Flexible electrode for long-life rechargeable sodium-ion batteries: effect of oxygen vacancy in MoO$_{3-x}$

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Layered molybdenum trioxide (MoO$_3$) has rarely been studied as an electrode material for sodium ion batteries due to its low electronic conductivity and irreversible phase transitions. Here we demonstrate that MoO$_{3-x}$ with a well-controlled oxygen vacancy, exhibits near theoretical capacity, excellent rate capability, and 2000 stable cycles with minimal capacity loss. The oxygen vacancy in MoO$_{3-x}$ is responsible for the two-plateau voltage profile, in contrast to the sloping feature observed in $\alpha$-MoO$_3$. This work highlights the importance of oxygen vacancies in enabling long-life rechargeable sodium-ion batteries.

The cost of lithium is expected to soar as it powers the next generation of electric vehicles due to limited resources, rendering the development of low-cost alternatives to lithium ion batteries of great importance.$^1$ The earthly abundance and low cost of raw materials has become of unparalleled superiority.$^2$ In this respect, ubiquitous distribution of sodium in the earth’s crust has stimulated extensive research interest towards sodium-ion batteries.$^{3-6}$

Molybdenum oxides have enabled a wide range of applications in gas sensing, catalysts, electronic devices and lubricants due to their low cost, resource abundance and nontoxicity. In particular, a layered molybdenum trioxide ($\alpha$-MoO$_3$) has been studied as an attractive electrode in rechargeable lithium-ion batteries due to its high theoretical specific capacity of 372 mA h g$^{-1}$, corresponding to two electrons reaction per formula.$^{7-12}$ However, the poor cycling stability so far has limited its application as a battery electrode for two reasons. One is the low electronic and ionic conductivity, and the other is the irreversible phase transition related to intralayer Li insertion.$^7$ Strategies were developed in the past to overcome such challenges: (i) nanosizing particle size to reduce the Li ion diffusion distance, (ii) carbon coating to increase the electronic conductivity,$^{13-17}$ and (iii) pre-intercalating Li, Na or K ions in layered MoO$_3$ to suppress intralayer Li insertion.$^{14-17}$

Oxygen deficient MoO$_{3-x}$ was reported to have fast intercalation and excellent electrochemical performance in lithium-ion batteries.$^{18}$ According to Law et al.$^{19}$ oxygen vacancies in MoO$_{3-x}$ led to increased electronic conductivity. Goodenough et al. showed that reduced MoO$_2$ had metallic conductivity as the Mo 4d orbitals split into $t_{2g}$ and $e_g$ orbitals and one extra electron per metal cation in MoO$_2$ partly populated the higher $t$ bands.$^{20}$ Therefore, partially reduced MoO$_{3-x}$ is beneficial for electrochemical applications.$^{21-24}$ To the best of our knowledge, MoO$_{3-x}$ so far has not been investigated as an electrode material in sodium-ion batteries.

In this work, we demonstrate partially reduced MoO$_{3-x}$ grown on flexible carbon cloth and investigate its electrochemical performance as a sodium-ion electrode material (Fig. 1), exploiting the reducing power of carbon cloth when heated with MoO$_3$. The electrochemical characterizations reveal improved electrochemical performance with a reversible capacity close to the theoretical specific capacity of MoO$_3$ (156.3 mA h g$^{-1}$) as well as a significantly improved cycling stability (92% capacity retention after 2000 cycles at 1000 mA g$^{-1}$).

Fig. 1 Schematic diagram of partially-reduced MoO$_{3-x}$, deposited on flexible carbon cloth to enable facile ion diffusion and electron conduction.

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To study the effect of the oxygen vacancy in MoO$_{3-x}$, Samples 1–3 were prepared as following. Carbon cloth (Fuel Cell Earth CCP40) was cleaned and punched to make discs of 1 cm in diameter. Sample 1 was prepared by annealing carbon cloth and 0.2 g MoO$_3$ powder in a corundum crucible at 690 °C for 30 min. Molybdenum oxide was deposited on the carbon cloth and became partially reduced (~5 mg). Sample 2 was prepared by annealing Sample 1 at 350 °C for 2 h in air. Sample 3 was prepared by annealing Sample 1 at the higher temperature of 450 °C for 2 h in air. All samples were characterized using X-ray diffraction (XRD, Rigaku MiniFlex 600) with Cu Kα radiation ($\lambda = 1.5406$ Å), X-ray photoelectron spectroscopy (XPS, VG MultiLab 2000), and scanning electron microscopy (SEM; Gemini LEO 1525).

