Unravelling the Origin of Irreversible Capacity Loss in NaNiO_2 for High Voltage Sodium Ion Batteries

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Abstract

Layered transition metal compounds have attracted much attention due to their high theoretical capacity and energy density for sodium ion batteries. However, this kind of material suffers from serious irreversible capacity decay during the charge and discharge process. Here, using synchrotron-based *operando* transmission X-ray microscopy and high-energy X-ray diffraction combined with electrochemical measurements, the visualization of the dissymmetric phase transformation and structure evolution mechanism of layered NaNiO_2 material during initial charge and discharge cycles are clarified. Phase transformation and deformation of NaNiO_2 during the voltage range of below 3.0 V and over 4.0 V are responsible for the irreversible capacity loss during the first cycling, which is also confirmed by the evolution of reaction kinetics behavior obtained by the galvanostatic intermittent titration technique. These findings reveal the origin of the irreversibility of NaNiO_2 and offer valuable insight into the phase transformation mechanism, which will provide underlying guidance for further development of high-performance sodium ion batteries.

Keywords: irreversible capacity loss; layered structure materials; high voltage; synchrotron-based techniques; sodium-ion batteries

1. Introduction

Lithium ion batteries have successfully powered portable electronic devices and electric vehicles due to their high energy density and stability over the past decades. Nevertheless, the limited lithium resources and the resultant cost have barred the lithium ion batteries from the large-scale electric energy storage applications, which motivate us to explore new energy storage systems. Sodium-based rechargeable batteries with similar intercalation electrochemistry to lithium ion batteries have attracted increasing attention due to the natural abundance of sodium resources and potentially lower cost, compared with lithium.[1-3] Numerous efforts on exploring electrode materials have been made and some remarkable achievements have been achieved in the capacity and cycle performance for sodium ion batteries.[4, 5] Inspired by the successful application of their analogies LiMO_2 (M = transition metal) in lithium-ion battery systems, layered transition metal compounds with a general formula of NaMO_2 have been investigated due to their relatively high capacity among the various cathode materials.[6, 7] With a similar crystal structure of lithium-containing layered transition metal compounds, many NaMO_2 materials can be considered as derivatives with so called “O3-type” structure based on cubic close-packed oxygen atom (ABCABC) arrays along c axis, where the octahedral sites in the interslab space are occupied by alkali ions or disordered transitional metal.[8, 9] Among the sodium transition-metal oxides of NaMO_2 cathode materials, nickel-based O3-type NaNiO_2 has been studied extensively owing to its relatively high operating voltage and theoretical capacity.[10-12] However, the low reversible capacity and poor cycle stability of NaNiO_2 impede their practical application in sodium ion batteries. Overcoming these challenges requires comprehensive understanding of the underlying structural evolution mechanism of NaNiO_2 during cycling.

The structure of NaNiO_2 was first determined by film method using a precession camera in 1954,[13] but the electrochemical behavior was not investigated until 1982 by Braconnier

et al.[14] It was found that the multiple phase transformation ($O'3$ - $P'3$ - $P''3$ - $O''3$) occurs at the voltage range of 1.8-3.4 V, corresponding to only 0.2 Na^+ extraction from the pristine material during the first charge process.[14] A significantly increased capacity was reported recently in which there were 0.85 Na^+ extraction and 0.62 Na^+ intercalation per formula unit during the first charge and discharge process with the voltage range of 2.0-4.5 V, respectively.[15] By the comparison of XRD patterns for $NaNiO_2$ electrodes charged to 3.75 and 4.5 V respectively, an unidentified new phase was observed at the highly charged state. More recently, the phase changes of $NaNiO_2$ cathode material during the first charge and discharge process at the voltage range of 1.5-4.0 V were reinvestigated by *in situ* lab XRD, and two new phases of $O'''3$ phase at the end of discharge and $P'''3$ structure at 3.38 V were identified.[16] Despite that this previous work brought up valuable information to help understand basically the phase evolution process during reversible intercalation and deintercalation process of sodium ions, the origin of the initial irreversible capacity loss related to the microstructure evolution has not been elucidated yet.

