpinnings of the enhanced cycling stability upon Al-substitution in LiNi_{0.45}Mn_{0.45}Co_{0.1-v}Al_vO₂ positive electrode materials for Li-ion batteries

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Abstract

Single-phase LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ layered oxide materials with $0 \le y \le 0.10$ were prepared using the glycine-nitrate combustion method. Al-substitution has a minimal effect on the defect concentration and rate capability of the materials, but raises the operating voltage and reduces the capacity fade of the materials during prolonged cycling compared to the unsubstituted system. *In situ* x-ray diffraction suggests the presence of Al has a significant structural impact during battery operation. It acts to limit the changes in lattice parameters observed during electrochemical charging and cycling of the materials. High-resolution x-ray diffraction reveals structural distortions in the transition metal layers of as-synthesized powders with high Alcontents, as well as a structural evolution seen in all materials after cycling.

Keywords: Li-ion, positive electrode, layered oxide, Al-substitution, in situ diffraction

TOC Summary

Al-substitution in layered oxides improves the cost, safety, and cycling stability of the electrode materials in Li-ion batteries. Synchrotron-based high-resolution and *in situ* X-ray diffraction techniques are used to elucidate the structural consequences of Al-substitution and the relation to improved electrochemical properties.



Introduction

With major efforts in recent years to develop and deploy electric transportation fleets, layered mixed transition metal oxides have been extensively investigated as positive electrode materials for Li-ion batteries. LiNi_zMn_zCo_{1-2z}O₂ (NMC hereafter) materials, with z commonly 0.33 or 0.4, have been shown to possess improved properties compared to LiCoO₂, the positive electrode material used in most portable electronics batteries, as well as alternatives such as trivalent Ni-based LiNi_{1-z}Co_zO₂.^{1,2,3,4,5} These phases all crystallize in the layered α -NaFeO₂ (R-3m) structure. In addition to a decrease in materials cost, the achieved improvements in practical energy density, stability, and cycle life are in line with the requirements for widespread use in electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs), which have necessary cost, safety, and lifetime constraints, and for which LiCoO₂ is inadequate.^{6,7,8,9,10,11,12,13}

Capacity fade over the operation lifetime of these electrode materials remains an issue, however, and the explicit mechanism is not fully understood.¹⁴ Reports on various layered oxide stoichiometries have referenced phase transformations or local structural disorder in the active particle bulk or surface,^{15,16,17,18} loss of contact or microcracking from cyclic volume changes,^{19,20,21} and reactivity with the electrolyte to produce surface films^{17,19,20,22} as positive-electrode-based capacity-fade schemes. The extent of each can vary based on the specific chemistry of the positive electrode and its environment, such as the operation temperature, voltage limits and composition of the electrolyte. Some, if not all, of these effects may certainly contribute to the decrease in capacity observed over the cycling life of the NMC materials.

Improved behavior is observed with the substitution of A1 in place of Co, leading to $LiNi_zMn_zCo_{1-2z-y}Al_yO_2$. The thermal stability and chemical reactivity properties are better upon substitution, resulting in overall safety enhancements.^{23,24,25} Notably, the presence of A1 in NMC

layered oxide systems has also been shown to improve the cycling stability of the electrodes.^{24,26,27,28,29} However, the means by which Al-substitution improves the material performance has not yet been definitively stated. To help design improved battery materials capable of powering an electrified fleet, the origin of the enhanced performance in the Al-substituted materials must be explicitly ascertained.

For the present study, the electrochemical and structural consequences of Al-substitution for Co in LiNi_zMn_zCo_{1-2z-y}Al_yO₂ (z=0.45) have been investigated. This stoichiometry is chosen because the Co-content is simultaneously decreased by both Al-substitution and the concurrent increase in Ni and Mn compared to the more common z=0.33 and 0.4 compositions. *In situ* xray diffraction (XRD) using synchrotron radiation allows for real-time tracking of the structural evolution of the materials during battery operation, and has been used here for an in-depth analysis of the system. Additionally, high-resolution synchrotron x-ray diffraction allows the observation of subtle structural consequences of Al-substitution in the materials, and changes occurring after repeated cycling.

