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Inhibiting effect of Na⁺ pre-intercalation in MoO_3 nanobelts with enhanced electrochemical performance



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Abstract

Layered molybdenum trioxide (α -MoO₃) has been widely investigated as a promising Li battery cathode material. However, its low conductivity and irreversible structure change during charge-discharge process leads to its poor electrochemical performance. Although several methods have been reported to increase its conductivity, the issue of structure degradation still hinders its practical application. Here, a Na⁺ pre-intercalation strategy was proposed. The Na ions were successfully pre-intercalated into MoO₃ nanobelts *via* a facile method, and the intercalation amount can be well controlled. Compared to pristine MoO₃, the Na⁺ pre-intercalated nanobelts exhibit significant improvement in cycling stability as well as rate capability. Through *in-situ* XRD analyses combined with the electrochemical tests, it is demonstrated that the Na ions between the Mo-O interlayers effectively inhibit the irreversible phase transition and stabilize the layered structure. The inhibiting effect and the proposed Na⁺ pre-intercalation strategy are fundamentally important to further promote the development of molybdenum based or other layered electrode materials. © 2015 Elsevier Ltd. All rights reserved.

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Introduction

As a typical layered transition metal oxide, α -MoO₃ has been extensively studied for decades in fundamental research and technological applications due to the unusual properties produced by the multiple valence states. [1-4] Especially when used as electrode material for lithium batteries, the advantages of high capacity, low cost, abundant resources and non-toxic make MoO₃ a promising candidate.[5,6] One of the most important necessities of lithium-ion batteries is the good sustainability.[7-19] But the problem of serious capacity fading for MoO₃ has been hampering its development and application. This should be attributed to the low-conductivity and structure-degradation, which lead to poor kinetics and serious capacity fading during cycling. [20-23] Coating a conductive layer has been reported as an effective way to increase the conductivity of MoO₃ and reduce the structure degradation.[24-27] However, the capacity fading in the initial cycles is still significant and unavoidable. The reason for irreversible capacity fading of MoO₃ in the initial cycles can be attributed to its structural characteristic. MoO₃ has two kinds of empty sites for lithium ion intercalation, viz. interlayer sites and intralayer sites. In the initial process, lithium ions insert not only into the interlayer sites (which is reversible) but also the intralayer sites (which is irreversible), and the irreversible Li insertion into the intralayers will lead to the structure rearrangement and severe capacity fading in the initial cycles. [28-30] Recently, pre-intercalation has been demonstrated as an effective way to increase the electrochemical performance of nanostructured materials.[31-36] Our group has also previously investigated the pre-lithiation method, which improved the electronic conductivity of MoO₃ and alleviated the initial capacity loss. [21] However, the function of pre-intercalation on its structure optimization still needs further research.

Here we designed and synthesized Na⁺ pre-intercalated MoO₃ nanobelts (Na-Mo-O nanobelts) *via* a facial method. The Na ions were intercalated into the MoO₃ crystal interlayers and the intercalation amount can be well controlled. After Na ions pre-intercalation, the nanobelts exhibit significantly improved cycling stability together with the enhanced rate capability. The structure change during a discharge/charge process was investigated by *in-situ* XRD tests, and it is found that the Na ions between the interlayers inhibit the irreversible structure change effectively.

Material and methods

Preparation of MoO₃ nanobelts

In a typical experiment, 40 mL H_2O_2 (30%) was stirring agitatedly, and 4 g molybdenum powder was added slowly under water-cooling until the clear orange peroxomolybdic acid sol was obtained, and then stirred in a 70 °C water bath for 4 h, and transferred into a 50 mL Teflon lined autoclave afterwards and kept at 180 °C for 6 h. The autoclave was left to cool, and the precipitate was filtered out and rinsed with deionized water for three times.

