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Ethanol reduced molybdenum trioxide for Li-ion capacitors

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ABSTRACT

Orthorhombic molybdenum trioxide (α-MoO$_3$) is a layered oxide with promising performance as electrode material for Li-ion capacitors. In this study, we show that expansion of the interlayer spacing (by $\sim 0.32 \text{ Å}$) of the structure along the b-axis, introduced by partial reduction of α-MoO$_3$ and formation of MoO$_{3-x}$ ($x\approx0.06–0.43$), results in enhanced diffusion of Li ions. Freestanding hybrid electrodes made of MoO$_{3-x}$ nanobelts and carbon nanotubes show excellent electrical conductivity. The combination of increased interlayer spacing and enhanced electron transport leads to high gravimetric and volumetric capacitances of about 420 F/g or F/cm$^3$ and excellent cycle life of binder-free MoO$_3$ electrodes.

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1. Introduction

Electrochemical capacitors (ECs) [1–6] are energy storage devices with higher power densities comparing to batteries. Electric double-layer capacitors (EDLCs) are the most common type of ECs [3], which store charge electrostatically at the electrode/electrolyte interface without any charge transfer. On the contrary, batteries [7–9] only benefit from the Faraday currents from redox reactions introducing phase transformations (nickel metal hydride battery [10,11] and lead-acid battery [12]) or intercalation reactions (Li-ion battery [13]). By studying the charge storage mechanism in ruthenium dioxide (RuO$_2$), Conway proposed the concept of redox current-induced pseudocapacitance [5]. Transition metal oxides such as RuO$_2$ and manganese dioxide (MnO$_2$) [14–16] show pseudocapacitive properties and are superior to EDLCs in terms of gravimetric and volumetric capacitance in aqueous electrolytes. However, the charge storage mechanism of pseudocapacitors limited to surface redox reaction determines the total amount of energy stored. Generally, volumetric capacitance is of significance for applications such as portable electronics and electric vehicles (EVs) due to the limited available space for the energy storage device. In order to achieve a higher volumetric capacitance, researchers are focusing on developing high mass density carbon or layered compounds such as 2D carbides (MXenes) [17] and Mo$_2$C [18] for EC electrodes [17,19]. It should be noted that these materials exhibit very high volumetric capacitances, but lower gravimetric capacitances compared to transition metal oxides. It is challenging to simultaneously obtain high gravimetric and volumetric capacitances.

Orthorhombic molybdenum trioxide (α-MoO$_3$) with a layered structure and redox active surface has been widely reported as a promising electrode material for ECs [20] and Li-ion batteries [21–23]. Previously, we reported amorphous MoO$_3$-x/WO$_3$-x hybrid structures, [24] which showed excellent gravimetric capacitance due to surface redox reactions. Later, we reported on hydrogenated MoO$_3$ with a high volumetric capacitance when used in an aqueous Li-ion capacitor [25] and in sea water electrolyte [26]. Unfortunately, the working potential window (V) for aqueous electrolytes is limited by electrolysis of water, which limits the energy (E) and power (P) of the supercapacitors ($E=CV^2/2$, $P=V^2/R$, where $C$ is capacitance and $R$ is resistance). The working voltage window of ECs can be extended by using organic electrolytes. [27,28] Moreover, the electrode structure has an important effect of capacitive performance, which was not studied intensively previously. By using nanocrystalline electrodes, Dunn et al. demonstrated the intercalation process in ordered mesoporous MoO$_3$ resulting in charge storage of 605 C/g in a 2 V voltage window in an electrolyte of 1 M LiClO$_4$ in propylene carbonate [20]. Although α-MoO$_3$ has showed some promise, its low rate capability and poor cycling life [29,30] impose restrictions on its application in various ECs.
use. These issues can be ascribed to slow ion diffusion in the pores of the material and also poor electron transport due to low electronic conductivity of MoO₃. Both problems result in a low rate capability of the electrodes, while the latter problem also affects the cycling stability due to the nonuniform polarization of the electrodes.

