Probing Microstructure and Phase Evolution of α -MoO₃ Nanobelts for

Sodium-Ion Batteries by *In Situ* Transmission Electron Microscopy

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Abstract:

The fundamental electrochemical reaction mechanisms and the phase transformation pathways of layer-structured α -MoO₃ nanobelt during the sodiation/desodiation process to date remain largely unknown. To observe the real-time sodiation/desodiation behaviors of α -MoO₃ during electrochemical cycling, we construct a MoO₃ anode sodium-ion battery inside a transmission electron microscope (TEM). Utilizing *in situ* TEM and electron diffraction pattern (EDP) observation, α -MoO₃ nanobelts are found to undergo a unique multi-step phase transformation. Upon the first sodiation, α -MoO₃ nanobelts initially form amorphous Na_xMoO₃ phase and are subsequently sodiated into intermediate phase of crystalline NaMoO₂, finally resulting in the crystallized Mo nanograins embedded within the Na₂O matrix. During the first desodiation process, Mo nanograins are firstly re-oxidized into intermediate phase NaMoO₂ that is further transformed into amorphous Na₂MoO₃, resulting in an irreversible phase transformation. Upon subsequent sodiation/desodiation cycles, however, a stable and reversible phase transformation between crystalline Mo and amorphous Na₂MoO₃ phases has been revealed. Our work provides an in-depth understanding of the phase transformation pathways of α -MoO₃ nanobelts upon electrochemical sodiation/desodiation processes, with the hope of assistance in designing sodium-ion batteries with enhanced performance.

Keywords: sodium-ion batteries; *in situ* TEM; MoO₃; sodiation/desodiation; multi-step phase transformation

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Introduction

Lithium-ion batteries (LIBs) have been widely used as power sources for electronic devices and renewable power stations in decades.[1, 2] Various anode materials that are believed to have high Li-uptake ability, high power density and good cyclability have been sought for improving the performance of next-generation LIBs.[3-9] However, the price of LIBs will be driven up since the resource of metal lithium in the earth is limited and the demand for large-scale energy storage becomes widespread.[10] Therefore, it is urgent to explore new charge carrier as an alternative of lithium to lower the cost of the electronics industry. Sodium, with the similar chemical properties and natural abundance as well as low redox potential, makes sodium-ion batteries (SIBs) great potential to the alternative of LIBs.[10, 11] With the guidance of LIBs, various materials, such as Sn,[12] SnO₂,[13] CuO,[14] MnO₂,[15] MoO₃,[16] Co₉S₈[17] *et al.*, have been investigated for the applications in SIBs in the past few years. The researches have shown that the reaction mechanisms between the insertion/extraction of sodium and lithium ions during electrochemical cycles are not completely equivalent as Na⁺ has larger ionic radius than Li⁺. Moreover, as it has a relatively short development history, the knowledge about the science of SIBs is lacking. Therefore, exploring the fundamental sodiation/desodiation electrochemical behaviors and the underlying failure mechanism are extremely urgent for designing suitable anode materials with improved performance for SIBs.

The α -MoO₃ has a unique layered structure: each layer is composed of two sub-layers which are formed by corner-sharing [MoO₆] octahedral along [001] and [100] directions and the two sub-layers are stacked together by sharing the edges of the [MoO₆] octahedral along [001] direction. An alternate stacking of these layers along the [010] direction with van der Waals interaction leads to the formation of the two-dimensional structure. The 1D α -MoO₃ nanobelt has been studied as a well-known lithium insertion compound for decades.[6, 18, 19] Growing attentions are focused on exploring the underlying failure mechanism and improving the performance for LIBs.[20-23] Although it has been proved that α -MoO₃ can also be used as host material to accommodate the insertion of Na ions,[24] the fundamental mechanism still remains largely unknown to date. No *in situ* work has been performed to indentify the nature of the electrochemical sodiation/desodiation behaviors. Furthermore, the information about dynamic morphology and microstructure evolutions of α -MoO₃ nanobelt during cycles is currently not reported yet, leading to the lacking knowledge of the underlying electrochemical reaction mechanism.

