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Microstructural Changes in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Positive Electrode Material during the First Cycle

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The microstructure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ positive electrode material before and after the first cycle was investigated by scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). STEM and EELS analysis shows that, before cycling, there are very thin layers of material at grain boundaries that contain a small amount of transition metal ions (particularly Ni) on Li sites. After the first cycle, the thickness of some grain boundary layers increases significantly, accompanied by formation of microcracks at grain boundaries. Also, from the grain interior to the grain boundary, the structure gradually changes from an ordered layer structure ($\alpha\text{-NaFeO}_2$ -type) to a partially ordered structure and then to a disordered rock-salt structure. We posit that these microstructural changes are primarily responsible for the irreversible capacity during the first cycle.

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Many lithium transition-metal oxides have been observed to exhibit reversible lithium extraction/insertion reactions without destruction of their “core” structure; such topotactic reactions have been utilized in positive and/or negative electrodes for lithium-ion batteries.^{1–3} Of these oxides, LiNiO_2 -based materials are considered to be a promising positive electrode material because of their high specific capacity, lower cost, and lower toxicity compared to LiCoO_2 .^{4–7} Because both LiCoO_2 and $\alpha\text{-LiAlO}_2$ are isostructural with LiNiO_2 , cobalt and aluminum ions can be substituted for nickel to form solid solutions of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($0 < y < 1$)^{8–11} and $\text{LiNi}_{1-z}\text{Al}_z\text{O}_2$ ($0 < z \leq 1/2$),^{12,13} respectively. Codoping is also possible, with the optimum composition with respect to thermal or structural stability and electrochemical reactivity in lithium cells reported to be $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.^{14–17} In electrochemically overlithiated or delithiated states, which correspond to the discharged and charged states, respectively, in lithium transition-metal oxide phases are not thermodynamically stable. This is one of the main reasons for deterioration of lithium-ion batteries, resulting in poor cyclability and low rate capability after long-term cycling, especially at elevated temperatures.^{18–25}

Abraham et al.²⁰ identified a less than 5-nm thick NiO-type layer with the rock-salt-type structure on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles after the cell formation cycles. They reported that the thickness of this surface layer increased to 30–40 nm after cycling at 60°C for 8 weeks. This was accompanied by a 43% power fade, which they attributed to the growth of the surface layer. Recently, Sasaki et al.²⁶ and Muto et al.²⁷ systematically studied the capacity fade of Li-ion batteries using $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ as the positive electrode. They found inactive divalent and trivalent Ni ions formed after long-term cycling and produced a spatial-distribution map of a NiO-type phase located near grain surfaces and grain boundaries. They concluded that the capacity fade is mainly caused by the formation of the inactive Ni ions, presumably accompanied by oxygen loss in the active materials at high temperature. However, most of the above results were obtained from long-term cycling tests at elevated temperatures, and the atomic scale microstructural changes during the first cycle at room temperature were not examined. To better understand this so-called irreversible capacity phenomenon,^{18,20,28–32} it is important to study the microstructural changes after the first cycle.

As it has been demonstrated previously that the microstructural changes initiate locally,^{20,27} an analytical method that can supply information with a high spatial resolution is necessary for this task.

Compared to conventional analytical approaches, such as x-ray absorption spectroscopy (XAS), x-ray diffraction (XRD), and conventional transmission electron microscopy, scanning transmission electron microscopy (STEM) not only has the advantage of high spatial resolution but can also be used to identify atomic species and their positions directly,³³ which is useful for observing order–disorder transitions of metal ions in LiNiO_2 -based materials. In this study, we use scanning electron microscopy (SEM), STEM, and electron energy loss spectroscopy (EELS) to examine microstructural changes in the positive cathode material $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder was prepared by a coprecipitation method and will be referred to as the “original” $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ hereafter. The powder was characterized with an x-ray diffractometer (RINT2200, Rigaku, Corp., Japan) using $\text{Cu K}\alpha$ radiation, equipped with a graphite monochromator to suppress background radiation. A positive electrode was prepared by casting black viscous slurry, which consisted of 85 wt % $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, 10 wt % carbon black, and 5 wt % polyvinylidene fluoride (PVdF) binder dissolved in N-methyl-2-pyrrolidone, onto an aluminum current collector with a blade. This painted sheet was dried at 120°C for 12 h under vacuum and pressed to form a dense electrode. A negative electrode was prepared by pressing a lithium metal sheet onto a stainless steel plate. A sandwich-type cell body consisting of the positive and negative electrodes separated by two sheets of polypropylene microporous membrane was immersed in 1 M LiPF_6 ethylene carbonate (EC)/diethyl carbonate (DEC) (3/7 v/v) electrolyte. This cell, referred to hereafter as cell 1, was used to characterize the electrochemical performance of the positive electrode material in terms of voltage profiles. Cell 1 was operated at 20°C within a voltage window of 2.5–4.2 V at a constant current of 0.1 mA/cm², which corresponds to a C/10 rate based on 175 mAh/g of capacity.

In order to examine the microstructural changes occurring in the positive electrode, another cell was also prepared, which we refer to as cell 2. In this cell, the positive electrode was formed by pressing $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder into a pellet without addition of carbon or binder; the materials used for the negative electrode and electrolyte were the same as cell 1. After a single charge–discharge cycle between voltages of 2.5 and 4.2 V at a constant current of 0.2 mA/cm², which corresponds to a C/50 rate based on 175 mAh/g of capacity, the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pellet was taken out of the cell in an Ar-filled glove box and then immersed in a DEC solution

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to remove the LiPF_6 salt. The sample obtained in this way will be called the “single-cycled” $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ hereafter.