Herein, we focus on enhancing the ionic and electronic conductivities of α-MoO₃ nanobelts by partial reduction of α-MoO₃ and introduction of oxygen vacancies into its structure. We found that the reduced form of α-MoO₃ (MoO₃ₓ/C₀ₓ) has a larger interlayer spacing along b-axis, which results in enhanced ion diffusion in the structure. Moreover, the MoO₃ₓ/C₀ₓ showed a higher electronic conductivity compared to α-MoO₃ before reduction. Freestanding and binder-free hybrid electrodes of carbon nanotubes (CNTs) and MoO₃ₓ/C₀ₓ nanobelts show an excellent specific capacitance of 418 F/g including CNTs in LiClO₄ ethylene carbonate/dimethyl carbonate electrolyte. Addition of CNTs to the electrode proved to be critical and about 90.2% of capacitance was retained after testing the hybrid electrode for 5000 cycles. Electrodes without CNT addition only retained 30% of their initial capacitance after the same number of cycles.

2. Experimental section

2.1. Materials

Mo powder (99.5%) and polyvinylidene fluoride (PVDF) were bought from Aladdin. The carbon black was bought from Alfa Aesar. Sodium dodecyl sulfate (SDS, 98%) and hydrogen peroxide (30%, H₂O₂) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis

The α-MoO₃ nanobelts were synthesized via a hydrothermal process as reported elsewhere. Briefly, 2 g molybdenum powder was added into 40 mL of deionized water and stirred to achieve a uniform mixture. Then, 20 mL of H₂O₂ was slowly dropped into the obtained mixed solution. After stirring for 30 min, the saffron yellow precursor solution was transferred to a Teflon lined stainless steel autoclave and heated at 180 °C for 12 h. The product precipitate was filtered and rinsed with deionized water, followed by drying at 60 °C for 12 h. For reduction of MoO₃ nanobelts, 0.3 g of MoO₃ was added into 15 mL of deionized water and 15 mL of ethanol in a Teflon lined stainless steel autoclave and 120 °C for 12 h. The product precipitate was filtered and rinsed with deionized water, followed by drying at 60 °C for 12 h. For reduction of MoO₃ nanobelts, 0.3 g of MoO₃ was added into 15 mL of deionized water and 15 mL of ethanol in a Teflon lined stainless steel autoclave and

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heated at different temperatures. Sample notation includes the reduction temperature; for example, MoO$_3$ reduced at 120°C is labeled as MoO$_{3-x}$-120.

2.3. Fabrication of electrodes

As shown in Fig. 1, the electrodes were prepared in two ways. For binder-free electrodes, MoO$_3$-x nanobelts, multiwalled carbon nanotubes (CNTs, prepared by a floating catalyst chemical vapor deposition; length ~500 µm) and sodium dodecyl sulfate (as surfactant) were added to deionized water in a 4:1:40 ratio. This mixture was the sonicated for 0.5 h and Na$_2$MoO$_4$ was added to deionized water in a 1:1 ratio. This resulted in a 4:1:40 ratio of the cyclic voltammograms (CVs) and using the equation $C = \frac{Q}{D_\alpha V}$.

The specific capacitance was calculated by integrating the discharge portions of the cyclic voltammograms (CVs) and using the equation $C = \frac{Q}{D_\alpha V}$.

3. Results and discussion

After hydrothermal treatment in ethanol, the color of MoO$_3$ powder was changed from light-gray to blue or black depending on the temperature of the hydrothermal treatment (Fig. 1a and Fig. S1a), suggesting a partial reduction of MoO$_3$ and introduction of oxygen vacancies in the structure [25]. Fig. 1b shows an SEM image of MoO$_{3-x}$-120 that has a similar morphology to the raw MoO$_3$ (Fig. S1b). The color of the MoO$_{3-x}$ was darker after hydrothermal treatment at higher temperatures due to further reduction by ethanol. Although a complete understanding of the reduction of MoO$_3$ by this method needs further studies, we suggest the following reduction mechanism. The α-MoO$_3$ has a layered structure, which consists of bilayers of MoO$_6$ octahedra that are held together by van der Waals forces in the (010) direction. [32,33]

