Formation and **effect** of orientation domains in layered oxide cathodes of lithium-ion batteries

Karalee A. Jarvis,* Chih-Chieh Wang, James C. Knight, Lew Rabenberg, Arumugam Manthiram, and Paulo J. Ferreira

Materials Science and Engineering Program & Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712 (USA)

Abstract

We show that in layered oxides that are employed as cathodes in lithium-ion batteries, the cation layers can order on different $\{111\}_{\text{NaCl}}$ planes within a single particle, which makes the lithium layer discontinuous across a particle. The findings challenge previous assertions that lithium undergoes 2-D diffusion in layered oxides and the data provide new insights into the decrease in rate capabilities for some layered oxides. Therefore, it is critically important to understand how these discontinuities form and how the loss of 2-D diffusion impacts the overall performance of the layered oxide cathode materials. Employing X-ray diffraction (XRD) and aberration-corrected scanning transmission electron microscopy (STEM), we find that as the material transitions from a disordered to an ordered state, it forms four orientation variants corresponding to the four $\{111\}_{\text{NaCl}}$ planes. This transition is not intrinsic to all layered oxides and appears to be more strongly affected by nickel. Furthermore, with energy dispersive spectroscopy (EDS), we show that there is an increase in the nickel concentration at the interface between each orientation variant. This reduces the rate of lithium diffusion, negatively affects the rate capability, and could be contributing to the overall capacity fade.

Keywords: Li-ion batteries, layered oxide cathodes, transmission electron microscopy, phase transition, nanodomains

* Corresponding author
Email: kjarvis@austin.utexas.edu
Phone: 512-232-1884; Fax: 512-471-3389

Introduction

With an aim to reduce the cost and improve the safety of Li-ion batteries, much focus has been directed in recent years towards novel materials composed of layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, generally designated as Li_2MnO_3 , and LiMO_2 [$\text{M} = \text{Mn}, \text{Ni}, \text{Co}$]. Among them, the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series has shown promise due to its high capacity[1–6]. We showed that compositions within the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series prepared by two different methods exhibits either an $R\bar{3}m$ phase, $C2/m$ phase, or both phases depending on the value of x [7]. More interestingly, we showed that regardless of composition, the cation layers in the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series order on different $\{111\}_{\text{NaCl}}$ planes in the base NaCl structure within a single particle. Initially, we will refer to areas of different ordering as domains. We also showed that particles with multiple domains are single-phase but appear to consist of multiple phases when viewed in projection[7].

As reported, we observed this phenomenon in four different compositions prepared with two different precursors. As we will show in this work, we see the same ordering in samples heat treated for different times and at different temperatures. In total, 14 different samples within the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series and over 70 different particles show changes in cation ordering, leading to an effective change in the orientation of the trigonal or monoclinic structure within the same particle. These domains result in discontinuities of the lithium layers across a single particle. Hence, particles in the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series can no longer be assumed to exhibit 2-D lithium diffusion, contrary to the previous assertion.

With this perspective, we focus here on how these domains form, if they are intrinsic to all layered oxides, and how they affect the overall electrochemical properties in lithium-ion cells. Accordingly, in this paper, we examine, by aberration-corrected scanning transmission electron

microscopy (STEM), two samples, LiCoO_2 and Li_2MnO_3 , in addition to the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series. We also investigate the disorder-to-order transition with X-ray diffraction (XRD) to explain the change in the ordering. Finally, we examine the rate capability of the system with and without the changes in ordering and consider the impact on capacity fade.

1. Experimental

1.1. Materials and synthesis

The $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ series was prepared with a sol-gel synthesis process. Required amounts of lithium acetate, manganese acetate, and nickel acetate were dissolved in deionized water. Ethylenediaminetetraacetic acid (EDTA) and citric acid, acting as complexing agents, were added to NH_4OH to form a homogeneous aqueous solution with $\text{pH} \sim 8$. The metal acetate solution was then added to the EDTA/citric acid solution. The mole ratio of EDTA : citric acid : metal ion was 1 : 1.5 : 1. The mixtures were then heat treated at 90°C for 12 h until a gel was formed. This gel was then fired at 450°C for 6 h to remove the residual organic impurities. The resulting powder was then heated at 900°C for 12 h to obtain the final powder, unless otherwise indicated.