Preparation of Na^+ pre-intercalated MoO_3 nanobelts

0.36 g as-synthesized MoO₃ nanobelts, 0.3 g polyethyleneglycol (PEG4000) and 1 mmol NaCl were added into 60 mL deionized water and stirred agitatedly for 2 h. Then the solution was transferred to a 100 mL Teflon lined autoclave and kept at 180 °C for 2 days to ensure complete reaction. The precipitate was filtered out and rinsed with deionized water for five times. Finally the precipitate was heated in air at 400 °C for 5 h to get the final product. To control the Na amount in the product, the NaCl added in the second step was tuned as 10 and 20 mmol. The samples were marked as Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O for 1 mmol, 10 mmol and 20 mmol NaCl, respectively.

Characterization

X-ray diffraction (XRD) measurements were performed to investigate the crystallographic information using a Bruker D8 Advance X-ray diffractometer with a non-monochromated Cu K α X-ray source. Scanning electron microscopy (SEM) images were collected using a JEOL JSM-7100F at an acceleration voltage of 15 kV. Transmission electron microscopic (TEM), high resolution transmission electron microscopic (HRTEM) and selected area electron diffraction (SAED) images were recorded using a JEOL JEM-2100F STEM/EDS microscope. The Na amount and Na/Mo ratio in the samples were characterized by Inductively Coupled Plasma (ICP) test using the PerkinElmer Optima 4300DV spectrometer.

The electrochemical properties were characterized in coin cells using lithium metal foil as the anode. The cathode electrodes were composed of 60% active material, 30% acetylene black and 10% poly(tetrafluoroethylene) (PTFE) binder. The specific capacity is calculated by multiplying a factor of 0.6 to calculate the active materials of Na-Mo-O. The acetylene black is used as a dispersing agent and a conducting additive to ensure the successful grinding of the as-prepared powders to cut into pellets. A solution (1 M) of $LiPF_6$ in EC-DEC (1:1 vol/vol) was used as the electrolyte. The cells were assembled in an argon-filled glove-box. Galvanostatic charge-discharge measurements were performed using a multichannel battery testing system (LAND CT2001A), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using an Autolab Potentiostat Galvanostat. All the measurements were carried out at room temperature.

For *in-situ* XRD measurement, the electrode was placed right behind an X-ray-transparent beryllium window which also acts as a current collector. The *in-situ* XRD signals were collected using the planar detector in a still mode during the dischargecharge process, and each pattern took 2 min to acquire.

Results and discussion

Figure 1 shows the crystal structure and intercalation sites of α -MoO₃. There are three kinds of oxygen atoms present in the crystal structure, which can be regarded as one-fold oxygen (O1), two-fold oxygen (O2) and three-fold oxygen (O3) based on the bonding state.[37] Among them, the one-fold terminal oxygen atoms form only one covalent bond,



Figure 1 Schematic illustration of MoO_3 structure along (a) *c* direction and (b) *a* direction.

revealing that it has the other free valence electron acting as a negative charge. Therefore, the intercalated Na ions will bond with the one-fold terminal oxygen atoms (O1) and be stabilized between interlayers, which in return act as pillars to reinforce the structure. Besides, the electronic conductivity of MoO_3 will also be improved as the pre-intercalation of ions will increase the carrier density. [21,38]

Figure 2a shows the XRD patterns of the pristine MoO₃ nanobelts in comparison with the Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts. Each diffraction pattern of Na-Mo-O nanobelts is in good correspondence to the characteristic diffraction peaks of pristine MoO₃ nanobelts. All the diffraction peaks can be assigned to a pure orthorhombic phase of MoO₃ (JCPDS No. 89-5108; a=3.9620 Å, b=13.8550 Å, and c=3.7010 Å). No obvious impurity phases or significant change of the peaks were detected for Na-Mo-O nanobelts, this may be attributed to the relatively minor Na⁺ amount and the random distribution of Na ions between the interlayers [29]. The comparison of the morphologies of MoO₃, Na(1)-Mo-O, Na (2)-Mo-O and Na(3)-Mo-O nanobelts is shown in Figure 2b I-IV. The morphologies have no significant change after Na⁺ intercalation and the widths of the nanobelts are in the range of 200-300 nm with good uniformity. TEM and HRTEM images (Figure 2c and d) reveal further information about the morphology and structure of the Na(1)-Mo-O nanobelts. The samples show typical nanobelt morphology in the TEM image. The HRTEM image of the Na(1)-Mo-O nanobelts shows the typical MoO₃ lattice fringes. The periodic fringe spacings of \sim 3.8 and \sim 3.3 Å agree well with the interplanar spacings of the (110) and (021) planes of orthorhombic MoO₃, respectively. Besides, some crystal defects and dislocations can be observed in HRTEM image, which is the evidence that the Na ions are indeed intercalated into the MoO₃ crystal. This can be further identified in the SAED image (Figure 2e). The Na(1)-Mo-O has good crystallinity, but different from that of pristine MoO₃ (Figure S1), there are obvious patterns of defects in the image, revealing the existence of Na ions in the structure.