During the hydrothermal treatment of the ethanol intercalated α-MoO$_3$, the Mo=O double bonds in between the layers in (010) direction can be reduced to Mo--O--H, resulting in an increased interlayer spacing and the observed color changes in the material. X-ray photoelectron spectroscopy (XPS) studies of the samples show two strong peaks corresponding to Mo$^{5+}$ for sample before and after reduction, and also two new weaker peaks corresponding to Mo$^{6+}$ that appears in the spectra for the reduced samples (Mo 3d spectrum in Fig. 1c and Fig. S2a). Also, comparison of the 01s spectra of the samples before and after reduction (Fig. S2) shows the appearance of a new peak after reduction, suggesting that Mo=O has changed to Mo--O--H [33]. By increasing the
Reduction temperature, Mo-O-Mo bonds could be ruptured, leading to formation of cracks in nanobelts, such as the case of MoO$_3$-x - 150 shown in Fig. 1c. For the samples treated at 180 °C (MoO$_3$-x - 180), the Mo-O-Mo bonds were heavily ruptured resulting in the damage of nanobelts and forming nanopowder (Fig. S1d). X-ray diffraction (XRD) patterns of the untreated MoO$_3$ powder and samples treated at various temperatures are shown in Fig. 1d. The patterns of MoO$_3$-x, MoO$_3$-x - 90, MoO$_3$-x - 120, and MoO$_3$-x - 150 closely match that of the orthorhombic MoO$_3$ (JCPDS reference card no. 05-0508). However, the treatment at 180 °C caused the phase transformation from orthorhombic MoO$_3$ to monoclinic MoO$_3$ (JCPDS reference card no. 78-1071). Fig. 1e shows the (020) peaks of all samples. The changes in b lattice parameter of α-MoO$_3$ can be calculated by the change in the position of the (020) peak, which increases from 13.80 Å for MoO$_3$-x to 14.12 Å for MoO$_3$-x - 120 and MoO$_3$-x - 150. This means that the reduction results in the increasing interlayer spacing of the oxide, which can facilitate Li intercalation and transport. Transmission electron microscopy (TEM) imaging was performed along the [010] crystal orientation (Fig. S3). According to the selected area electron diffraction (SAED) of MoO$_3$-x and MoO$_3$-x - 120, the crystal face [010] kept its structure after the reduction. It is inferred that the ethanol more easily reacts with oxygen shared by neighboring octahedra of two bilayers. With the temperature rising, the kinetic control of ethanol reduction changes to the thermodynamics one and ethanol begins to react with the oxygen neighbors of two bilayers. With the temperature rising, the kinetic control of ethanol reduction changes to the thermodynamics one and ethanol begins to react with the oxygen neighbors of two bilayers. Hence, the two bilayers and their neighbors were ruptured easily. Hence, the enhanced ionic conductivity of the samples after reduction, electrochemical performance of the MoO$_3$-x, MoO$_3$-x - 120 and MoO$_3$-x - 150 was studied systematically in a three-electrode configuration in a potential window of −1.6 V to 0.4 V vs. Ag/AgCl (1.5 V to 3.5 V vs. Li/Li$^+$) in an electrolyte of 1 M LiClO$_4$ in 1:1 mixture of ethylene carbonate and dimethyl carbonate. All electrodes were fabricated by vacuum filtration of a mixture of MoO$_3$-x and carbon nanotube (CNT) at 4:1 ratio, resulting in freestanding and binder-free electrodes. The electrodes with 20 wt% CNT content show an electrical conductivity of 4 S/cm, which is much higher than the conductivity of the electrodes without CNTs (< 10$^{-5}$ S/cm), measured by the four-point probe method. Fig. 2a shows the CV curves of different electrodes recorded at 20 mV/s. As explained by Augustyn et al.[34], a charging time ranging from 10 s to 10 min is appropriate for intercalation pseudocapacitor materials and devices performing on this time-scale can bridge the gap between batteries and EDLCs. We recorded CV curves at 20 mV/s, which is equivalent to 100 s charging time for the 2 V voltage window. The CV curve of CNT-MoO$_3$-x - 120 clearly shows Li intercalation (A) and deintercalation (B) peaks. These peaks are broader and smaller in the case of CNT-MoO$_3$-x with enhanced interlayer spacing, but no cracking of MoO$_3$ formation occurs.

