**Na-Ion Batteries** 



# Capturing Reversible Cation Migration in Layered Structure Materials for Na-Ion Batteries

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Na-ion batteries are promising for large-scale energy storage due to the low cost and earth abundance of the sodium resource. Despite tremendous efforts being made to improve the battery performance, some fundamental mechanism issues still are not sufficiently understood. One such issue in the most popularized layered structure materials is the potential cation migration into sodium layers, which would highly affect the energy efficiency thus hindering its widespread use in the future. Here a systematic study of the cation migration in layered structure materials is presented and its relationship with voltage hysteresis is disclosed. Using the high-angle annular dark fieldscanning transmission electron microscopy and in operando X-ray diffraction as implements, for the first time, the reversible migration of the transition metal between transition metal layers and sodium layers is captured. The research inspires a novel insight into the cation migration related layered materials, which should be considered for future battery design toward conventional use.

The fast development of electrochemical energy storage, especially the wild application of Li-ion batteries, has facilitated today's portable electronic equipment and is essential for realizing the hybrid and electrical vehicles.<sup>[1]</sup> Nevertheless, the state-of-the-art Li-ion batteries still could not meet the requirement of large scale energy storage since it suffered from the

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inherent drawbacks including the high price of Li metal, the less abundance and the nonuniformly distribution of Li resources.<sup>[2]</sup> Lifting the difference between supply and demand extensively inspired the interest of alternative strategy.

Na-ion batteries, the potential alternative to prevailing Li-ion batteries, have attracted considerable interest and have been vastly studied nowadays, due to the abundance of sodium resource and the comparability of chemical properties to lithium.<sup>[3]</sup> The practical use of Na-ion batteries is largely dependent on the electrode materials that are able to host sodium in their crystal structures.<sup>[4–6]</sup> However, compared with Li-ion batteries, the larger ionic size of sodium and higher hygroscopicity of synthesized materials affect the phase stability, transportation properties as well as the energy density of Na-ion bat-

teries, holding back their further development. In the last few years, remarkable amount of materials has been introduced as cathode materials for Na-ion batteries including layered type transition metal oxides, Prussian blue analogues, polyanionic compounds, and so on.<sup>[7,8]</sup>

Among these potential cathode materials candidates, layered structure transition metal oxides, denoted as  $Na_xTMO_2$ (TM = Mn, Fe, Co, Ni, etc.), have attracted great attention and have been extensively investigated because of their potential high capacity and relatively simple synthesis method.<sup>[5,6,9,10]</sup> Besides, the success and wide commercialization of Li-based layered transition metal oxides materials stimulated the intensively interest of  $Na_xTMO_2$  as well. Yet, still a lot of issues need to be solved before practical use. Tremendous attempts have been made aiming at improving the electrochemical stability of  $Na_xTMO_2$  originated from its inherent stacking sequence of host structure.<sup>[8,11]</sup>

However, some fundamental mechanism issues still have not been sufficiently understood. One such issue associated with the layered structure Na-ion battery materials is the possible cation migration into the sodium layer leading to a large unexpected capacity fading and structural deterioration upon cycling. This phenomenon was proposed earlier in the layered lithium storage materials, which is known as cation disorder or cation migration. The similar ionic radii of Li<sup>+</sup> and the transition metal ions facilitates the cation migration behavior.<sup>[12]</sup> Normally, this cation migration behavior is irreversible and will give



rise to various drawbacks including poor thermal stability, large surface side reaction, fast capacity fading, and so on. Therefore, considerable efforts have been made to overcome the disadvantages caused by the irreversible cation migration. Although sodium layers are generally thought to be resistant to the migration of transition metal owing to the larger ionic radii of Na<sup>+</sup> compared with the transition metal ions, latest researches carried out by different groups reveal the irreversible migration of partial transition metal into sodium layer would happen in Na-ion batteries.<sup>[13-16]</sup> Based on the peak intensity evolution of X-ray diffraction (XRD) patterns, Komaba and co-workers demonstrated the loss of electrode reversibility in O3-Na<sub>v</sub>CrO<sub>2</sub> and O3-Na<sub>x</sub>FeO<sub>2</sub> were highly correlated with possible transition metal migration into layered host structure.<sup>[15,16]</sup> Employed in operando X-ray diffraction combined with pair distribution function technique, Nazar and co-workers suggested the possible cation migration in Mn/Fe-based layered P2 structure Na-ion battery materials based on the electrochemical performance.<sup>[13]</sup> However, to the best of our knowledge, direct observation of reversible cation migration in the layered structure Na-ion batteries has not yet been proposed.