Experimental

LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ ($0 \le y \le 0.1$) layered oxide materials were prepared using the glycine-nitrate combustion method.³⁰ Stoichiometric amounts of LiNO₃ (Mallinckrodt), Ni(NO₃)₂•6H₂O (Sigma Aldrich), Co(NO₃)₂•6H₂O (Sigma Aldrich), Al(NO₃)₃•9H₂O (Sigma Aldrich), and Mn(NO₃)₂ (45-50 wt% solution in dilute nitric acid, Sigma Aldrich) were mixed with glycine (98.5%, Sigma Alrich) in an aqueous solution using distilled water. A 5% excess of LiNO₃ was used in all samples to account for Li loss during the synthesis procedure. The precursor solution was transferred to a heated stainless steel beaker, where it was concentrated

by the evaporation of water and a subsequent self-sustaining combustion reaction ensued. The combustion product was planetary ball-milled in acetone and dried under flowing N_2 gas before being annealed at 800°C for 4 hours in air.

Composite electrodes were composed of 84 wt% active oxide, 8 wt% polyvinylidine flruoride (PVdF) binder (Kureha Chemical Ind. Co. Limited), 4 wt% synthetic flake graphite (SFG-6, Timcal Ltd.), and 4 wt% acetylene black (Denka). Slurries were mixed in 1-methyl-2pyrrolidinone (NMP, Sigma Aldrich) and cast onto carbon-coated aluminum current collectors (Exopack Advanced Coatings). Typical active material loadings were 5-8 mg cm⁻². The electrodes were dried for at least 24 hours in air, then overnight in a vacuum oven at 120°C. Size 2032 coin cells were assembled in a helium-filled glovebox with Li-metal counter electrodes, porous polypropylene separators (Celgard 3401), and electrolyte composed of 1 M LiPF₆ in 1:2 (v/v) ethylene carbonate (EC):dimethyl carbonate (DMC) solution (Ferro). Electrochemical testing was performed using a VMP3 potentiostat/galvanostat (BioLogic) by cycling the coin cells gavlanostatically between voltage limits.

High resolution XRD was performed *ex situ* at beamline 11-BM of the Advanced Photon Source (APS).^{31,32} Fresh powder, fresh electrode materials (including carbon and PVDF), and electrode materials recovered from coin cells after 20 and 50 cycles (2-4.3V, C/18.5 = 15 mA g⁻¹) were placed in Kapton capillaries. The high-resolution beamline utilizes 30 keV xrays (λ =0.413 Å), a sample mount spinning at 90 Hz to reduce preferred orientation, and 12 discrete Si(111) single crystal analyzer detectors. The entire detector construction was scanned over a 34° 20 range at a rate of 0.01°/s, with data collected every 0.001° 20. The data were refined using GSAS/EXPGUI with a fitting range of 2.8°-32° 20 with Li at the 3a sites, transition metals at the 3b sites, and oxygen at the 6c sites within the R-3m unit cells.^{33,34} The antisite Ni concentrations were refined by constraining the total Ni content (occupancy in both the lithium and transition metal layers) to the stoichiometric value in the $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ materials. An isotropic displacement parameter (U_{iso}) was refined for each crystallographic site. Values of 1.10(1) x 10⁻² and 0.63(5) x 10⁻² Å² were typically found for U_{iso} at the anion and transition metal cation sites, respectively. Scanning electron microscopy was performed with a JSM-7500F field-emission SEM (JEOL, Ltd.).

In situ synchrotron x-ray diffraction studies were performed at beamline 11-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). Pouch cells were assembled with Li-metal counter electrodes, Celgard 2400, and 1 M LiPF₆ in 1:1 ethylene carbonate (EC):diethyl carbonate (DEC) electrolyte solution (Ferro) in an argon-filled glovebox. They were cycled galvanostatically using an FAS2 Femtostat (Gamry Instruments, Inc.) at ~C/13 or ~C/21 depending on beamtime constraints. To maintain pressure, the pouch cells were constrained within an aluminum frame with a small 2 mm diameter hole to allow for transmission of the xray beam through the electrode. Transmission XRD ring patterns were detected using a MAR image plate and an exposure time of approximately 10 s. Linescans were generated by integrating the calibrated image patterns. The significant background signal contributed by the polyester pouch material throughout the angular range observed, along with the periodic overlap of the active material and Al current collector peaks during cell operation, make perfect background subtraction and refinement of the entire diffraction patterns difficult. To circumvent this problem, backgrounds were manually subtracted and specific peaks (7 in total) that were not obscured by the current collector during cell operation were fit with pseudo-Voigt lineshapes to The unit cell lattice parameters at various states-of-charge (SOC, determine positions.

