Probing microstructure and phase evolution of \( \alpha \)-MoO\(_3\) nanobelts for sodium-ion batteries by \textit{in situ} transmission electron microscopy

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1. 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], SnO\(_2\) [13], CuO [14], MnO\(_2\) [15], MoO\(_3\) [16], CoS\(_2\) [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/insertion 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 \( \alpha \)-MoO\(_3\) has a unique layered structure: each layer is composed of two sub-layers which are formed by corner-sharing \([\text{MoO}_6]\) octahedral along [001] and [100] directions and the two sub-layers are stacked together by sharing the edges of the \([\text{MoO}_6]\) octahedral along

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ABSTRACT

The fundamental electrochemical reaction mechanisms and the phase transformation pathways of layer-structured \( \alpha \)-MoO\(_3\) nanobelt during the sodiation/desodiation process to date remain largely unknown. To observe the real-time sodiation/desodiation behaviors of \( \alpha \)-MoO\(_3\) during electrochemical cycling, we construct a MoO\(_3\) anode sodium-ion battery inside a transmission electron microscope (TEM). Utilizing \textit{in situ} TEM and electron diffraction pattern (EDP) observation, \( \alpha \)-MoO\(_3\) nanobelts are found to undergo a unique multi-step phase transformation. Upon the first sodiation, \( \alpha \)-MoO\(_3\) nanobelts initially form amorphous Na\(_2\)MoO\(_3\) phase and are subsequently sodiated into intermediate phase crystalline NaMoO\(_2\), finally resulting in the crystallized Mo nanograins embedded within the Na\(_2\)O matrix. During the first desodiation process, Mo nanograins are firstly re-oxidized into intermediate phase Na\(_2\)MoO\(_3\) that is further transformed into amorphous Na\(_2\)MoO\(_3\), resulting in an irreversible phase transformation. Upon subsequent sodiation/desodiation cycles, however, a stable and reversible phase transformation between crystalline Mo and amorphous Na\(_2\)MoO\(_3\) phases has been revealed. Our work provides an in-deepth understanding of the phase transformation pathways of \( \alpha \)-MoO\(_3\) nanobelts upon electrochemical sodiation/desodiation processes, with the hope of assistance in designing sodium-ion batteries with enhanced performance.

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[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-MoO$_3$ 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-MoO$_3$ 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 identify the nature of the electrochemical sodiation/desodiation behaviors. Furthermore, the information about dynamic morphology and microstructure evolutions of α-MoO$_3$ 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-MoO$_3$ 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-MoO$_3$ 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-MoO$_3$ nanobelts are found to undergo a unique multi-step phase transformation. Upon the first sodiation, the α-MoO$_3$ nanobelts initially form amorphous Na$_3$MoO$_4$ and subsequently convert into crystalline NaMoO$_2$, finally resulting in the formation of crystallized Mo nanograins embedded within a Na$_x$O matrix. During the first desodiation process, Mo nanograins are firstly re-oxidized into crystalline NaMoO$_2$ followed by the conversion to amorphous Na$_3$MoO$_4$, 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 Na$_3$MoO$_4$. Our work reveals the detailed information about the sodiation/desodiation process, providing an in-depth understanding of the fundamental mechanism of α-MoO$_3$ nanobelts during electrochemical cycles.

2. Experimental section

2.1. Preparation of α-MoO$_3$ nanobelts

The α-MoO$_3$ nanobelts were synthesized according to the previous reports [21]. Briefly, 2.0 g ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) 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 HNO$_3$ (5 M). 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 MoO$_3$ was filtered and washed with distilled water, followed by drying in a hot air oven at 60 °C for 12 h.

2.2. 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-MoO$_3$ 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-MoO$_3$ 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 Na$_2$O 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$_x$Na$_2$O and α-MoO$_3$ nanobelt in contact by fine steps. A constant −2 V/3 V potential was then applied to the α-MoO$_3$ nanobelts anode with respect to sodium counter electrode to drive the transport of sodium ions through the solid-state electrolyte Na$_2$O layer, thereby initiating the electrochemical sodiation/desodiation process.