Fig. 2a shows the XRD patterns of Samples 1–3 as well as the MoO$_2$ and MoO$_3$ standards. Monoclinic MoO$_2$ (JCPDS no. 01-086-0135, $a = 5.6096$ Å, $b = 4.8570$ Å, $c = 5.6259$ Å and $\beta = 120.9120^\circ$) has a distorted rutile structure that has two O sites labeled as O1 and O2 in Fig. 2c. In comparison, orthorhombic $\alpha$-MoO$_3$ is a stable bilayered structure (JCPDS no. 00-001-0706, $a = 3.9540$ Å, $b = 13.8250$ Å, $c = 3.6940$ Å and $\alpha = \beta = \gamma = 90^\circ$) with the space group $Pnma$. Each bilayer consists of two sub-layers of distorted octahedral MoO$_6$ (Fig. 2c). There are three oxygen sites O1, O2 and O3 in the MoO$_3$ structure. O1 oxygen is bonded to one Mo atom, O2 is asymmetrically placed between two Mo centers with a two-fold symmetry, while O3 is located between two Mo centers in one sublayer and another Mo center in the neighboring sublayer. Comparing with the XRD standards, Sample 1 is mainly the monoclinic MoO$_2$ phase, Sample 3 is mainly the orthorhombic $\alpha$-MoO$_3$ phase, while Sample 2 is a mixture of the MoO$_2$ and MoO$_3$ phases.

In order to quantify the concentration (x) of the oxygen vacancy in the MoO$_{3-x}$ samples, we conducted XPS measurements and the results are shown in Fig. 2b and summarized in Table 1. Deconvolution of the Mo 3d spectra in Sample 1 reveals simultaneous existence of peaks from Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$.

**Table 1** Deconvolution of the XPS spectra of Samples 1–3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo$^{4+}$</th>
<th>Mo$^{5+}$</th>
<th>Mo$^{6+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>3d$_{5/2}$ 260</td>
<td>3d$_{5/2}$ 4700</td>
<td>3d$_{5/2}$ 1700</td>
</tr>
<tr>
<td>Sample 2</td>
<td>3d$_{5/2}$ 440</td>
<td>3d$_{5/2}$ 6600</td>
<td>3d$_{5/2}$ 1300</td>
</tr>
<tr>
<td>Sample 3</td>
<td>3d$_{5/2}$ 440</td>
<td>3d$_{5/2}$ 6600</td>
<td>3d$_{5/2}$ 1300</td>
</tr>
</tbody>
</table>

Mo$^{4+}$ consists of two well-defined peaks located at 229.4 eV for Mo$^{4+}$ 3d$_{3/2}$ and 232.6 eV for Mo$^{4+}$ 3d$_{5/2}$.7,26,27 Peaks at 235.1 and 231.6 eV for Mo$^{5+}$ and 236.0 and 232.9 eV for Mo$^{6+}$ exist with smaller percentages. Through fitting the peak area ratio in the XPS spectra, we find that the average valence state of Mo in Sample 1 is 5.0 and that x is 0.5 in MoO$_{3-x}$. In Sample 2, the peaks corresponding to Mo$^{5+}$, located at 236.0 eV and 232.9 eV, become dominant, while the Mo$^{5+}$ peaks are suppressed and the Mo$^{4+}$ peaks disappear. The average valence state of Mo in Sample 2 is 5.94 and thus x is 0.03 in MoO$_{3-x}$. In Sample 3, the XPS spectrum shows a sharp Mo 3d$_{3/2}$ peak at 232.9 eV and a Mo 3d$_{5/2}$ peak at 236 eV, suggesting x is 0 in Sample 3. Therefore, it is clear that carbon cloth reduces MoO$_3$ to MoO$_{2.5}$ during synthesis, while thermal annealing in air partially oxidizes Mo back and results in a mixture of Mo$^{5+}$ and Mo$^{6+}$.

Fig. 3a–c show the SEM images of Samples 1–3, in which carbon fibers are clearly visible. At intermediate magnification (Fig. 3d–f), MoO$_{3-x}$ nanoplates uniformly cover the surface of the carbon fibers. They are several micrometers in length and a few hundred nanometers in thickness (Fig. 3g–i). The nanosized MoO$_{3-x}$ plates would allow fast kinetics for Na-ion diffusion due to the short diffusion distance. In addition, the conductive carbon fiber network is retained very well during the annealing process. All three MoO$_{3-x}$ samples show similar nanoscale morphology, therefore allowing us to compare electrochemical performance solely based on the differences in oxygen vacancies in the structure.