Recently, the rapid development of *in situ* transmission electron microscopy (TEM) technique makes it possible to directly observe the dynamic process of nanomaterials during electrochemical reaction.[25-29] Here, we construct an all-solid nanobattery within an individual α -MoO₃ nanobelt anode inside TEM to visualize the morphology, size and microstructure evolutions during electrochemical sodiation/desodiation cycles. Upon the first sodiation process, the sodiation displacement of the α -MoO₃ nanobelts exhibits axial stepwise propagation with time, indicating that the sodium ions firstly wet the anode surface and then insert into the anode which led to fast sodiation ratio. Utilizing *in situ* TEM and EDP observations, α -MoO₃ nanobelts are found to undergo a unique multi-step phase transformation. Upon the first sodiation, the α -MoO₃ nanobelts initially form amorphous Na_xMoO₃ and subsequently convert into crystalline NaMoO₂, finally resulting in the formation of crystallized Mo nanograins embedded within a Na₂O matrix. During the first desodiation process, Mo nanograins are firstly re-oxidized into crystalline NaMoO₂ followed by the conversion to amorphous Na₂MoO₃ which is confirmed by EELS and EDPs measurements, resulting in an irreversible phase transformation after the first cycle. We also find that the phase transformation during subsequent cycles is reversible between crystalline Mo nanograins and amorphous

Na₂MoO₃. Our work reveals the detailed information about the sodiation/desodiation process, providing an in-depth understanding of the fundamental mechanism of α -MoO₃ nanobelts during electrochemical cycles.

Experimental Section

Preparation of α -MoO₃ Nanobelts

The α -MoO₃ nanobelts were synthesized according to the previous reports.[21] Briefly, 2.0 g ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved into 15 mL deionized water and formed a clear solution, in which the PH value was adjusted to about 1 by slowly adding a certain amount of HNO₃ (5M). After that, the mixed solution was sealed in a Teflon-lined stainless autoclave at 180 °C for 30 h. The obtained thick white colored precipitate of MoO₃ was filtered and washed with distilled water, followed by drying in a hot air oven at 60 °C for 12 h.

In situ TEM Experiments for Electrochemical Sodiation/Desodiation

A high-resolution TEM (FEI Titan, 80-300 KV) with a fast responding charge-coupled device (CCD) camera was carried out for *in situ* observing the electrochemical behaviors of the α -MoO₃ nanobelts during sodiation/desodiation cycles with the assistance of electron diffraction pattern (EDP), HRTEM image and EELS spectrum measurements. The details of electrochemical experiment setup inside TEM are described as followings. The α -MoO₃ nanobelts, which were attached to an Au rod by conductive silver colloid to ensure a good electrical contact, were used as anode. Metal sodium was adhered to a tungsten probe and regarded as the counter electrode and sodium source. The natural oxide layer Na₂O which was generated in the holder loading process acted as the role of solid electrolyte, allowing the transport of sodium ions. Building the nanobattery was accomplished in a glovebox filled with Ar-gas, as sodium is a very active metal and can be oxidized easily. Afterward, the holder was immediately transferred into a TEM column. The tungsten probe was driven by a piezo-positioner inside TEM to make the Na/Na₂O and α -MoO₃ nanobelt in contact by fine steps. A constant -2 V/3 V potential was then applied to the α -MoO₃ nanobelts anode with respect to sodium counter electrode to drive the transport of sodium ions through the solid-state electrolyte Na₂O layer, thereby initiating the electrochemical sodiation/desodiation process.

Half Cell Measurement

Galvanostatic electrochemical performance of the as-prepared MoO₃ nanobelts was performed with a 2025-type coin cell in the voltage window 0.04-3.0V at room temperature on a Neware battery cycler at various current densities. The working electrode for SIBs is the slurry mixture of active material (MoO₃ nanobelts), acetylene black, and polyvinylidene fluoride (PVDF) (75:15:10 weight ratio) in N-methyl pyrrolidone which has been stirred for 12 h. The slurry was coated onto Cu foam current collector and dried at 240°C for 4h under Argon gas. Metal Na was used as the counter electrode and reference electrode, meanwhile, the electrolyte was 1.0 M NaClO₄ in the mixture of ethylene carbonate (EC)/ propylene carbonate (PC) (1:1 volume ratio).