To confirm the enhanced ionic conductivity of the samples after reduction, electrochemical performance of the MoO$_3$-x, MoO$_3$-x - 120 and MoO$_3$-x - 150 was studied systematically in a three-electrode configuration in a potential window of −1.6 V to 0.4 V vs. Ag/AgCl (1.5 V to 3.5 V vs. Li/Li$^+$) in an electrolyte of 1 M LiClO$_4$ in 1:1 mixture of ethylene carbonate and dimethyl carbonate. All electrodes were fabricated by vacuum filtration of a mixture of MoO$_3$-x and carbon nanotube (CNT) at 4:1 ratio, resulting in freestanding and binder-free electrodes. The electrodes with 20 wt% CNT content show an electrical conductivity of 4 S/cm, which is much higher than the conductivity of the electrodes without CNTs (< 10$^{-5}$ S/cm), measured by the four-point probe method. Fig. 2a shows the CV curves of different electrodes recorded at 20 mV/s. As explained by Augustyn et al.[34], a charging time ranging from 10 s to 10 min is appropriate for intercalation pseudocapacitor materials and devices performing on this time-scale can bridge the gap between batteries and EDLCs. We recorded CV curves at 20 mV/s, which is equivalent to 100 s charging time for the 2 V voltage window. The CV curve of CNT-MoO$_3$-x - 120 clearly shows Li intercalation (A) and deintercalation (B) peaks. These peaks are broader and smaller in the case of CNT-MoO$_3$-x with enhanced interlayer spacing, but no cracking of MoO$_3$ formation occurs.

Choice of CNT – MoO$_3$– C caused the phase transformation from orthorhombic MoO$_3$– C0 to orthorhombic MoO$_3$– C150 closely match that of the orthorhombic MoO$_3$– C0x shown in Fig. 1c. For the samples treated at 180 °C (MoO$_3$– C0x - 180), the Mo–O–Mo bonds were heavily ruptured resulting in the damage of nanobelts and forming nanopowder (Fig. S1d). X-ray diffraction (XRD) patterns of the untreated MoO$_3$ powder and samples treated at various temperatures are shown in Fig. 1d. The patterns of MoO$_3$– x, MoO$_3$– x - 90, MoO$_3$– x - 120, and MoO$_3$– x - 150 closely match that of the orthorhombic MoO$_3$ (JCPDS reference card no. 05-0508). However, the treatment at 180 °C caused the phase transformation from orthorhombic MoO$_3$ to monoclinic MoO$_3$ (JCPDS reference card no. 78-1071). Fig. 1e shows the (020) peaks of all samples. The changes in b lattice parameter of α-MoO$_3$ can be calculated by the change in the position of the (020) peak, which increases from 13.80 Å for MoO$_3$– x to 14.12 Å for MoO$_3$– x - 120 and MoO$_3$– x - 150. This means that the reduction results in the increasing interlayer spacing of the oxide, which can facilitate Li intercalation and transport. Transmission electron microscopy (TEM) imaging was performed along the [010] crystal orientation (Fig. S3). According to the selected area electron diffraction (SAED) of MoO$_3$– x and MoO$_3$– x - 120, the crystal face [010] kept its structure after the reduction. It is inferred that the ethanol more easily reacts with oxygen shared by neighboring octahedra of two bilayers. With the temperature rising, the kinetic control of ethanol reduction changes to the thermodynamics one and ethanol begins to react with the oxygen between the Mo atoms of the same (010) layer. Therefore, it was concluded that a reduction temperature of 120 °C is the optimum choice, since MoO$_3$– x - 120 crystals keep the layered structure of MoO$_3$– x with enhanced interlayer spacing, but no cracking of MoO$_3$ formation occurs.

