**Supporting information**

**Li3V(MoO4)3 as a novel electrode material with good lithium storage properties and improved initial coulombic efficiency**

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**A definition for ICE**

ICE is the abbreviation of initial coulombic efficiency. It represents charge-discharge efficiency of electrode in the first cycle. For cathode material, it is the ratio of the discharge capacity/charge capacity; For anode material, it is the ratio of charge capacity/discharge capacity.

**In-situ XRD**

For time-resolved in situ X-ray diffraction (XRD), the electrode was placed right behind an X-ray-transparent beryllium window which is also acted as a current collector. The in situ XRD signals were collected using the planar detector in a still mode during the discharge-charge process, and each pattern took 2 min to acquire. Using in situ XRD measurement, we can clearly elucidate the reaction mechanism and structural change of Li3V(MoO4)3 during the charge-discharge process.

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Figure S1 Core level XPS spectra of Li3V(MoO4)3 material: (a) Total curve, (b) Mo 3d, (c) V 2p, (d) O 1s, (e) Li 1s, and (f) C 1s.

The XPS analysis is employed to elucidate the chemical composition and oxidation state of the resultant sample. As shown in Figure S1(a), the survey spectrum indicates that the sample consists of the elements C, Mo, V, Li and O. The high-resolution Mo 3d spectrum [Figure S1(b)] shows two obvious signals at 232.7 and 235.9 eV, which is attributed to the Mo 3d5/2 and Mo 3d3/2 of Mo6+, in good agreement with previous reports.[1](#_ENREF_1) The high-resolution O 1s spectrum [Figure S1(c)] can be resolved into two peaks at 529.8 and 532.0 eV. The former (529.8 eV) is ascribed to the lattice-oxygen and the latter (532.0 eV) is related to the adsorbed-oxygen. Figure S1(d) shows the presence of zero-valent carbon on the surface (peak at 284.8 eV) which results from the pyrolysis of excess oxalic acid. This BE value of C 1s compares well with that of amorphous carbon. In addition, a low-density peak with a BE value of 286.3 eV is observed, which may be due to C–O–H bonds.[2](#_ENREF_2) The high-resolution V 2p spectrum in Figure S1(e) shows two peaks with binding energies at 517.0 and 524.3 eV, which are associated with V 2p3/2 and V 2p1/2, respectively. This indicates that the V(+5) is reduced to V(+3) by oxalic acid dehydrate during synthetic process. In Figure S1(f), the Li 1s has a BE value of 55.3 eV, indicating no obvious change of BE value for Li 1s from Li–O in CH3COOLi (55.5 eV) to Li–O in Li3V(MoO4)3. The BE value of Li 1s is similar to that in LiVPO4F[2](#_ENREF_2) and LiFePO4[3](#_ENREF_3). These results further reflect successful fabrication of Li3V(MoO4)3 with expected valence state.

Table S1 Refined length of metal-O bonds in Li3V2(MoO4)3

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Atom 1 | Atom 2 | Count | d1,2 (Å) | Average d1,2 (Å) |
| Mo1 | O4 | 2x | 1.7688 | 1.7837 |
| O7 | 1x | 1.7940 |
| O5 | 1x | 1.8032 |
| Mo2 | O3 | 1x | 1.7317 | 1.7617 |
| O2 | 1x | 1.7516 |
| O1 | 1x | 1.7701 |
| O6 | 1x | 1.7934 |
| Li1|V1 | O5 | 1x | 2.0233 | 2.0481 |
| O1 | 2x | 2.0395 |
| O1 | 2x | 2.0491 |
| O5 | 1x | 2.0882 |
| Li2|V2 | O4 | 1x | 2.0267 | 2.0481 |
| O6 | 1x | 2.0367 |
| O3 | 1x | 2.0457 |
| O6 | 1x | 2.0673 |
| O7 | 1x | 2.1242 |
| O4 | 1x | 2.1780 |
| Li3 | O2 | 2x | 2.0123 | 2.2119 |
| O3 | 2x | 2.2532 |
| O2 | 2x | 2.3700 |

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Figure S2 rate capability of as-prepared Li3V(MoO4)3

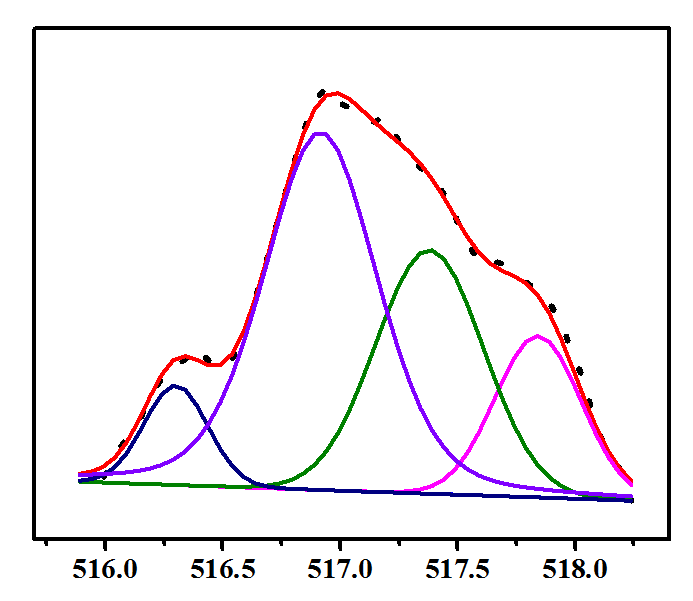


Figure S3 High-resolution XPS curve of V 2p in Li3V(MoO4)3 after 1st cycle.

The high resolution XPS analysis further proved that after the reaction the single peak of the multi-valance of vanadium with binding energies at 517.0 dividing to four small peaks with a distribution of 15%, 28%, 50% and 7%, respectively. This means that higher percent of vanadium tends to higher binding energy, or higher valence state.

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Figure S4 (a, b) TEM and (c) HRTEM images of Li3V(MoO4)3 after 1st cycle.

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Figure S5 (a) Selected galavanostatic discharge curve in the potential range of 0.01-3.0 V and charge curve in the potential range of 0.01-1.0 V at 100 mA g-1; (b) Profiles of specific capacity vs. cycle number at 100 mA g-1.

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Figure S6 (a-d) Galavanostatic discharge curves in the potential range of 0.01-3.0 V and charge curves in the potential range from 0.01 to 1.0 V, 1.2 V, 1.5 V and 2.0 V at 100 mA g-1.

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Figure S7 Profiles of specific capacity vs. cycle number at 0.4V-3V at 100 mA g-1.

The electrochemical reaction mechanism assumption

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