Results and Discussion

The schematic illustration of the *in situ* experimental setup inside TEM, as shown in Figure 1a, consists of three parts: anode α -MoO₃ nanobelt, counter electrode sodium and all-solid electrolyte Na₂O. The α -MoO₃ nanobelts were attached to an Au wire by conductive epoxy to ensure good electrical contacts, while the metal Na was scratched by a sharp tungsten probe in the glovebox filled with Ar gas to avoid over oxidation. The thin layer of Na₂O formed on the surface of Na metal as a result of the short time air

exposure during the holder loading procedure can perfectly serve as the solid electrolyte and allow the transport of sodium ions. The tungsten probe was driven by a piezo-positioner inside TEM to make the Na/Na₂O layer and the α -MoO₃ nanobelts in contact with each other by fine steps. Afterwards, a constant -2 V/3V potential was applied to the α -MoO₃ nanobelts anode with respect to sodium to drive the transport of sodium ions through the Na₂O layer, thereby initiating the electrochemical sodiation/desodiation process. Figure 1b displays the corresponding TEM image of a nano-battery within α -MoO₃ anode which has a uniform width and belt-like morphology (Figure S1 in Supplementary Material), and the yellow arrow denotes the transport direction of sodium ions. The diffraction spots in the EDP of an individual α -MoO₃ nanobelt (Figure 1c) that can be perfectly index as the orthorhombic MoO₃ (α -MoO₃) phase (JCPDS no. 35-0609), revealing its single crystalline feature. Insert in Figure 1c is the HRTEM image of α -MoO₃, in which the lattice spacing of 3.81 Å can be assigned as the (110) plane.

The time sequences of TEM images of two α -MoO₃ nanobelts during the first sodiation process are given in Figure 1(d₁-d₄) and (e₁-e₄) (Movie S1 and S2 in Supplementary Material), where we can see the morphology and size evolution. Apparently, sodiation began from one side in contact with the Na/Na₂O layer and propagated toward to the other side, leading to obvious radial expansion and axial elongation as a result of the intercalations of sodium ions. The huge axial elongation can result in the bend of the nanobelts as the distance between Au electrode and Na/Na₂O is limited. The radial expansion of the two α -MoO₃ nanobelts during sodiation in Figure 1d and 1e can be respectively estimated as 26.6% and 29.1% on the basis of their size increases, meanwhile, the axial elongation of the nanobelt in Figure 1e is about 27.4% with the assistant reference marked by black arrow in Figure 1e₁. However, we have no idea about the size expansion in the thickness direction as the image we observed during the *in situ* TEM experiment is the projection of the real object and the belt-like MoO₃ may show very different size expansion in diameter and thickness directions. Therefore, the specific volume expansion of the nanobelt-like MoO₃ is almost impossible to be estimated just from the TEM experiments.

The positions of reaction front that are labeled with red arrows by following the swelling of the nanobelt at different time can be used to measure the relationship between sodiation length and time. Figure 1f shows the plotted sodiation length vs time of the two nanobelts in Figure 1d and 1e. From that we find the sodiation ratio which can be reflected by the slope does not follow the rule of parabolic shape but exhibits stepwise increase feature. In detail, the sodiation ratio of the sample in Figure 1d during the first 27 s was 21.6 nm/s, and decreased to 3 nm/s during the following 11 s. Afterward, the value increased to 14.5 nm/s and then decreased to 1 nm/s and then increased to 2.84 nm/s. The sample in Figure 1e also showed the similar sodiation behavior. We believe this behavior should be attributed to the different sodiation mechanism of α -MoO₃ nanobelt compared with other anode materials. The sodium ions maybe wet the anode surface firstly followed by inserting and reacting which will lead to fast sodiation ratio. In the meantime, the overall movement speed of the reaction front still decreased since the transport distance for sodium ions became longer as the sodiation process proceeded. We also found the irregular Na₂O around the both two nanobelts in the sodiation parts and this behavior can be ascribed to the fast diffusion of Na species along the nanobelts surface, which is the consequence of the nature in the *in situ* TEM experiments.[12, 13] However, it will not affect the intrinsic electrochemical behaviors during the sodiation/desodiation processes. Moreover, no fracture and cracking were observed in spite of obvious size expansion, which is beneficial to keeping a good electronic contact between the anode material and current collector and thus enhanced performance.