In this study, high-angle annular dark field (HAADF)scanning transmission electron microscopy (STEM) is employed to monitor the cation migration in the layered structure Na-ion batteries. Due to the sufficient spatial resolution, the nearly reversible cation migration from the TMO<sub>2</sub> layers into the sodium interlayer spaces was unambiguously observed. This result was further approved by the in operando XRD structure analyses combined with Fourier mapping of difference electron density between the observed and the calculated XRD reflections. The fundamental understanding of the reversible migration process is proposed based on our results. It shows that the previously believed irreversible cation migration could be reversible. This reversible cation migration phenomenon differs from what has been founded before, gives new insights into the structure evolution. Our research inspires a completely new perspective into the cation disordered related electrode materials, which is imperative for the potential improvement of battery design and could be considered for advanced energy storage.

The material we studied here is Na<sub>0.8</sub>Co<sub>0.4</sub>Ti<sub>0.6</sub>O<sub>2</sub> (NCT), which was synthesized through the traditional solid-state method as described in the Experimental Section. The assynthesized material was first examined by the X-ray powder diffraction, which was further refined by the Rietveld method to confirm the pristine structure. As it is shown in Figure 1a, all the diffraction peaks were successfully assigned by the hexagonal O3 phase with  $R\overline{3}m$  space group, without any diffraction lines from impurity phase, indicating that sodium ions occupy the octahedral (O) site according to the classification by Delmas et al.<sup>[17]</sup> The refinement showed a good agreement with experimental diffraction pattern with the  $R_{wp} = 4.58\%$ . Based on the refinement, the calculated lattice parameters of NCT are a = b = 3.00005(9) Å and c = 16.44205(67) Å (Table S1, Supporting Information). Scanning electron microscopy (SEM) images (Figure 1b) indicate the secondary particle size of assynthesized NCT material is around 5 µm with irregular morphology. Moreover, the XRD results indicate the mixing atomic structure did not exist initially before the charging process (Figure S1, Supporting Information).

The initial three cycles electrochemical tests of NCT material are shown in Figure 1c. The tests were performed



**Figure 1.** Characterization and electrochemical tests of  $Na_{0.8}Co_{0.4}Ti_{0.6}O_2$  (NCT) materials. a) XRD pattern and Rietveld refinement of as-synthesized NCT sample with experimental data in black line, calculated data in red dots, difference curve in blue, and standard Bragg diffraction peaks in pink vertical bars. b) SEM image of  $Na_{0.8}Co_{0.4}Ti_{0.6}O_2$  (NCT) with an average size of around 5  $\mu$ m. c) Electrochemical performance at 0.1 C rate and d) the dQ/dV plot of NCT electrode during first 3 cycles. The black, red, and blue lines indicate first, second, and third cycle, respectively.

galvanostatically at 0.1 C rate (1 C = 250 mAg<sup>-1</sup> based on the total mass of NCT) within a voltage window of 1.1 and 4.0 V. Note that the smaller charge capacity at the first cycle is the consequence of the sodium deficiency that left 20% of vacancy in the sodium layer. The first charge and discharge activated the potential sodium intercalation position and giving rise to a reversible capacity of around 100 mAh g<sup>-1</sup> for the following electrochemical cycling as can be seen in the second and third cycles. Particularly, the threshold of electrochemical tests is chosen based on the dQ/dV plot (Figure 1d), which shows a pair of distinct peaks corresponding presumably to the redox couple upon cycling.

