High-Rate Charging Induced Intermediate Phases and Structural Changes of Layer-Structured Cathode for Lithium-Ion Batteries

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Using fast time-resolved in situ X-ray diffraction, charge-rate dependent phase transition processes of layer structured cathode material LiNi\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} for lithium-ion batteries are studied. During first charge, intermediate phases emerge at high rates of 10C, 30C, and 60C, but not at low rates of 0.1C and 1C. These intermediate phases can be continuously observed during relaxation after the charging current is switched off. After half-way charging at high rate, sample studied by scanning transmission electron microscopy shows Li-rich and Li-poor phases' coexistence with tetrahedral occupation of Li in Li-poor phase. The high rate induced overpotential is thought to be the driving force for the formation of this intermediate Li-poor phase. The in situ quick X-ray absorption results show that the oxidation of Ni accelerates with increasing charging rate and the Ni\textsuperscript{4+} state can be reached at the end of charge with 30C rate. These results give new insights in the understanding of the layered cathodes during high-rate charging.

1. Introduction

In the efforts of expanding lithium-ion batteries from widely used in consumer electronics to large-scale applications such as electric vehicles, hybrid electrical vehicles, and clean energy storage, the rate capability and energy density are two very important issues. In order to improve the rate capability of the electrode materials in battery operation, practical approaches have been reported, such as using nanoparticle composed electrode materials and surface coatings to reduce ion diffusion length and increase electronic conductivity. Although relationships between the high-rate capabilities and nanometer-size effects as well as chemical compositions and structures of nanostructured materials have been studied, the fundamental understanding about the structural changes of the electrode materials during high rate cycling in real time is quite limited, partly due to experimental difficulties in ultrafast data collection requirement under operando conditions. Recently, metastable structures (a continuous solid solution phase, rather than the two-phase separation) in nanosized LiFePO\textsubscript{4} (LFP) electrodes were captured experimentally during high-rate cycling using synchrotron based time-resolved X-ray diffraction (XRD) techniques. The results were analyzed and interpreted as nonequilibrium state for LFP during fast delithiation process. It is very interesting to see that the phase transition behavior of the electrode materials at high rate cycling is quite different from that at the low rate, as reported earlier (see literature about the metastable transient crystal phase in Li\textsubscript{x}FePO\textsubscript{4} observed by time-resolved XRD). Furthermore, a new “lithium staging”

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structure of Li$_0.5$FePO$_4$ was observed by an aberration-corrected annular-bright-field scanning transmission electron microscopy (STEM) technique. Although this Li-staging phase was not observed in situ, and the cycling rate was not high, the direct observation of the existence of intermediate phase with atomic resolution is very important for understanding the complicated structural changes of cathode materials during cycling.

The advantage of XRD is the large penetration depth of the photon probe into the sample and the statistical reliability due to averaging over the whole sample area illuminated by X-rays. The disadvantage is the limitation on new phase identification caused by peak broadening, due to the short coherence length (crystal grain size, not particle size) and/or large distribution of atomic interlayer distances. Unfortunately, such short coherence length (as newly formed crystal) and lattice parameter distribution (newly formed crystal grains with varying lattice parameters) are very likely to occur during high rate cycling and XRD alone may not be able to give us a full picture. On the other hand, STEM is a great complementary technique to XRD. It is capable to catch new crystal structures even with very small quantity and very short coherence length with atomic resolution. The disadvantage of STEM is the lack of statistical reliability, since the sample area being probed is usually too small. Therefore, using the combination of XRD and STEM techniques will provide a more detailed full picture about the structural changes of the materials being studied. In addition, in situ quick X-ray absorption spectroscopy (Q-XAS) is another powerful technique for studying the high rate behavior of electrode materials. It has the capability to distinguish the charge compensation contribution by different transition metal ions in the electrode materials during high rate charge-discharge, reflected by their valence state and local environment changes, such as in local symmetry and coordination numbers.