Here, we combined synchrotron-based *in operando* transmission X-ray microscopy (TXM), high-energy X-ray diffraction (HE-XRD), high-resolution X-ray diffraction (HR-XRD) and electrochemical measurements to visualize the phase transformation during the first two cycles. The structure of pristine $NaNiO_2$ material was investigated by the refined HR-XRD. Phase mappings at various states of charge were directly obtained by the TXM-XANES technique, and a correlation between the phase transformation and electrochemical performance has been addressed. The irreversible structure evolution primarily occurs in the charge/discharge voltage zones of below 3.0 V and over 4.0 V by *in situ* HE-XRD phase transformation tracking during the first cycle. It is also indicated that the irreversibility of $NaNiO_2$ material is related to the low Na^+ diffusion and reaction kinetics confirmed by galvanostatic intermittent titration technique (GITT) measurement.

2. Experimental Section

Synthesis of NaNiO₂ Samples: The NaNiO₂ cathode material was synthesized by a high-temperature solid-state method of 12 h heated treatment at 650 °C in oxygen atmosphere, based on previous work.[17, 18] Briefly, NiO (0.03 mol) and Na₂O₂ (0.0165 mol) were mixed by ball-milled process at 350 rpm for 5 h under argon atmosphere at room temperature. The powder was pelleted under 11 MPa for 10 min, and the NaNiO₂ was obtained by heating the pellet at 650 °C for 12 h.

Characterization: HR-XRD data were collected at beamline 11-BM-B, Advanced Power Source, Argonne National Laboratory, using X-ray wavelength of 0.4142 Å. The SEM images were recorded using field-emission scanning electron microscope (FESEM, FEI Helios Nanolab600i). Electrochemical tests were performed on CR2032-type coin cells by a multichannel potentiostat (Biologic VMP3) controlled by EC-Lab software. The electrode consists of 80 wt% active material, 10 wt% carbon black and 10 wt% PVDF binder. The coin cells were assembled in an argon-filled glovebox with both moisture and oxygen levels less than 0.5 ppm using the 1 M NaPF₆ in a solvent of PC as the electrolyte. All the cells used for this article were cycled at room temperature. The GITT experiments were performed at a rate of C/20 for 10 min with a 30-min relaxation immediately.

In operando 2D TXM experiment: *In operando* 2D TXM experiments were performed on a traditional 2032-type coin cell with 3 mm diameters Kapton windows,[19-21] at beamline 8-BM-B of APS (ANL) as a transition program at the National Synchrotron Light Source II (NSLS II). These electrode in the coin cell for *in operando* tests was made of 40 wt% active material, 40 wt% carbon black and 20 wt% binder (PVDF). Thin carbon papers (~ 60 μm thickness) were used as current collectors for the NaNiO₂ electrodes. It should be noted that hard X-rays can transmit though the binder and carbon material including carbon black and carbon papers. Therefore, these inactive materials, which are necessary for electrode fabrication, cannot be recorded on the TXM. The cell was fixed in a battery holder mounted

on a motorized stage with X , Y , Z , and θ dimension and aligned for X-ray transmitting. The cell was continuously cycled at a rate of about 1/10 C during the absorption-contrast imaging, and the background images was collected under dynamic conditions. A $2\text{ k} \times 2\text{ k}$ CCD camera with a field of view of $40 \times 40\text{ }\mu\text{m}^2$ was used. To record the phase transformations in the material, a full series of XANES images were collected at each state of charge. The full XANES images were collected by scanning Ni K -edge (8,333 eV) from 8,313 to 8,413 eV at every 2 eV, which generated 512×512 XANES spectra with 4×4 binned pixels, corresponding to $\sim 80\text{ nm}$ output pixel size. The exposure time for every XANES image was 20 s. Three areas and one reference background area were recorded at every state of charge.

In situ HE-XRD: The *in situ* high energy X-ray diffraction experiments were performed at beamline 11-ID-D in Advanced Power Source of Argonne National Laboratory, using a traditional 2032-type coin cell with 3 mm-diameter Kapton windows. The X-ray wavelength was 0.799898 Å. 50 wt% active materials, 40 wt% carbon black, and 10 wt% PTFE binder were pelleted to obtain a 10 mm-diameter electrode. The diffraction patterns were collected at each state of charge with 3 s exposure time for each pattern. After recording the data sets, the sample was allowed to rest for 600 s to minimize any negative impact by the high energy X-ray beam.