![Fig. 2](image_url) **Fig. 2** (a) XRD patterns of Samples 1–3 and standard PDFs for monoclinic MoO$_2$ and orthorhombic MoO$_3$. (b) XPS of Samples 1–3. (c) Crystal structures of MoO$_2$ and $\alpha$-MoO$_3$ with different oxygen atoms highlighted.

![Fig. 3](image_url) **Fig. 3** (a, d and g) SEM images for Sample 1. (b, e and h) SEM images for Sample 2. (c, f and i) SEM images for Sample 3. Insets show the optical images of Samples 1–3.
To shed light on the effect of oxygen vacancy concentration on the electrochemical performance, the three samples were measured using CR2032 coin cells with sodium metal as the counter electrode and 1 M NaClO4 in propylene carbonate as the electrolyte. No additional conductive agent or binder was used. Fig. 4a–c display the discharge–charge voltage profiles of the three samples at the 1st, 50th, and 100th cycles at a low rate (current density of 100 mA g⁻¹). Sample 1 shows negligible capacity at the first cycle, and slowly increases to ~60 mA h g⁻¹ after 100 cycles. Interestingly, the voltage profile develops a two-voltage plateau but with a higher capacity of 264 mA h g⁻¹. For Sample 2, the capacity shows a two-voltage plateau but with a higher capacity of 290 mA h g⁻¹. The sloping profile suggests the amorphous structure of α-MoO3 after the first cycle. The sloping profile suggests the amorphous structure of α-MoO3 after the first cycle. No additional conductive agent or binder was used. Sample 2 also shows a two-voltage plateau but with a higher capacity of 156 mA h g⁻¹, close to the theoretical specific capacity of MoO3. For Sample 3, the capacity shows a capacity as high as 156 mA h g⁻¹ in the first cycle. However only 40% capacity retention is observed after 50 cycles, which is comparable to the performance of orthorhombic α-MoO3.18 These results indicate that a 3% oxygen vacancy (Sample 2) is optimal for both high capacity and stable cycling. Too many (Sample 1) or too few (Sample 3) oxygen vacancies result in a reduced electrochemical performance.

The rate capabilities of Samples 1–3 are further tested at various current densities (50 to 1000 mA g⁻¹) within the voltage window of 1.0–4.0 V vs. Na/Na⁺ (Fig. 4d). Sample 2 delivers the highest capacity among the three samples with its discharge capacity of 176.6, 122.9, 98.4 and 79.2 mA h g⁻¹ at current densities of 50, 200, 500 and 1000 mA g⁻¹, respectively. Fig. 4e and f show the cycling performance of the three samples at 100 and 1000 mA g⁻¹, respectively. With an initial capacity drop at 100 mA g⁻¹, the capacity of Sample 2 increases over cycling and eventually reaches 156.3 mA h g⁻¹ after 200 cycles, corresponding to 0.84 sodium ions per MoO3-x. The excellent stability in Sample 2 arises from a balanced mixture of the conductive MoO3 phase and a Na-intercalating MoO3 phase. A fluctuation in the specific capacity during cycling is observed and is possibly due to the uneven electrolyte wetting of the phases of MoO3 and MoO2. This phenomenon has been previously observed in amorphous MnO2–carbon nanocomposites,31 and in α-Fe2O3/B-MnO2 nanorods32 during lithium-ion storage. Sample 1 approaches a specific capacity of 64 mA h g⁻¹ after 80 cycles. Sample 3 has an initial specific capacity of 157 mA h g⁻¹, but decays very fast with only 63.4 mA h g⁻¹ after 100 cycles. A similar decay is well known for MoO3 in lithium-ion batteries due to the irreversible phase transition and intralayer trapping of Li ions.33–37 At a current density of 1000 mA g⁻¹ (Fig. 4f), Sample 2 still shows the best performance. The discharge capacity of Sample 2 increases to 92.6 mA h g⁻¹ after 500 cycles and then shows minimal capacity loss over 2000 cycles, with 92% capacity retention compared to the capacity at the 500th cycle.

Conclusions

In summary, partially reduced MoO3-x grown on flexible carbon cloth has been synthesized via a facile thermal reduction method. The obtained MoO3-x with well-controlled oxygen vacancies exhibits near theoretical capacity, good rate capability and much enhanced cycling stability. Moreover, it presents very small capacity loss over 2000 cycles at a high rate (1000 mA g⁻¹). Further investigations of XRD and XPS reveal that the best performing electrode features a 3% oxygen vacancy in the structure of MoO3-x. This study demonstrates the importance of controlling the oxygen vacancy in optimizing materials for long-life rechargeable sodium-ion batteries.

Acknowledgements

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Notes and references