To investigate the effect of the first cycle on the microstructure of the positive electrode, both the original and the single-cycled $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ were studied by SEM, STEM, and EELS. SEM observation was performed on a high-resolution Hitachi SU-8000 scanning electron microscope with a field emission electron source. Transmission electron microscopy specimens were prepared by epoxy embedding, followed by mechanical grinding and ion milling (Gatan 691, operated at 3–1 kV and cooled with nitrogen liquid). STEM observation was performed on a Cs-corrected JEM-2100F transmission electron microscope equipped with a Gatan image filter for EELS analysis.

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ has an ordered layer structure ($\alpha\text{-NaFeO}_2$ -type), in which Li ions and transition metal ions occupy alternating cation layers parallel to (0001). In the $[11\bar{2}0]$ direction, Li layers and transition metal layers can be distinguished easily in a STEM image. Consequently, in this study, all the high resolution STEM images were acquired with $[11\bar{2}0]$ as the zone axis.

Results and Discussion

Materials characterization.—The morphology of the original $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles was studied by SEM. As shown in Fig. 1, the original sample comprises large particles about 10 μm in diameter with a narrow size distribution. These particles are agglomerates of small grains about 1 μm in diameter. The original $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles exhibit the typical morphology of LiNiO_2 -based particles prepared by the coprecipitation method.

Figure 2 shows the XRD pattern of the original $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder, which can be indexed as an $\alpha\text{-NaFeO}_2$ -type structure belonging to space group $R\bar{3}m$. The lattice parameters of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ were calculated to be $a = 2.864$ Å and $c = 14.171$ Å in the hexagonal setting.

Generally, the integrated intensity ratio of (003) to (104), i.e., $I_{(003)}/I_{(104)}$, is used as a simple criterion to estimate the amount of contamination by rock-salt domains in the bulk rhombohedral phase, which can tell us whether the samples are battery-active or not.⁸ According to Ohzuku et al.,⁸ the presence of rock-salt structured domains, in which Ni and Li ions randomly occupy the octahedral sites, weakens the integrated intensity of the (003) peak indexed to the rhombohedral LiNiO_2 structure, while the integrated intensity of the (104) peak remains unchanged. When the integrated intensity ratio $I_{(003)}/I_{(104)}$ is less than 1.2, the (108) and (110) peaks become indistinguishable and the capacity is decreased; together these two

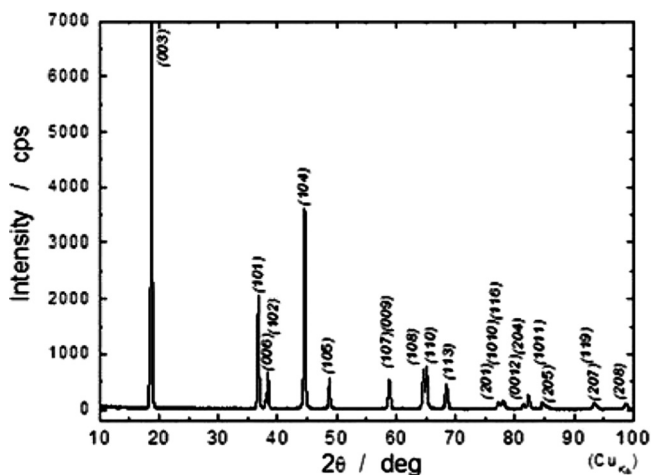


Figure 2. XRD pattern of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder. The lattice parameters are $a = 2.864$ Å and $c = 14.171$ Å in the hexagonal setting of space group $R\bar{3}m$.

observations can be used to determine the degree of contamination by the rock-salt domains.⁸ In our case, the $I_{(003)}/I_{(104)}$ ratio is 1.36, and (108) and (110) peaks show a clear split, indicating that the original $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder does not contain an appreciable amount of rock-salt domains in the bulk phase.

Figure 3 shows the voltage profile of cell 1. The open-circuit voltage of the freshly fabricated cell was about 3.2 V. When a constant current of 0.1 mA/cm² was applied, the voltage rapidly rose to 3.6 V, increasing to 4.2 V at the end of charging. Based on the weight of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ used to form the electrode, the first-charge capacity was 203 mAh/g, and the first-discharge capacity was 178 mAh/g. This corresponds to an irreversible capacity loss of 25 mAh/g during the first cycle, which is typical of Li cells using an LiNiO_2 -based positive electrode.^{18,28–32} The cell showed a good reversible capacity of about 175 mAh/g in subsequent cycles.

The SEM, XRD, and charge–discharge cycling tests indicate that the original $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder was high purity, exhibiting suitable electrochemical performance for use as an electrode material. An electrode made from this material should thus be a good specimen for observing the microstructural changes that occur during the first cycle of a lithium-ion battery.

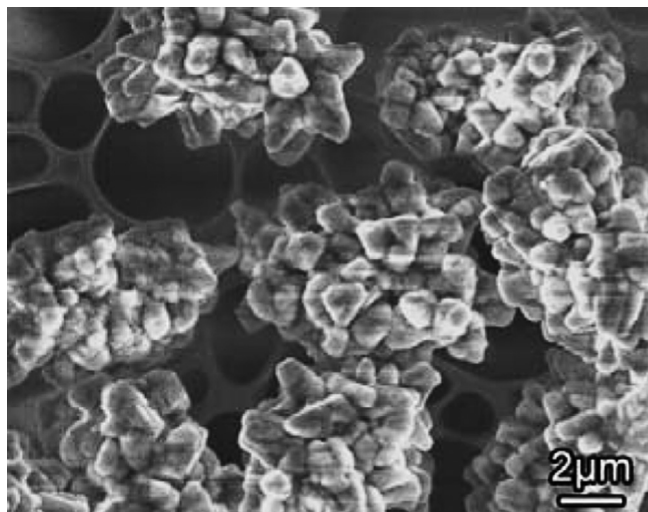


Figure 1. SEM micrograph showing the typical morphology of particles in the original powder.