2.3. Half cell measurement

Galvanostatic electrochemical performance of the as-prepared MoO$_3$ nanobelts was performed with a 2025-type coin cell in the voltage window 0.04–3.0 V at room temperature on a Neware battery cycler at various current densities. The working electrode for SIBs is the slurry mixture of active material (MoO$_3$ nanobelts), acetylene black, and polyvinylidene fluoride (PVDF) (75:15:10 wt ratio) in N-methyl pyrrolidine which has been stirred for 12 h. The slurry was coated onto Cu foam current collector and dried at 240 °C for 4 h under Argon gas. Metal Na was used as the counter electrode and reference electrode, meanwhile, the electrolyte was 1.0 M NaClO$_4$ in the mixture of ethylene carbonate (EC)/propylene carbonate (PC) (1:1 vol ratio).

3. Results and discussion

The schematic illustration of the in situ experimental setup inside TEM, as shown in Fig. 1(a), consists of three parts: anode α-MoO$_3$ nanobelt, counter electrode sodium and all-solid electrolyte Na$_2$O. The α-MoO$_3$ 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 oxidation. The thin layer of Na$_2$O 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$_x$Na$_2$O layer and the α-MoO$_3$ nanobelts in contact with each other by fine steps. Afterwards, a constant −2 V/3 V potential was applied to the α-MoO$_3$ nanobelts anode with respect to sodium to drive the transport of sodium ions through the Na$_2$O layer, thereby initiating the electrochemical sodiation/desodiation process. Fig. 1(b) displays the corresponding TEM image of a nano-battery within α-MoO$_3$ anode which has a uniform width and belt-like morphology (Fig. 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-MoO$_3$ nanobelt (Fig. 1(c)) that can be perfectly index as the orthorhombic MoO$_3$ (α-MoO$_3$) phase (JCPDS no. 35-0609), revealing its single crystalline feature. Insert in Fig. 1(c) is the HRTEM image of α-MoO$_3$ 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-MoO$_3$ nanobelts during the first sodiation process are given in Fig. 1(d1–d4) and (e1–e2) (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$_2$O 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 \( \alpha \)-MoO3 nanobelts during sodiation in Fig. 1(d) and (e) 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 Fig. 1(e) is about 27.4% with the assistant reference marked by black arrow in Fig. 1(e1). However, we have no idea about the size expansion in the thickness direction as the image we observed during the \textit{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.

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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. Fig. 1(f) shows the plotted sodiation length vs. time of the two nanobelts in Fig. 1(d) and (e). 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 Fig. 1(d) 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 Fig. 1(e) also showed the similar sodiation behavior. We believe this behavior should be attributed to the different sodiation mechanism of \( \alpha \)-MoO3 nanobelt compared with other anode materials. The sodium ions maybe wet the anode surface firstly 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 spices along the nanobelts surface, which is the consequence of the nature in the \textit{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 \( \alpha \)-MoO3 nanobelt, as given in Fig. 2(a1)–(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 \( \alpha \)-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 \( \frac{C}{24} \) (247 Å) can be identified as Na2O from the HRTEM image of a fully sodiated anode in Fig. 2(b), in which the lattice fringe is \( \frac{C}{24} \) Å and in good agreement with the (200) plane of Na2O (JCPDS no. 03-1074). As we can see from the Fig. 2(b), 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 Fig. 2(c10). 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:

$$\text{MoO}_3 + x\text{Na}^+ + xe^{-} \rightarrow \text{Na}_x\text{MoO}_3$$

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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 Fig. 2(c). The original anode shows obvious single crystalline feature (Fig. 2(c1)), 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 24 s and 2.32 nm at 56 s, confirming the insertion of sodium ions. Meanwhile, the measured angle continually changed, as Fig. 2(c1)–(c3) 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 (Fig. 2(c3)–(c4)), suggesting the existence of disordered structure induced by Na⁺ intercalation. The reaction in this stage can be expressed as follows:

$$\text{MoO}_3 + x\text{Na}^+ + xe^{-} \rightarrow \text{Na}_x\text{MoO}_3$$

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 Fig. 2(c5). And as the sodiation proceeded, more and more diffraction rings and spots that can be indexed as Na2O and NaMoO2 were acquired (Fig. 2(c5)–(c8)), in the meantime, the amorphous phase was vanished gradually, indicating the conversion from amorphous Na$_x$MoO$_3$ to crystalline Na$_2$O and NaMoO2, which can be expressed as:

$$\text{Na}_x\text{MoO}_3 + (3 - x)\text{Na}^+ + (3 - x)e^{-} \rightarrow \text{Na}_x\text{MoO}_2 + \text{Na}_2\text{O}$$

Subsequently, Mo phase was captured (JCPDS no. 01-1207), while most diffraction rings represent Na$_x$MoO$_2$ tapers off and only the (107) plane can be found at 638 s, as shown in Fig. 2(c6). The EDP that can be assigned to Mo and Na$_2$O (Fig. 2(c9)) never changed after 812 s, indicating that the nanobelt has been fully sodiated and the final sodiation product is the mixture of Mo and Na$_2$O, agreeing well with the HRTEM result. So the electrochemical reaction involved in this stage is:

$$\text{NaMoO}_2 + 3\text{Na}^+ + 3e^{-} \rightarrow \text{Mo} + 2\text{Na}_2\text{O}$$

Consequently, the sequential phase transformations of the α-MoO3 nanobelts during the first sodiation can thus be expressed as: c-MoO3→a-NaxMoO3→c-NaMoO2→c-Mo.

After the full sodiation, a constant positive potential of 3 V was applied on the anode to initiate the desodiation behaviors. Fig. 3(a1)–(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 Fig. 3(a4). The morphology and size evolution is the result of phase
change caused by the sodium ions extraction and electron transmission during desodiation process.

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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 Fig. 3(b1)-(b8). As Fig. 3(b1) 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 (Fig. 3(b2)) at the early desodiation stage. As the desodiation time went on, the feature of Mo disappeared, instead, the diffraction rings that represent crystalline NaMoO2 became more and clearer, as given in Fig. 3(b3). This result indicates that the first stage desodiation reaction is:

\[
\text{Mo} + 2\text{Na}_2\text{O} \rightarrow \text{NaMoO}_2 + 3\text{Na}^+ + 3\text{e}^-\]

Afterwards, these diffraction rings/spots continually decreased, and in the meantime, diffused rings that represent amorphous phase started to arise (Fig. 3(b4)-(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 (Fig. 3(b8)). 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-M3,2 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 Fig. 3(c), we can find the value of \(I_{\text{M3}}/I_{\text{M2}}\) is 2.18, corresponding to the state of +4 [31]. Consequently, we believe that the form of the final desodiation product is \(\text{Na}_{2y-4}\text{MoO}_6\) (\(2 \leq y \leq 3\)) 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:

\[
\text{NaMoO}_2 \rightarrow \text{MoO}_2 + \text{Na}^+ + \text{e}^-\]

\[
\text{NaMoO}_2 + 2\text{Na}_2\text{O} \rightarrow \text{Na}_2\text{MoO}_3 + \text{Na}^+ + \text{e}^-\]

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

\[
\text{Mo} + 2\text{Na}_2\text{O} \rightarrow \text{MoO}_2 + 4\text{Na}^+ + 4\text{e}^-\]

\[
\text{Mo} + 3\text{Na}_2\text{O} \rightarrow \text{Na}_2\text{MoO}_3 + 4\text{Na}^+ + 4\text{e}^-\]

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 form the EDP in Fig. 3(b8). 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 Na3MoO3 and the reactions involved during the first desodiation process would be as follows: c-Mo \(\rightarrow c\text{-NaMoO}_2 \rightarrow \alpha\text{-Na}_2\text{MoO}_3\). 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 \(\alpha\text{-MoO}_3\) nanobelt during the first three electrochemical sodiation/desodiation processes was investigated and displayed in Fig. 4 to well understand the conversion mechanism during charging/discharging cycles. We also showed the dynamic microstructure evolution of the anode during

