New Insights into Electrochemical Lithiation/Delithiation Mechanism of $\alpha$-MoO$_3$ Nanobelt by in Situ Transmission Electron Microscopy

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ABSTRACT: The $\alpha$-MoO$_3$ nanobelt has great potential for application as anode of lithium ion batteries (LIBs) because of its high capacity and unique one-dimensional layer structure. However, its fundamental electrochemical failure mechanism during first lithiation/delithiation process is still unclear. Here, we constructed an electrochemical setup within $\alpha$-MoO$_3$ nanobelt anode inside a transmission electron microscope to observe in situ the microstructure evolution during cycles. Upon first lithiation, the $\alpha$-MoO$_3$ nanobelt converted into numerous Mo nanograins within the Li$_2$O matrix, with an obvious size expansion. Interestingly, $\alpha$-MoO$_3$ nanobelt was found to undergo a two-stage delithiation process. Mo nanograins were first transformed into crystalline Li$_{1.66}$Mo$_{0.66}$O$_2$ along with the disappearance of Li$_2$O and size shrink, followed by the conversion to amorphous Li$_4$MoO$_3$. This irreversible phase conversion should be responsible for the large capacity loss in first cycle. In addition, a fully reversible phase conversion between crystalline Mo and amorphous Li$_2$MoO$_3$ was revealed accompanying the formation and disappearance of the Li$_2$O layer during the subsequent cycles. Our experiments provide direct evidence to deeply understand the distinctive electrochemical lithiation/delithiation behaviors of $\alpha$-MoO$_3$ nanobelt, shedding light onto the development of $\alpha$-MoO$_3$ anode for LIBs.

KEYWORDS: lithium ion batteries, in situ TEM, MoO$_3$, electrochemical behavior, two-stage delithiation

1. INTRODUCTION

As a kind of promising rechargeable batteries, lithium ion batteries (LIBs) require new anode materials with high energy density, power density and good cyclability to meet the rapid development of electronic industry. Various metal oxides, such as SnO$_2$, TiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, MoO$_3$, Co$_3$O$_4$, and ZnO, are possible anode candidates for LIBs due to their high lithium-taken abilities (>500 mAh g$^{-1}$), low cost, and environmental friendliness compared with the commercial anode material graphite (372 mAh g$^{-1}$). Among them, MoO$_3$ has been studied for decades as a well-known lithium insertion compound with the high theoretical lithium storage capacity of 1117 mAh g$^{-1}$. The orthorhombic MoO$_3$ ($\alpha$-MoO$_3$) nanobelt, as the thermodynamically stable phase among various polymorphs, offers improved performance and thus be investigated as anode material for LIBs most widely. These improvements can be attributed to its unique one-dimensional (1D) layer structure, which provides enhanced accommodation of the transformation strains caused by the lithium insertion/extraction, efficient 1D electron transport pathways and large contact area between electrode and electrolyte. However, $\alpha$-MoO$_3$ shows poor ionic and electronic conductivity, resulting in limited electrochemical activity. Moreover, the large volume expansion/constriction during lithiation/delithiation process can lead to anode pulverization and, thus, capacity loss. A variety of strategies have been adopted to overcome the restrictions, including the use of carbon-based (MWCNT, graphene) nanocomposites, and the modification of MoO$_3$ with MnO$_2$/SnO$_2$/In$_2$O$_3$. In a well-designed anode, these modifications can not only improve the lithium diffusion and the electronic conductivity but also accommodate the volume change associated with the lithium insertion and extraction, achieving a high capacity retention and stable cycling performance.

Although the improved electrochemical performance has been acquired by the above-mentioned methods, a few fundamental mechanisms concerning lithiation/delithiation processes still remain ambiguous due to the lack of direct evidence. It is well-known that the $\alpha$-MoO$_3$ nanobelt anode suffers from a huge capacity fading in first charging/discharging cycle which can be attributed to the irreversible lithiation/delithiation process such as the irreversibility of the lithiated product, the formation of the solid electrolyte interphase (SEI) layer and the possible loss of electrical contact caused by the anode pulverization. Although the previous reports indicate that MoO$_3$ can be transformed into Mo and Li$_2$O after being lithiated completely, little attention has been focused on the delithiation process. It still has no direct evidence to

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confirm the final delithiation product. Furthermore, no experimental data can provide the information on dynamic morphology and microstructure evolution of $\alpha$-MoO$_3$ nanobelt during cycles. That is to say, the nature of the irreversible electrochemical processes of $\alpha$-MoO$_3$ nanobelt anode and its influence on rapid capacity fading are still not understood completely.