TXM chemical mapping construction: The customized program written in Matlab (MathWorks, R2011b) was used to analyze the XANES data. The background TXM images collected at each energy step were applied on all the corresponding XANES images, and then we can extract the full XANES spectrum data (x-ray intensity *v.s.* energy) for each pixel. According to the Beer's Law, the x-ray attenuation for the given phase with attenuation coefficient μ and thickness t can be defined as follows:

$$\frac{I}{I_0} = \exp(-\mu(E)t) = \exp(-\mu_{\text{NaNiO}_2} t_{\text{NaNiO}_2}) \cdot \exp(-\mu_{\text{Na}_0.19\text{NiO}_2} t_{\text{Na}_0.19\text{NiO}_2}) \quad (1)$$

where I_0 is the incident X-ray intensity and I is corresponding transmitted X-ray intensity.

The scaled $-\ln(I/I_0)$ at each of the 512 x 512 pixels was then fitted with the linear combination of two μ values of NaNiO_2 and $\text{Na}_{0.19}\text{NiO}_2$. The ratio of the weighting factor is analogous to the thickness fraction and therefore represents their volume fraction.

$$-\ln\left(\frac{I}{I_0}\right) = \mu_{\text{NaNiO}_2} t_{\text{NaNiO}_2} + \mu_{\text{Na}_{0.19}\text{NiO}_2} t_{\text{Na}_{0.19}\text{NiO}_2} \quad (2)$$

The spectrum fitting was carried out by minimizing the measure misfit (R value) for each spectrum at each pixel, and the R value is defined as:

$$R = \sum_{Ei}^{Ef} (\text{data}E - \text{ref}E)^2 / \sum_{Ei}^{Ef} \text{data}E^2 \quad (3)$$

where Ei is 8,313 eV, Ef is 8,413 eV, $\text{data}E$ is the $-\ln(I/I_0)$ value for the given energy E at each pixel, and $\text{ref}E$ is the reference $-\ln(I/I_0)$ value that is a linear combination of X-ray attenuation of NaNiO_2 , Na_xNiO_2 and $\text{Na}_{0.19}\text{NiO}_2$. In addition, the pristine NaNiO_2 , Na_xNiO_2 (3.2 V charged-state material) and $\text{Na}_{0.19}\text{NiO}_2$ (fully charged-state material) were selected as the reference materials for the fitting results.

3. Results and discussion

The NaNiO_2 material was prepared by a solid-state method, and the pristine phase of NaNiO_2 is identified by HR-XRD as shown in Figure 1a. The as-prepared NaNiO_2 material has a layered monoclinic structure with a $C_12/m1$ symmetry space group, which is similar to the electrochemically active structure as proved previously.[15] The lattice parameters of $a = 5.313 \text{ \AA}$, $b = 2.845 \text{ \AA}$, $c = 5.575 \text{ \AA}$, and $\beta = 110.39^\circ$ for NaNiO_2 , which are close to the previous work,[15] are obtained by the Rietveld refinement performed with GSAS-II software package,[22] indicating a distorted O3-type structure owing to the a/b ratio (1.87) deviated from that of the ideal hexagonal system ($\sqrt{3} \approx 1.73$),[23, 24] and the crystal structure of a O3-type NaNiO_2 is also illustrated in Figure 1c. The atomic positions and cell parameters are listed in Table S1. The edge-sharing of NiO_6 octahedral forms the NiO_2 layer with Ni-O

distances of 1.951(5) Å (4x) and 2.167(5) Å (2x). Between these layers, the Na atoms also exhibit a distortion at the octahedral coordination with 2.290(9) Å (4x) and 2.342(3) Å length of Na-O bonds. Besides the pristine NaNiO₂ phase, an additional phase shown at 2θ=4.38 and 12.5 degree is identified as Na_{0.91}NiO₂ (Figure 1a and b, marked with orange triangle), which is due to possible reactivity with air during sample preparation or transportation for HR-XRD experiments.[15]

