Mo-doped LiV₃O₈ nanorod-assembled nanosheets as a high performance cathode material for lithium ion batteries

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Supporting Information

The calculation of oxygen vacancies and true molecular formula for Mo doped LiV₃O₈ calcined at 400°C: The relative atomic ratio of V⁵⁺ and V⁴⁺ is 3:1 which was calculated based on the peak areas of V2p high resolution XPS. This means that the content of V⁴⁺ is 25% in vanadium ions and there are 0.71 V⁴⁺ per Mo doped LiV₃O₈ molecular. On the other hand, the substitution of a Mo⁶⁺ ion for a V⁵⁺ ion produces a V⁴⁺ ion, as dictated by the electroneutrality condition. 0.15 Mo⁶⁺ replaces V⁵⁺ in per molecular. The excess 0.56 V⁴⁺ come with the emergence of 0.28 oxygen vacancies. Therefore, the formula of Mo doped LiV₃O₈ is LiMo₀.₁₅ V₂.₈₅O₇.₇₂ (V⁴⁺)₀.₂₈.

Figure S1 (a) Mo-doped LiV₃O₈ cryogel obtained by freeze drying. (b) Mo-doped LiV₃O₈ nanorod-assembled sheets obtained by annealing the cryogel in ambient atmosphere at 400°C for 2 h. (c) Mo-doped LiV₃O₈ nanorod-assembled nanosheets obtained after ball milling.
Figure S2 Current-voltage curves obtained by the DC four-probe measurements for LiV$_3$O$_8$ calcined at 400°C and Mo-doped LiV$_3$O$_8$ (400) samples at room temperature. Linear responses of the applied voltage range spectra were seen in Figure S2, which indicate that the electrical transports are within the ohmic region for LiV$_3$O$_8$ calcined at 400°C and Mo-doped LiV$_3$O$_8$ (400) samples. The current (I) and voltage (V) in Figure S2 can be used to calculate the conductivity by the following expression

$$\sigma_{dc} = \frac{I}{V} \frac{L}{A} \text{ (S cm}^{-1})$$

In above equation, L is the distance between the probes and A is the area of the sample. The electrical conductivity values were calculated to be $3.52 \times 10^{-6}$ S cm$^{-1}$ and $2.89 \times 10^{-5}$ S cm$^{-1}$ for LiV$_3$O$_8$ calcined at 400°C and Mo-doped LiV$_3$O$_8$ (400) samples, respectively.
Figure S3 FE-SEM images of Mo-doped LiV$_3$O$_8$ cryogel (a, b), Mo-doped LiV$_3$O$_8$ calcined at 400 °C (c, d) and milled Mo-doped LiV$_3$O$_8$ calcined at 300 °C (e), 350 °C (f), 400 °C (g) and 450 °C (h).

Figure S4 XRD pattern of milled Mo-doped LiV$_3$O$_8$ cryogel obtained by freeze drying.
The calculation of the NH₃ and O₂ partial pressure produced by the hydrothermal reaction: During the reaction, the volume of stainless steel autoclave is 100 ml, the amount of liquid is 60 ml and the V₂O₅ is 0.01mol. The number of moles of NH₃ and O₂ would be 0.0009 mol and 0.0003 mol based on the following formula.

\[
28LiOH + 39.9V₂O₅ + 0.6(NH₄)ₙMo₉O₄₄ \xrightarrow{180°C} 28LiMo₀.₁₁V₂₃₅O₈ + 15.8H₂O + 3.6NH₃ + 1.05O₂
\]

The partial pressure of NH₃ and O₂ would be 113.02 Pa according to the ideal-gas equation, which is much smaller than the vapor pressure of water (1001900 Pa) and the pressure of air (153990 Pa) at 180 °C. Therefore, the effects of NH₃ and O₂ were negligible on the total pressure in stainless steel autoclave.

\[
P = \frac{nRT}{V}
\]

\[
P = \frac{[(0.0009 + 0.0003) \times 8.314 \times (273.15 + 180)]}{0.04}
\]

\[
P \approx 113.02(Pa)
\]

Figure S5 Illustration of the calculation method to get the surface area of LiV₃O₈ (a) and MDLVO calcined at 400°C (a, b).

The following is the calculation of LiV₃O₈ nanosheet surface area. The average length of LiV₃O₈ nanosheets is estimated to be 1.15 μm, the width and thickness are about 1 μm and 5 nm, respectively. The density of LiV₃O₈ is 3.48 g cm⁻³. Therefore, the calculated surface area of LiV₃O₈ nanosheet is 116 m² g⁻¹ based on the following equations.
Gas-adsorption derived surface area (13.9 m² g⁻¹) occupies only 11.98% of the calculated surface area. That is, only 11.98% of the calculated surface area can be in contact with the electrolyte supposing all of the LiV₃O₈ are nanosheets.