We further achieved a close view of the microstructure evolution of a segment α -MoO₃ nanobelt, as given in Figure 2a₁-a₄ and movie S3 in Supplementary Material. The nanobelt with a uniform width of

138.5 nm was fully sodiated within 600 s and has a radial expansion of 27.7 % depending on its size increase. During the sodiation process, the α -MoO₃ nanobelt just swelled and then coated with a crystalline layer which thickened as the sodiation time went on. The crystalline layer with a size of ~5-7 nm can be identified as Na₂O from the HRTEM image of a fully sodiated anode in Figure 2b, in which the lattice fringe is ~2.76Å and in good agreement with the (200) plane of Na₂O (JCPDS no. 03-1074). As we can see from the Figure 2b, the single crystal nanobelt has converted into numerous nanograins that were marked by white dashed circles embedded into the Na₂O matrix after sodiation process. These nanograins with size of less than 1 nm can be validated as metal Mo from EDP of a fully sodiated anode in Figure 2c₁₀. Overall, the sodiation process involves the reduction of MoO₃ to Mo and the formation of crystalline Na₂O, which can be expressed by the following equation:

To deeply understand the fundamental reaction mechanism and confirming the intermediate products of MoO₃ during the first sodiation process, time-lapsed EDPs were achieved and displayed in Figure 2c. The original anode shows obvious single crystalline feature (Figure 2c₁), in which the distance between two symmetrical diffraction spots marked by red arrows is 10.1 1/nm and can be indexed as the (200) plane of MoO₃. In the meantime, the measured angle between the line determined by the two spots and horizontal is about 82.3°. Once sodiation began, the spots blurred and the (200) spacing increased from 1.98 nm to 2.13 nm at 24s and 2.32 nm at 56s, confirming the insertion of sodium ions. Meanwhile, the measured angle continually changed, as Figure 2c₁-2c₃ show, which can be attributed to the rotation of zone axis caused by the volume expansion during sodiation. Besides that, we also find the disappearance of diffraction spots and the formation of amorphous phase (Figure 2c₃-2c₄), suggesting the existence of disordered structure induced by Na⁺ intercalation. The reaction in this stage can be expressed as follows:

This behavior is similar to that in lithiation process.[30] Afterwards, a broad diffraction ring which can be indexed as (200) plane of Na₂O (JCPDS no.03-1074) and (006) plane of NaMoO₂ (JCPDS no.23-0687) was detected, as shown in Figure 2c₅. And as the sodiation proceeded, more and more diffraction rings and spots that can be indexed as Na₂O and NaMoO₂ were acquired (Figure 2c₅-c₈), in the meantime, the amorphous phase was vanished gradually, indicating the conversion from amorphous Na_xMoO₃ to crystalline Na₂O and NaMoO₂, which can be expressed as:

Subsequently, Mo phase was captured (JCPDS no.01-1207), while most diffraction rings represent NaMoO₂ tapers off and only the (107) plane can be found at 638s, as shown in Figure 2c₉. The EDP that can be assigned to Mo and Na₂O (Figure 2c₁₀) never changed after 812s, indicating that the nanobelt has been fully sodiated and the final sodiation product is the mixture of Mo and Na₂O, agreeing well with the HRTEM result. So the electrochemical reaction involved in this stage is:

Consequently, the sequential phase transformations of the α -MoO₃ nanobelts during the first sodiation can thus be expressed as: $c\text{-MoO}_3 \rightarrow a\text{-Na}_x\text{MoO}_3 \rightarrow c\text{-NaMoO}_2 \rightarrow c\text{-Mo}$.