determined by the current passed) were subsequently calculated by a least-squares refinement using the available peak positions and the program CelRef.³⁵

Results and Discussion

Materials Characterization

The glycine-nitrate combustion (GNC) method allows intimate mixing of metalcontaining precursors, resulting in the synthesis of homogeneous Al-substituted products. This route avoids the issues described by other authors in using a mixed hydroxide precursor to incorporate Al into the NMC lattice.^{36,37} The GNC method, which utilizes an Al³⁺-nitrate precursor, neither requires formation of an intermediate M^{2+} (*M*=Ni, Mn, Co) hydroxide phase, nor relies on solid-state diffusion to generate a uniform metal distribution, as in more common solid-state synthesis methods. Rather, the metal homogeneity is mainly determined by the mixing in solution prior to combustion.

High-resolution synchrotron XRD patterns for as-synthesized LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ powders with *y*=0, 0.05, and 0.10 are shown in Figure 1, indexed with the hexagonal description of the rhombohedral R-3m symmetry (α -NaFeO₂ structure). Subtle structural variations were observed due to the small wavelength (0.413 Å), unparalleled resolution (<0.0002 Δ Q/Q, Q=2 π /d), and large angular range used in the measurements – data was recorded and analyzed that is inaccessible by common laboratory-scale systems. The small shoulder peaks not indexed (Fig. 1a, inset) are indicative of cation ordering in the transition metal layer and are discussed below. Substitution of Co by Al causes an expansion of the crystal lattice along the *c*-direction, as observed by a shift of the R-3m 003 peak at ~4.96° 20 (Fig. 1b), and a slight corresponding contraction within the *ab* plane (Table 1). The former is related to the interlayer spacing, while

the latter is primarily determined by the bonding distances within the transition metal plane. The changes are attributed in part to the slightly smaller size of the Al^{3+} ion in an octahedral environment (0.535 Å) as compared to the low spin Co³⁺ ion (0.545 Å) it replaces,³⁸ though electronic effects relating to the differences in Al-O and Co-O bonding character may also contribute.³⁹

Closer observation of the XRD patterns reveals the existence of splitting at certain reflections for the fully substituted y=0.10 sample. Figure 1c shows the region around the 1 2 11 reflection in the R-3m system, with further examples shown in Figure S1. These specific occurrences indicate a suppression of the degeneracy of the hexagonally indexed *hkl* and *kh-l* reflections, signifying a symmetry-lowering distortion within the transition metal plane. Indeed, while the XRD patterns for y=0 and y=0.05 can be adequately fit using the R-3m space group, the diffractogram for y=0.10 is best fit using the monoclinic C2/m symmetry (space group #12). C2/m symmetry is a maximal non-isomorphic subgroup of R-3m, simply generated by the removal of the 3-fold axis of the hexagonal structure through a slight expansion of one in-plane metal-metal distance relative to the other.

The results of Rietveld refinements of pristine powder samples are presented in Table 1 and Figures 2, S2, and S3. The refinement of the y=0.10 sample was performed using C2/m symmetry, but the results are additionally presented in the table after conversion to R-3m using geometry and averaging the calculated a_{mon} and b_{mon} lattice parameters. All materials were observed to contain approximately 9-10% Ni ions residing in the Li sites between the transition metal layers. The errors on the refined Ni_{Li} concentration values are <0.1% for all samples. It is assumed that full intersite mixing occurs, leading to an equivalent amount of Li residing on the transition metal sites. A slight increase in antisite concentration (~1%) is observed as the Al-

substitution is increased, though the change is not large enough to significantly affect the electrochemical properties. This is consistent with previous reports,^{25,27} and is further discussed below.