Introducing in situ TEM technique to solve the above-mentioned issues is an excellent option as it has the ability to monitor the dynamic processes of anode material during electrochemical reactions in real time.$^{24-30}$ Here, an all-solid nanobattery was constructed with an individual $\alpha$-MoO$_3$ nanobelt as anode inside TEM to visualize the microstructure, morphology and phase evolutions during lithiation/delithiation processes. The $\alpha$-MoO$_3$ nanobelt was transformed into many Mo nanograins embedded in the crystalline Li$_2$O matrix during lithiation. Cracking and pulverization, which would lead to the loss of electrical contact between active material and current collector, was not observed in anode during lithiation process despite the obvious volume expansion. Meanwhile, we found that the anode cannot be converted to its original state, namely, orthorhombic MoO$_3$, but suffered a two-step phase change from Mo to crystalline Li$_{1.66}$Mo$_{0.66}$O$_2$ and then transformed to amorphous Li$_2$MoO$_3$ during first delithiation process. This reversible phase conversion can be responsible for the huge capacity loss and low coulomb efficiency of MoO$_3$ anode in first cycle. Our experiments provide direct observations for deeply understanding the electrochemical mechanisms of $\alpha$-MoO$_3$ nanobelt anode, which is beneficial for the successful design of advanced performance anode material.

2. EXPERIMENTAL SECTION

2.1. Preparation of $\alpha$-MoO$_3$ Nanobelts. The $\alpha$-MoO$_3$ nanobelts were synthesized according to the previous reports.$^{17}$ Briefly, 2.0 g ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) were 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$_3$ (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 MoO$_3$ were filtered and washed with distilled water, followed by drying in a hot air oven at 60 °C for 12 h.

2.2. Characterization. The as-prepared solid products were identified by X-ray diffraction (XRD) at room temperature using a diffractometer (ARL XTRA, Thermo Electron Corp., Waltham, MA) with Cu K$_\alpha$ radiation as the X-ray source. Scanning electron microscopy (SEM) images were obtained on a microscope (JSM-7600F, JEOL, Japan) operated at 15 kV to study the morphology of the samples. TEM images and selected area electron diffraction (SAED) were taken on a high-resolution field emission transmission electron microscope (FEI Titan, 300 kV).

2.3. In Situ Electrochemical Experiments. A high-resolution TEM (FEI Titan) with a fast responding charge-coupled device (CCD) camera was carried out for in situ observing the electrochemical behaviors of $\alpha$-MoO$_3$ nanobelt with the assistance of electron diffraction pattern (EDP), HRTEM imaging and EELS spectrum measurements. The $\alpha$-MoO$_3$ nanobelts, which were attached to a Au rod by conductive silver colloid to ensure a good electrical contact, were used as anode. Metal lithium was adhered to a tungsten probe and regarded as the counter electrode and lithium source. The natural oxide layer, Li$_2$O that generated in the holder loading process, acted as the solid electrolyte, which allows the transport of lithium ions. Building the nanobattery was accomplished in a glovebox filled with argon gas, as lithium 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 Li/Li$_2$O and $\alpha$-MoO$_3$ nanobelt in contact with each other.