After the full sodiation, a constant positive potential of 3 V was applied on the anode to initiate the desodiation behaviors. Figure 3a₁-a₄ shows the size and morphology evolution of a segment of an individual α -MoO₃ nanobelt during the first desodiation process. This dynamic desodiation behavior can also be seen in the Movie S4 in Supplementary Material. The sodiated anode of 114.5 nm shrunk its size to 95.7 nm, with a contraction of ~19%, accompanying with the disappearing of Na₂O layer. Meanwhile, the morphology of numerous Mo nanograins within Na₂O matrix vanished and converted into a smooth

surface, as given in Figure 3a₄. The morphology and size evolution is the result of phase change caused by the sodium ions extraction and electron transmission during desodiation process.

For deeply understanding the fundamental electrochemical desodiation mechanism, the following two crucial questions must be considered. (1) Whether the desodiation process can convert the sodiated anode to its pristine state? (2) Is there any intermediate phases appeared during the desodiation process? To solve these problems, we acquired EDPs of another sodiated anode at variable intervals during whole desodiation process and displayed them in Figure 3b₁-b₈. As Figure 3b₁ shows, the final sodiation product is the mixture of crystalline Mo and Na₂O. And the diffraction spots that can be indexed as (107) plane of NaMoO₂ appeared (Figure 3b₂) at the early desodiation stage. As the desodiation time went on, the feature of Mo disappeared, instead, the diffraction rings represent crystalline NaMoO₂ became more and clearer, as given in Figure 3b₃. This result indicates that the first stage desodiation reaction is:

Afterwards, these diffraction rings/spots continually decreased, and in the meantime, diffused rings that represent amorphous phase started to arise (Figure 3b₄-b₇). After the full desodiation, the EDP exhibits obvious amorphous feature and no diffraction rings/spots can be detected, suggesting the final desodiation product is amorphous (Figure 3b₈). However, we cannot identify the nature of the desodiated anode due to the limited information provided by the diffused rings. To further confirm the specific desodiation product, we used the intensity ratio of Mo-M_{3,2} that can be calculated from the electron energy-loss spectroscopy (EELS) spectrum to identify the valence state of element Mo in the fully desodiated anode. From the EELS spectrum in Figure 3c, we can find the value of I_{M3}/I_{M2} is 2.18, corresponding to the state of +4.[31] Consequently, we believe that the form of the final desodiation product is Na_(2y-4)MoO_y (2 ≤ y ≤ 3) and the amount of extraction sodium is thus about four in each cell after the first desodiation process. Considering about this, we believe that the possible reaction from intermediate NaMoO₂ to final amorphous phase may be expressed by the following two equations.

Accordingly, the overall electrochemical reaction during desodiation process can be expressed as:

If the real reaction follows the former one, we should detect crystalline Na₂O phase from the desodiated anode as only four Na₂O in each cell participated in the reaction. However, no Na₂O feature can be found from the EDP in Figure 3b₈. And with the latter reaction equation, crystalline Na₂O was consumed up during the desodiation process, in well agreement with the EDP result. Base on above analysis, we believe that the final desodiation product is amorphous Na₂MoO₃ and the reactions involved during the first desodiation process would be as follows: *c*-Mo → *c*-NaMoO₂ → *a*-Na₂MoO₃. The desodiation process cannot convert the anode into its original state, resulting in an irreversible microstructure change which should be responsible for the huge capacity loss during the first cycle.