The electrochemical performance of the NaNiO₂ material was evaluated in the sodium half-cell. Galvanostatic measurements of NaNiO₂ electrode at the rate of 0.1 C (1 C = 235 mAh·g⁻¹) at various cycles are shown in Figure 2a. During the first cycle, the NaNiO₂ electrode shows the charge and discharge capacity of ~190 and 131 mAh·g⁻¹ respectively, corresponding to 0.81 Na⁺ extraction and 0.56 Na⁺ intercalation per formula unit. The first charge/discharge Coulombic efficiency is approximately 68.9%, but it increases to 93.3% and 96.1% for the second and fifth cycle, respectively. It can be seen that the initial charge profile at low and high voltage zones shows distinctive behaviors from the subsequent cycles. At low voltage zone below 3 V, the accessible capacity during the first charge process is higher than that for the subsequent charge cycles. At a high voltage zone above 4 V during the first charging process, a charging plateau is clearly shown, and the plateau can be negligible for the following cycles. The capacity evolution corresponding to the charging voltage plateau at the beginning (below 3 V) and the ending stage (above 4 V) is mainly related to the structural evolution during the first deintercalation process of sodium ions. In addition, during the first charging process, there is an obvious voltage dropping at about 2.87V, which is caused by the reduced polarization mainly related to the surface chemistry and phase transformation of NaNiO₂ materials at the beginning of charging process. To further understand phase transformation for the first cycle and correlate it with sustainable capacity over cycling, cyclic voltammetry (CV) experiment was performed at a scan rate of 0.4 mV·s⁻¹ (Figure 2b). The

CV plots of NaNiO₂ electrode show five couples of reversible oxidation/reduction reaction peaks at the voltage of 2.68/2.38, 3.07/2.93, 3.39/3.23, 3.52/3.40 and 4.07/3.47 V, respectively. The CV curve of the first cycle is remarkably different from the following cycles, indicating the distinctive oxidation/reduction reactions between the first and the subsequent cycles. In addition to the unique characteristics and irreversibility during the first cycling, the other phenomenon for the subsequent cycles is that the electrochemical reversibility is found to be related to the upper cutoff voltage. According to the CV curves from the second cycle, the NaNiO₂ material shows relatively good reversibility of electrochemical redox reactions occurred at the voltage zone of below 4.0 V in terms of the reduction process, showing the decreasing electrochemical polarization as marked with yellow arrows in the figure, and the electrochemical polarization corresponding to the peak potential differences (ΔE_p) for NaNiO₂ electrode increases dramatically for the reduction reaction occurred at above 4.0 V, as shown in the redox reaction peaks marked with grey arrow. This irreversibility at the high voltage zone is mainly due to the irreversible phase transformation and side reactions such as the electrolyte decomposition.

To illuminate the electrochemical reaction mechanism, we firstly studied the NaNiO₂ cathode in the sodium half-cell using *in operando* TXM technique. The typical 2032-type coin cell with 3mm-diameter Kapton windows on both sides was used for the *in operando* test.[25, 26] Figure 3a shows the TXM measurement setup for the *in operando* investigation of NaNiO₂ electrochemical reaction. We prepared the large-size (*ca.* 15 μm , Figure 3b) particles for the reaction evolution observation at the individual-particle scale. A mosaic image in Figure S1 shows a large area of the NaNiO₂ electrode consisting of multi-particles in the battery.

TXM-XANES images were collected in dynamic conditions at various states of charge, as marked in Figure 3c by colorful circles. The *operando* cell was cycled at a constant current of 1/10 C (23.5 mA $\cdot$ g⁻¹) at a voltage range of 2.0-4.5 V. The recorded data were processed and