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Notably, a remarkable voltage hysteresis showed up quickly after the sodium (de)intercalation start. At the beginning of charging process, the voltage curve jumped to the 3.8 V abruptly followed by a relative flat voltage plateau with smooth charging curve straight after the craggy slop. The flat plateau could be ascribed to the well accepted sodium ion transition from the octahedral site to the prismatic site and will be further studied afterward. Upon discharging, the curve behavior exhibited high symmetric as its antecedent charging process. The discharging curve directly dived till it reached 1.2 V keeping up with the similar voltage plateau within 1.1 and 1.2 V. Despite the significant polarization, the parallelogram like charge-discharge curve, as shown in Figure 1c, displayed relatively reversible behaviors, which could hardly be explained by the formation of irreversible rock-salt phase or the irreversible transformation of cation ion into the sodium layered structure as shown in the previously studies.[15,18]

To disclose the thermodynamic stable state of our NCT electrode, galvanostatic intermittent titration technique (GITT) was performed in Figure S2 (Supporting Information). GITT is a conventional used electrochemical technique that enables us to determine both kinetic and the thermodynamic behavior in solid state electrode.<sup>[19]</sup> For the GITT test, a fixed current, usually very small amount, was employed followed by a long-time relaxation. The voltage was recorded with regard to the time. The thermodynamic equilibrium potential could be obtained by tracing the open-circuit voltage at the end of each relaxation step. In our experiment, the NCT electrode was charged/discharged under very low current about 0.02 C for 1 h followed by a 10 h rest. As it showed in Figure S2 (Supporting Information), the polarization emerged at the early stage of charge (and discharge) process and gradually decreased till the end of charging/discharging. In spite of the decreasing, the polarization did not vanish at nearzero currents and was still very large with the average  $\approx 2.5$  V. The experiments implied rather than the kinetic polarization,<sup>[15]</sup> the hysteresis has to be originated from the inherent structure<sup>[20]</sup> change and the explanation will be expansion hereafter.

To further disclose the local structure and the origin of the large voltage polarization, HAADF-STEM technique was employed, which allows direct visualization of the structure change from the atomic point of view. For all the TEM measurements, both of the pristine material as well as the electrochemically operated material, i.e., charged and discharge electrode, a sealed sample holder was used as implement for the sample transform after taken out from the glove box to avoid the potential surface contamination with the air. The results of HAADF-STEM images and their corresponding FFT patterns are shown in **Figure 2** and Figure S3 (Supporting Information), respectively, where the sodium and oxygen atoms are not visible in the *Z*-contrast HAADF-STEM images due to their low atomic masses.<sup>[21]</sup> Therefore, the bright dots are corresponding to the transition-metal ions and depict the transition-metal ion arrangement.



**Figure 2.** The STEM images and their corresponding line profiles of NCT electrode at different stages. a–c) STEM image of (a) the pristine, (b) fully charged, and (c) fully discharged NCT electrodes viewed along the [010] direction. d–f) The corresponding line profiles of NCT electrodes where the red arrows point out the intensities that referred to the transition metal migration from the transition metal layers to the sodium layers.



**Figure 3.** Structure evolution of NCT electrode during the first cycle. a) Left: in-operando XRD patterns collected at a constant current rate of 10 mA  $g^{-1}$ . Middle: schematic of phase evolution upon cycling where the pristine O3 phase, O3 and P3 coexistence biphase, and P3 sole phase areas are depicted in red, orange, and blue color bars, respectively. Right: the corresponding electrochemical performance during XRD measurement. b) Evolution of *c*-lattice parameter as a function of the sodium content during the first charge (left) and discharge (right). The electrochemical profile, *c*-lattice parameter of O3 phase, and *c*-lattice parameter of P3 phase are represented by green line, blue hollow sphere, and red hollow sphere, respectively.

