Full paper
Li$_3$V(MoO$_4$)$_3$ as a novel electrode material with good lithium storage properties and improved initial coulombic efficiency

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A R T I C L E   I N F O

Keywords:
Li$_3$V(MoO$_4$)$_3$
Pre-lithiation
Anode
Lithium storage
Initial coulombic efficiency

A B S T R A C T

It is of great significance to discover new negative electrode materials featuring a low operating voltage, high capacity and improved initial coulombic efficiency for lithium ion batteries. This is the first report on the use of orthorhombic Li$_3$V(MoO$_4$)$_3$ as a promising anode material that exhibits natural advantages over reported traditional metal oxides. High-crystalline Li$_3$V(MoO$_4$)$_3$ nanoparticles decorated with carbon are synthesized by a facile mechanochemical route followed by low-temperature (480 °C) calcination. The lithium storage ability of the prepared Li$_3$V(MoO$_4$)$_3$ anode is fully tapped at 3.0–0.01 V vs. Li$^+$/Li, displaying a lower voltage plateau than the conversion-type metal oxides. It delivers a high reversible specific capacity of 999 mAh g$^{-1}$ at 50 mA g$^{-1}$ and a high coulombic efficiency of 82.6%. Moreover, it maintains a capacity retention of 92% after 75 cycles at 500 mA g$^{-1}$. The GITT-determined Li$^+$ diffusion coefficient ranges from 10$^{-11}$ to 10$^{-13}$ cm$^2$ s$^{-1}$ along with the voltage. The lithium storage mechanism indicates that Li$_3$V(MoO$_4$)$_3$ can be considered a pre-lithiated material. In-situ XRD testing during the first cycle reflects the conversion reaction of Li$_3$V(MoO$_4$)$_3$. These insights will benefit the discovery of novel anode materials for lithium-ion batteries.

1. Introduction

The growing demand for renewable energy storage devices has generated mainstream interest in lithium-ion batteries (LIBs) for their high energy and power densities [1–4]. As one of the crucial components, anode material plays an important role in LIBs’ performance [5–9]. Among the various anode materials, graphite is one of the most common in commercial applications [10,11]. However, the graphite’s limited theoretical capacity (372 mAh g$^{-1}$) has proven too low to satisfy the increasing energy requirement [12–15]. Due to their high capacity, low cost and facile preparation, conversion-type transition metal oxides (TMOs) have been widely investigated as promising anodes [16–23]. However, these materials suffer from structural instability and low coulombic efficiency during the first cycle due to a large volume change, irreversible electrolyte decomposition and solid electrolyte interface (SEI) film formation [24,25]. In addition, TMO’s high operating voltage makes it hard to significantly increase the energy density of batteries composed of TMO anodes [26,27]. Therefore, it is of great significance to develop new anode materials with large specific capacity, low operating voltage and improved initial coulombic efficiency (ICE).

Complex lithium- and molybdenum-containing oxides, such as Li$_2$Co$_2$(MoO$_4$)$_3$ [28], Li$_2$Ni$_2$(MoO$_4$)$_3$ [29], LiFe(MoO$_4$)$_2$ [30], Li$_3$V (MoO$_4$)$_3$[31] and LiVO$_2$Mo$_4$[32] have exhibited reversible Li$^+$ insertion/extraction over a wide voltage range. Among these materials, lithium vanadium molybdate, Li$_3$V(MoO$_4$)$_3$, was discovered by the D. Mikhailova group in 2010 as a novel mixed molybdenum-vanadium oxide with an orthorhombic structure and large channels half-filled with Li atoms [31]. The Li$^+$ insertion/extraction ability of Li$_3$V(MoO$_4$)$_3$ was discovered in the potential window of 1.4–4.9 V, delivering a specific capacity of 250 mAh g$^{-1}$. Interestingly, given the various oxidation states of V and Mo, it is expected that Li$_3$V(MoO$_4$)$_3$ has the ability to deliver a high specific capacity. Therefore, it is worth finding an effective way to develop the lithium storage ability of Li$_3$V(MoO$_4$)$_3$ under a suitable conditions. Moreover, the particle size of the Li$_3$V (MoO$_4$)$_3$ reported in the above-mentioned literature is as large as

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https://doi.org/10.1016/j.nanoen.2017.11.079
Received 28 September 2017; Received in revised form 26 November 2017; Accepted 30 November 2017
Available online 05 December 2017
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several micrometers, inhibiting both Li\(^+\) ion transfer and electronic conductivity. Considering this, grain refining might be very useful for improving the electrochemical performance of Li\(_3\)V(MoO\(_4\))\(_3\).