1.2. Characterization

For transmission electron microscopy (TEM) analysis, the powders were suspended in ethanol or methanol and placed on a carbon lacey grid. The samples were imaged at The University of Texas at San Antonio, with a JEOL ARM200F TEM/STEM, equipped with a CEOS GmbH corrector for the illuminating lenses, and a high-angle annular dark-field (HAADF) detector. Selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) was performed on a JEOL 2010F TEM equipped with an Oxford energy dispersive X-ray detector.

2. Results and Discussion

As we showed in our previous work, a change in the ordering of the cation layers on the $\{111\}_{\text{NaCl}}$ planes occurs in samples of various compositions and prepared with different precursors and heat treated at 900 °C for 12 h[7]. We see the same trend with samples of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.2}]\text{O}_2$ heat treated at 850 °C for 24 h and heated at 900 °C for 6 h, 24 h, and 72 h (Fig. 1). In order to understand how these domains form, we must identify the type of domains and the respective boundaries.

2.1. Domain formation

For this discussion, we again use the rock-salt (NaCl)-structure for comparison because it is the basic structure for layered oxides[8] and allows us to more easily compare different compositions and their resulting phases. Fig. 2 shows the interface between two domains of different ordering for the material $\text{Li}[\text{Li}_{0.067}\text{Mn}_{0.533}\text{Ni}_{0.4}]\text{O}_2$, in particular, region 1 is ordered on the $(111)_{\text{NaCl}}$ plane, while region 2 is ordered on the $(1\bar{1}1)_{\text{NaCl}}$ plane. The boundary between these two regions is clearly not sharp and has characteristics of both domains. In fact, the transition-metal layer of region 1 slowly changes from bright atomic columns, spaced by 1.4 Å to bright atomic columns spaced by 2.8 Å, until it reaches region 2. In addition, the interfacial region shows that the transition metals begin to occupy the lithium layer of region 1 until it fully transforms to region 2.

By initial observation, the boundary appears to be a type of high-angle grain boundary. Grain boundaries form during solidification, deformation and recrystallization, or phase transformation due to macroscopic diffusion (diffusion of more than a few nearest neighbors)[9]. This material never went through solidification or deformation and macroscopic diffusion would require heterogeneous compositional variations on a large scale. Although we cannot yet rule out grain boundaries entirely, there are two boundaries that are more likely to form in these

materials during disorder-order transitions. As these materials go through a disorder-to-order process, orientation variants and/or anti-phase domains can form [10,11]. The type of domain formed will depend on the starting and final structures.

In the case of our samples, which were first heated at 450 °C for 6 h to remove the organic residues, XRD shows that $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.2}]\text{O}_2$ exhibits a spinel-like structure with an $Fd\bar{3}m$ space group, as indicated by the single broad X-ray peak near 65° (Fig.3). These results are similar to the previous work by Lu et al for $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$ synthesized at 600°C [6]. Due to the broad nature of the peak near 65° and the peaks in the 25-35° range, which indicate lithium ordering in the transition-metal layer, some of the material may have already formed a layered structure. As we have shown in a previous work, these materials have less homogeneity at lower temperatures [12]. Therefore, we propose that this material contains some particles with spinel-like structure while others exhibit an ordered layered structure. However, after heat treatment at 900 °C, the sample has fully transitioned from the initial $Fd\bar{3}m$ space group to either an $R\bar{3}m$ or $C2/m$ space group, depending on the composition [7]. Furthermore, *in-situ* XRD heating at 900 °C for 12 h indicates that the material is mostly layered, as indicated by the peak splitting near 64° (Fig. S1). The *in-situ* XRD shows a small amount of a spinel-like phase, as indicated by the shoulder on the peak at 44.2°, and a NaCl-like phase, as indicated by the small peaks around 37.5°, 43° and 62.6°; however, these could be the result of the loss of lithium during the *in-situ* XRD heating [12]. Overall, the material does not significantly disorder at 900°C and, therefore, the disorder-to-order transition happens mostly when the material orders after the initial heat treatment.