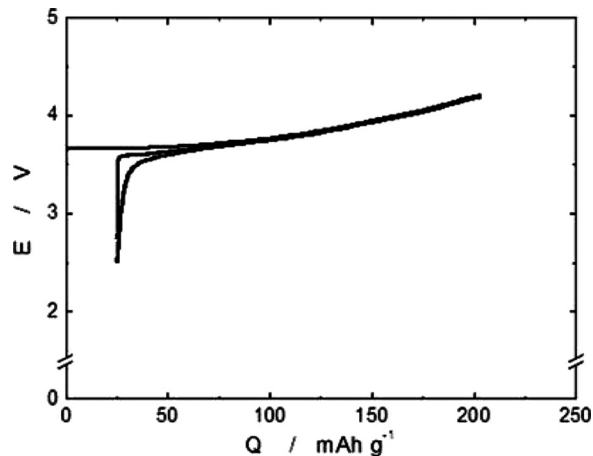


Figure 3. Voltage profile for cell 1 operated at a C/10 rate over a voltage window of 2.5–4.2 V at 20°C. The positive electrode was a mixture of 85 wt % $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, 10 wt % carbon black, and 5 wt % PVdF binder, and 1 M LiPF_6 dissolved in EC/DEC (3/7 v/v) was used as the electrolyte.

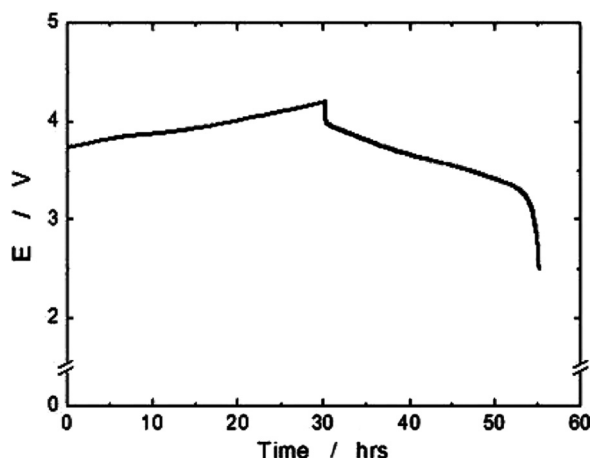


Figure 4. Voltage profile for cell 2 operated at a C/50 rate over a voltage window of 2.5–4.2 V at 20°C. The positive electrode consisted of pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder, and 1 M LiPF_6 dissolved in EC/DEC (3/7 v/v) was used as the electrolyte.

Preparation of the single-cycled $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.—As mentioned above, cell 2 was prepared using pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder. The cell was operated within a voltage window of 2.5–4.2 V at 0.2 mA/cm^2 , as shown in Fig. 4. The charge current was applied to the cell for 30 h until a voltage of 4.2 V was reached; the battery was then discharged at constant current for 25 h until the voltage dropped to 2.5 V, which corresponds to charge and discharge capacities of 110 and 90 mAh/g , respectively. A voltage drop occurred upon switching from a charge current to discharge current because the positive electrode did not contain carbon or binder. Charge and discharge capacities of the pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (cell 2) are limited in comparison to the positive electrode with carbon and binder (cell 1) because of the large polarization of cell 2. In this case, the capacity loss during the first cycle was 20 mAh/g , which is reasonable and can be attributed to the positive electrode itself. The single-cycled $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was subsequently removed from the battery as described above for further detailed characterization.

Morphological changes during the first cycle.—Using low magnification STEM imaging with a detection angle of 52–140 mrad, microstructural changes near grain boundaries were studied. We define a grain boundary layer as a layer along a grain boundary, which deviates structurally from the ordered layer structure of the grain interior. Figure 5a shows a typical STEM image of grain boundaries in the original sample. The grain boundaries have thin grain boundary layers, producing bright contrast (indicated by arrows in Fig. 5a). After the first cycle, the thickness of some grain boundary layers, indicated by arrows in Fig. 5b, increased drastically. Some microcracks also appear at triple junctions and grain boundaries. The thicker grain boundary layers and microcracks are more common in the case of regions near the surfaces of large agglomerates in the single-cycled sample.

Grain boundary layers in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder particles.—In order to analyze the microstructure with atomic detail, high resolution STEM was performed. Figure 6a shows a STEM image of a typical grain boundary in the original sample using a detection angle of 52–140 mrad. The grain boundary layer shows a stronger bright contrast. Figure 6b shows a magnified portion of Fig. 6a. Two Li layers marked with two single-headed arrows in the grain boundary layer show a stronger contrast than the Li layers marked with two double-headed arrows far from the boundary. The region marked with double-headed arrows, where Li layers are invisible due to their low atomic weight, has an ordered layer structure. However, the transition metal layers next to the Li layers marked with single-headed arrows also show a stronger contrast than that in the region marked with double-headed arrows.