To further quantify the Na⁺ amount in the structure, ICP measurement was performed and the results are shown in

Table S1. The sodium amount and molybdenum amount can be characterized and the molar ratios of Na/Mo are 0.072, 0.259 and 0.386 for Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts, respectively. Therefore, by changing the NaCl amount during the preparation process, the Na⁺ amount in Na-Mo-O can be well controlled.

To investigate the effect of Na⁺ pre-intercalation on the electrochemical property, the cyclic voltammetric (CV) performance was measured at a sweep rate of 0.1 mV s^{-1} in the potential range from 4.0 to 1.5 V vs. Li/Li⁺ (Figure 3a). For pristine MoO₃ nanobelts, an irrevesible cathodic peak located at around 2.6 V was observed, which can be assigned to the irreversible lithium insertion into the intralayer sites. [39] Note that this irreversible lithium insertion causes unrecoverable structure transformation of MoO₃. For Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts, the cathodic peaks around 2.6 V almost disappeared, indicating the irreversible intercalation process is inhibited after Na ions pre-intercalation. The cathodic peaks located at around 2.1 V for both the pristine MoO₃ nanobelts and the Na-Mo-O nanobelts correspond to the reversible insertion of lithium ions into the interlayer spacings (van der Waals spacings). Besides, it can be clearly seen that nanobelts after Na⁺ intercalation exhibit sharper redox peaks than pristine MoO₃, indicating the better electrochemical kinetics of Na-Mo-O.

The rate performances of MoO₃ and Na-Mo-O nanobelts are shown in Figure 3b. The electrodes are cycled at various rates from 0.1 to 3.0 Ag^{-1} . It can be seen that at higher current rates, the Na-Mo-O nanobelts have better performance than that of pristine MoO₃ nanobelts. Particularly at very high current rate (3 Ag^{-1}), the capacity of Na(1)-Mo-O still reaches up to 146.6 mA h g⁻¹, higher than 75.0 mA h g⁻¹ of Na(2)-Mo-O and 51.6 mA h g⁻¹ of Na(3)-Mo-O nanobelts. For pristine MoO₃ nanobelts, the capacity at 3 Ag^{-1} is only 10.1 mA h g⁻¹. The rate performance clearly indicates the better kinetics and electrochemical properties after Na⁺ intercalation.

The cycling performance of the pristine MoO_3 and Na-Mo-O nanobelts (voltage range of 1.5-4 V and current density of 500 mA g⁻¹) is demonstrated in Figure 3c. The initial



Figure 2 XRD patterns (a) and SEM images (b) of pristine MoO_3 , Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts; TEM (c), HRTEM (d) images and SAED patterns (e) of Na(1)-Mo-O nanobelts.