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the first three cycles in Movie S5 (Supplementary Material), including the vanishment and formation of Na$_2$O 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 $-2 \text{V}/3 \text{V}$ was applied to the $\alpha$-MoO$_3$ nanobelt to initiate the electrochemical sodiation/desodiation behaviors. Fig. 4(a) is a pristine $\alpha$-MoO$_3$ nanobelt 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 Fig. 4(b)–(g). The $\alpha$-MoO$_3$ nanobelt anode has an obvious size expansion, meanwhile, the anode converted into numerous nanograins within Na$_2$O matrix after full sodiation. During desodiation processes, the lithiated anode shrunken its volume and the Na$_2$O layer disappeared as a result of the extraction of sodium ions. The anode diameter changes after each electrochemical process were plotted in Fig. 4(h). 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.

Fig. 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 $\alpha$-MoO$_3$ nanobelt being repetitively cycled; The numeric percentages are for the diameter expansion/ contraction during each event.
Consequently, we hold the opinion that the reaction mechanism dominating the first sodiation is different from the mechanism during the subsequent (de)sodiation cycles.

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Fig. 4(a1)–(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 (Fig. 4(a1)) was converted into the mixture of crystalline Mo and Na2O (Fig. 4(b1)). During the subsequent desodiation process, the sodiated anode did not turn into its pristine state but exhibited amorphous feature (Fig. (c1)). 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 Fig. 4(d1) displays. The second sodiation reaction can thus be expressed by the following equation:

\[
\text{Na}_2\text{MoO}_3 + 4\text{Na}^+ + 4\text{e}^{-1} \rightarrow \text{Mo} + 3\text{Na}_2\text{O}
\]

As expected, the second desodiation product exhibited the same characteristic (Fig. 4(e1)) with that in Fig. 4(b1). From Fig. 4 (f1) and (g1), 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 Fig. 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: α-Na2MoO3 → c-NaMoO2 → c-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 MoO2 (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 Lever, can be used to quantitatively analyze the chemical element at nanoscale inside TEM. Here, the intensity ratios of M4,5,6 edges with distinct valence specific shapes (Iₓ/ₓᵧ) of element Mo collected from the anode were obtained and given in Fig. 5 to reveal the valence state evolution during the first three electrochemical sodiation/desodiation cycles. Fig. 5(a) shows the EELS spectrum of the original MoO3 nanobelt, in which the Iₓ/ₓᵧ 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 (Fig. 5(b)) and corresponded to the state of 0, indicating the MoO3 nanobelt was reduced into metal Mo. The Iₓ/ₓᵧ was lowered to 2.19 after first desodiation, as Fig. 5(c) displays, indicating the valence state of Mo is +4. The obvious difference of Iₓ/ₓᵧ between Fig. 5(a) and (c) 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 Iₓ/ₓᵧ was increased to 2.51 again after second full sodiation process (Fig. 5(d)), similar to that after the first sodiation, suggesting the sodiation product was still metal Mo although the different starting material. As given in Fig. 5(e), the Iₓ/ₓᵧ was decreased to 2.22 again after second desodiation process, implying the valence state of Mo in the anode is +4. The Iₓ/ₓᵧ evolution during the third cycles (Fig. 5(f)–(g)) is identical to the second one, indicating the reversible microstructure evolution between Mo6+ and Mo4+ during subsequent cycles. The EELS results that the evolution of valence state of Mo follows Mo6+ → Mo4+ → Mo4+, agreeing well with the conclusion that α-MoO3 nanobelts undergo irreversible microstructure evolution from MoO3 to amorphous Na2MoO3 during the first cycle and reversible phase change between Mo and Na2MoO3 during subsequent cycles. Consequently, the overall electrochemical reactions can be expressed as the followings:

\[
\text{MoO}_3 + 6\text{Na}^+ + 6\text{e}^{-1} \rightarrow \text{Mo} + 3\text{Na}_2\text{O} \quad \text{(first sodiation)}
\]

\[
\text{Mo} + 3\text{Na}_2\text{O} \rightarrow 2\text{Na}_2\text{MoO}_3 + 4\text{Na}^+ + 4\text{e}^{-1} \quad \text{(subsequent desodiation/sodiation)}
\]