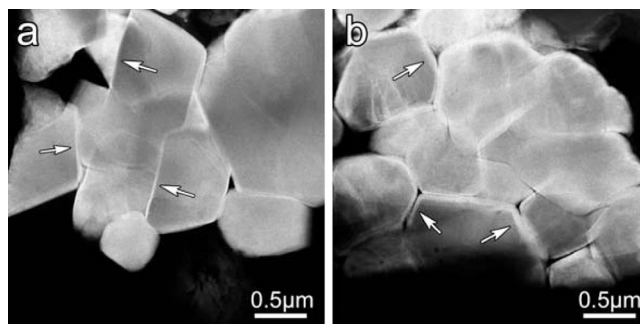


Figure 5. STEM images taken with a detection angle of 52–140 mrad showing the microstructure of (a) the original sample and (b) the single-cycled sample. The thickness of the grain boundary layers (white contrast indicated by arrows) increased dramatically after the first cycle.

Figure 6c is a STEM image of the same grain boundary taken using a detection angle of 92–228 mrad. In this image, although all the transition metal layers show similar contrast, the Li layers marked with single-headed arrows still show stronger contrast than those marked with double-headed arrows.

At low detection angles, the contrast of a STEM image is sensitive to both strain and atomic number, while at high detection angles it mainly depends on atomic number.³⁴ In our case, because all the transition metal layers show similar contrast in Fig. 6c, their elemental composition can be concluded to be essentially constant. On the other hand, the contrast of Li layers increases gradually from the grain interior to the grain boundary. The stronger contrast of some of the Li layers in Fig. 6c indicates the presence of heavier elements, namely extra transition metal ions, on Li sites; the larger Ni ions will also induce strain in the grain boundary layer. The stronger contrast of the grain boundary layer in Fig. 6a can thus be attributed to both strain and the presence of some transition metal ions on Li sites. This is not surprising, given the propensity for Ni to occupy Li sites if synthesis conditions are not carefully controlled.³⁵

According to the definition of grain boundary layers given earlier, the width of the grain boundary layer (from the Li layer showing obvious contrast caused by transition metal ions to the grain boundary) is about 5 nm. In the grain boundary layer, the strongest contrast of Li layers is still weaker than the contrast of transition metal layers. Thus, in the grain boundary layers of the original sample, only a small amount of extra transition metal ions are present in

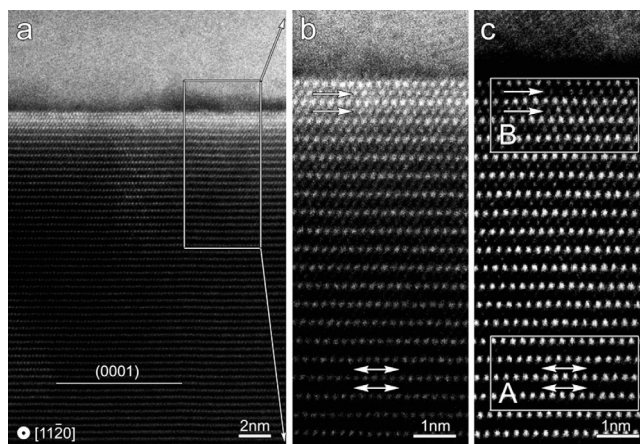


Figure 6. (a) STEM image taken with a detection angle of 52–140 mrad showing a typical grain boundary in the original sample; (b) a magnified image of the framed region in (a); (c) STEM image of the same grain boundary as in (a) taken with a detection angle of 92–228 mrad. In (b) and (c), two Li layers each in the grain interior and grain boundary layer are indicated with double-headed arrows and single-headed arrows, respectively.

Li layers. In order to verify these compositional and structural differences, EELS spectra were obtained for regions A and B in Fig. 6c. The results are discussed below.

Microstructural changes at the grain boundary layer during the first cycle.—For comparison, high resolution STEM was also performed on the single-cycled sample. Figure 7a shows a STEM image of typical grain boundaries in this sample using a detection angle of 52–140 mrad. The grain boundary layers showing a strong white contrast are about 25 nm in thickness, which is much larger compared to those in the original powder. At the grain boundaries, the dark regions correspond to microcracks.

Figure 7b is a STEM image of the region in Fig. 7a bounded by the white frame, taken with a detection angle of 52–140 mrad. Figures 7A1–7C1 are high resolution STEM images using a detection angle of 92–228 mrad acquired from regions A–C in Fig. 7b, respectively, and Figs. 7A2–7C2 are the corresponding microdiffraction patterns. From the grain interior (Fig. 7A1) to the boundary (Fig. 7C1), the contrast of the Li layers increases steadily, and the corresponding diffraction spots marked with arrows in Figs. 7A2–7C2 become weaker, until the contrast of the Li layers is the same as the transition metal layers in Fig. 7C1, and the corresponding diffraction spots are completely absent in Fig. 7C2. The diffraction pattern of Fig. 7C2 can be indexed using the [110] zone axis of the rock-salt structure, indicating that, near the boundary, the Li ions and transition metal ions are randomly distributed over the cation sites. Between the ordered layer structure in the grain interior and the disordered rock-salt structure near the boundary, there is a partially ordered structure in a transitional region, represented by Fig. 7B1. In this region, the structure consists of alternating transition metal-rich and Li-rich layers. The structure gradually changes from the ordered layer structure to the partially ordered structure and to the disordered rock-salt structure with increasing extra transition metal ions on Li ion sites from the grain interior to the grain boundary.