The transition metal planes are composed of edge-sharing MO_6 octahedra, with M = Ni, Mn, Co, Al, or Li ions at the octahedral centers. Depending on the central ion species and oxidation state, each octahedron has different equilibrium *M*-O bond distances.³⁸ The edgesharing configuration therefore leads to a degree of inherent octahedral strain within the transition metal layer. There is also evidence of at least some extent of metal ordering by the existence of a small shoulder peak on the high-angle side of the 003 (R-3m) reflections of all samples (Fig. 1 inset). Intensity in this region is commonly attributed to Li₂MnO₃-like domains within the structure,⁴⁰ which is anticipated in materials with significant concentrations of antisite defects, such as the ones described here. This Li₂MnO₃-like character exists in all of the LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ ($0 \le y \le 0.1$) electrode materials, as they all contain a similar antisite defect concentration.

The nanoscale dimensions of the primary particles in all samples (~40 nm diameter) cause significant peak broadening, which can mask smaller distortions in the peak profiles despite the unparalleled resolution of the measured XRD patterns. It is possible that the lower Al-content materials such as y=0.05, which is well-fit using the R-3m structure, may also contain local-scale distortions that are not resolved on average here.

Previous results from neutron pair distribution function (PDF) analysis and nuclear magnetic resonance (NMR) spectroscopy have indicated that Ni and Mn ions have a thermodynamic tendency to form short range ordered clusters, while the presence of Co in NMC breaks this correlation and leads to extensive long and short range disorder.⁴¹ It is hypothesized

that the incorporation of Al into the lattice induces a local-scale ordering of the metals, possibly through the reduction of Co and its driving force toward disordering. This ordering relieves some of the inherent strain within the edge-sharing octahedral layer, and results in the observed monoclinic distortion. This, however, is different from the monoclinic symmetry observed in Li₂MnO₃, caused by the ordering of Li and Mn in the transition metal planes. The monoclinic distortion due to Al-substitution is the result of the breakage of the three-fold symmetry of the transition metal-oxide sheets, perhaps due to changes in the distortion of the transition metal-oxide sheets, perhaps due to changes is supported by X-ray absorption spectroscopy results, which will be reported in an upcoming publication.

Samples observed using scanning electron microscopy indicate average primary particle sizes are ~40-45 nm diameter (Fig. 3), and show that the primary particles are organized into larger agglomerates. The powder morphologies are similar for all synthesized materials. Thus, performance comparisons between the materials sets are complicated neither by size effects nor significant differences in antisite mixing (as implied by Rietveld refinement of the high resolution XRD patterns) amongst the compositions.

Electrochemical Characterization

Electrochemical characterization using Li-metal half-cells shows that Al-substitution increases the reaction potential at which Li⁺ is both removed and replaced in the LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ materials by 50-75 mV during both charge and discharge, consistent with results obtained for other NMC compositions (Fig. 4).^{26·27} This is clearly observed by a shift in the peaks of the derivatives of the specific capacity curves (normalized dQ/dV), shown in Figure 4b. This systematic increase in both the charge and discharge operating potentials is

additional evidence of the full incorporation of Al in the NMC lattice, with the increase in the discharge potential specifically indicating a change in operating potential as opposed to a polarization effect. The presence of a secondary phase (such as insulating γ -LiAlO₂),⁴² in contrast, would most likely increase the impedance of the system, (if it has any effect at all), resulting in higher charge potentials but lower discharge potentials. The incorporation of Al potentially causes an increase in the ionicity of some or all of the *M*-O bonds (where *M*=Ni, Mn, or Co), which in turn lowers the relative redox energy and increases the operating voltage.⁴³

Practical charge and discharge capacities between the set voltage limits decrease somewhat in proportion to the Al content, due to the rising potential as a function of state-ofcharge (SOC). The impact is, however, minimal for $y \le 0.05$. Al substitution has no effect on the rate capability (Fig. 5a); the decrease in the delivered capacities as the current density increases remains constant as the Al content rises. Decreased rate capability in NMC materials is usually indicative of significantly greater Ni/Li antisite mixing, which acts to block Li diffusion during battery operation.^{44,45} The limitation is exaggerated at higher rates and leads to greater declines with current density in the Peukert plots, which relates the delivered capacities as a function of discharge current densities. The lack of any such major differences amongst the materials in this study, therefore, corroborates the assertion that the very slight increase in antisite defect concentration with Al-substitution has a minimal effect on the electrochemical performance.