In this work, we are the first to present the synthesis of Li\(_3\)V(MoO\(_4\))\(_3\) particles via a facile method using the soft chemical route with mechanical activation assist, and further study its lithium storage properties at low voltage. The synthetic method is simple, with the broad adaptability to the Li, Mo and V sources. Herein, oxalic acid is used not only as a selective reductant that reduces vanadium from a high oxidation state to V (+3) without reducing Mo (+6), but also as a carbon source depositing homogeneously on the surface of the Li\(_3\)V(MoO\(_4\))\(_3\) particles [4,33,34]. The residual carbon is able to enhance the electronic conductivity of the sample. With the assistance of mechanical activation, the as-prepared Li\(_3\)V(MoO\(_4\))\(_3\) particles are well-refined to submicron or nanoscale, which is beneficial to the lithium ion diffusion [35–37]. To explore the use of Li\(_3\)V(MoO\(_4\))\(_3\) in LIBs, the prepared Li\(_3\)V (MoO\(_4\))\(_3\) material is introduced as an anode material at the potential window ranging from 0.01 to 3.0 V. We expect to excavate the lithium ion storage properties of Li\(_3\)V(MoO\(_4\))\(_3\) at a low potential for practical applications.

2. Experimental section

2.1. Synthesis of Li\(_3\)V(MoO\(_4\))\(_3\) material

The Li\(_3\)V(MoO\(_4\))\(_3\) material was prepared through a soft chemical route with mechanical activation assist followed by low temperature annealing. First, stoichiometric amounts of V\(_2\)O\(_5\) (A.R., 99%), CH\(_3\)COOLi:2H\(_2\)O (A.R., 98%), (NH\(_4\))\(_6\)MoO\(_4\)2H\(_2\)O (A.R., 99%), and 10% excess oxalic acid (H\(_2\)C\(_2\)O\(_4\)·2H\(_2\)O, A.R., 99.5%) were mixed and dispersed into alcohol to form a homogeneous slurry. After that, the slurry was treated by high energy ball milling (ND6−1. The obtained slurry was dried in the vacuum oven at 120 °C overnight. Finally, the precursor was sintered at 300 °C for 3 h, and then at 480 °C for 10 h in a tube furnace under an argon atmosphere to obtain Li\(_3\)V(MoO\(_4\))\(_3\).

2.2. Characterization of Li\(_3\)V(MoO\(_4\))\(_3\)

Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Cu K\(_\alpha\)) was used to determine the purity and crystalline phases of the synthesized products. Field emission scanning electron microscope (FESEM, Hitachi S4800, 20 kV) and transmission electron microscopy (TEM, Titan G2 60–300 with image corrector) were used to observe the morphologies. The surface elemental valence states were determined by an X-ray photoelectron spectrometer (XPS, Kratos Model XSAM800) equipped with an Mg K\(_\alpha\) achromatic X-ray source (1235.6 eV). The elemental distributions were evaluated by energy dispersive spectrometer (EDS) mapping analysis. The carbon content in the composite was determined by C-S analyzer (Elta, Germany). For in-situ XRD measurement, an electrochemical cell module with a beryllium window directly cast with slurry was used. The XRD patterns of the cell at various discharge–charge states were then collected by a D8 Advance X-ray diffractometer using Cu-K\(_\alpha\) radiation (\(\lambda = 1.5418 \text{ Å}\)).

2.3. Electrochemical tests

To fabricate the working electrodes, 10% conductive agent (acetylene black), 10% binder (polyvinylidene fluoride) and 80% as-prepared active material were mixed into the N-methyl pyrrolidinone (NMP) solution to form slurry. Then, the resultant slurry was pasted on a copper foil current collector and dried at 120 °C for 6 h in a vacuum oven. Electrodes were punched into 12-mm-diameter disks. The quality of active material in each electrode was about 1.5 mg. The coin 2025 half cells were assembled in a dry Ar-filled glove box using Li\(_3\)V(MoO\(_4\))\(_3\) as a working electrode, lithium foil as a counter electrode and a porous polypropylene film as the separator. The electrolyte was a mixture solvent of 1 mol L\(^{-1}\) LiPF\(_6\) in EC/EMC/DMC (1:1:1 in volume). The electrochemical tests were conducted using a NEWARE battery circler, between 0.01 V and 3.0 V vs. Li\(^+\)/Li at room temperature. When calculating the specific capacity, the prepared sample with carbon layer directly amounted to the total mass of active material. A CHI660A electrochemical analyzer was used to conduct the electrochemical impedance spectroscopy and cyclic voltammetry measurements. A CV test was conducted in a voltage range of 0.01–3.0 V vs. Li\(^+\)/Li electrode at a scanning rate of 0.05 mV s\(^{-1}\). The impedance spectra were recorded by applying an AC voltage of 5 mV amplitude in the 0.01 Hz–100 kHz frequency range. For the galvanostatic intermittent titration technique (GITT) measurement, the cell (pre-activated for 2 cycles) was discharged/charged with a constant current flux (100 mA g\(^{-1}\)) for 10 min followed by an open-circuit stand for 100 min.