In order to show the change in structure more clearly, profiles of image intensity ratio of Li layers to neighboring transition metal layers are plotted in Fig. 8. The image intensity ratio is related to the ratio of transition metal ions in the Li layers to those in the transition metal layer and thus reveals the overall change in distribution of

transition metals across the grain. The profiles for the original and the single-cycled samples correspond to grain boundary layers shown in Figs. 6a and 7b, respectively. In the profile of the single-cycled sample, three sections, corresponding to the ordered layered structure, the partially ordered structure, and the disordered rock-salt structure, are apparent. The region with a disordered rock-salt structure is about 5 nm in width, while the transition region with a partially ordered structure is about 20 nm in width. During the first cycle, a substantial volume of material with the transitional structure forms near the grain boundary. The profile from the original sample corresponds to the middle section of the profile of the single-cycled sample, but with a lower intensity ratio of 0.6. Thus, during the first cycle, the region with a partially ordered structure expands significantly, and a disordered rock-salt structure forms at the boundary.

EELS analysis.—Results from EELS analysis are consistent with the structural changes described in the previous section. Figures 9a–9c show EELS profiles of O-K, Co- $L_{2,3}$, and Ni- $L_{2,3}$ edges, respectively, acquired at regions A and B in the original sample (Fig. 6c), while Figs. 9d–9f show the corresponding EELS profiles acquired at regions A, B, and C in the single-cycled sample (Fig. 7b). In Figs. 9d–9f, compared with that in region A, the first peak of the O-K edge in region C becomes weaker and shifts to a higher energy, while Co- $L_{2,3}$ and Ni- $L_{2,3}$ edges shift to lower energies. These changes are consistent with the presence of inactive divalent cations in the Li layers, as well as a structural change from an ordered layer structure to a disordered rock-salt structure.^{20,36,37} In region B of the single-cycled sample, which corresponds to the partially ordered structure, the intensity change and energy shift of the first peak of the O-K edge and energy shift of Co- $L_{2,3}$ and Ni- $L_{2,3}$ edges are halfway between those of the ordered layer structure and the disordered rock-salt structure. This suggests that EELS profiles also change continuously as the number of extra transition metal ions occupying Li sites increases gradually.

Because the amount of extra transition metal ions on Li sites is small in the grain boundary layer of the original sample, which corresponds to the initial state before the structural changes due to cycling occur, EELS profiles from the grain boundary layer show only small differences compared to that of the ordered layer structure. As shown

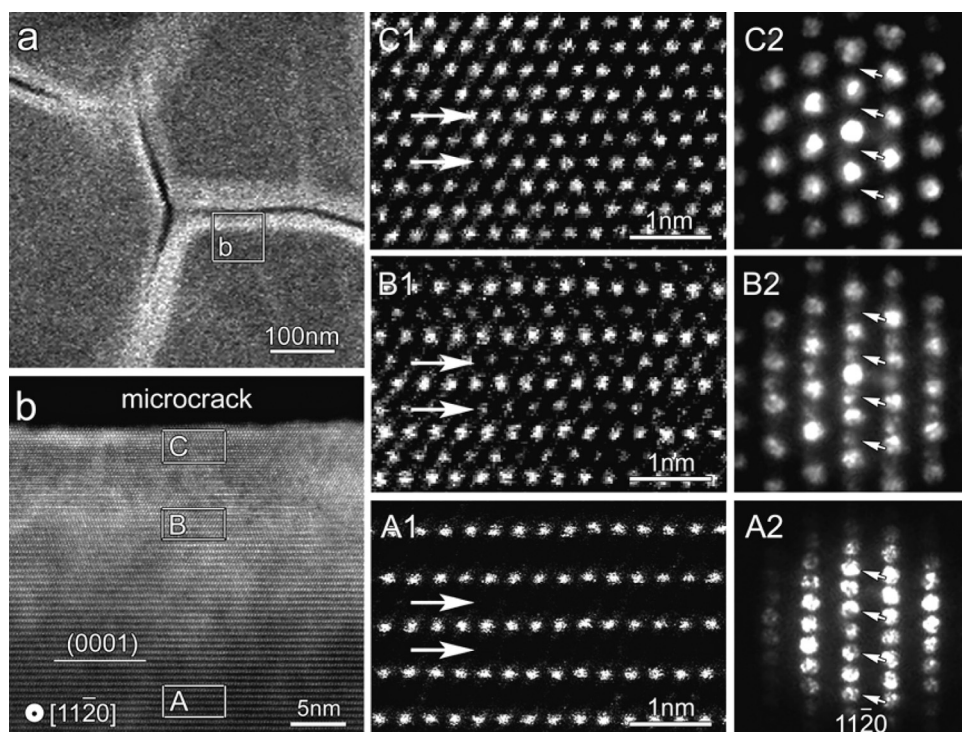


Figure 7. (a) STEM image taken with a detection angle of 52–140 mrad showing typical grain boundaries in the single-cycled sample, in which grain boundary layers show strong white contrast; (b) a high magnification STEM image taken with a detection angle of 52–140 mrad corresponding to the framed region in (a); (A1)–(C1) STEM images (detection angle 92–228 mrad) acquired from regions A–C in (b), respectively, in which two Li layers are marked with arrows; (A2)–(C2) microdiffraction patterns corresponding to STEM images (A1)–(C1), respectively.

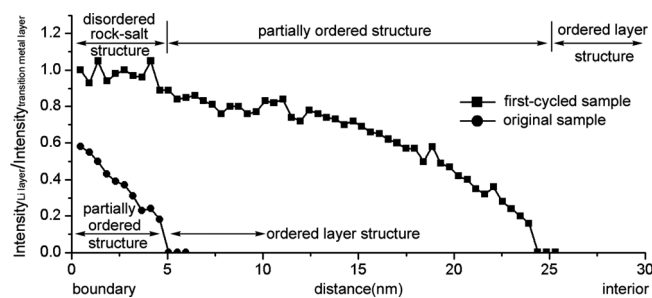


Figure 8. Image intensity ratios of Li layers to neighboring transition metal layers showing the increase in transition metal ion concentration on the Li sites. The ratios were measured for the original and the single-cycled samples from Figs. 6 and 7b, respectively.

in Figs. 9a–9c, relative to region A, in region B of the original sample, the first peak of the O-K edge becomes weaker, with a small energy shift, while the Co- $L_{2,3}$ edge does not show any obvious change, and the Ni- $L_{2,3}$ edge only shows a slight energy shift.