There is, importantly, a clear enhancement in the cycling stability with the presence of Al, as seen in Figure 5b. After approximately 30 cycles at 12 mA g⁻¹ (~C/23) between 2-4.3 V, the material with y=0.05 provides a higher discharge capacity, while the fully substituted sample (y=0.10) outperforms the parent material after about 100 cycles. Both materials have first cycle discharge capacities slightly lower than that of the unsubstituted material, as discussed above,

but the presence of Al limits the rate of capacity fade in the substituted materials. A faster rate of capacity fade is seen upon cycling between 2-4.7 V at 18 mA g^{-1} (~C/16, Fig. 5c). The stabilizing effect of Al is still observed, with the Al-substituted samples out-performing the parent material after about 25 cycles. Cycling between 2-4.0 V at 18 mA g^{-1} also results in some capacity fade of the LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ materials, though at a slower rate than the higher voltage cycling (Fig. 5d). A stabilizing effect of Al, however, is not readily apparent within 30 cycles when operated in this relatively low voltage range.

Structural Evolution During Cycling

In situ x-ray diffraction was used to probe the structural evolution of the materials during battery cycling. This sort of experiment is an excellent tool to observe the changes occurring during the charge and discharge processes of single cells, eliminating the uncertainties that could arise from the use of numerous *ex situ* samples to observe different SOC's. When a high throughput image plate detector is used, the material need only be exposed for <10 seconds to generate a diffraction ring pattern, which can subsequently be integrated to produce a linescan for analysis. The short exposure time allows for the continuity of the electrochemical processes, as in real battery operation, without having to stop the cycling procedure and allow the cells to relax during a lengthy θ -2 θ scan. This ensures minimal changes occur during pattern acquisition. Thus, essentially instantaneous snapshots of the material structure at any and all discreet stages of cycling can be generated to investigate the changes occurring over wide ranges of Li⁺ content.

Figures 6 and S4 show plots of potential vs. composition (x) for Li/Li_xNi_{0.45}Mn_{0.45}Co_{0.1-} _yAl_yO₂ for the y=0 and y=0.5 electrode materials, respectively, electrochemically charged and discharged in pouch cells during the *in situ* XRD experiments. The points at which integrated linescans were analyzed for this work are specified on each plot; these correspond to 5% changes in Li content for all cells (calculated based on the current passed), an interval considered small enough to capture the details of the structural changes occurring in the positive electrode materials. The top plots correspond to a full cycle with Li-removed on charge in an amount equivalent to a 4.3 V cut-off in an optimized coin cell. The bottom plots show the voltage profiles of cells containing $Li_xNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ (*y*=0, 0.05) charged to the nominally *x*=0 state.

The structural evolution of $Li_xNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ (*y*=0, *y*=0.05) materials during charge and discharge is presented in Figure 7. Three separate regions are shown for each material during oxidation (black) and reduction (green). Neither the *y*=0 (Fig. 7a) nor *y*=0.05 (Fig. 7b) materials undergo an observable phase change or form any secondary phases, as evidenced by the absence of new peaks at any point in the redox processes. Peak shifting due to changing lattice parameters as Li-ions are removed and reinserted can clearly be observed for both materials, as expected for layered oxide systems in which Li-ions reside within Van der Waal's gaps between MO_6 planes.

Although they behave very similarly, the y=0.05 material returns closer to the initial state at the end of discharge than the unsubstituted material in terms of both peak position and shape, as shown in Figure 8. There is significantly increased peak broadening in the fully discharged y=0 material, seen especially in the 101, 110, and 113 reflections. This broadening indicates a larger degree of disorder or electrode inhomogeneity, a decrease in particle size, or increased strain after the first charge/discharge cycle. The Li-content after discharge is similar for both materials, validating the comparison.