Inspired by the interesting studies introduced above, we carried out a structural study using the in situ time-resolved XRD and Q-XAS, as well as ex situ STEM on a commercially important LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) cathode material during and after high rate cycling. The reason of selecting this particular NMC material is based on the importance of this material in today’s commercial Li-ion batteries (much more widely used than LFP) and the totally different crystal structure from LFP (layer structured for NMC vs olivine structured for LFP). In addition, NMC exhibits a more complex phase diagram with different phase transition pathways during charge and discharge, when compared with LFP. The particle size of the NMC samples in this study is in the micron range (particle size: 0.8–1.0 μm, Figure S1 (Supporting Information)), which is the optimized particle size in the commercial Li-ion batteries using NMC materials. As we know, the crystal structure of the layer structured cathodes such as LiCoO$_2$, LiNiO$_2$, LiNi$_{0.5}$Mn$_{0.5}$O$_2$, and LiNi$_{1.1}$Mn$_{1.1}$Co$_{1.1}$O$_2$ generally undertake a “solid solution – two-phase reaction – solid solution” phase transition pathway during the first charge process. Two hexagonal O3 phases (H1 and H2) are usually involved for the normal charge range (the formation of the O1 phase resulted from high voltage charging should be avoided for good cycle performance). It is well known that layer structured cathode materials LiMO$_2$ (M = Ni, Co, Mn) have better rate capability comparing with olivine LFP systems due to their higher electronic conductivity, higher lithium ion diffusion coefficient, and 2D diffusion paths. However, to the best of our knowledge, not much systematic studies have been reported on the phase transition behavior of the layer structured cathode materials during high current rate charging. In the present work, the structural changes of NMC in a wide range of current rates (from 0.1C to 60C) are systematically studied using synchrotron based time-resolved in situ XRD. The contribution from each transition metal ions (Ni, Mn, Co) to charge compensation on charging is obtained by in situ Q-XAS. The details of atomic arrangement and local phase distributions for NMC samples harvested from half-way charged cell at 30C rate are studied by the aberration-corrected STEM technique. Intermediate phases are observed using in situ time resolved XRD during the first charging cycle when current rates higher than 10C are applied.

2. Results and Discussion

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) has a typical NaFeO$_2$-type layered structure with a space group of R-3m. Detailed information about the crystal structure is shown in Figure S2 and Table S1 (Supporting Information). By using specially designed in situ cells and optimized X-ray diffraction technique for high rate characterization, the in situ XRD patterns of the NMC cathode were captured during the first charge at different current rates of 0.1C, 1C, 10C, 30C, and 60C (the C rate is calculated based on a specific capacity of 160 mA h g$^{-1}$). In order to collect data with good signal-to-noise ratio and 2θ angle resolution in a very short time, most data were collected in a narrow 2θ angle range near the 003 reflection only. Figure 1 shows the 003 diffraction
peak evolution of Li$_{1-x}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode from $x = 0$ to 0.7 ($x$ value is calculated from the charging curve, $x = 0$ is the pristine sample, and $x = 0.7$ is considered as the fully charged sample. Charge curves during the in situ XRD experiments are shown in Figure S3, Supporting Information). At 0.1C, a typical “solid solution – two phase – solid solution” phase transition behavior is observed, involving two hexagonal phases (H1 and H2). This agrees well with the previous in situ XRD study via synchrotron X-ray.[22,30–32] Some research groups[23–29] also studied the structure change of NMC during initial charge process via ex situ XRD by lab X-ray, but they did not reveal the two-phase coexistence region. We believe this is because of the low angle resolution and time resolution of the ex situ lab XRD, compared with in situ synchrotron XRD. Very interestingly, when the C rate increases to 10C, a new, broad peak emerges between the H1 and H2 phases with a low intensity at 10C, and becomes more pronounced at 30C and 60C, indicating the formation of intermediate phases. Comparing to the metastable phase in LFP system,[12,13] the intermediate phases in NMC system cover a much wider range of 2θ angles and $x$ values bridging the H1 and H2 phases. This could be caused by either the solid-solution behavior or the multiphase nature of the intermediate phases, and very likely by both. It is worth noting that the appearance of the new H2 phase and the disappearance of the initial H1 phase occur at an earlier stage of charging process (lower $x$ values) when the C rate is increased. This high rate accelerated phase transition is very interesting. The high rate charging can create high inhomogeneity of Li content, which in turn could enhance the new phase formation. On the other hand, the extra driving force provided by the overpotential effect of high rate should be helpful in overcoming the energy barrier for phase transition. Such extra driving force together with the high inhomogeneity may also play very important roles in forming the intermediate structures, as will be discussed later using the STEM results. Full XRD patterns of NMC over an extended range of 2θ angles and at a high charge rate (30C) are shown in Figure S4 (Supporting Information). They agree well with the diffractogram of Figure 1 and the signature of the intermediate phase can be observed for all the Bragg peaks, although the 2θ angle peak separation is a little poor due to the short wavelength used. It should be noted that for 60C charge, the peak is broader than those for low rate charge at the high potential range. This indicates that high rate charging creates high inhomogeneity of Li content, resulting in a wider distribution of lattice parameter at the high potential range. In addition, NMC is fully converted into the H2 phase at the end of charge, even at 60C rate charge, indicating the excellent rate capability. In comparison, the LFP at a rate of 10C charge still shows residues of the pristine LFP phase at the fully charged state.[11–13]