Further, it is found that Ni ions and Co ions behave differently. In Figs. 9e and 9f, in contrast to the obvious energy shift of the Ni- L_2 edge in both regions B and C, the Co- L_2 edge shows no distinct energy shift; while the Ni- L_3 edge in region B is close to that in region C, the Co- L_3 edge in region B is close to that in region A. The different behavior of Ni and Co ions indicates that Co^{3+} is much more stable than Ni^{3+} on the 3a site of the ordered layer structure, which is consistent with previously reported XAS analyses.^{25,38}

Lack of dependence of structural changes on grain boundary orientation.—The $\alpha\text{-NaFeO}_2$ -type structure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ allows two-dimensional lithium-ion conduction parallel to the

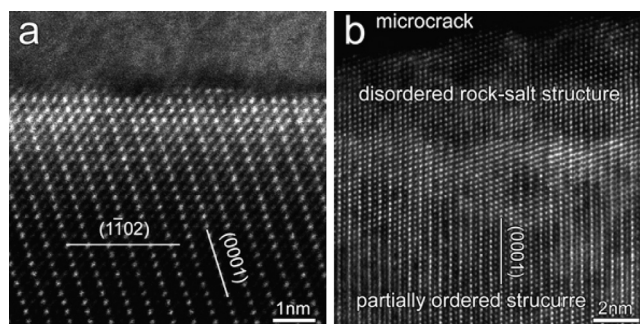


Figure 10. (a) A STEM image showing a $(1\bar{1}02)$ -terminated grain boundary layer in the original sample; (b) a STEM image showing a typical grain boundary layer in the single-cycled sample.

(0001) plane. However, the grain boundary layers in the original sample and the structural changes during cycling do not depend on the grain boundary orientation or its relation to the (0001) plane. As shown in Fig. 5a, in the original sample, the grain boundary layer thickness is similar, regardless of the degree of grain boundary misorientation or the nature of the boundary plane. Similar observations are made for the single-cycled sample from the micrographs in Figs. 5b and 7a.

In order to demonstrate this more clearly, high resolution STEM images of two grain boundary layers with different crystal orientations from that in Figs. 6 and 7b are shown in Fig. 10. Figure 10a shows a grain boundary layer terminated by a $(1\bar{1}02)$ plane in the original sample. Although the angle between the terminating plane and (0001) plane is about 70° , the grain boundary layer shows the same characteristic structure as the (0001) terminated grain boundary layer shown in Fig. 6. Similarly, in Fig. 10b, the grain