Figure 9 presents integrated linescans (in increments of 5% Li⁺) for both positive electrode materials upon complete Li-ion removal. In the case of the Al-substituted sample, a current was passed for an amount of time corresponding to 100% Li⁺ extraction despite the fact that the Al³⁺ ion is redox inactive in this voltage range. Theoretical calculations, however, have suggested that Li⁺ can be extracted from layered LiAlO₂, with oxidation occurring in the oxygen 2p band at ~5.4 V vs. Li/Li⁺.^{39,46} Most likely at high potentials, irreversible side reactions such as oxidation of the electrolyte, contribute to the charge capacity, so that not all of the lithium is actually removed from the layered structure. Neither material undergoes an observable phase change upon reaching a nominally 100% SOC (i.e. complete Li⁺ extraction). This is consistent with previous observations on related phases such as Li_xNi_{0.4}Mn_{0.4}Co_{0.2}O₂, which maintains the rhombohedral structure to about x=0.05.¹¹ In both cases, the lattice undergoes an initial expansion, followed by a contraction above 50% SOC along the c direction, as indicated, for instance, by the shift in the 003 reflection. However, significant structural evolution differences between $Li_xNi_{0.45}Mn_{0.45}Co_{0.1}O_2$ and $Li_xNi_{0.45}Mn_{0.45}Co_{0.05}Al_{0.05}O_2$ are apparent. The 003, 006/102, and 108 peaks move to higher q (smaller d-spacing) at the end of charge in the unsubstituted material as compared to that containing Al. The shift of these peaks suggests a greater change of the structure in the basal direction (c_{hex}) within the parent compound at high states-of-charge.

The normalized changes in lattice parameters, calculated from the integrated linescans, are shown in Figures 10 and 11 as a function of nominal Li-content. The results show that both materials undergo a contraction within the *ab*-plane due to the formation of highly charged transition metal ions, which have smaller ionic radii than the initial states. Comparative analysis indicates that the presence of Al limits the changes in the *c*-parameter, and to some extent the

contraction in a_{hex} , during charging. Similar behavior has previously been observed for an Alfree NMC compound.¹⁰ The difference in *c* parameter contraction with Al-substitution at 100% SOC mentioned above is clearly observed in Figure 11b. Moreover, the "turnover" point – the charge state at which the lattice begins to contract along the axial direction – is shifted to a higher SOC for the Al-substituted material. Figures 5c and d show that samples charged to 4.3 or 4.7 V during the cycling experiments displayed improved discharge capacities compared to the Al-free electrodes. A similar effect was not observed for a maximum voltage of 4.0 V. The 4.3 and 4.7 V bounds (for the cycling of optimized coin cells) correspond to about 60 and 75% SOC, respectively, while the 4.0 V limit only cycles to an SOC of approximately 40%. Comparing with the measured lattice parameters, it seems plausible that the delay in lattice contraction, owing to the structural stability conveyed by the Al, correlates with the improved electrochemical properties.

High-resolution XRD patterns for LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ (y=0) electrodes in the pristine state and after 20 and 50 cycles are shown in Figure 12, while those for y=0.05 and 0.10 are shown in Figure S5. Note that all patterns, including the pristine samples, correspond to measurements taken on composite electrodes, as opposed to the as-synthesized powder data shown in Figure 1. The cycled electrodes were harvested from coin cells in the fully discharged state and measured *ex situ*. No new peaks indicating any new phase growth are observed with cycling. All samples do, however, show a relative expansion of all lattice parameters with cycle number. This enlargement is clearly observed by the shifting of all peaks to lower 20 values, examples of which are shown in Figure 12b-d.

Results from Rietveld refinements are presented in Table 2. The expansion in *c*-parameter (indicated, for example, by the shift of the 003 reflection) can possibly be explained

by an incomplete re-lithiation of the materials upon discharge. However, the expansion within the *ab*-plane compared to the pristine material cannot be similarly explained. This plane only undergoes contraction during cycling, as seen during *in situ* measurement. As the materials are charged, a number of peaks (for example the 101, 104, and 113 reflections) shift to higher 20 values (smaller *d*-spacing). The peak shifts due to extended cycling observed here are in the opposite direction, towards lower 20, suggesting a structural change that is not simply due to Li content. The refinements also indicate a decrease in antisite concentration of all samples due to cycling (error <0.1%). It is noted that the relative changes in lattice parameters are the smallest, and the decrease in antisite concentration is highest, in the *y*=0.05 sample, which also shows the best cycling performance. These results suggest that the presence of Al in LiNi_{0.45}Mn_{0.45}Co_{0.1-} *y*AlyO₂ positive electrodes has beneficial structural effects that have a positive impact on cycle life.