Now that we know the starting and ending phases of the disorder-to-order transition, we can predict what type of boundaries are present between the different orientations. $R\bar{3}m$ is a

“translationengleiche” subgroup of $Fd\bar{3}m$ and $C2/m$ is a “translationengleiche” subgroup of $R\bar{3}m$ [13]. Only point group symmetry operators of the parent phase are lost during the disorder-to-order transition of “translationengleiche” subgroups[13]. Accordingly, the interfaces observed in these materials should be orientation variant boundaries, not anti-phase boundaries, which require a loss of translational symmetry[10].

To confirm that the domains are orientation variants, we must verify that each variant can transition into the other from one of the lost point group symmetry operators[10,14]. The $Fd\bar{3}m \rightarrow R\bar{3}m$ transition should produce four orientation variants as the material transitions from 48 symmetry operators to 12 symmetry operators[10,15]. This explains the changes in cation ordering occurring in four different $\{111\}_{NaCl}$ planes. The lost symmetry operators of the $Fd\bar{3}m \rightarrow R\bar{3}m$ transition are the 4^+ , 4^- , $\bar{4}^+$, $\bar{4}^-$, and d . To begin, let us first consider if any of the orientation variants can translate into one another by a fourfold axis of rotation in the clockwise direction. The three 4^+ axes of rotation in $Fd\bar{3}m$ are on the three $\langle 001 \rangle_{NaCl}$ zone axes[13], which correspond to the $[841]_T$, $[\bar{4}41]_T$, and $[\bar{4}\bar{8}1]_T$ axes in the $R\bar{3}m$ space group. Due to the overlap of different types of atoms along these zone axes, it is not possible to depict the transitions with a simple schematic. Instead, let us consider the $[210]_T$ zone axis, in which like atoms stack on top of each other (Fig. 4a). When rotated 90° clockwise about the $[841]_T$ axis, the crystal is now aligned along the $[8101]_T$ zone axis (Fig. 4b), which corresponds to configuration A_3 as defined in a previous paper (Fig. S2)[7]. Another 90° clockwise rotation about the $[841]_T$ axis brings the crystal to the $[211]_T$ zone axis (Fig. 4c), which corresponds to configuration A_4 [7]. The last 90° clockwise rotation produces an $[8\bar{2}1]_T$ zone axis (Fig. 4d), which also corresponds to A_3 [7]. Thus, when viewed along any of the $\langle \bar{2}11 \rangle_{NaCl}$ zone axis, which corresponds to the zone axis of the STEM image shown in Fig. 2, four orientation variants are then observed in the $LiMO_2$

system, namely $[210]_T$, $[8101]_T$, $[211]_T$, and $[8\bar{2}1]_T$, each capable of transitioning into another by the symmetry operator 4^+ . Since the domains only need to translate into another by one of the lost point group symmetry operators, which we have shown is true for the 4^+ symmetry operator, we do not need to test the other lost symmetry operators.