The microstructure evolution of a segment of α-MoO₃ nanobelt during the first three electrochemical sodiation/desodiation processes was investigated and displayed in Figure 4 to well understand the conversion mechanism during charging/discharging cycles. We also showed the dynamic microstructure evolution of the anode during the first three cycles in Movie S5 (Supplementary Material), including the vanishment and formation of Na₂O layer, the expansion and constriction of the anode, as well as the appearance and vanish of the Mo nanograins. In the following cycles, the constant potential of -2V/3V was applied to the α-MoO₃ nanobelt to initiate the electrochemical sodiation/desodiation behaviors. Figure 4a is

a pristine α -MoO₃ nanobelt anode with a diameter of 55.5 nm. The size expansion/contraction and morphology evolution of the anode after the first three electrochemical cycles are shown in Figure 4b-g. The α -MoO₃ nanobelt anode has an obvious size expansion, meanwhile, the anode converted into numerous nanograins within Na₂O matrix after full sodiation. During desodiation processes, the lithiated anode shrunk its volume and the Na₂O layer disappeared as a result of the extraction of sodium ions. The anode diameter changes after each electrochemical process were plotted in Figure 4h. From that we can see the size expansion after the first sodiation process is about 27%, while the first desodiation process only leads to 16% contraction. In the subsequent cycles, the expansion and contraction rates are only in the range of 16%-19.5%. In the range of the errors permitted, we believe that the anode has a reversible size change after the first cycle. Consequently, we hold the opinion that the reaction mechanism dominating the first sodiation is different from the mechanism during the subsequent (de)sodiation cycles.

Figure 4a₁-g₁ show the EDPs recorded from the anode in the planes a-g, revealing the phase change during the first three cycles. After the first fully sodiated process, the single crystal MoO₃ (Figure 4a₁) was converted into the mixture of crystalline Mo and Na₂O (Figure 4b₁). During the subsequent desodiation process, the sodiated anode did not turn into its pristine state but exhibited amorphous feature (Figure 4c₁), suggesting that an irreversible microstructure phase change happened during the first cycle. Although the starting anode material during the second sodiation process was different from that in the first cycle, the sodiation product was still same as the first sodiated one, as Figure 4d₁ displays. The second sodiation reaction can thus be expressed by the following equation:

As expected, the second desodiation product exhibited the same characteristic (Figure 4e₁) with that in Figure 4b₁. From Figure 4f₁ and 4g₁, we can find the phase evolution during the third cycle is identical to the second one. The repeated EDPs indicate that the microstructure evolution after the first cycle is reversible between crystalline Mo and amorphous Na₂MoO₃ which has been verified by the discussions about Figure 3. The results can also confirm that the different size change during the first sodiation process and subsequent (de)sodiation cycles is resulted by the electrochemical reaction mechanism difference. We also *in situ* observed the EDPs of another anode during the second cycle, and we found that the phase change also can be expressed as followings: $a\text{-Na}_2\text{MoO}_3 \leftrightarrow c\text{-NaMoO}_2 \leftrightarrow c\text{-Mo}$. This behavior indicates that the anode after the first cycle also undergo a multi-step phase change during the subsequent cycles. With the above analysis, we can attribute the low coulomb efficiency and large capacity loss in the first cycle to the incompletely re-oxidized process of Mo to Na₂MoO₃ (Mo⁴⁺) rather than MoO₃ (Mo⁶⁺), meanwhile, the better capacity retention and cycling performance during the subsequent cycles can be ascribed to the relatively reversible phase and size changes.

EELS white lines of transition metals, which contain rich information about the chemical bonding and density of unoccupied states near the Fermi Level, can be used to quantificationally analyze the chemical element at nanoscale inside TEM. Here, the intensity ratios of M_{3,2} edges with distinct valence specific shapes (I_{M3}/I_{M2}) of element Mo collected from the anode were obtained and given in Figure 5 to reveal the valence state evolution during the first three electrochemical sodiation/desodiation cycles. Figure 5a shows the EELS spectrum of the original MoO₃ nanobelt, in which the I_{M3}/I_{M2} is 1.89, undoubtedly agreeing well with the valence state of +6. [31] After the first sodiation process, the value was increased to 2.53 (Figure 5b) and corresponded to the state of 0, indicating the MoO₃ nanobelt was reduced into metal Mo. I_{M3}/I_{M2} was lowered to 2.19 after first desodiation, as Figure 5c displays, indicating the valence state of Mo is +4. The obvious difference of I_{M3}/I_{M2} between Figure 5a and Figure 5c confirms that the MoO₃ nanobelt cannot be back to its original state of Mo⁶⁺ after the first desodiation process. This irreversible