fitted with the selected standard reference spectra (Figure 3d) to obtain the chemical phase mapping during the charge and discharge process, as shown in Figure 3f and g.[26] Three consecutive phases from the de-intercalation of NaNiO_2 were investigated during the first charge process. The pristine NaNiO_2 (Ni, +3), partly charged Na_xNiO_2 (Ni, +3 and +4, 3.2 V charged-state material), and fully charged-state $\text{Na}_{0.19}\text{NiO}_2$ (Ni, mostly +4, the nominal formula corresponding to the charge capacity of NaNiO_2 during the first cycling) were selected as the standard reference phases for quantitative analysis. It was found that the phase transformation occurs at all directions and a “core-shell” reaction mechanism is suggested by the in operando quantitative chemical mapping.[27] From the open circuit voltage (OCV) of 2.65 V to 3.20 V, the red pixels (NaNiO_2) were replaced by green pixels (Na_xNiO_2) gradually (Figure 3f, from i to Vi), which illustrates the Na^+ extraction from pristine material NaNiO_2 with the valence of Ni element being oxidized to +IV (green color pixels). Then, with further deintercalation from 3.20 V to 4.50 V, blue pixels ($\text{Na}_{0.19}\text{NiO}_2$) appear and substitute the green pixels (Figure 3 f, from Vi to X), indicating the formation of the charged phase ($\text{Na}_{0.19}\text{NiO}_2$) during the de-intercalation reaction of NaNiO_2 . For the first discharge process (Figure 3g, from i to V), most Na^+ ions intercalate back into the material. However, the phase mapping of the fully discharged particles after the first cycle is not the same as the one of the pristine particles (V in Figure 3g VS i in Figure 3f), exhibiting some mixed color pixels in the middle of the particles, which shows an irreversible phase conversion in the first charge and discharge cycle. From the second cycle, the phase transformation seems to be reversible according to the restorable phase mapping of the particles during cycling as shown in Figure S2. Therefore, through the *in operando* TXM-XANES experiment, it reveals that the partly irreversible phase transformation predominately occurs at the first charge and discharge process.

To quantitatively understand the phase transformation, we analyzed the XANES spectra of the NaNiO_2 sample at the full field of view (Figure 4a-d). The weak pre-edge absorption

peaks, as marked by the dash arrow in Figure 4b, are associated with non-centrosymmetric environment or local symmetry structural distortion between oxygen coordination and the transition metal (Ni).[28, 29] The enlarged selected shadow area (Figure 4c) shows the continuous shift of Ni K-edge XANES spectra to the higher absorption energy by 2.0 eV, as highlighted by the arrows, indicating that Ni^{3+} ions are oxidized to the higher oxidation state (+4) during the first deintercalation process. Interestingly, at high voltage zones of above 4.0 V, the XANES spectra just exhibits a slight shape change with little absorption edge shift (Figure 4d),[30] which means that the absorption peak moves in one direction, and there is a isosbestic point shared by all the spectra. This phenomenon suggests that few Ni elements are oxidized, but a possible local structure change during the charging process to high cutoff voltage. For instance, partial Ni ion migration from octahedral sites to the interslab space has been proved in $\text{Na}_x[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($0 < x < 2/3$) and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3-x}\text{Ti}_x]\text{O}_2$ ($0 < x < 2/3$) by Ni K-edge spectra. [31, 32] This kind of structural distortions may be responsible for the irreversible capacity loss when NaNiO_2 is charged to above 4.0 V. Quantification of the chemical phase composition was achieved by fitting XANES spectra with the three standard references (see Experimental Section for details). The average Na composition over every particle (determined spectroscopically) corresponds to the electrochemically-determined composition of Na_xNiO_2 , assuming that all the primary NaNiO_2 particles are electrochemically active for sodiation and desodiation. The representative 2D chemical phase mapping at 2.8 V and 3.4 V are shown in Figure 4e and f. The phase composition of the selected area clearly shows the two-phase coexistence and phase boundaries. The phase distribution along a line profile was also analyzed at various states of charge for the initial cycle (Figure S3). At the discharge state after the first cycling (Figure 3g, V), the NaNiO_2 phase (red pixels) accounts for 70%. If we consider the other colors as an average phase, the composition of the average phase is $\text{Na}_{0.17}\text{NiO}_2$, which is very close to the fully charged phase of $\text{Na}_{0.19}\text{NiO}_2$, illustrating that the irreversible capacity loss can be caused by the

deintercalation phase. Therefore, the quantitative phase composition analysis clearly illustrates the “core-shell” reaction model and the origin of irreversible capacity loss during the intercalation and deintercalation process.