The lithium-excess composition Li_2MnO , will undergo an additional transition, $R\bar{3}m \rightarrow C2/m$, which has been previously discussed [11]. This transition produces three orientation variants [11]. Thus, the full transition from $Fd\bar{3}m \rightarrow C2/m$ will produce 12 orientation variants with the lost symmetry operators, 3^+ , 3^- , $\bar{3}^+$, $\bar{3}^-$, 4^+ , 4^- , $\bar{4}^+$, and $\bar{4}^-$. These lost fourfold symmetry operators are on the three $\langle 100 \rangle_{\text{NaCl}}$ axes [13], which correspond to the $[\bar{3}2\bar{3}]_M$, $[323]_M$, and $[10\bar{1}]_M$ axes in the $C2/m$ system. Again, due to the overlap of different types of atoms along these zone axes, it is not possible to depict the transitions with a simple schematic. Therefore, let us start by considering the first orientation variant from the $R\bar{3}m \rightarrow C2/m$ transition, which is the $[100]_M$ direction rotated about a four-fold axis along the $[10\bar{1}]_M$ axis (Fig. 5a). The crystal normal changes to a $[3\bar{2}\bar{3}]_M$ zone axis after the first clockwise 90° rotation (Fig. 5b). This is equivalent to the A_3 configuration previously defined [7]. Two more 90° rotations about the $[10\bar{1}]_M$ axis produce $[001]_M$ and $[\bar{3}\bar{2}3]_M$ zone axes (Figs. 5c and 5d, respectively), which correspond to arrangements A_5 and A_3 , respectively [7]. If we now consider one of the other orientation variants from the $R\bar{3}m \rightarrow C2/m$ transition, namely the $[110]_M$, a rotation of 90° about the $[323]_M$ axis produces zone axes $[011]_M$, $[316]_M$, and $[613]_M$, which correspond to arrangements A_6 , A_4 , and A_3 , respectively [7]. Finally, for the same orientation variant $[110]_M$, a rotation of 90° about the $[\bar{3}2\bar{3}]_M$ axis produces zone axes $[6\bar{1}3]_M$, $[3\bar{1}6]_M$, and $[0\bar{1}1]_M$, which correspond to configurations A_3 , A_4 , and A_6 , respectively [7]. In

summary, when the $C2/m$ phase is viewed along any of the $\langle \bar{2} 11 \rangle_{\text{NaCl}}$ zone axis, there are 12 possible orientation variants, namely $[100]_M$, $[110]_M$, $[1\bar{1}0]_M$, $[3\bar{2}\bar{3}]_M$, $[0\bar{1}0]_M$, $[\bar{3}\bar{2}3]_M$, $[011]_M$, $[316]_M$, $[613]_M$, $[6\bar{1}3]_M$, $[3\bar{1}6]_M$, and, $[0\bar{1}1]_M$. Each variant transforms into the other by either a fourfold or threefold rotation of axis, which are the **symmetry operators** lost in the $Fd\bar{3}m \rightarrow C2/m$ transition. Accordingly, we can conclude that the domains in this material are orientation variants and their boundaries are orientation variant boundaries formed during a disorder-order process.

2.2. Effect of composition

Now that we have determined that orientation variants formed during the disorder-to-order transition are the **source** of the changes in ordering on the $(111)_{\text{NaCl}}$ plane, we need to determine if this behavior is intrinsic to all lithium-ion layered oxides. Therefore, we chose to examine two of the common end members of the $\text{Li}[\text{Li}_x\text{M}_{1-x}]\text{O}_2$ ($0 \leq x \leq 1$) series, namely, LiCoO_2 ($x = 0$), and Li_2MnO_3 ($x = 1$). We intentionally chose compositions without Ni because Ni has been reported to cause disordering with Li in these materials[6]. No orientation variants were detected in any of the particles examined for either LiCO_2 or Li_2MnO_3 (Fig. 6). Both LiCO_2 and Li_2MnO_3 show clear peak splitting near 65° (Fig. 3), just after a heat treatment at 450°C for 6 h, indicating well-formed layered structures, unlike those containing Ni. This confirms that they do not go through the disorder-to-order transition from the $Fd\bar{3}m$ phase and, therefore, do not form orientation variants. Overall, the orientation variants are not intrinsic to all lithium-ion layered oxides but can form if the material starts in a disordered spinel state, which is more likely when nickel is present.

It should be noted that under certain low-temperature conditions, LiCO_2 (LT- LiCoO_2) will form a spinel structure ($\{\text{Li}_2\}_{16c}[\text{Co}_2]_{16d}\text{O}_4$)[16]. Thus, it is possible that a material starting out as LT-

LiCoO₂ will form orientation variants when it transitions from $Fd\bar{3}m$ to $R\bar{3}m$. This will require further investigation. Ultimately, the formation of orientation variants is affected by the phase of the starting material, and thus will be affected by the composition.