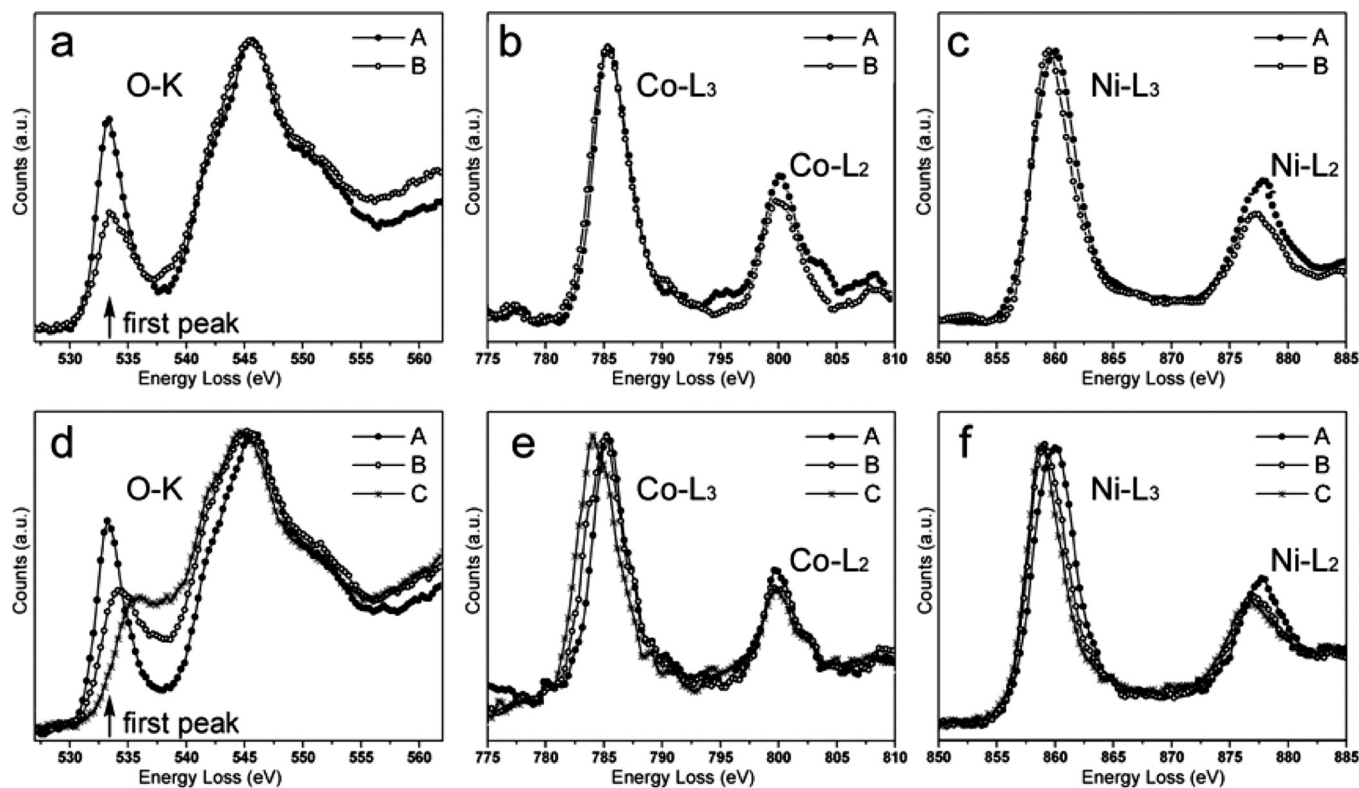


Figure 9. EELS profiles of (a) O-K, (b) Co- $L_{2,3}$, and (c) Ni- $L_{2,3}$ edges for the original sample taken from regions A and B in Fig. 6; EELS profiles of (d) O-K, (e) Co- $L_{2,3}$, and (f) Ni- $L_{2,3}$ edges corresponding to regions A, B, and C in the single-cycled sample shown in Fig. 7b.

boundary layer in the single-cycled sample with an arbitrary terminating plane, which lies at about 80° relative to the (0001) plane, also shows the same structural changes as the (0001)-terminated grain boundary layer shown in Fig. 7b.

Structural changes in LiNiO_2 -based materials.—The structure of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ solid solutions depends on the value of x .^{39,40} For $x \leq 0.3$, Li and Ni ions randomly occupy octahedral sites in the O close-packed rock-salt structure; for $x > 0.3$, Li and Ni ions begin to separate into alternating (111) planes of the rock-salt structure and form a partially ordered structure; for $x \sim 0.5$, Li and Ni ions form an ordered layer structure (α - NaFeO_2 -type).

Similarly, the Li content also affects the structure of doped LiNiO_2 materials. An NiO -type (rock-salt structure) phase has been observed in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ positive electrode materials.^{20,26,27,37} In this study, not only the disordered rock-salt structure but also the partially ordered structure was identified by STEM and EELS. As seen in Fig. 8, while the concentration of transition metal ions on Li sites increases gradually from the grain interior to the grain boundary, the structure changes from an ordered layer structure to a partially ordered structure and then to a disordered structure in a continuous fashion, while the Li content also decreases gradually. For the composition $\text{Li}_x\text{M}_{1-x}\text{O}$ ($\text{M} = \text{Ni}, \text{Co}$, and/or Al), the disordered structure region is likely to have a Li content of $x \sim 0.3$. Because the Li and transition metal ions are randomly distributed over cation sites, the image intensity ratio is about 1. In the partially ordered region, where $0.3 \lesssim x \lesssim 0.5$, the structure comprises alternating Li-rich and transition metal-rich layers, and the image intensity ratio is between 1 and 0. In the ordered region, x is about 0.5, and the image intensity ratio is close to 0.

It also can be deduced that the degradation of the positive electrode material initiates at the grain boundary. In the original sample, a small amount of transition metal ions, especially Ni ions, are present in the Li layers in the grain boundary layer. During charging, Li ions are extracted from the positive electrode, and presumably some transition metal ions migrate onto the vacant Li sites, accompanied by some release of O. Consequently, near these grain boundaries, the structure transforms to the disordered rock-salt structure, and the thickness of the corresponding grain boundary layers increases dramatically after cycling. Owing to the volume shrinkage caused by Li extraction, migration of transition metal ions and release of oxygen, microcracks form at some triple junctions and grain boundaries, and some agglomerates break up. During discharging, because of the presence of thick grain boundary layers, which do not exhibit a good ionic conductivity,³⁷ the Li ions are not easily inserted back into the positive electrode in this voltage range. Based on these results, the changes in microstructure are expected to occur in all LiNiO_2 -based positive electrode materials. We conclude that these changes are one of the main causes of the irreversible capacity in lithium-ion batteries during the first cycle.

Conclusions

Microstructural changes in the positive electrode material $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ during the first cycle were investigated by STEM and EELS. It was found that microcracks formed at some grain boundaries during the first cycle. Grains in the original sample contain very thin grain boundary layers with a partially ordered crystal structure, where a small amount of transition metal ions, especially Ni ions, are present on Li sites. After the first cycle, the thickness of some grain boundary layers increased dramatically. STEM and EELS analysis revealed a continuous change from the layered structure in the grain interior, to a partially ordered structure, and then to the disordered rock-salt structure adjacent to the boundary in the single-cycled sample. The irreversible capacity during the first cycle may be attributed to these microstructure changes.