In situ synchrotron HE-XRD experiments were performed to track the structural evolution of NaNiO₂ cathode as shown in Figure 5. The first scan corresponds to the pristine material with distorted O3-phase (O'3-type), which has been clearly characterized by HR-XRD as discussed above in Figure 1. The *in situ* HE-XRD patterns were fitted with both O3 and P3 structures to analyze the structure. At the beginning of deintercalation, the pristine O'3 phase disappears gradually and a new phase (P'3-type) emerges at the same time, indicated by the shift of (002) reflections to lower two-theta degree. When approximately 0.4 Na⁺ per formula unit are extracted from the pristine NaNiO₂ at around 3.1 V, the layer spacing along the *c* direction (*c* spacing) increases, indicated by the disappearing (002) peak and growing intensity for the new phase diffraction peak at 2θ=16.6 degree,[33] which is quantitatively analyzed by the changing *c* lattice parameter during the first charge and discharge process as shown in Figure 6b. At the same time, the *d*-spacing along the *a* and *b* direction shrinks as the (110) reflection shifts to a higher two-theta degree caused by increasing Ni⁴⁺ ions (the enlarged rectangle area in Figure 5, and the contour plots in Figure 6a). These cell parameter changes indicate serious structural distortion accompanying with phase transformation. The significant distortion around 3 V also leads to transformation of the pristine structure O'3 into O''3 accompanying with the appearance of new phase (P'3-type) as mentioned above, which is marked in the *in-situ* XRD patterns as shown in Figure 5. Between 3.1 V and 3.8 V, the peak intensity of P'3 phase increases dramatically with a slightly reducing *d*-spacing, such as the peaks of (200), (110), (020) and (001) as shown in Figure 5 and 6a. Whereas, the *d*-spacing of *c* direction increases significantly with the consequent deintercalation (Figure 6b) owing to the increased repulsion between oxide layers as the extraction of positively charged sodium ions.[34] At 3.8 V, the diffraction peaks at both left and right shoulders of (111)

disappear, indicating the conversion of the $P''3$ phase into a new phase ($O'''3$) as marked by the circle at $2\theta=6.5$ (Figure S4a) and 21.5 degree (Figure 5). When the electrode is charged above 4.0 V, the domain peaks such as the magnified peaks (110) in Figure 5 slightly move to the higher two-theta degree, and all the peaks shown as contour plots in Figure 6a, representing a small reduction in the cell parameters at all directions, correspond to another distorted O3-type ($O''''3$) phase.[16] It can be seen that nearly all the diffraction peaks for the fully discharged-state Na_xNiO_2 return back reversibly in comparison with the charged-state material, and the values of a , b lattice parameters for the full discharged-state and charged-state Na_xNiO_2 with the same state of charge (SOC) are almost identical. However, c value of the fully discharged-state Na_xNiO_2 is higher than that of charged-state material with the same SOC, which is mainly caused by the gliding of NiO_2 slabs during the charge process at the high-voltage zone of above 4.0 V, resulting in the irreversible phase transformation reaction.

In addition, we performed the GITT experiments (see Figure S5) to further understand the sodium ion diffusion process and the corresponding phase transformation kinetics. For the voltage response of each charge pulse (see the enlarged one of charge pulse in Figure S5b), the voltage suddenly drops as soon as the current is terminated, and then gradually decreases to the equilibrium potential.[35] The discharge process (blue curve in Figure S5a) exhibits the opposite behaviors. Two parameters of IR drop and reaction overpotential can be obtained from each charge pulse. The IR voltage drop shown in Figure S5b is the sudden voltage change after the current is removed, which is typically caused by the ohm impedance of the electrode at the different states of charge. The reaction overpotential related to the nucleation, new phase growing and mass transport is calculated by the end pulse-voltage minus the ohm impedance caused by the IR drop (Figure S5c). [36, 37] For the first charge process, the overpotential reduces firstly at $x \approx 0.9$ in Na_xNiO_2 , which may be related to the increased c spacing, and a high charge capacity is obtained at the same time. Then the reaction overpotential increases gradually due to the structural distortion, phase transformation and