![Graphical abstract](image_url)

Fig. 3. (a) Cyclic voltammograms of CNT-MoO$_3$– x - 120 from 2 mV/s to 200 mV/s. (b) The peak current of peak A vs. the scan rate. (c) The Nyquist plots for MoO$_3$– x. (d) The charge storage capability of CNT-MoO$_3$– x - 120 compared with previously reported materials.

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sign of a better reversibility in the former case. As Fig. S1c shows, the nanobelts were cracked at 150 °C, leading to poor contact between MoO$_2$$_{\text{x}}$−150 nanobelts and CNTs, which is probably the reason for smaller and broader peaks for MoO$_2$$_{\text{x}}$−150 compared to MoO$_2$$_{\text{x}}$−120. At lower scan rates, the intercalation peaks in CVs became sharper with a smaller difference between intercalation and deintercalation potentials (Fig. S7a). Fig. 2b shows the calculated specific capacitances of all samples at various scan rates. At a low scan rate of 2 mV/s, the specific capacitance values of CNT-MoO$_2$$_{\text{x}}$−120 and CNT-MoO$_2$$_{\text{x}}$−150 are 418 F/g and 375 F/g, respectively, which are much higher than the specific capacitance of the untreated sample (182 F/g). The similar (010) peaks in XRD patterns of CNT-MoO$_2$$_{\text{x}}$−120 and CNT-MoO$_2$$_{\text{x}}$−150 (Fig. 1d), can be interpreted as similar interlayer spacings for these samples. Therefore, under a slow scan rate of 2 mV/s there is only a small difference in their specific capacitances. However, as the scan rate increases to 200 mV/s, specific capacitance of CNT-MoO$_2$$_{\text{x}}$−120 (152 F/g) becomes about two times higher than CNT-MoO$_2$$_{\text{x}}$−150 (79 F/g). This is related to a lower electronic conductivity of cracked CNT-MoO$_2$$_{\text{x}}$−150 (shorter belt length). The untreated CNT-MoO$_2$$_{\text{x}}$ shows a much lower capacitance (182 F/g at 2 mV/s), which constantly decreases to a very small value of 19 F/g at 200 mV/s. This indicates that the untreated CNT-MoO$_2$$_{\text{x}}$ samples should be mainly regarded as a Li-ion battery electrode material and cannot be used at rates expected from Li-ion capacitors.

We further studied the kinetics of Li intercalation into CNT-MoO$_2$$_{\text{x}}$−120 samples following a method suggested by Dunn et al. to distinguish surface- and diffusion-controlled responses of pseudocapacitive materials [20,35,36]. CV curves of CNT-MoO$_2$$_{\text{x}}$−120 samples at scan rates ranging from 2 mV/s to 200 mV/s are shown in Fig. 3a. The following equation was used to analyze the CV discharge peak position:

$$i = av^n$$  \hspace{1cm} (1)

where $i$ is current at peak position, $v$ is scan rate, $a$ and $n$ are adjustable values. $n$ value of 0.5 corresponds to a diffusion-controlled process and $n = 1$ means that the process is surface-controlled. Theoretically the $n$ value for an ideal capacitor should be equal to one, but in practice it is less than one due to the effects of ion diffusion and/or ohmic contribution. As Fig. 3b shows, for CNT-MoO$_2$$_{\text{x}}$−120 the $n$ value was about 0.9 (nonlinear curve.