Figure 2a showed HAADF-STEM image of the pristine material in which all the transition metals are well aligned indicating the fine layered structure of the raw materials. After charge, the HAADF-STEM characterization showed (see Figure 2b) remarkable spots popped up between the neighboring transition-metal slabs, which indicated to the existence of transition metal ions in the sodium layers. This can be seen clearly in the corresponding intensity plot (see line profile in Figure 2e) where some pronounce peak intensities emerged between the transition metal peaks. The HAADF-STEM figure shows direct proof of the migration of transition metal ions into the sodium layers which is proposed as an assumption in the previous researches.<sup>[15,16]</sup> STEM-EELS suggested most of the migration was coming from Co atoms (Figure S4, Supporting Information). Besides, QSTEM simulate disclose around 20% transition metal (Co) migrated to the sodium layered (Figure S5, Supporting Information). Since the STEM-EELS measurement was also sensitive to the detect area and other factors, the further research is needed to confirm the dominant migration species. This cation migration behavior also provides the reasonable explanation of the large overpotential upon cycling in our system. To confirm the exist of P3 structure after charge, electron diffraction patterns from several direction were provided, which can be found in Figure S6 (Supporting Information).

It is noteworthy that, the unexpected reversible migration of transition metal occurred during the subsequent discharge process. Figure 2c presents the HAADF-STEM image after discharge. The result was distinguished with the characterization of charged sample in Figure 2b, represented for the migrated transition metal ion, decreased drastically. The corresponding intensity plot in Figure 2e,f provided better comparison from the quantity aspect. The slightly intensity between the transition metal peaks referred to a small amount of residual transition metal ion in the sodium layer position (Figure 2f). The reservation of TM in the sodium layer would slightly affect the cycling performance leading to a gradually decreased capacity (Figure S7, Supporting Information). Moreover, this highly reversible cation migration behavior also existed in the subsequent electrochemical performance that can be found in Figure S8 (Supporting Information). Despite of these residual ions, our results revealed the transition metal ion could reversibly migrate between the sodium layers and the transition metal layers in our case which did not directly be observed in the early research.

In operando XRD was performed to trace the structure evolution upon galvanostatic charge-discharge process. Figure 3a depicts the evolution of XRD pattern for the NCT electrode over the first charge-discharge between 1.1 and 4.0 V at a constant current rate of 10 mA g<sup>-1</sup>. As can be seen in Figure 3a the NCT electrode underwent the phase transition between O3 and P3 stacking pattern illustrated by the mutual intensity shifting of both 003 as well as 006 diffraction. The operando XRD analyse showed the O3-to-P3 conversion occurs at the beginning of charging process leading to the coexistence of O3 and P3 biphase stage. As the charge went on the O3 phase gradually vanished, instead, the P3 phase grew steadily and became the sole phase in the system until the end of charge stage. Upon discharging, the reversible P3-to-O3 transformation occurred making the system O3 again. The phase fraction of O3 calculated by the Rietveld refinement (Figure S9, Supporting Information) confirmed this transition tendency, which is also consistent with previous studies regarding the reversible phase transition between O- and P-type stacking.<sup>[5,9,22]</sup>

As described in the local structure study by HAADF-STEM, although sodium layers are generally thought to be resistant to migration of transition metal, our experiments showed the large hysteresis will induce cation migration from the transition metal layer to the sodium layers. This phenomenon was further confirmed from the structure evolution analysis especially expressed by the *c*-lattice parameter.

Figure 3b displays the evolution of *c*-lattice parameter for both O3 and P3 phase in the NCT during the first cycle along with the electrochemical performance. The charge and discharge stage are manually separated for a better understanding. Considering the cation migration was disclosed by the STEM as mentioned above, therefore, the structure evolution could be deduced as below. At the beginning of charge, the *c*-lattice parameter of O3 phase (*c*-O3) gradually increased due to the extraction of sodium ion. For the O3 stacking strategy, sodium ions occupied the octahedral site and have strong attraction for the oxygen atoms standing around them making the layered structure closely packed. Upon charging, deintercalation of sodium ion gave rise to the electrostatic repulsion between adjacent oxygen layers, leading to the increase of the *c*-O3. At the same stage, P3 phase emerged as a new phase and the *c*-lattice parameter of P3 (*c*-P3) also exhibit similar increasing tendency. This is ascribed to the different of stacking way of P3, which brings more open framework than O3 structure and possesses larger expansion along *c* direction. The transformation from O3 to P3 leads to the *c*-P3 increase as well.