discharge capacities of Na(1)-Mo-O, Na(2)-Mo-O, Na(3)-Mo-O are 233.2, 188.1 and 164.0 mA h g^{-1} , respectively, compared to the 243.9 mA h g^{-1} of MoO₃. Since the preintercalated Na ions will occupy some active sites between the MoO₃ interlayers, the initial discharge capacity of Na-Mo-O are lower than the pristine MoO_3 , and the more Na ions are between the interlayer, the lower the initial capacity is. The capacity of MoO3 nanobelts decreases rapidly in the initial cycles, which is caused by the irreversible structure destruction resulting from the Li⁺ insertion into the intralayers. For Na-Mo-O, interestingly, the capacities increase for several cycles initially and then start to decrease. The increased capacity should be arise from the extraction of Na ions during the charge-discharge process. Similar phenomenon has been reported in sodium vanadate system. [40] And this is also consistent with the fact that the more Na ions are in the structure, the longer the increase period is. The capacity increase lasts for 7 cycles, 9 cycles and 11 cycles for Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O, respectively (Figure S3). To clarify the Na⁺ extraction amount of Na-Mo-O, the Na/Mo ratio of Na (1)-Mo-O electrode after different cycles was detected by ICP test (Table S2). Based on the ICP results, it is calculated that 61.1% Na is lost in the first 20 cycles. However, only 16.7% Na is lost in the next 130 cycles, indicating that the Na extraction mainly occurs in initial stage. Importantly, the Na/Mo ratio of Na(1)-Mo-O electrode still keeps at 0.016 after 150 cycles, thus, although the capacity fading still exists for Na-Mo-O, it is greatly alleviated and the capacity was kept at a relatively high level. After 150 cycles, the capacities of Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O maintains at 124.0, 113.1 and 101.7 mA h g⁻¹, respectively, compared to 62.0 mA h g⁻¹ for pristine MoO₃.

To further understand the influence of Na⁺ preintercalation on the rate performance, we studied the Li diffusion rate of the pristine MoO₃ and Na-Mo-O nanobelts through electrochemical impedance spectroscopy (EIS) measurements (Figure 3d). The diffusion coefficient values of the lithium ions (D) can be calculated using the equation D=0.5 $(RT/AF^2\sigma_w C)^2$, where R is the gas constant, T is the temperature, A is the area of the electrode surface, F is Faraday's constant, σ_w is the Warburg factor, and C is the molar concentration of Li ions.[41] The calculated lithium diffusion coefficient value for pristine MoO_3 is 1.38×10^{-13} $cm^2 s^{-1}$, while for Na⁺ intercalated nanobelts, the lithium diffusion coefficient values are 8.91×10^{-11} , 3.27×10^{-11} and $7.91\times 10^{-12}\,cm^2\,s^{-1}$ for Na(1)-Mo-O, Na(2)-Mo-O, Na(3)-Mo-O nanobelts, respectively, which are about two orders of magnitude larger than that of pristine MoO₃ nanobelts. The results demonstrate the significantly increased lithium diffusion rate after Na⁺ pre-intercalation, which leads to the improved rate capability of Na-Mo-O nanobelts. Notably, among the Na-Mo-O, Na(1)-Mo-O (which has the lower Na amount) shows the largest diffusion coefficient value, indicating that overmuch Na ions pre-intercalation is not beneficial to the Li ion diffusion. Since Na ions and Li ions are both cations, excessive Na ions between interlayers will produce repulsive interaction to the Li ions during charge-discharge.



Figure 3 Electrochemical properties of pristine MoO₃, Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts. (a) Cyclic voltammetry (CV) curves at a sweep rate of 0.1 mV s⁻¹ in the potential range from 4.0 to 1.5 V vs. Li/Li⁺. (b) Rate performance of pristine MoO₃, Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts cycled from 0.1 to 3 A g⁻¹. (c) The cycling performance at the current density of 500 mA g⁻¹. (d) Electrochemical impedance spectra of the pristine MoO₃, Na(1)-Mo-O, Na(2)-Mo-O and Na(3)-Mo-O nanobelts.

Therefore, the Na(1)-Mo-O shows better kinetics than Na(2)-Mo-O and Na(3)-Mo-O.