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1. T. Ohzuku and A. Ueda, *Solid State Ionics*, **69**, 201 (1994).
2. M. S. Whittingham, *Chem. Rev.*, **104**, 4271 (2004).
3. B. L. Ellis, K. T. Lee, and L. F. Nazar, *Chem. Mater.*, **22**, 691 (2010).
4. J. R. Dahn, U. V. Sacken, M. W. Juzkow, and H. Al-Janaby, *J. Electrochem. Soc.*, **138**, 2207 (1991).
5. T. Ohzuku, A. Ueda, and M. Nagayama, *J. Electrochem. Soc.*, **140**, 1862 (1993).
6. M. Broussely, F. Pertion, P. Biensan, J. M. Bodet, J. Labat, A. Lecerf, C. Delmas, A. Rougier, and J. P. Peres, *J. Power Sources*, **54**, 109 (1995).
7. C. Delmas, M. Menetrier, L. Croguennec, I. Saadoun, A. Rougier, C. Poullierie, G. Prado, M. Grune, and L. Fournes, *Electrochim. Acta*, **45**, 243 (1999).
8. T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, and H. Komori, *Electrochim. Acta*, **38**, 1159 (1993).
9. C. Delmas, I. Saadoun, and A. Rougier, *J. Power Sources*, **44**, 595 (1993).
10. A. Ueda and T. Ohzuku, *J. Electrochem. Soc.*, **141**, 2010 (1994).
11. A. Rougier, I. Saadoun, P. Graveriau, P. Willmann, and C. Delmas, *Solid State Ionics*, **90**, 83 (1996).
12. T. Ohzuku, A. Ueda, and M. Kouguchi, *J. Electrochem. Soc.*, **142**, 4033 (1995).
13. M. Guilmard, C. Poullierie, L. Croguennec, and C. Delmas, *Solid State Ionics*, **160**, 39 (2003).
14. J. Shim, R. Kostecki, T. Richardson, X. Song, and K. A. Striebel, *J. Power Sources*, **112**, 222 (2002).
15. C. H. Chen, J. Liu, M. E. Stoll, G. Henriksen, D. R. Vissers, and K. Amine, *J. Power Sources*, **128**, 278 (2004).
16. C. J. Han, J. H. Yoon, W. I. Cho, and H. Jang, *J. Power Sources*, **136**, 132 (2004).
17. I. Bloom, S. A. Jones, V. S. Battaglia, G. L. Henriksen, J. P. Christophersen, R. B. Wright, C. D. Ho, J. R. Belt, and C. G. Motloch, *J. Power Sources*, **124**, 538 (2003).
18. D. P. Abraham, E. M. Reynolds, E. Sammann, A. N. Jansen, and D. W. Dees, *Electrochim. Acta*, **51**, 502 (2005).
19. Y. Ito and Y. Ukyo, *J. Power Sources*, **146**, 39 (2005).
20. D. P. Abraham, R. D. Twisten, M. Balasubramanian, J. Kropf, D. Fischer, J. McBreen, I. Petrov, and K. Amine, *J. Electrochem. Soc.*, **150**, A1450 (2003).
21. K. Nikolowski, N. N. Bramnik, C. Baecht, H. Ehrenberg, and H. Fuess, *J. Power Sources*, **174**, 818 (2007).
22. T. Nonaka, C. Okuda, Y. Seno, K. Koumoto, and Y. Ukyo, *Ceram. Int.*, **34**, 859 (2008).
23. W. S. Yoon, K. Y. Chunga, J. McBreen, D. A. Fischer, and X. Q. Yang, *J. Power Sources*, **174**, 1015 (2007).
24. Y. C. Zhang and C. Y. Wang, *J. Electrochem. Soc.*, **156**, A527 (2009).
25. T. Nonaka, C. Okuda, Y. Seno, H. Nakano, K. Koumoto, and Y. Ukyo, *J. Power Sources*, **162**, 1329 (2006).
26. T. Sasaki, T. Nonaka, H. Oka, C. Okuda, Y. Ito, Y. Kondo, Y. Takeuchi, Y. Ukyo, K. Tatsumi, and S. Muto, *J. Electrochem. Soc.*, **156**, A289 (2009).
27. S. Muto, Y. Sasano, K. Tatsumi, T. Sasaki, K. Horibuchi, Y. Takeuchi, and Y. Ukyo, *J. Electrochem. Soc.*, **156**, A371 (2009).
28. J. P. Peres, C. Delmas, A. Rougier, M. Broussely, F. Pertion, P. Biensan, and P. Willmann, *J. Phys. Chem. Solids*, **57**, 1057 (1996).
29. K. Dokko, M. Nishizawa, S. Horikoshi, T. Itoh, M. Mohamedi, and I. Uchida, *Electrochem. Solid-State Lett.*, **3**, 125 (2000).
30. K. K. Lee and K. B. Kim, *J. Electrochem. Soc.*, **147**, 1709 (2000).
31. J. R. Mueller-Neuhaus, R. A. Dunlap, and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 3598 (2000).
32. S.-H. Kang, W.-S. Yoon, K.-W. Nam, X.-Q. Yang, and D. P. Abraham, *J. Mater. Sci.*, **43**, 4701 (2008).
33. S. J. Pennycook, *Ultramicroscopy*, **30**, 58 (1989).
34. X. Wu, M. Robertson, J. Gupta, and J.-M. Baribeau, *Microsc. Microanal.*, **13**, 830 (2007).
35. C. Delmas, J. P. Peres, A. Rougier, A. Demourgues, F. Weill, A. Chadwick, M. Broussely, F. Pertion, P. Biensan, and P. Willmann, *J. Power Sources*, **68**, 120 (1997).
36. Y. Koyama, T. Mizoguchi, H. Ikeno, and I. Tanaka, *J. Phys. Chem. B*, **109**, 10749 (2005).
37. D. P. Abraham, R. D. Twisten, M. Balasubramanian, I. Petrov, J. McBreen, and K. Amine, *Electrochem. Commun.*, **4**, 620 (2002).
38. T. Nonaka, C. Okuda, Y. Seno, Y. Kondo, K. Koumoto, and Y. Ukyo, *J. Electrochem. Soc.*, **154**, A353 (2007).
39. J. B. Goodenough, D. G. Wickham, and W. J. Croft, *J. Phys. Chem. Solids*, **5**, 107 (1958).
40. J. B. Goodenough, D. G. Wickham, and W. J. Croft, *J. Appl. Phys.*, **29**, 382 (1958).