Figure 1. (a) Photograph, (b) XRD spectrum, and (c) the crystal structure of the as-prepared MoO$_3$, (d) Scanning electron microscope (SEM) image and (e) TEM image confirm that the $\alpha$-MoO$_3$ is belt-like morphology. (Inset, d) HRTEM image of a MoO$_3$ nanobelt, in which the clear and ordered lattice fringes suggest the good crystallinity. (f) EDP indicates that the $\alpha$-MoO$_3$ nanobelt shows single crystalline feature.
which all diorthorhombic MoO₃ (commonly known as the transport of lithium ions and electrons. From the SEM parallel to the (010) direction and providing open channels for resulting in a unique two-dimensional layer structure that is 1a. Figure 1b is the XRD spectrum of the as-prepared MoO₃, in several micrometers. TEM image in Figure 1e further con

investigate the lithiation/delithiation mechanism of α

anode material.

that the as-prepared MoO₃ phase has a unique layer structure in which each layer is

with lattice parameters of \( a = 0.963 \text{ nm}, b = 1.385 \text{ nm}, \) and \( c = 0.3696 \text{ nm} \) (JCPDS no. 35-0609). As Figure 1c shows, the α-MoO₃ phase has a unique layer structure in which each layer is composed of two sublayers. The two sublayers are constituted by corners-sharing and edges-sharing octahedra \([\text{MoO}_6]\), resulting in a unique two-dimensional layer structure that is parallel to the (010) direction and providing open channels for the transport of lithium ions and electrons. \(^{55}\) From the SEM image presented in Figure 1d and Figure S1, we can observe that the as-prepared α-MoO₃ represent a belt-like morphology, with a width in the range of about 50–500 nm and a length of several micrometers. TEM image in Figure 1e further confirms its nanobelts morphology, which is in good agreement with the SEM image. HRTEM image in the inset of Figure 1e exhibits clear and ordered lattice fringes of 3.81 and 2.7 Å, in accordance with the (110) and (101) planes of α-MoO₃, respectively (JCPDS no. 35-0609), indicating the good crystallinity of the α-MoO₃ nanobelts. The electron diffraction pattern (EDP) of an individual α-MoO₃ nanobelt is shown in Figure 1f, which reveals the single crystalline feature for the anode material.

The electrochemical experimental setup that was used to investigate the lithiation/delithiation mechanism of α-MoO₃ nanobelt inside TEM is illustrated in Figure 2a. Briefly, it contains α-MoO₃ nanobelt anode, lithium counter electrode and solid electrolyte Li₂O. The Li/Li₂O layer was applied to a sharp tungsten tip that was attached to the piezo-driven biasing-probe which can make the α-MoO₃ nanobelt and Li/Li₂O in contact with each other by fine steps. A constant potential of −2 V was applied to the α-MoO₃ nanobelt with respect to the lithium counter electrode to initiate the lithiation process. Movie S1 (Supporting Information) and Figure 2b₁–b₃ show the morphology evolution of an individual α-MoO₃ nanobelt with an original width of 74.5 nm in a low magnification, in which the red arrows denote the lithiation front. Obviously, lithiation began from the side that in contact with the Li/Li₂O layer and propagated toward to the other side, resulting in a gray contrast. The straight α-MoO₃ nanobelt undergone both width swelling and elongation as a result of the lithium ions intercalations. The final width of the lithiated anode was expanded to 98.9 nm, with an obvious width expansion of 32%. We further calculated five other nanobelts, and their width expansions range from 26 to 34%, with an average value of 29%, while the mean elongation is about 27%. 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 nanobelt-like MoO₃ may show very different size expansion in width and thickness directions. Therefore, the specific volume expansion of the nanobelt-like MoO₃ is almost impossible to be estimated from the experiments.

To further explore the microstructure change during lithiation, we achieved a close view of the microstructure evolution of a segment of another MoO₃ nanobelt (Figure 2c₁–c₄ and Movie S2, Supporting Information). The MoO₃ nanobelt was just swelled at the initial stage of lithiation, and then coated with a crystalline layer, which was increased as the lithiation process proceeded. The width expansion is about 34% depending on its size increase from 66.6 to 89.7 nm, similar to

![Figure 2](https://example.com/figure2.png)

Figure 2. Experimental setup and the microstructure evolution of the MoO₃ nanobelt during first lithiation. (a) Schematic illustration of the in situ TEM cell. (b₁–b₃) Typical morphology change during lithiation with both width swelling and axial elongation in low magnification. (b₄) The pristine MoO₃ nanobelt was straight and bending deformation occurred during lithiation. The red arrows indicate the lithiation fronts. (c₁–c₄) Close view of the microstructure evolution of a segment of another MoO₃ nanobelt during lithiation. The (c₁) straight MoO₃ nanobelt was (c₂) just swelled at the beginning of lithiation and then (c₃) coated with Li₂O layer, which was increased as the lithiation process proceeded. Insets in panels c₂ and c₃ is the enlargement of the anode marked by the red boxes in panels c₂ and c₃, respectively. (d) HRTEM image and (e) EDP of a lithiated anode show that the lithiation product is the mixture of Mo and Li₂O.