2.3. Effects of orientation variants on performance

Now we must examine the effects of orientation variants on charge and discharge cycles. Due to the four {111} type planes in the NaCl-base structure, a single particle can have four different lithium layers, each rotated 109° to one another. This means there are four different 2-D layers for lithium to diffuse in and out of the particle, not one, as previously thought. This effectively provides a 3-D diffusion path for Li for every single particle. Yet, at the junction of any of the four {111}_{NaCl} planes, there is a barrier to lithium diffusion. When examined more closely, high angle annular dark field (HAADF) STEM images reveal that at the interface between two orientation variants, there is a region, a few nanometers thick, where Ni buildup seems to occur. This is shown in Figs. 2 and 7. In Fig. 2, the bright columns, which correspond to either Mn or Ni under HAADF STEM imaging, begin to occupy the lithium layer of one domain before fully transforming to the second domain. Furthermore, the interface between orientation variants is often slightly brighter than the bulk (Fig. 7), indicating less Li and more Mn and/or Ni. To be able to distinguish between Ni and Mn at the interface, we collected EDS line scans from two orientation variant interfaces and two orientation variants. Fig. 7 shows that the nickel content from the averaged interfaces is slightly higher than the nickel amount from each averaged orientation variant. Thus, the interface between two orientation variants is slightly higher in nickel content, with nickel occupying some of the lithium sites in the lithium layers. This buildup of Ni at the interface could be due to the higher diffusivity of nickel ions compared with lithium ions down the lithium layer, as reported by Gu et al [17]. Gu et al. also showed that

the energy barrier for diffusion of nickel ions between the metal layer and the lithium layer is much higher than that for lithium ions. Accordingly, when an orientation variant interface is present, the nickel ions will have a larger energy barrier to diffuse across the barrier than lithium ions. This results in a pileup of nickel ions at the interface between orientation variants.

It should be noted that this buildup of nickel ions likely forms during or after ordering. Nickel build up at the orientation variant boundaries would require long-range diffusion and, orientation variant formation is diffusionless on a macroscale [9]. Therefore, the buildup most likely occurs after the orientation variants form. Since the nickel ions diffuse faster, the buildup could have occurred during cooling, while resting at room temperature after cooling, or by the STEM probe during analysis. Great care was taken to not damage the sample, and while nickel diffusion was not directly observed during the STEM imaging, it cannot be ruled out entirely yet.

If the buildup of nickel at the orientation variant boundaries is present during cycling, it will slow lithium diffusion and, therefore, have an impact on the rate capability of the material. Fig. 8 shows the rate capabilities of LiCoO_2 and $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$. Here we can see that LiCoO_2 , which does not exhibit orientation variants, has a better rate capability, while changing the cations to Mn and Ni causes a drop in capacity retention at higher charge rates. This suggests that the nickel buildup was formed during material synthesis. Given this insight, we propose a new explanation for the poor rate capability of the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series.

While it is reported that Ni present in the Li layer of the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series will slow Li diffusion, with only about 8% Ni in the Li layer of $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$ [3], it would not be expected to have such a significant impact on capacity retention with a random distribution. Gu et al. suggested that nickel buildup at the surface limits the charge rate [17]. While this buildup will impact the rate capability, it can be seen in Gu et al.'s work that the

buildup is not continuous over the entire surface. In fact, a large amount of surface appears to not exhibit nickel buildup[17]. Therefore, a large amount of surface will still be available for delithiation/lithiation. Furthermore, we find that Ni build up at the surface depends on the synthesis route and does not always occur (Fig. 9). We show here that the nickel buildup occurs in thin strips throughout the particles, which is consistent with the EDS maps shown by Gu et al.[17]. We, therefore, propose that the poor rate capability of nickel-containing layered oxides is largely the result of nickel-rich boundaries throughout the particles, which form as a result of orientation variants, not solely the result of nickel ions in the lithium layer or a buildup of nickel at the surface.

We must also consider the effects of orientation variants on the capacity retention of the battery during repeated cycling, which has been shown to be problematic in layered oxides[18]. Explanations of the capacity retention have all been based on the assumption that the lithium layer is continuous across the entire particles in these materials. However, the influence of multidomain orientation variants on capacity decay must also be considered. Low symmetry materials are known to have anisotropic thermal expansion, which will introduce strain in the orientation variants upon heating and cooling[19]. Therefore, if there are temperature fluctuations during cycling, the built-up strains could contribute to a degradation in voltage. Future work could focus on making materials of identical composition with and without orientation variants to understand how multidomain orientation variants will impact the voltage retention over multiple cycles.