Conclusions

When Al is substituted for Co in LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO₂ compounds, solid solutions form over the entire composition range, $0 \le y \le 0.10$, though a monoclinic distortion is observed in the fully substituted (*y*=0.10) sample. This distortion indicates a removal of the degeneracy of the a_{hex} and b_{hex} (nearest metal-neighbor) distances, and is distinct from the monoclinic ordering observed in Li₂MnO₃-containing materials. There is almost no impact on the initial discharge capacity when the *y*=0.05 compound is used as a positive electrode in lithium batteries compared to the baseline material, and Al substitution in general does not adversely affect rate capability. Enhanced capacity retention is observed for the Al-containing positive electrode materials compared to the unsubstituted material during prolonged cycling in lithium cells, when charged to voltages greater than 4 V.

In situ x-ray diffraction on cells containing the y=0 and y=0.05 materials shows a definite structural effect of Al-substitution during the first cycle. Substantially more peak broadening is seen in diffraction linescans of the y=0 materials after a single cycle than in the y=0.05 system. Calculated lattice parameters indicate the presence of Al especially acts to limit the changes in c_{hex} as the materials are charged and discharged. The charge-state at which the lattice begins to contract along the layered direction is pushed to a higher SOC in the Al-substituted materials, which possibly correlates with the improved electrochemical properties. High-resolution XRD of cycled cells indicates an expansion of all lattice parameters with cycling, and a concurrent decrease in antisite concentration for all samples. Among them, the sample with y=0.05 shows the smallest swings. Further experiments probing the local structural and electronic effects of Al in this system have been underway and will be reported in a future publication. Continuing work is focused on locally resolved characterization of the substitution effects.

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Supporting Information Available: Further examples of peak splitting due to structural distortion, Rietveld refinements of as-synthesized powder and fresh and cycled electrode materials. This material is available free of charge via the internet at <u>http://pubs.acs.org</u>.

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Al content (%)	Symmetry	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Ni_{Li} (%)	Rwp	Rp	χ^2
0	R-3m	2.88045(3)	-	14.2772(2)	-	102.588(2)	9.06	8.19	6.24	3.954
5	R-3m	2.87964(2)	_	14.2812(2)	_	102.558(2)	9.49	7.96	6.09	3.853
10	C2/m	4.9984(1)	2.87200(5)	5.0447(1)	109.258(4)	68.368(2)	10.08	7.34	5.50	3.313
10	R-3m	2.8789	-	14.2873	_	102.552	10.08	_	-	_

Table 1: Results of Rietveld refinement of high-resolution XRD patterns of as-synthesized $LiNi_{0.45}Mn_{0.45}Co_{0.1-}$ $_yAl_yO_2$ (y=0, 0.05, 0.1) powders.

Table 2: Results of Rietveld refinement of high-resolution XRD patterns of the fresh and cycled $LiNi_{0.45}Mn_{0.45}Co_{0.1}$, $_{y}Al_{y}O_{2}$ (*y*=0, 0.05, 0.1) electrodes.

Al content (%)	# Cycles	Symmetry	a (Å)	b (Å)	c (Å)	β (°)	$Ni_{Li}(\%)$	Rwp	Rp	χ^2	Δa (%)	Δb (%)	Δc (%)
0	0	R-3m	2.88080(3)	_	14.2771(2)	_	9.17	7.98	6.17	2.565	0	_	0
0	20	R-3m	2.88274(3)	-	14.2884(2)	-	8.3	7.92	6.1	2.746	0.067	_	0.079
0	50	R-3m	2.88331(3)	-	14.2923(2)	-	8.36	7.73	5.95	2.499	0.087	_	0.106
5	0	R-3m	2.87994(3)	-	14.2810(2)	-	9.62	7.98	6.26	2.545	0	-	0
5	20	R-3m	2.88126(3)	-	14.2894(2)	-	8.48	7.73	6.03	2.340	0.046	_	0.058
5	50	R-3m	2.88190(3)	-	14.2917(2)	-	8.37	7.92	6.15	2.466	0.068	-	0.075
10	0	C2/m	4.9991(1)	2.87234(5)	5.0449(1)	109.259(4)	10.2	7.38	5.66	2.641	0	0	0
10	20	C2/m	5.0043(1)	2.87503(6)	5.0490(1)	109.267(3)	9.23	7.55	5.66	3.022	0.102	0.094	0.082
10	50	C2/m	5.0084(1)	2.87689(7)	5.0511(1)	109.282(3)	9.3	7.78	5.77	3.023	0.185	0.159	0.123