To further reveal the function mechanism of Na⁺ preintercalation on the cycling performance, in-situ XRD test was performed on both Na(1)-Mo-O and pristine MoO₃ electrodes. The in-situ XRD result of Na(1)-Mo-O is shown in Figure 4, and the pattern can be divided into four parts. Region I represents the initial first discharge process. In this process, the (060) peak at about 38.3°, corresponding to the characteristic plane of the layered structure, shifts toward 36.0° at the start (Figure S4 for the zoom in image), but turn back to 40.9° at the end of the discharge, indicating that the lithium intercalation leads to an expansion-contraction process of the Mo-O layered structure. The contraction may be attributed to the distortion of Mo-O single bonds on the surface of the layers caused by the increased interactions between the Li ions and one-fold oxygen atoms after large amount of Li intercalation [5,28]. Region II represents the relaxation process, in which the peaks shift toward low angle slowly, demonstrating the gradual layer spacing expansion, which indicates the metastable property of the lithiated structure in thermodynamics. Region III can be regarded as the reversible charge-discharge

process, although the large expansion-contraction of the layer spacing is still observed. The reversibility is attributed to the existence of Na ions between the interlayers, which inhibits the irreversible structure change (as demonstrated by the CV results) and acts as pillars to prevent the collapse of the layered structure. However, what should be noticed is that the peak position in the discharge state shifts toward high angle as the charge-discharge cycling. Combined with the cycling performance and the ICP results of Na(1)-Mo-O, it further confirms that partial Na ions between the interlayers extract accompanied by the extraction of Li ions, thus the pillar effect of Na ions weakened and the layer spacing in lithiated structure (discharge state) decreased. After several cycles, the irreversible structure transformation was observed (Region IV), revealing the collapse of the layered structure, corresponding to the fast capacity fading in the cycling. For pristine MoO₃, the irreversible structure degradation occurs after the first lithium intercalation/de-intercalation (Figure S5), consistent with the fast capacity decrease initially. The in-situ XRD results match well with the cycling performance and clearly illustrate that Na ions effectively inhibit the initial irreversible structure change and stabilize the Mo-O layered structure.

Based on the *in-situ* XRD tests and the electrochemical results, the charge-discharge mechanism in the initial cycles for MoO_3 and Na-Mo-O can be expected and be displayed briefly as Figure 5. For pristine MoO_3 nanobelts, the lithium ions will intercalate into the MoO_3 intralayer sites in the initial cycles, leading to an irreversible structure transformation and severe structure degradation and resulting in fast capacity loss. After Na^+ pre-intercalation treatment, the Na ions will bond with the one-fold oxygen atoms and act as pillars to stabilize the structure. During the initial cycles, the irreversible insertion process into intralayers is inhibited and the layered structure is maintained, which prevents the fast capacity fading initially even though partial Na ions

will extract in this process. Although the structure degradation still occur for Na-Mo-O after several cycles, it can give us a great inspiration that a more stable pre-intercalation (such as bigger K⁺/Rb⁺ or bivalent Mg² ⁺/Ca²⁺ pre-intercalation) will lead to a greater performance improvement.

Conclusion

In summary, we have designed and prepared Na^+ preintercalated MoO_3 nanobelts *via* a facile method, and the Na^+ intercalation amount can be well controlled. It is found that the Na^+ pre-intercalated nanobelts showed the



Figure 4 *In-situ* XRD pattern of Na(1)-Mo-O electrode and the corresponding charge/discharge profile during the initial 9 cycles. The horizontal axis represents the 2θ region and voltage, and the vertical axis represents the time. The diffraction intensity is color coded with the scale bar shown on right.



Figure 5 Schematic illustration of lithium intercalation/deintercalation process of MoO₃ and Na-Mo-O for the initial cycles, respectively. The red balls, purple balls and gray balls represent the one-fold oxygen atoms, Li ions and Na ions, respectively.

improved cycling stability as well as rate capability. This is due to the enhanced structure stability together with the increased lithium diffusion ability. Besides, through *in-situ* XRD analyses combined with the electrochemical tests, it is demonstrated that Na⁺ pre-intercalation can effectively inhibit the irreversible phase transition of the MoO₃ nanobelts, which is fundamentally important for the further investigation of molybdenum trioxide or other layered metal oxides as high performance electrode materials. In addition, our study suggests that the Na-Mo-O nanobelts are promising candidates for the next-generation lithium battery cathodes.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.04.015.

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