The crystal structure evolution of the MoO3 anode during the first electrochemical sodiation/desodiation process is schematically given in Fig. 6. Upon the initial sodiation, sodium ions firstly inserted into MoO3 under the drive of the negative potential, which can lead to a reasonable volume expansion and disordered structure, forming amorphous phase Na2MoO3. According to the previous reports [32], the lithium ions can insert not only into the interlayer spacing between [MoO3] octahedron layers but also into the [MoO6] 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 MoO3, we therefore believe that the insertion of sodium ions into the MoO3 structure is similar to that of lithium ions, as Fig. S2 (Supplementary Material) shows. Upon the further sodiation, Na2MoO3 phase was converted into another intermediate phase of crystalline NaNdMoO2. Finally, the full sodiation resulted in the formation of crystalline Mo dispersed in Na2O matrix.

Afterwards, a potential of 3 V was applied to initiate the first desodiation process, forming fully desodiated product of Na2MoO3 phase, rather than the original MoO3. The intermediate NaMoO2 phase also occurred during the desodiation process. Once the NaMoO2 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 desodiation (sodiation) cycles, a stable and reversible phase transformation between the Na2MoO3 and Mo phases would be established. We also provide the schematic view of the microstructure evolution of α-MoO3 nanobelt during the electrochemical cycles, as displayed in Fig. S3 (Supplementary Material).

A coin cell with MoO3 nanobelts as working electrode was constructed to test its electrochemical performance for SIBs and the result of its rate performance was provided in Fig. 7. From that we can see the MoO3 electrode delivers an initial discharge (sodiation) capacity of 545 mA h g−1 and charge (desodiation) capacity of 330 mA h g−1 at the current density of 100 mA g−1, with a low Coulomb efficiency of 60.6% in the first cycle. Afterwards, the electrode shows similar capacity retention under same current density during subsequent cycles with the Coulomb 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 MoO3 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 186 mA h g−1 at a high current density of 1000 mA g−1, and the capacity can recover to about 280 mA h g−1 when the current density is reset to 100 mA g−1, suggesting that MoO3 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−1, from which we find the electrode still has an acceptable reversible capacity of ~ 280 mA h g−1 after further 50 cycles, confirming the good cycling performance of α-MoO3 nanobelts.
Fig. 5. EELS spectra of Mo/M$_{2,3}$ 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.
4. Conclusions

In summary, the electrochemical sodiation/desodiation behaviors of \( \alpha \)-MoO\(_3\) nanobelts have been revealed by \textit{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 \textit{in situ} TEM and EDP observations, \( \alpha \)-MoO\(_3\) nanobelts are found to undergo a multi-step phase transformation during electrochemical processes. In detail, \( \alpha \)-MoO\(_3\) nanobelts are initially sodiated to amorphous \( \text{Na}_x\text{MoO}_3 \) and then converted into crystalline \( \text{NaMoO}_2 \) which are further sodiated to the crystallized Mo nanograins embedded within \( \text{Na}_2\text{O} \) matrix after full the first sodiation process. During the first desodiation process, Mo nanograins are firstly re-oxidized to crystalline \( \text{NaMoO}_2 \) followed by the conversion to amorphous \( \text{Na}_2\text{MoO}_3 \), which is confirmed by EELS and EDPs measurements. The irreversible phase transformation from \( \text{MoO}_3 \) to \( \text{Na}_2\text{MoO}_3 \) 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 \( \text{Na}_2\text{MoO}_3 \). Our experiment results provide direct evidences for deeply understanding the underlying mechanism of \( \alpha \)-MoO\(_3\) nanobelts 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. These authors contributed equally to this work.

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Appendix A. Supplementary material

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