To improve the rate capability of the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series and better understand the role of multidomains on capacity fade, future work could focus on reducing the formation of orientation variants during synthesis. Altering the synthesis thermal treatment has

been shown to reduce amount of the orientation variants along the c axis [12,20]. Thus, certain thermal heat treatments during synthesis may help alleviate orientation variants and improve rate capabilities.

3. Conclusions

We have shown that particles within the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series form four orientation variants in which the cation layers order along different $\{111\}_{\text{NaCl}}$ planes due to the disorder-to-order phase transition. These orientation variants are only formed in layered oxides containing nickel. As a result, particles in the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series are likely to provide a pseudo-3D path for lithium diffusion. However, the overall lithium diffusion is inhibited due to a buildup of Ni at the interface between orientation variants. These orientation variants must be removed, most likely through thermal heat treatments, in order to improve the rate capability of the $\text{Li}[\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{Ni}_x]\text{O}_2$ ($0 < x \leq 1/2$) series.

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Fig. 1. SAED patterns from single particles of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ viewed down the $\{\bar{2}11\}_{\text{NaCl}}$ zone axis heat treated at (a) 850 °C for 24 h, (b) 900 °C for 24 h, (c) 900 °C for 6 h, and (d) 900 °C for 72 h showing the cation layers ordering on different $\{111\}_{\text{NaCl}}$ planes in a single particle. (7) The phases are all monoclinic.

Fig. 2. STEM images of $\text{Li}[\text{Li}_{0.067}\text{Mn}_{0.533}\text{Ni}_{0.4}]\text{O}_2$ viewed down the $\{\bar{2}11\}_{\text{NaCl}}$ zone axis, showing the interface between two areas with the cation layers ordered on different $\{111\}_{\text{NaCl}}$ planes as indicated. The dark-grey circles outlined in white are transition metals, the light-green circles are lithium and the dark circles outlined in light-green are a mixture of transition metals and lithium.

Fig. 3. XRD patterns of the $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, Li_2MnO_3 , and LiCoO_2 powders before heat treatment.

Fig. 4. Schematic of LiMO_2 showing the result of 4^+ rotations about a $[841]_{\text{T}}$ axis starting on the (a) $[210]_{\text{T}}$ zone axis and transitioning to the (b) $[810]_{\text{T}}$, (c) $[211]_{\text{T}}$, and (d) $[8\bar{2}1]_{\text{T}}$ zone axes. The large dark-grey atoms are transition metals and the small light-green atoms are lithium.

Fig. 5. Schematic of Li_2MnO_3 showing the result of 4^+ rotations about a $[10\bar{1}]_{\text{M}}$ axis transition starting on the (a) $[100]_{\text{M}}$ zone axis and transitioning to the (b) $[3\bar{2}\bar{3}]_{\text{M}}$, (c) $[001]_{\text{M}}$, and (d) $[\bar{3}\bar{2}3]_{\text{M}}$ zone axes. The larger dark-purple atoms are manganese and the small light-green atoms are lithium.

Fig. 6. HAADF-STEM images of (a) LiCoO_2 and (b) Li_2MnO_3 and corresponding SAED patterns. The inset images show the structures at higher magnification.

Fig. 7. HAADF-STEM image of a particle of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ showing the interface between two orientation variants, $(111)_{\text{NaCl}}$ and $(1\bar{1}1)_{\text{NaCl}}$ and the corresponding EDS spectra normalized to the Mn K- α peak. The solid black spectrum is the average of 36 points from two orientation variants and the dotted grey spectrum is the average of 36 points on two different orientation variant interfaces.

Fig. 8. Rate capability and cyclability of LiCoO_2 and $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$ with upper cut-off voltages of 4.5 and 4.8 V.

Fig. 9. EDS data of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.2}]\text{O}_2$ heated at (a) 900°C for 24 h and (b) 850°C for 5 h averaged over 25 different particles from both the centers of the particles and the surfaces of the particles.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9