microstructure change should be responsible for the huge capacity loss after the first cycle. The value of I_{M3}/I_{M2} was increased to 2.51 again after second full sodiation process (Figure 5d), similar to that after the first sodiation, suggesting the sodiation product was still metal Mo although the different starting material. As given in Figure 5e, the I_{M3}/I_{M2} was decreased to 2.22 again after second desodiation process, implying the valence state of Mo in the anode is +4. The I_{M3}/I_{M2} evolution during the third cycles (Figure 5f-g) is identical to the second one, indicating the reversible microstructure evolution between Mo^0 and Mo^{+4} during subsequent cycles. The EELS results that the evolution of valence state of Mo follows $Mo^{+6} \rightarrow Mo^0 \leftrightarrow Mo^{+4}$, agreeing well with the conclusion that α - MoO_3 nanobelts undergo irreversible microstructure evolution from MoO_3 to amorphous Na_2MoO_3 during the first cycle and reversible phase change between Mo and Na_2MoO_3 during subsequent cycles. Consequently, the overall electrochemical reactions can be expressed as the followings:

The crystal structure evolution of the MoO_3 anode during the first electrochemical sodiation/desodiation process is schematically given in Figure 6. Upon the initial sodiation, sodium ions firstly inserted into MoO_3 under the drive of the negative potential, which can lead to a reasonable volume expansion and disordered structure, forming amorphous phase Na_xMoO_3 . According to the previous reports,[32] the lithium ions can insert not only into the interlayer spacing between $[MoO_6]$ octahedron layers but also into the $[MoO_6]$ octahedron interlayers. Because sodium ion and lithium ion possess the same amount of charge and similar chemical properties as well as the enough space for the insertion of sodium ions in the MoO_3 , we therefore believe that the insertion of sodium ions into the MoO_3 structure is similar to that of lithium ions, as Figure S2 (Supplementary Material) shows. Upon the further sodiation, Na_xMoO_3 phase was converted into another intermediate phase of crystalline $NaMoO_2$. Finally, the full sodiation resulted in the formation of crystalline Mo dispersed in Na_2O matrix.

Afterwards, a potential of 3V was applied to initiate the first desodiation process, forming fully desodiated product of Na_2MoO_3 phase, rather than the original MoO_3 . The intermediate $NaMoO_2$ phase also occurred during the desodiation process. Once the Na_2MoO_3 phase was formed, the nanobelt never changed in size and morphology, implying that the anode material has been desodiated completely. Note that upon the subsequent sodiation/desodiation cycles, a stable and reversible phase transformation between the Na_2MoO_3 and Mo phases would be established. We also provide the schematic view of the microstructure evolution of α - MoO_3 nanobelt during the electrochemical cycles, as displayed in Figure S3 (Supplementary Material).

A coin cell with MoO_3 nanobelts as working electrode was constructed to test its electrochemical performance for SIBs and the result of its rate performance was provided in Figure 7. From that we can see the MoO_3 electrode delivers an initial discharge (sodiation) capacity of 545 mAhg^{-1} and charge (desodiation) capacity of 330 mAhg^{-1} at the current density of 100 mA g^{-1} , with a low Coulombic efficiency of 60.6% in the first cycle. Afterwards, the electrode shows similar capacity retention under same current density during subsequent cycles with the Coulombic efficiency of $> 90\%$, suggesting a good cycling performance after the first cycle. This result is in well agreement with the conclusion from *in situ* TEM experiments that the MoO_3 nanobelts show an irreversible phase change during the first cycle while a reversible microstructure evolution during the subsequent cycles. Except the irreversible phase conversion, the capacity loss during cycles can also be attributed to the irreversible formation of SEI membrane and electrode pulverization. Besides that, we can also find that the capacity keeps about 188 mAhg^{-1} at a high current density of 1000 mA g^{-1} , and the capacity can recover to about 280 mAhg^{-1} when the current density

is reset to 100 mAg^{-1} , suggesting that MoO_3 nanobelts can tolerate high current density charge/discharge cycling and have great potential to be charged and discharged rapidly. After 50 cycles with various current densities, we also performed the cycling performance measured at a current density of 100 mA/g , from which we find the electrode still has an acceptable reversible capacity of $\sim 280 \text{ mAhg}^{-1}$ after further 50 cycles, confirming the good cycling performance of $\alpha\text{-MoO}_3$ nanobelts.