Figure 2 shows the contour plot of the 003 diffraction peak of Li$_{1-x}$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ as a function of time during a 55 s charge ($x \approx 0.35$) at a current rate of 30C and then relaxed over a time period of 480 s when no charging current is applied. In order to see the changes during relaxation more clearly, the detailed in situ XRD patterns in three different time zones are also plotted in Figure 2. At the moment the charging current is just cut off, relatively sharp H1 and H2 peaks and a broad intermediate phase peak can be clearly identified. With increasing relaxation time in the first 200 s, the H1 peak gradually

![Figure 2](image-url)
disappears, the intermediate phase peak broadens, and the H2 peak shifts to higher \( 2\theta \) angles and sharpens. Between 200 and 480 s, the H2 peak changes course from sharpening to broadening and ends up as a quite broad peak at 480 s. At the same time, in the broad peak region representing the intermediate phase, two or three peaks are gradually developed, as indicated by the yellow areas in the counterplot. These results show that the structural relaxation after high rate charging is a quite complicated process. The high rate charging creates very steep Li concentration gradients and large inhomogeneities from the surface to the center of the particles, as well as a large number of structural defects. With the help of extra driving force provided by the higher overpotential, multiple intermediate phases with different Li contents and lattice parameter \( c \) can be nucleated and grown. During relaxation, with the rearrangement of Li ions, some of the newly nucleated intermediate phases can continuously grow up. It should be noted that these intermediate phases can be maintained several hours, even several days after the charging current was cut off, well beyond the 480 s time period shown in Figure 2. This is different from the relaxation behavior of the metastable structure in some LFP systems, where the lifetime was estimated to be \( \approx 30 \) min.[12] In fact, the intermediate phases should be relaxed to the thermodynamically stable phase after a certain time. Unfortunately, we did not follow the relaxation process to the end, since we were more interested in how long it can be maintained to do our ex situ STEM study. Our results suggest the developed intermediate phases can be maintained more than several days to give us enough time to do the TEM study. Taking advantage of these relatively stable intermediate phases in the half way charged NMC samples (\( x \approx 0.35 \)), we were able to carry out ex situ STEM studies on these intermediate phases with atomic level resolution.

In order to visualize the structural changes of NMC caused by high rate charge, pristine NMC and samples harvested from cells after 30C charge were studied using the STEM technique. More than 20 images were collected for each sample at different spots to get better statistics, but only a few representative ones with good quality are presented here. The results of pristine NMC are shown in Figure 3. Figure 3a presents a schematic of the atom arrangement along [010] projection, which is the best direction for observing the layer structured cathode material, since separated columns of Li, O, and transition metal (TM = Ni, Co, and Mn) ions are aligned. An extensive number of atomic resolution high-angle annular dark-field (HAADF) and annular-bright-field (ABF) STEM images of NMC were obtained and two representative images are shown in Figure 3b,c. It should be noted that the contrast varies as \( Z^{1.7} \) where “Z” is the atomic number for the HAADF images, but varies as \( Z^{1/3} \) for the ABF images. Since HAADF is more sensitive to the heavy atoms, TM ions (3b sites) are clearly observed from the HAADF image in bright dots in Figure 3b, while the lighter atoms of Li (3a sites) and O (6c sites) are showed more clearly in the ABF image (Figure 3c). Figure 3d shows the line contrast profile of TM columns along the [42T] direction projected at the [010] zone axis. It demonstrates that pristine NMC exhibits a well-defined layered structure, and the positions of TM (3b sites) are well resolved at the atomic level along the [010] zone axis. Figure 3e shows the line contrast profiles also along the [42T] direction. It shows a very uniform distribution of the “TM-O-Li-O-TM” ordering, indicating a perfect layered structure without observable Li-TM antisite defects, which are

![Figure 3. Structure of pristine NMC materials. a) A schematic of lattice structure, b) HAADF, and c) ABF STEM images of pristine NMC from the [010] projection. The corresponding line profiles of d) TM (TM = Ni, Co, and Mn) atoms in HAADF image and e) TM, Li, and O atoms in ABF image acquired along the black line. In the ABF line profile, image contrast of the dark dots is inverted and displayed as peaks.](image-url)
frequently observed in Ni containing layer-structured cathode materials.\(^\text{[33]}\)