nonhomogeneous composition as visualized in TXM-XANES. When the material is charged to the high voltage (above 4.0 V, $x \approx 0.4$), there is clearly increased overpotential mainly caused by the serious structural distortion, leading to the irreversible capacity of the NaNiO_2 material. However, the average overpotential is smaller during the intercalation process than that for the deintercalation process, which is mainly related to the large c spacing as proved by *in situ* HE-XRD experiments. Furthermore, sodium ion diffusion coefficients (D_{Na^+}) can be obtained at different states of charge from the charge pulse processes (Figure S5d). Similarity to the overpotential changes during intercalation and deintercalation process, the average D_{Na^+} during the discharge process is larger than that for the charge process, which is in conformity with the overpotential values and *in situ* HE-XRD results. In addition, the diffusion kinetics of NaNiO_2 materials charged to 4.5 V and 3.8 V after a few cycles was also investigated respectively. The sodium ion diffusion coefficient of NaNiO_2 cathode cycled at 2.0-3.8 V is over three times higher than that of the electrode cycled at 2.0-4.5 V (Figure S6), and the sluggish diffusion kinetics of sodium ions for the electrode charged to a high cut-off voltage is mainly caused by the irreversible phase transformation of layered Na_xNiO_2 at high-voltage zone of over 4.0 V.

To further reveal the irreversibility during charge process at the high-voltage zone, we tested the electrochemical properties of the NaNiO_2 electrode with a charge cutoff voltage of 3.8 V (Figure S7). At the voltage range of 2.0-3.8 V, the first charge profile (Figure S7a) is the same as the profile mentioned above in Figure 2a, exhibiting a high charge capacity at low voltage (approximately 3.0 V) compared with the subsequent cycling. This high charge capacity illustrates a kind of irreversibility of NaNiO_2 electrodes with the first discharge columbic efficiency of 72 %, which is related to the structural distortion and phase transformation during this process. However, from the second cycle, the discharge capacity is maintained at $79 \text{ mAh} \cdot \text{g}^{-1}$ (the same as the first discharge capacity) with the coulombic efficiency close to 100 % (Figure S7c), indicating a good reversibility during the subsequent

cycling. Even after 40 cycles, the electrode just exhibits a slight capacity fading compared with the electrode cycled to the high cutoff voltage. The reversibility at the voltage range of 2.0-3.8 V is also confirmed by the nearly overlapped CV curves except the first cycle (Figure S7b). In other words, the irreversible capacity of NaNiO₂ electrode is mainly attributed to the phase transformation and structural distortion when the material is charged to a high voltage of over 4.0 V.

The phase transformation of the NaNiO₂ cathode material is schematically illustrated in Figure 7. Figure 7a shows the nonhomogeneous reaction mechanism (“core-shell” reaction mechanism) with the existence of the irreversible phase (blue middle spot) at the end of the first discharge process. The phase transformation with *c* spacing of the selected phase is schematized in Figure 7b. The increased *c* spacing after the first charge process cannot shrink back to that of the pristine material, corresponding to an irreversible phase transformation and structural distortion.

4. Conclusions

In conclusion, combining with synchrotron-based *operando* TXM and HE-XRD techniques as well as the electrochemical experiments, we visualize the structural evolution of the NaNiO₂ cathode material in sodium ion batteries and elucidate the irreversible phase transformation mechanism during the initial electrochemical cycling. At the single-particle level, the electrochemically active phase transformation exhibits a dissymmetric spatial distribution with a “core-shell” reaction mechanism from the visualization obtained by *in operando* TXM-XANES, which shows a different discharge behavior due to the existence of the irreversible phase (Na_{0.17}NiO₂). The origin of initial irreversibility is associated with the charge process at the voltage range of below 3.0 V and above 4.0 V. At the low-voltage zone below 3.0 V, the irreversibility is mainly attributed to the increasing *c* spacing confirmed by synchrotron *in situ* HE-XRD. The irreversibility at the high voltage zone is caused by the irreversible structural

distortion and possible electrolyte decomposition during the first charge process. The correlation of the capacity evolution with reaction kinetics during the first charge and discharge process is also confirmed by GITT experiments. According to the analysis on the origin of irreversible capacity loss of NaNiO_2 material, optimizing the charge-discharge cutoff voltage to avoid the obvious irreversible phase transformation and stabilizing the phase structure by cation-doping are straightforward methods to improve the electrochemical reversibility for layered cathode materials. These findings could provide new insights into the reaction mechanism and the irreversibility of the other layered structure electrode materials to explore low cost and high-performance sodium ion batteries.