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Note that all the potentially migrated transition metals can hardly jump to the sodium host layer or interlayer at the same time due to the large energy barrier required for the metalstable transformation, we assume this migration would happen step by step once the local current is large enough to activate the reaction. In our case the large hysteresis showed up at the initial stage of charge (and discharge) hence supplied large local current to the system. Therefore, we suggest at the beginning of charge the transition metals also transferred to the sodium layer along with the sodium extraction. In principle, the cation transferred to the sodium layer (or the interlayer) will also decrease the value of *c*-lattice parameter as the cation have larger positive charge state than sodium ions. Nevertheless, the fairly small amount cation migration at the beginning of charging did not have obviously influence of the overall behavior. As the charging went on, this impact became more pronounced gradually. The decreasing of *c*-P3 (also *c*-O3) in the subsequent charge process can be explained by the accumulation of certain amount of transition metal ions in the sodium layer.

During discharge c-P3 evolution displayed opposite tendency compared with the charge course, first increased then decreased, which implied that the migration of transition metal is almost reversible. The reaction can be depicted as below. When the sodium inserted into the system, the fast moving of sodium ion prefer to grasp oxygen since the fast moving species favor the formation of a selective equilibrium state.<sup>[23]</sup> The transition metal ions were expelled by the sodium ions. Moreover, the voltage polarization was still very large which provide sufficient kinetic power for the transition metal reversing back to the transition metal layer. The weaker attraction of sodium toward to the oxygen caused the increasing of c-lattice parameter of both c-P3 and c-O3. Yet, after the P3 phase vanished, the continuous sodiation induced the decreasing of c-O3 till even smaller than pristine c-O3 (16.44 Å). This can be explained by the extra amount of sodium (~Na0.9Co0.4Ti0.6O2) that insert into the O3 NCT structure leading to the contraction of c direction since the more sodium exhibited larger attraction for the adjacent oxygen layers. The good agreement with measurement and the calculation show the cation migration is almost reversible in our case. Moreover, it has to be emphasized that

the variation of nonlinear *c*-lattice parameter change is not the solely evidence that refers to the cation migration.<sup>[24]</sup> The combination with STEM and in situ XRD results provide the opportunity to disclose the structure evolution described above.

As it explicated above, both HAAD-STEM and in operando XRD studies showed the direct evidence that transition metal migrated to the sodium layered structure upon cycling. To confirm our observation from the experiment and further explored the possible occupancy space of the transition metal ions, Fourier density difference maps were performed based on the ex situ XRD pattern of cycled electrode.

From the ex situ XRD pattern of charged and discharged we can see clearly that the cycled electrode displayed fine P3 and O3 structure respectively without any new phase (Figure S10, Supporting Information). Rietveld refinement exhibited some intensity differences between the calculated results and the experimental observation, especially for the charged P3 diffraction pattern, which could refer to the missing atoms in the global frame. Our Fourier mapping were obtained by Fourier transformation based on those intensity difference. To generate the Fourier map focusing on the transition metal ion, the transition metal atoms occupancy were set to zero and performing the difference Fourier between calculated and the observed patterns from the ex situ XRD data.<sup>[25]</sup> The results are shown in **Figure 4**.

In Figure 4 the difference of electron density for the transition metal ions are plotted as green color. It can be visualized clearly, after charging, ignoring the electron density from the original transition metal space, the ball-like electron density for the transition metal ions appeared in the sodium innerlayer.