3. RESULTS AND DISCUSSION

The color photo image of the MoO₃ smaples is shown in Figure 1a. Figure 1b is the XRD spectrum of the as-prepared MoO₃, in which all diffraction peaks can be perfectly indexed as the orthorhombic MoO₃ (commonly known as α-MoO₃) phase with lattice parameters of \( a = 0.963 \text{ nm}, b = 1.385 \text{ nm}, \) and \( c = 0.3696 \text{ nm} \) (JCPDS no. 35-0609). As Figure 1c shows, the α-MoO₃ phase has a unique layer structure in which each layer is composed of two sublayers. The two sublayers are constituted by corners-sharing and edges-sharing octahedra \([\text{MoO}_6]\), resulting in a unique two-dimensional layer structure that is parallel to the (010) direction and providing open channels for the transport of lithium ions and electrons. \(^{55}\) From the SEM image presented in Figure 1d and Figure S1, we can observe that the as-prepared α-MoO₃ represent a belt-like morphology, with a width in the range of about 50–500 nm and a length of several micrometers. TEM image in Figure 1e further confirms its nanobelts morphology, which is in good agreement with the SEM image. HRTEM image in the inset of Figure 1e exhibits clear and ordered lattice fringes of 3.81 and 2.7 Å, in accordance with the (110) and (101) planes of α-MoO₃, respectively (JCPDS no. 35-0609), indicating the good crystallinity of the α-MoO₃ nanobelts. The electron diffraction pattern (EDP) of an individual α-MoO₃ nanobelt is shown in Figure 1f, which reveals the single crystalline feature for the anode material.

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32% for the above-mentioned MoO3 nanobelt. The crystalline layer coated on the anode with a thickness of 3–5 nm was identified to be Li2O from the EDP of lithiated anode in Figure 2e. From the HRTEM image of the lithiated anode given in Figure 2d, lattice fringe is found about 2.66 Å, in good agreement with the (111) plane of Li2O (JCPDS no. 12-0254), also confirming the formation of crystalline Li2O layer. Furthermore, the lattice spacing marked with the white circles in Figure 2d is measured to be 2.22 Å and can be assigned to the (110) plane of Mo (JCPDS no. 01-1208), indicating the conversion of MoO3 to Mo nanograins. Therefore, we can conclude that MoO3 nanobelt has evolved from a single crystal to a belt with numerous Mo nanograins within the Li2O matrix after lithiation process. Figure 2e shows the EDP of a lithiated MoO3 nanobelt, in which the diffraction rings can be indexed as the mixture of Li2O and Mo, further confirming the formation of crystalline Li2O layer. Overall, the first lithiation reaction involves the reduction of MoO3 to Mo and the formation of crystalline Li2O, which can be expressed by the following equation:

\[
\text{MoO}_3 + 6\text{Li}^+ + 6e^{-} \rightarrow \text{Mo} + 3\text{Li}_2\text{O}
\]

Despite the obvious size expansion, no crackings and fractures were observed in the MoO3 anode during the lithiation process, which is beneficial to the electrical contact between the anode material and current collector. Because the fracture can only be observed for Si nanoparticles over 150 nm in diameter,30 we further used MoO3 nanobelts with various sizes to explore the effect of width size on the microstructure of nanobelt during lithiation and no fractures were found. These results suggest that the MoO3 nanobelt exhibit promising potential as anode material for LIBs.