To observe the intermediate phases of NMC formed by high rate charging at the atomic scale, ex situ STEM images were collected on the relaxed sample (48 h relaxation) after half-way charge (\(x = 0.35\)) at 30C rate. The typical HAADF and ABF images taken along the \([110]\) zone axes are shown in Figure 4. The uniformly distributed TM layers can be seen from the HAADF image (Figure 4a–c), which is identical to the TM layers in pristine NMC (Figure 3b). It indicates that the structure of TM layers is well preserved after half-way charge at high rate. On the other hand, the ABF image taken at the same sample position shows two different types of domains in the green and red dashed squares in Figure 4d, and in more details in Figure 4e,f. The location of the Li columns in the green dashed square region in Figure 4e is different from that in the red dashed square region in Figure 4f. In Figure 4f, the Li columns are no longer located in the middle position of two TM columns (actually, it should be in the middle of two oxygen columns, but the TM layers have much stronger contrast). The middle position corresponds to the typical octahedral sites as shown in the pristine sample. It looks like the lithium ions in Figure 4f are located at the pseudotetrahedral sites, as identified in the pristine sample. It looks like the lithium ions in the middle position corresponds to the typical octahedral sites as columns, but the TM layers have much stronger contrast. The TM columns (actually, it should be in the middle of two oxygen slabs, and no more intermediate phase sites) can be observed at the surface region.

The valence state and local environment of each transition metal element in NMC are monitored by in situ quick X-ray absorption technique. To avoid the lag of reaction near the window part of the cell,\(^\text{[37]}\) glassy carbon is used to enhance the pressure of the window of the in situ cells. Figure 5a–c shows the changes of the X-ray absorption near edge spectroscopy (XANES) at the Ni, Co, and Mn K-edges during 30C charge, respectively. The K-edge of Ni shifts continuously to higher energy, indicating the oxidation of Ni ions from Ni\(^{2+}\) to Ni\(^{4+}\) during the charging process. In contrast, the K-edges of Co and Mn exhibit almost no energy shift. The Co and Mn K-edge features change shape, indicating that the local environment changes around Co and Mn ions, but Co and Mn do not contribute much to the charge compensation. Same results are obtained at 1C and 10C rates presented in Figure S7 (Supporting Information). These results suggest that charge compensation during charging mainly arises from Ni. Charge compensation is not affected much by the different C rates. Figure 5d shows the edge shift of Ni K-edge XANES as functions of the state of charge (\(x\) values) at different C rates. Interestingly, comparing the rate effects at the same charge state (same \(x\) value), the oxidation state of Ni ions is higher at faster charging rates, especially in the half-way charge state (\(x = 0.35\)). If all the charges passed to the sample were equally used to extract Li, and Ni is the only charge compensation contributor, the oxidation state of Ni should be linear to the \(x\) value and independent to the charge rate. In fact, these three curves are not linear and also charge rate dependent, showing that the effectiveness of Li extraction is different at different charge states and also rate dependent. The plotted higher oxidation state of Ni at the same nominal \(x\) value actually means that when the total charge passed are
the same, the higher rate has higher efficiency to extract more Li (higher x value) than the lower rates. This is also consistent with the in situ XRD results shown in Figure 2. Since no rigid K-edge shift for Mn and Co during charge, the information shown in Figure Sd for Ni cannot be obtained for Mn and Co. From the Fourier-transformed extended X-ray absorption fine structure spectra shown in Figure S8 (Supporting Information), the most noticeable spectral changes occur at the Ni-edge, indicating the significant changes of coordination shell and bond length around Ni during high rate charging. This is in good agreement with the XANES results as well as with our previous study.[38]

Based on the data above, we unveil the real-time phase transition behavior of layer structured NMC cathode during fast charging. Intermediate phases are first observed when a 10C rate is applied, which become more pronounced at higher charging rates of 30C and 60C. They bridge the H1 and H2 phases. It can be assumed that high rate induced large overpotential could provide extra driving force to overcome the energy barrier for the nucleation of the intermediate phases and facilitate the multiphase reactions. From the STEM results, we observe abnormal regions with tetrahedral Li ion occupation (Li poor region), in addition to the normal regions with octahedral Li occupation (Li rich region) in samples at half-way charged state (x = 0.35) after high rate charging. The lattice parameter c of the Li poor region is larger than that of the Li rich region. In contrast, for the pristine (x = 0) or fully charged sample (x = 0.7), only one type of region with octahedral Li occupation is observed. Theoretical calculations of the Li occupation in layer structured cathode materials showing that the free-energy variation of octahedral and tetrahedral Li occupation in relation to the distance between adjacent oxygen layers was reported in the literature.[39] It was suggested that the activation energy for tetrahedral occupation becomes lower than that for octahedral occupation, when the interlayer distance between adjacent oxygen layers of Li increases to a certain value (2.9 Å for LiCoO2). This suggests that the preferred occupation sites for Li could be the tetrahedral site, when such interlayer distance is larger than a certain value. Table S2 (Supporting Information) shows the measured lattice parameters of the phases observed from STEM images. It can be seen that the parameter c in Figure 4f is larger than that in Figure 4c. This agrees well with the prediction of the published calculation study.[39]