Figure 1: a) High-resolution XRD patterns of as-synthesized $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{O}_2$ (*y*=0, 0.05, 0.1) powders. A magnification of the indicated region is shown in the inset. b, c) Magnified regions of the patterns shown in (a). Al-substitution causes a slight structural distortion in the materials, seen as peak splitting in (c).

Figure 2: High-resolution XRD patterns and Rietveld refinement of the $LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$ (unsubstituted) material.

Figure 3: SEM images of as-synthesized $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ powders with a) y=0.025 and b) y=0.075. All materials had similar primary particle sizes and agglomeration. Scale bars are 100 nm.

Figure 4: a) Voltage vs. specific capacity plots for the first cycles of $LiNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ ($0 \le y \le 0.10$) electrodes cycled 2.0-4.3 V vs. Li/Li^+ . The inset shows the increased operating potential of the electrodes due to Al-substitution. b) Differential capacity vs. voltage shows the increase occurs on both oxidation (top) and reduction (bottom).

Figure 5: a) Modified Peukert plot showing the similar rate capabilities of materials with different Al-contents. b) Discharge capacity vs. cycle number for $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{O}_2$ (*y*=0, 0.05, 0.1) materials cycled between b) 2.0-4.3 V vs. Li/Li^+ , c) 2/0-4.7 V, d) 2.0-4.0 V. Alsubstitution leads to enhanced cycling stability when electrodes are charged \geq 4.3 V.

Figure 6: Voltage vs. *x* in $Li_xNi_{0.45}Mn_{0.45}Co_{0.1}O_2$ (unsubstituted) for the first cycle during *in situ* XRD testing. Pouch cells were a) cycled, b) fully charged. The points at which diffraction data is presented are indicated. The corresponding profiles for the y=0.05 material are shown in Figure S4.

Figure 7: Selected regions of *in situ* XRD patterns for $Li_xNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ electrode materials during the first cycle. a) *y*=0, b) *y*=0.05. Each pattern corresponds to a 5% change in Li-content during charge (black) and discharge (green). Values of *x* correspond to the Li-content in the materials.

Figure 8: Comparison of diffraction peaks between fresh (black) and fully discharged (green) $Li_xNi_{0.45}Cn_{0.1-y}Al_yO_2$ electrodes with a) y=0 and b) y=0.05, before and after the first cycle. Increased broadening is observed in the unsubstituted sample, while the Al-substituted sample (b) appears more reversible. The red spots indicate reflections from the Al current collector.

Figure 9: Selected regions of *in situ* XRD patterns for $Li_xNi_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ electrode materials during full Li extraction. a) *y*=0, b) *y*=0.05 during the first charge. Each pattern corresponds to a 5% change in Li-content during charge from the fresh state (blue) to complete Li-deintercalation (red). Values of *x* correspond to the Li-content in the materials. The red spots indicate reflections from the Al current collector.

Figure 10: Relative chances in the calculated lattice parameters for the $Li_{1-x}Ni_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ (*y*=0, 0.05) materials during the first cycle. More variation is observed in the Al-free (*y*=0) material.

Figure 11: Relative chances in the calculated lattice parameters for the $Li_{1-x}Ni_{0.45}Mn_{0.45}Co_{0.1-y}Al_yO_2$ (*y*=0, 0.05) materials during first charge full Li deintercalation. Al-substitution limits the structural changes observed at high states-of-charge along the layer-stacking direction.

Figure 12: a) High-resolution XRD patterns of fresh and cycled $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1}\text{O}_2$ (*y*=0) electrodes. The small peak at ~7° 2 θ is due to graphite. b, c, d) Magnified regions of the $\text{LiNi}_{0.45}\text{Mn}_{0.45}\text{Co}_{0.1}\text{O}_2$ (*y*=0) XRD patterns showing the shift of all peaks to lower 2 θ with cycling. A similar trend is observed in the Al-substituted materials.