During the delithiation process, a constant positive potential of 3 V was applied on the lithiated anode with respect to the lithium counter electrode. Figure 3a–a3 show the electrochemical delithiation behaviors of a lithiated MoO3 nanobelt. Interestingly, we found that the delithiation process occurs in two stages. During the first stage (Figure 3a1–a2), the anode shrank in width from 208 to 176 nm and the coated Li2O layer was gradually disappeared, and the size of the lithiated anode shrank as the delithiation process proceeded. In this stage, Mo nanograins were converted into crystalline Li1.66Mo0.66O2. Afterward, Li1.66Mo0.66O2 vanished followed by the formation of amorphous Li2MoO3 accompanying the shrinking of the anode.
under the drive of the potential, while the atomic ratio of Mo/O remains constant at 1:3, the same as that in Li_{1.66}Mo_{0.66}O_{2.3}, suggesting that the final delithiation product of MoO_{3} nanobelt anode is Li_{x}MoO_{3}. The EDP (Figure 3d) of the final anode after delithiation process shows diffused ring which reveals the amorphous delithiation product. EELS spectrum can be used to investigate the valence states of Mo as the M_{3,2} edges exhibit distinct valence-specific shapes. Herein, we revealed that α-MoO_{3} nanobelt undergoes a unique two-stage delithiation process and pointed out that the specific final product is amorphous Li_{x}MoO_{3} by HRTEM, EDP, and EELS techniques for the first time. The result is credible, as EELS technique is an accurate tool to investigate the valence states of chemical elements. On the basis of the above analysis, we hold the opinion that the lithiated anode undergoes a two-stage phase change from Mo nanograins to Li_{1.66}Mo_{0.66}O_{2} nanograins followed by the transformation to amorphous Li_{x}MoO_{3} during the first delithiation process, which can be expressed by the following equations:

\[
\text{Mo} + 3\text{Li}_{2}\text{O} \rightarrow 1.5\text{Li}_{1.66}\text{Mo}_{0.66}\text{O}_{2} + 3.5\text{Li}^{+} + 3.5\text{e}^{-}
\]

\[
1.5\text{Li}_{1.66}\text{Mo}_{0.66}\text{O}_{2} \rightarrow \text{Li}_{2}\text{MoO}_{3} + 0.5\text{Li}^{+} + 0.5\text{e}^{-}
\]

Accordingly, the overall reaction during delithiation can be expressed as Mo + 3Li_{2}O \rightarrow Li_{2}MoO_{3} + 4 Li^{+} + 4e^{-}. This result is consistent with the previous conclusion that the amount of extraction lithium is about four in each cell during first delithiation process. The delithiation process cannot convert the anode into its original state, resulting in an irreversible microstructure change and thus huge capacity loss during first cycle.

Previous studies indicate that the decomposition of Li_{2}O is attributed to the electrocatalysis of the nanograins in the Li_{2}O matrix. In the initial stage of the delithiation process, the small size effect of the Mo nanograins caused by the increased number of surface atoms can greatly enhance the electrochemical reactivity and make the conversion from Li_{2}O to Li^{+} and O^{2-}. Then, Mo nanograins reacted with O^{2-} and parts of Li^{+}, thus forming Li_{1.66}Mo_{0.66}O_{2} nanograins during first stage. Meanwhile, about 3.5 Li^{+}/Mo were extracted from the lithiated anode, accounting for the volume shrink during delithiation process. After the full conversion from Mo to Li_{1.66}Mo_{0.66}O_{2}, Li^{+} were continually extracted from Li_{1.66}Mo_{0.66}O_{2} under the drive by the positive potential with the volume shrink, consequently resulting in amorphous Li_{x}MoO_{3}.