Conclusions

In summary, the electrochemical sodiation/desodiation behaviors of $\alpha\text{-MoO}_3$ nanobelts have been revealed by *in situ* TEM technique for the first time. Upon the first sodiation process, the sodiation displacement exhibits axial stepwise increase with time, indicating that the sodium ions wet the anode surface firstly and then insert into the anode which can lead to fast sodiation ratio. Meanwhile, no fracture and cracking are observed in spite of obvious size expansion. By virtue of *in situ* TEM and EDP observations, $\alpha\text{-MoO}_3$ nanobelts are found to undergo a multi-step phase transformation during electrochemical processes. In detail, $\alpha\text{-MoO}_3$ nanobelts are initially sodiated to amorphous Na_xMoO_3 and then converted into crystalline NaMoO_2 which are further sodiated to the crystallized Mo nanograins embedded within Na_2O matrix after full the first sodiation process. During the first desodiation process, Mo nanograins are firstly re-oxidized to crystalline NaMoO_2 followed by the conversion to amorphous Na_2MoO_3 , which is confirmed by EELS and EDPs measurements. The irreversible phase transformation from MoO_3 to Na_2MoO_3 should be responsible for the large capacity loss after the first cycle. We also find that the phase transformation during subsequent cycles is reversible between Mo nanograins and amorphous Na_2MoO_3 . Our experiment results provide direct evidences for deeply understanding the underlying mechanism of $\alpha\text{-MoO}_3$ nanobelt anode for SIBs, which are beneficial to designing SIBs with enhanced performance.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ¹These authors contributed equally to this work.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version at XXXXXX.

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Figure 2. (a₁-a₄) Microstructure evolution of a segment of α -MoO₃ nanobelt during the first sodiation process. (b) HRTEM image of a fully sodiated anode. (c₁-c₁₀) *In situ* electron diffraction for identifying the phase evolutions of α -MoO₃ nanobelt during the first electrochemical sodiation process.

Figure 3. (a₁-a₄) Microstructure evolution of a segment of α - MoO_3 nanobelt during the first desodiation process. (b₁-b₈) *In situ* electron diffraction for identifying the phase evolutions of α - MoO_3 nanobelt during the first electrochemical desodiation process. (c) EELS spectrum of Mo/M_{3,2} edge for a fully desodiated anode.

Figure 4. Microstructure evolution of MoO_3 nanobelt in the first three sodiation and desodiation processes. (a) The pristine MoO_3 nanobelt with a size of 55.5 nm. (b) The first sodiated and (c) delithiated MoO_3 nanobelt. (d) The second sodiated and (e) desodiated MoO_3 nanobelt. (f) The third sodiated and (g) desodiated MoO_3 nanobelt. (a₁-g₁) The EDPs recorded from the anode in the planes (a-g), revealing the phase change during the first two cycles. (h) The measured diameter versus electrochemical reaction time of the α - MoO_3 nanobelt being repetitively cycled; The numeric percentages are for the diameter expansion/contraction during each event.

Figure 5. EELS spectra of Mo/M_{3,2} edges in the first three electrochemical sodiation/desodiation cycles. (a) Original stage; after the first (b) sodiation and (c) desodiation processes; and after the second (d) sodiation and (e) desodiation processes; and after the third (f) sodiation and (g) desodiation processes.

1st Electrochemical Sodiation

1st Electrochemical Desodiation

Figure 6. Crystal structure evolution of the anode material during the first electrochemical sodiation/desodiation process.

Figure 7. Electrochemical rate performance of MoO₃ nanobelts as anode material in SIBs at various current densities.