**Figure 4.** Electron density maps of density difference resulting from Fourier transformation. The Fourier transform of the density difference between the observed and calculated reflections was performed based on the model where no transition metals present in the structures. The occupancy of transition metals was set to zero. a) Reference O3 structure of pristine electrode with no density difference. b) Charged P3 structure and c) discharged O3 structure electron density maps of density difference resulting from ex situ XRD reflections and calculated reflections. The results represent the potential transition metal density in NCT electrodes. The red, blue, and pink solid balls represent of oxygen atoms, transition metal atoms, and sodium atoms, respectively, whereas the green imaginary contours plot represent the possible transition metals migrated positions.







**Figure 5.** Schematic plot of reversible transition metal migration upon cycling. The as-synthesized O3 type NCT electrode underwent  $O3 \rightarrow P3$  phase transition upon charging combined with a fraction of cation migration into the sodium layers from the transition metal layers. After discharge, the electrode became O3 phase again indicated a reversible phase transition behavior. Meanwhile, most of the transition metals that occupied in the Na layers moved back to the transition metal layers.

This means, besides the original place, considerable transition metal ions migrated to the sodium layers (see Figure 4b). Moreover, rather than the sodium place, these transited ions seems favor of moving to the interstice site and face toward to the oxygen atoms. This place can hardly refer to the classic octahedral or prismatic site. Upon discharging, these electron densities disappeared again which refer to the highly reversible of the transition metal ion migration (see Figure 4c).

Further analysis within wider voltage window<sup>[15,16]</sup> disclosed charging to the higher voltage range would significantly increased the irreversibility of cation migration (Figures S11–S13, Supporting Information). Fourier mapping of different charge density at different discharge states indicated more and more TM ions would occupied at the sodium state (octahedral site) at the end of discharging, leading to a larger irreversible of cation migration when discharged from the higher voltage state.

In conclusion, for the first time, a complete and consistent picture of the reversible cation metal ion migrating to the sodium layer in the layered materials is presented based on the HAAD-STEM and in operando XRD technique combined with the Fourier mapping of difference electron density. This reversible migration is depicted by monitoring the evolution of *c*-lattice parameter upon cycling. It is demonstrated that during charging, the transition metal ion transferred into the sodium layers due to the large voltage polarization. The extraction of the sodium ion from the host structure leads O3-to-P3 conversion and makes c-O3 and c-P3 increasing at the beginning. The small amount of cation migration does not strongly affect the structure at the start. As the charge goes on, the accumulation of transition metal ion in the sodium layer contributing strongly to the attraction of the oxygen slab, giving rise to the decreasing of the c-P3 at the end of charging process. The opposite evolution of *c*-lattice parameter shows up during the subsequent discharge process which refers to the migration of the transition metal ion back to its transition metal layer. The schematic plot of this process can be found in Figure 5. Fourier difference density mapping further disclosed the occupancy of transition metal ions existing in the sodium layers at the interstice site facing toward to the oxygen atoms. Moreover, despite the large hysteresis found in the NCT material, the novel insights regarding the driving force and de/intercalation mechanisms are very important for cathode materials of sodium ion batteries, the materials with superior electrochemical performance can be developed from this aspect.

#### **Experimental Section**

Sample Preparation: The O3 structure NCT material was prepared by simple solid-state reaction. All the chemical compounds used come from Wako Pure Chemicals Industries Ltd., Japan. The starting materials of Na<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub>, and CoO were well ground in an agate mortar with stoichiometric proportion at a rotation rate of 200 r min<sup>-1</sup> for 20 h. An excess 5 wt% of Na<sub>2</sub>CO<sub>3</sub> was added. The obtained powders were pressed using the 16 mm diameter of presser, and then heat-treated at the temperature of 900 °C for 15 h in the Ar atmosphere. The heated materials were quenched to the room temperature and then transport into an argon-filled glove box. The molar ratios of the metal ions in the O3-NCT sample was chemically analyzed by laser ablation inductively coupled plasma mass spectrometry. The Na/Co/Ti ratios were finally exhibit to be 0.83:0.40:0.59, which matching well with the designed materials.