The microstructure evolution of a segment of α-MoO_{3} nanobelt during first two electrochemical lithiation/delithiation processes were investigated and displayed in Figure 4 to well understand the conversion mechanism during charging and discharging cycles. Figure 4a1a confirms the single crystalline feature of the pristine α-MoO_{3} nanobelt anode with a width of 56.1 nm. In the following cycles, the constant potential of -2 V/3 V was applied to the α-MoO_{3} nanobelt to initiate the electrochemical lithiation/delithiation behaviors. After first lithiation, the width size of the anode was increased to 71.3 nm with a size expansion of 27.1%, and a thin Li_{2}O layer was visible on the surface of the lithiated nanobelt. This size expansion is a little smaller than the MoO_{3} nanobelts in Figure 2, which mainly attribute to the difference of local Li^{+} concentration. Meanwhile, the microstructure of the α-MoO_{3} nanobelt was evolved to numerous Mo nanograins in the Li_{2}O matrix from a single crystal. The diffraction rings in the EDP of a lithiated anode (Figure 4b1) further confirmed that the lithiation products are the mixture of Mo and Li_{2}O. During first-stage delithiation, the Li_{2}O layer disappeared and the anode shrunk to 58.2 nm, as Figure 4c shows. The EDP (Figure 4c1) with diffraction rings confirmed the product of...
Li$_{1.66}$Mo$_{0.66}$O$_3$. For the second delithiation stage, the anode further shrank to 56.2 nm (Figure 4d) and the final delithiation product are amorphous Li$_3$MoO$_3$ by the EDP in Figure 4d1. The anode after the second lithiation process is displayed in Figure 4e, from that we can see the width size was expanded to 67.9 nm and Li$_2$O layer was formed on the anode surface again. The size expansion is only about 20.8%, smaller than 27.1% during first lithiation process. This behavior may be mainly attributed to the fact that the formed Li$_3$MoO$_3$ after first cycle can accommodate less lithium ions than MoO$_3$. EDP recorded from the second lithiated anode (Figure 4e) indicates that the products are Mo and Li$_4$O, just like the first lithiation process. The second lithiation reaction can thus be expressed by the following equation: Li$_3$MoO$_3$ + 4Li$^+$ + 4e$^-$ → Mo + 3Li$_2$O. Druing the second delithiation process, the Li$_2$O layer disappeared again and the anode shrank in width to 57.1 nm after fully delithiation, as shown in Figure 4f,g. The corresponding EDPs in Figure 4f,g represent the similar feature with those in Figure 4e, suggesting that the electrochemical behavior during second delithiation process is the same as the first one. With the above discussions, we can conclude that the low coulomb efficiency and large capacity loss in first cycle is mainly due to the incompletely reoxidized process of Mo to Li$_3$MoO$_3$ (Mo$^{4+}$) rather than MoO$_3$ (Mo$^{6+}$). Meanwhile, the better capacity retention and cycling performance during the subsequent cycles can be attributed to the relatively reversible phase and size change, as well as the improved conductivity of Li$_2$MoO$_3$ compared to $\alpha$-MoO$_3$ nanobelt.37

EELS performed in TEM is a well-established technique to quantitatively analyze the chemical at the nanoscale by calculating the intensity ratio from white-lines edges. Here, we used M$_{2,3}$ edges to obtain the valence state information on Mo element in the first two lithiation/delithiation processes as it can keep a low experimental dispersion caused by the proximity between O−K and Mo−M$_{2,3}$ edges and shows distinct valence-specific shapes.32 Figure 5a shows the EELS spectrum of an initial $\alpha$-MoO$_3$ nanobelt in which the Mo−M$_{2,3}$/M$_{1,4}$ intensity ratio is about 1.95, corresponding to the valence state of 6+.32 The Mo−M$_{2,3}$/M$_{1,4}$ intensity ratio increased to 2.54 after first lithiation process (Figure 5b), suggesting the formation of metal Mo. From the EELS spectrum of a delithiated anode in Figure 5c, we can see the Mo−M$_{2,3}$/M$_{1,4}$ intensity ratio decreased to 2.2, which agrees well with the valence state of 4+.32 The result implies the amount of the extraction lithium ions is only four for each cell, resulting in an irreversible phase conversion and thus large capacity fading in the first cycle, in agreement with the above conclusions. Figure 5d shows that the Mo−M$_{2,3}$/M$_{1,4}$ intensity ratio was 2.5 after the second lithiation process, similar to the first lithiation result, indicating that the second lithiation product is the same as the first lithiation one. In addition, from the EELS spectrum in Figure 5e, the Mo−M$_{2,3}$/M$_{1,4}$ intensity ratio after second delithiation process is calculated to 2.23, elucidating the 4+ valence state of Mo element, which is identical to the result after first cycle. The repeated valence state evolution of Mo elements revealed the reversible phase change between Mo$^{6+}$ and Mo$^{4+}$ during electrochemical lithiation/delithiation processes. These observations further confirmed the results that anode shows an irreversible microstructure evolution during first cycle but a reversible phase change between Mo and Li$_3$MoO$_3$ during subsequent cycles that from HRTEM images and EDP. Overall, the electrochemical reactions of $\alpha$-MoO$_3$ during lithiation and delithiation processes can be expressed as:

$$\text{MoO}_3 + 6\text{Li}^+ + 6\text{e}^- \rightarrow \text{Mo} + 3\text{Li}_2\text{O} \quad \text{(first lithiation)}$$

$$\text{Mo} + 3\text{Li}_2\text{O} \leftrightarrow \text{Li}_3\text{MoO}_3 + 4\text{Li}^+ + 4\text{e}^- \quad \text{(subsequent delithiation/lithiation)}$$

The theoretical lithium storage capacity of Li$_3$MoO$_3$ is calculated to be about 734 mAh g$^{-1}$ according to its weight and the ability of accommodating lithium ions, which is much lower than MoO$_3$ of 1117 mAh g$^{-1}$. That is to say, the irreversible phase conversion during first electrochemical lithiation/delithiation cycle will lead to a theoretical capacity loss of 383 mAh g$^{-1}$ after first cycle. To study the influence of irreversible phase conversion on capacity fading in first cycle, we checked other reports that used pure $\alpha$-MoO$_3$ as anode material for LIBs. The first cycle capacity loss was found to 760 mAh g$^{-1}$ for ball-milled MoO$_3$, 370 mAh g$^{-1}$ for porous MoO$_3$ film, 650 mAh g$^{-1}$ for MoO$_3$ nanoparticles, 370 mAh g$^{-1}$ for MoO$_3$ nanorods, 560 mAh g$^{-1}$ for short-bar-like MoO$_3$ particles, 728 mAh g$^{-1}$ for MoO$_3$ nanobelt film, 406 mAh g$^{-1}$ for MoO$_3$ nanobelt, and so on. The average capacity loss in first cycle can thus be calculated to about 568 mAh g$^{-1}$ for pure MoO$_3$. This result suggests that about 68% of the capacity loss of MoO$_3$ in the first cycle can be attributed to the irreversible phase conversion. Meanwhile, about 32% of the initial capacity loss is caused by other irreversible electrochemical behaviors such as the formation of SEI layer. The good capacity retention and cycling performance during subsequent cycles can be attributed to the reversible microstructure change between Mo and Li$_3$MoO$_3$ and to the enhanced conductivity of Li$_2$MoO$_3$ than MoO$_3$. 

Figure 5. EELS spectra of Mo/M$_{3,2}$ edges in the first two electrochemical lithiation/delithiation cycles. (a) Original stage; after the first (b) lithiation and (c) delithiation processes; and after the second (d) lithiation and (e) delithiation processes.
4. CONCLUSIONS

In summary, the electrochemical lithiation/delithiation behaviors of an individual α-MoO₃ nanobelt was studied by in situ TEM technique for the first time. It was found that the α-MoO₃ nanobelt was converted into many Mo nanograins within the Li₂O matrix after first lithiation process. Interestingly, we found that the delithiation process, where the anode shrank in volume, occurred in two stages. Mo nanograins were first transformed into crystalline Li₁₆6Mo₀₆₆O₂ nanograins which further converted into the amorphous Li₂MoO₃. The irreversible phase conversion from original MoO₃ (1117 mAh g⁻¹) to the final Li₂MoO₃ (734 mAh g⁻¹) is suggested to be responsible for ~68% total capacity loss of MoO₃ anode in first cycle, while the remaining ~32% capacity loss can be attributed to other irreversible electrochemical behaviors such as the formation of SEI layer. Our results also revealed a reversible phase conversion between amorphous Li₂MoO₃ and crystalline Mo, accounting for the good capacity retention and improved cycling performance during the subsequent cycles. Overall, our findings provide direct evidence and new insights about the fundamental nature of electrochemical lithiation/delithiation behaviors of the α-MoO₃ nanobelt, with the hope that it will assist the design of improved performance LIBs anode material.

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