As for the Mo-doped LiV₃O₈ material calcined at 400°C (MDLVO (400)), its structure comprises of nanorod-assembled nanosheets. The calculation surface area is as follows supposing all of the MDLVO (400) are nanorods. The average length of the MDLVO (400) nanorods is estimated to be 150 nm, the width is 50 nm and the thickness is about 5 nm. The nanorod is assumed to be cuboid. Therefore, the calculated surface area of LiV₃O₈ nanorod is 131 m² g⁻¹ based on the following equations.

\[
S = 2 \times (L \times W + L \times T + W \times T) = 2 \times (150 \times 50 + 50 \times 5 + 150 \times 5) \\
	imes 10^{-18} = 1.70 \times 10^{-14} (m^2)
\]

\[
V = L \times W \times T = 150 \times 50 \times 5 \times 10^{-21} = 3.75 \times 10^{-17} (cm^3)
\]

\[
m_S = \rho V = 3.48 \times 3.75 \times 10^{-17} \approx 1.30 \times 10^{-16} (g)
\]

\[
S_T = \frac{S_S}{m_S} = \frac{2.32 \times 10^{-12}}{2.00 \times 10^{-14}} = 116 (m^2 g^{-1})
\]

Gas-adsorption derived surface area (24.8 m² g⁻¹) occupies 18.93% of the calculated surface area, and the corresponding ratio of calculated surface area can be in contact with the electrolyte. The ratio of active surface area increases 58.01% comparing with LiV₃O₈ nanosheets.
If all of the MDLVO (400) are nanosheets, the gas-adsorption derived surface area (24.8 m\(^2\) g\(^{-1}\)) would take 21.38% of the calculated surface area. And the ratio of active surface area would increase 78.46% comparing with that of LiV\(_3\)O\(_8\) nanosheets. Collectively, the BET surface area has increased 78.42% after Mo doped LiV\(_3\)O\(_8\) nanosheets and the ratio of active surface area has also an increase of 58.01%-78.46% comparing with that of LiV\(_3\)O\(_8\) nanosheets. Therefore, the different electrochemical performance would be obtained due to the doping of Mo.

![Figure S6](image)

Figure S6 The first-cycle CV curves for pure LiV\(_3\)O\(_8\) calcined at 400\(^\circ\)C and Mo-doped LiV\(_3\)O\(_8\) (400) electrodes at a scan rate of 0.1 mV s\(^{-1}\) over the range of 2.0-4.0 V (vs. Li/Li\(^+\)).

<table>
<thead>
<tr>
<th>Table S1. Impedance parameters calculated from equivalent circuit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs (Ω)</td>
</tr>
<tr>
<td>LiV(_3)O(_8)</td>
</tr>
</tbody>
</table>
Table S2. BET surface areas of Mo-doped LiV$_3$O$_8$ samples calcined at different temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MDLVO(300)</th>
<th>MDLVO(350)</th>
<th>MDLVO(400)</th>
<th>MDLVO(450)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET/ m$^2$ g$^{-1}$</td>
<td>29.5</td>
<td>27.3</td>
<td>24.8</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Table S3. Comparison of electrochemical performance of different LiV$_3$O$_8$ electrode materials.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>The highest capacity (mA h g$^{-1}$)</th>
<th>Capacity after cyclings (mA h g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo doped LiV$_3$O$_8$</td>
<td>4-2 V: 269.0 at 300 mA g$^{-1}$</td>
<td>205.9 after 100 cycles</td>
<td>This work</td>
</tr>
<tr>
<td>Pure LiV$_3$O$_8$</td>
<td>4-2 V: 292.0 at 300 mA g$^{-1}$</td>
<td>97.8 after 100 cycles</td>
<td>This work</td>
</tr>
<tr>
<td>LiV$_3$O$_8$ nanorods on graphene</td>
<td>4-1.5 V: ~ 226 at 300 mA g$^{-1}$</td>
<td>~197 after 100 cycles</td>
<td>Ref [1]</td>
</tr>
<tr>
<td>Li$_x$V$_2$O$_5$/LiV$_3$O$_8$ nanoflakes</td>
<td>4-1.5 V: 195.4 at 300 mA g$^{-1}$</td>
<td>163.4 after 200 cycles</td>
<td>Ref [2]</td>
</tr>
<tr>
<td>Al$_2$O$_3$ coated LiV$_3$O$_8$</td>
<td>4-2 V: 283.1 at 100 mA g$^{-1}$</td>
<td>205.7 after 100 cycles</td>
<td>Ref [3]</td>
</tr>
<tr>
<td>LiV$_3$O$_8$/polythiophene</td>
<td>4-1.8 V: ~255 at 300 mA g$^{-1}$</td>
<td>216.7 after 50 cycles</td>
<td>Ref [4]</td>
</tr>
<tr>
<td>LiV$_3$O$_8$ nanosheets</td>
<td>4-1.5 V: 232.4 at 300 mA g$^{-1}$</td>
<td>~195 after 100 cycles</td>
<td>Ref [5]</td>
</tr>
<tr>
<td>Al$_2$O$_3$-modified LiV$_3$O$_8$</td>
<td>4-1.5 V: ~200 at 300 mA g$^{-1}$</td>
<td>191.0 after 200 cycles</td>
<td>Ref [6]</td>
</tr>
</tbody>
</table>
References