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Figure Captions

Figure 1. Structural analysis of NaNiO_2 material. (a) Rietveld refinement of the HR-XRD results of the prepared NaNiO_2 material. The black (red) line represents the experimental (calculated) data. The pink bar shows the standard Bragg peak positions. The residuals are shown as the blue line in the bottom. (b) The magnification of selected area (purple square) in Figure 1a. The orange triangle stands for the $\text{Na}_{0.91}\text{NiO}_2$ phase due to the exposure to air for the prepared materials. (c) Schematic illustration of the O3-type NaNiO_2 crystal structure.

Figure 2. Electrochemical performance of the NaNiO_2 electrode. (a) The first five charge-discharge profiles at the rate of 0.1 C. (b) The first five cyclic voltammetry (CV) curves at the scan rate of 0.4 mV/s. The arrow shows the tendency of voltage changes from 1st to 5th cycle.

Figure 3. *In operando* hard X-ray spectro-imaging of two-dimensional microstructural evolution of NaNiO_2 cathode. (a) Schematic illustration of the TXM experimental setup. (b) Scanning electron micrographs of the NaNiO_2 . Inset is the magnified graph of the NaNiO_2 . (c) Charge and discharge profiles of the *operando* cell. The cell was cycled at the rate of 1/10 C between 2.0 V and 4.5 V. The small circles correspond to the states of charge where the data were collected and fitted as chemical mapping. (d) Reference XANES spectra selected from three different *operando* charged states. (e) The reference color indicates the three phases in the chemical mapping. (f) and (g) are the two-dimensional chemical phase mapping during the first charge and discharge process. Scale bar: 10 μm .

Figure 4. *In operando* XANES spectra and phase composition analysis during the first charge process. (a) The charge profile of *in operando* cell. (b) The *in operando* XANES spectra collected at various states of charge. (c, d) The enlarged profiles from the selected area (the

shadow section in b). The dash arrow shows the pre-edge tendency after deintercalation. The phase composition analysis of (e) 2.8 V charged state (f) 3.4 V charged state. Scale bar: 10 μm . The red, green, and blue line and column bar correspond to NaNiO_2 , Na_xNiO_2 and $\text{Na}_{0.19}\text{NiO}_2$, respectively, and the black line represents the corresponding XANES spectra of the selected zones in e and f.

Figure 5. *In situ* synchrotron HE-XRD patterns for the first cycle. Time-resolved HE-XRD experiment was performed on the $\text{Na}|\text{NaNiO}_2$ coin cell during the first cycle corresponding to the charge and discharge profiles with voltage range of 2.0-4.5 V at the rate of 1/10 C. The diffraction peaks (002) and (-202) are highlighted by dash circles due to their disappearance after one cycle and the arrows represent the change direction of diffraction peaks. At right of the *in situ* diffraction patterns, the phase transformation for the first charge was marked by three color bars. The right inset is the enlarged selected rectangle area, corresponding to (110) diffraction peaks.

Figure 6. Quantification analysis of lattice parameters during the first cycle. (a) Contour plots of around (001), (200) and (020) diffraction peaks and their corresponding charge and discharge profiles. (b) The lattice parameters (a , b and c values) at different Na compositions during the first intercalation and deintercalation process.

Figure 7. Schematic illustration of the electrochemical reaction mechanism for the NaNiO_2 material. (a) The single particle reaction mechanism and (b) the schematic illustration of the structure evolution during intercalation and deintercalation process.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Graphical Abstract

The dissymmetric phase transformation and structure evolution mechanism of layered NaNiO_2 material during initial charge and discharge cycling were comprehensive understood with transmission X-ray microscopy and synchrotron-based X-ray diffraction. We directly observed the structural evolution of the NaNiO_2 cathode in sodium-ion batteries and elucidated the irreversible phase transformation mechanism during the initial electrochemical cycling.