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Fig. 4. (a) The cycle life testing of MoO$_2$$_{\text{x}}$−120 in the traditional (mixed with 5%wt PVDF and 25%wt carbon black) electrode and binder-free electrode. (b) SEM images of the electrode with binder after 500 cycles. (c) and (d) SEM images of binder-free electrode before and after 5000 cycles.
fitted from 2 to 100 mV/s), which means a surface-controlled process is dominant at all scan rates. As explained by Dunn et al. [35], the current response of the electrodes at a fixed potential can be expressed as the as combinations of the contributions of the surface-controlled capacitive processes and diffusion-controlled processes according to:

\[
 i(V) = k_1 \sqrt{V} + k_2 V 
\]

where \( i(V) \) is the current at a specific potentials, \( V \) is scan rate, \( k_1 \) and \( k_2 \) are reaction rate coefficients, and \( V \) is the potential at which \( i \) is measured. For analytical purposes, Eq. (2) can be rearranged to:

\[
 i(V)\sqrt{V} = k_1 + k_2 V \sqrt{V}
\]

from which \( k_1 \) and \( k_2 \) can be determined from the slope and intercept of the \( i(V)\sqrt{V} \) vs. \( V \) graph. Fig. S5 shows this graph calculated for the CV peak current at various scan rates, \( k_1 \) and \( k_2 \) were calculated from this graph to be equal to 0.089 and 0.79, respectively. This means that about 76% of the current at peak potentials are from capacitive surface-controlled processes at 100 mV/s. This explains the high rate capability of the reduced samples as the charge storage in these samples is not limited by diffusion of ions (Fig. 2b).

The high-rate ion intercalation/deintercalation into the structure of the reduced samples can also be observed by the electrochemical impedance spectroscopy (EIS) in Fig. 3c. The high-frequency (200 kHz to 50 Hz) region of the Nyquist plot shows a smaller Warburg region related to ion diffusion resistance for the reduced sample. Its low frequency region of the Nyquist plot is smaller Warburg region related to ion diffusion resistance for the high rate inorganic electrolyte (200 mV/s scan rate). Cycling stability of the samples was also heavily influenced by the electrode structure and preparation method. In order to demonstrate the importance of uniform electronic conductivity in the electrodes, the two types of electrodes were subjected to 5000 cycle tests by GCPL at a current density of 5 A/g. As shown in Fig. 4a, the traditionally fabricated electrode lost 70% of its initial capacitance after 500 cycles, while the binder-free electrode retained 90% of its initial capacitance after 5000 cycles. The morphologies of both electrodes were examined by SEM before and after cycling. The inhomogeneous distribution of carbon black particles (conductive additive in conventional made electrode) and partial contact between the particles and nanobelts (Fig. S8) results in an uneven lithium intercalation and electrode expansion of MoO3 nanobelts, leading to their cracking and mechanical failure during consecutive cycling. The binder may also affect the fracture of electrodes as uneven distribution of binder on the surface of nanobelts may result in an uneven volume expansion. In other words, parts of the nanobelts that are covered with binder are more constrained and expand less during Li intercalation. Consequently, this results in transformation of nanobelts to nanoparticles after 500 cycles (as shown in SEM image of Fig. 4b). In contrast, the binder-free electrodes, which are free to move during expansion/contraction while being charged/discharged, keep their initial morphology after 5000 charge and discharge cycles (Fig. 4c and d). The high conductivity of CNTs in the network of CNTs and MoO3 nanobelts results in a uniform polarization and expansion of the electrodes during charging. Moreover, the increased conductivity of the electrodes promotes their rate capability, as discussed above.

The results presented here illustrate the benefits from both, improved ion diffusion and electron transport in the partially reduced MoO3-x (x=0.06-0.43) electrode that are required for rapid charging of electrodes [37]. The enhanced capacitance, rate capability and cyclic performance of the electrode are the results of (1) increased Li ion intercalation/deintercalation rates due to a larger interlayer spacing (from 13.80 Å to 14.12 Å) in the oxide structure, and (2) fast electron transport in the electrodes as a result of formation of a CNT/MoO3-x network. The best performance was achieved for samples reduced at 120 °C (MoO3-x – 120) that showed excellent capacitive behavior at a high scan rate in organic electrolyte (152 F/g at 200 mV/s). The importance of the CNT addition for uniform polarization of the electrode and its effects on cyclic stability of the electrodes has been shown.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.05.004.

References