In situ quick X-ray absorption spectra provide useful information about the contribution of each transition metal element (Ni, Co, Mn) to the charge compensation at different C rates. The fully oxidation of Ni from Ni²⁺ to Ni⁴⁺ during charge, even at a high rate of 30C, indicates the electrochemical reaction and ion diffusion within the particles of NMC is rather fast. Ni oxidation is faster and more effective than that of Co and Mn, when higher rate charging is applied. This is in good agreement with the calculated lower activation barrier surrounding Ni²⁺ (210 meV) comparing with Co³⁺ (310 meV) and Mn⁴⁺ (340 meV) for Li motion in the layer structure cathode.

Figure 5. In situ quick XAS of NMC during the first charge. The X-ray absorption near edge spectroscopy (XANES) results of NMC at a) Ni, b) Co, and c) Mn K-edges during 30C charge, respectively. d) The Ni K-edge energy shift as a function of nominal lithium content x in NMC during initial charge process at the current rates of 1C, 10C, and 30C.
systems. These results provide an important guidance for designing NMC for high rate cycling: higher Ni content in NMC could be beneficial to high rate capability, as long as the negative effects of structural stability and cation mixing caused by high Ni content can be well managed.

3. Conclusion

In summary, we present the exploratory study of the nonequilibrium phase transition behavior in layer structured NMC cathode system during high rate cycling. It provides direct evidence for the different phase transition behaviors than those during low rate charging. Intermediate phases were observed at high rate charging at 10C, 30C, and 60C by in situ XRD. In contrast, such intermediate phase formation was not observed during low rate charging. Since the formation of intermediate phases is strongly related to the larger overpotential generated by high rate charging, during the low rate charge, the overpotential may not be high enough to facilitate the formation of intermediate phases. Phase coexistence heterogeneities and tetrahedral occupation of Li in the Li-poor phase, which could be one of the intermediate phases, were observed in the half-way charged NMC using ex situ STEM. By using the in situ quick X-ray absorption technique, we find that the charge compensation contribution by Ni ions is faster and more effective at the higher C rate, suggesting the benefit of higher Ni content in NMC for rate capability. These results show that the high rate induced intermediate phase formation process reported in the literature for olivine structured LFP system, also exist in layer structured NMC system. This raises the question about the presence of such intermediate states in other systems, such as layered structured LiCoO₂ and cubic spinel structured LiMn₂O₄. These important results will further inspire theoretical and experimental studies on the high rate induced structural changes for a wide spectrum of cathode materials.

4. Experimental Section

Samples and Cell Test: The LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials were provided by an industrial partner. The electrode was prepared by slurrying the active material, carbon black, and polyvinilidenefluoride with a weight ratio of 70:14:16 in N-methyl-2-pyrrolidone solvent, then coating the mixture onto aluminum foil current collectors. The electrode was dried in a filled glove box. High-purity lithium foil was used as the anode.

In Situ XRD Characterization: The Q-XAS experiment was performed at beamline X18A of the NSLS (BNL). The in situ Mn, Co, and Ni K-edge spectra were collected separately in the transmission mode. About 16–17 XAS spectra were recorded in a 30 s time interval, with the best achievable temporal resolution of 2 s per scan. Eight successive spectra were merged into one to get a better signal-to-noise ratio. Therefore, the real temporal resolution in this work was about 15 s. Energy calibration was carried out using the first inflection point of the reference spectrum of metal foils which were simultaneously collected during each measurement during the in situ experiments.

STEM Characterization: STEM specimens were prepared by sonicating the charged cathode in anhydrous dimethyl carbonate and drop-coating the materials individually onto carbon lacy films and sealed in airtight bottles before immediate transfer into the STEM column. A JEM-ARM200F STEM operated at 200 kV and equipped with double aberration-correctors for both probe-forming and imaging lenses was used to perform HAADF and ABF imaging. The attainable spatial resolution of the microscope was 78 pm at the incident semialonge of 25 mrad. To observe Li directly using ABF collection geometry, the acceptance semialonge in this study was fixed between 12 and 25 mrad. The STEM ABF and HAADF images were taken simultaneously at the optimal defocus value of the HAADF imaging condition, which was more defocused than the optimal ABF imaging condition on this instrument. Thus, the contrast in the ABF image was reversed with the bright area corresponding to the atomic positions.

Supporting Information

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

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