Electrochemistry: The electrochemistry tests were carried out using CR2032 coin-type cells, where NCT material was used as the cathode and the sodium metal was used as the anode. The slurry with 75% NCT material, 20% teflonized acetylene black and 5% polytetrafluoroethylene was coated into the aluminum screens. The coated cathode electrodes were  $\approx$ 2 mg in mass and 7 mm in diameter with the loading mass around 1.3 mg cm<sup>-2</sup>. All the electrodes were dried under the vacuum condition at about 110 °C for 24 h until cells assembling. All the electrodes were pressed before use to enhance the contact between electrode composite and current collector and then assembled in a glove box filled with dried argon gas ( $O_2$  and  $H_2O < m0.1$  ppm). The electrolyte used in the experiments was 1 mol dm $^{-3}$  NaClO4 dissolved in propylene carbonate (Tomiyama Pure Chemical Industries, Japan) with 2 vol% fluorinated ethylene carbonate as an electrolyte additive.<sup>[26]</sup> A glass fiber disks were used as the separator. All the electrochemical tests were performed using Hokuto Denko HJ1001SD8 (Japan) battery tester. The cells were operated at different current densities within a selected cut-off voltage window of 1.1-4.0, 1.1-4. 2, or 1.1-4.5 V versus Na/Na<sup>+</sup> at room temperature after a 12 h rest of equilibrium. The current density of 1 C corresponds to 250 mA  $g^{-1}$ .

Material Characterizations: The XRD data were recorded using Cu  $K\alpha$  radiation on a Bruker D8 Advance Diffractometer (Germany). For the ex situ XRD characterization, the cycled samples were loaded in the air-tight sample holder to avoid potential oxidation from the air exposure. Operando X-ray diffraction tests were performed in the coin-type cells with diffraction window on the cathode side. The cell was cycled at a constant current rate of 10 mA g<sup>-1</sup>. The diffraction data were refinement. All the ex situ and in operando diffraction data were refinement. All the ex situ and in operando diffraction data were refinement in GSAS software.<sup>[27]</sup>

To observe the morphology of the NCT electrode, SEM was done on the TOPCON DS-720 instrument (Japan). A JEOL-2100F STEM (Japan) equipped with a double aberration-corrector was used to perform HAADF imaging for both probe-forming and imaging lenses. The HAADF-STEM was operated at 200 KV. The convergence angle was 25 mrad



and the angular range of collected electrons for HAADF imaging was  $\approx$ 60–250 mrad. The Gatan Quantum spectrometer on the microscope was used to keep the track of STEM-EELS line scan data were recorded using. The probe current was 40 pA in 0.1 nm probe with the acceleration voltage of 60 kV. The measurement of the charge and the discharged samples were obtained from the electrodes which were subjected to ex situ XRD, STEM, and STEM-EELS line scan mentioned above. For all the TEM measurements, both of the pristine material as well as the electrochemical operated material, i.e., charged and discharge electrode, an air-tight sample holder was used as implement for the sample transformation after taken out from the glove box to avoid the potential surface contamination with the air. HAADF-STEM images are simulated by using the QSTEM, which is a suite of software for quantitative image simulation of electron microscopy images, including model building.<sup>[28]</sup>

The TEM specimen preparation by FIB lift out was conducted on an FEI Helios Dualbeam 600 operation at 2–30 kV. First, 1.2  $\mu$ m thick Pt layer (200 nm e-beam deposition followed by 1  $\mu$ m ion beam deposition) was deposited on the particles to be lifted out to avoid Ga ion beam damage. After lift out, the specimen was thinned to 200 nm using 30 kV Ga ion beam. A final polishing was performed using 2 kV Ga ion to remove the surface damage layer and the surface damage layer was believed to be <1 nm. The FIB-prepared samples were placed on the TEM holder in 99.99% N<sub>2</sub> atmosphere and then investigated by using an FEI Titan G2 Cubed 60–300 microscope at 300 kV. This microscope is equipped with double aberration correctors, enabling sub-angstrom imaging using HAADF-STEM detector.

## **Supporting Information**

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

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### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

Fourier mapping, HAADF-STEM, reversible cation migration, sodium-ion batteries

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