3. Results and discussion

3.1. Structure and morphology

The structural characterization of the as-prepared Li\(_3\)V(MoO\(_4\))\(_3\) anode material was conducted using X-ray diffraction. The XRD pattern and Bragg peak position of the synthesized Li\(_3\)V(MoO\(_4\))\(_3\) are shown in Fig. 1(a). The XRD data are refined with Fullprof. According to the fitting results, as-prepared Li\(_3\)V(MoO\(_4\))\(_3\) is isosctructal to
orthorhombic (Pnma space group) NASICON-type NaCo$_{2.31}$(MoO$_4$)$_3$ [30,38]. In Li$_3$V(MoO$_4$)$_3$ structure, there are many cation vacancies which is good for the transmission of Li$^+$ ions [39]. No impurity phase is detected and a pure Li$_3$V(MoO$_4$)$_3$ phase can be synthesized using the current approach. As shown in [Fig. S1], the high-resolution V 2p spectrum shows two peaks with binding energies at 517.0 (V 2p$_{3/2}$) and 524.3 eV (V 2p$_{1/2}$), indicating the formation of V(+3) during synthetic process. While in Mo 3d spectrum, two obvious signals at 232.7 and 235.9 eV are separately attributed to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of Mo(VI). In L$i$_3$V$(MoO_4)_3$ structure, there are many cation vacancies which are a little larger than those in the previous report. The enlarged cell parameters may benefit lithium ion diffusion and storage. From the structural view, the composition of the as-prepared sample can be described as Li[Li$_{0.558}$V$_{0.442}$]$_4$[Li$_{0.652}$V$_{0.348}$]$_8$[MoO$_4$]$_3$. As shown in the inset of Fig. 1(a), two types of (Li, V) octahedral are found in the structure. One is face-sharing [Li$_{0.558}$V$_{0.442}$]$_4$MoO$_4$ in the b-c plane [Fig. 1(b)]; the other is edge- and corner-sharing [Li$_{0.652}$V$_{0.348}$]$_8$MoO$_4$ that are linked with MoO$_4$ tetrahedra by vertices sharing [Fig. 1(c)]. Both [Li$_{0.558}$V$_{0.442}$]$_4$MoO$_4$ and [Li$_{0.652}$V$_{0.348}$]$_8$MoO$_4$ are linked with MoO$_4$ tetrahedra by sharing vertices. Similar to the structure of Mg$_{2.5}$Fe$_4$(VO$_4$)$_6$, the Li$_{4+}$ atoms in the Li$_3$V(MoO$_4$)$_3$ occupy the channel with a half-filled state. Part of the lithium positions are vacant along the infinite chain of face sharing octahedra, and the lithium atoms likely alternate with cation vacancies along the chain. As revealed by Table S1, the Li-O bond length of LiO$_6$ in the half-filled channel is larger than that in (Li, V)O$_6$, indicating easier transport for Li$^+$ in the channel.

Fig. 2 presents the morphologies of the Li$_3$V(MoO$_4$)$_3$ sample using SEM and TEM. The SEM images in Fig. 2(a) and (b) show the agglomerations of primary submicron-sized Li$_3$V(MoO$_4$)$_3$ particles with clean, smooth surfaces. The particle size of the as-prepared Li$_3$V(MoO$_4$)$_3$ exhibits a narrow distribution ranging from 200 to 400 nm. In addition, the agglomeration of the primary particles builds a porous structure in the prepared sample that is beneficial to the electrical contact between the electrode material and electrolyte. As a result, the lithium ion diffusion is enhanced by shortened transportation [5,27,41]. From the TEM and HRTEM images of Li$_3$V(MoO$_4$)$_3$ in Fig. 2(c) and (d), it can be seen that the surfaces of the well-crystallized Li$_3$V(MoO$_4$)$_3$ particles are wrapped loosely by a 5-nm pyrolytic amorphous carbon layer, forming a core/shell structure with an integral and uniform carbon shell. The content of carbon in the composite is about 0.95%. The FFT image of the selected area “1” [bottom right of Fig. 2(d)] and the corresponding IFFT image [Fig. 2(e)] show a lattice.
distance of 0.331 nm, corresponding to the (104) plane of the Li$_3$V(MoO$_4$)$_3$ crystal. The elemental EDS mappings in Fig. 2(f-j) further confirm that the bulk core material (as shown in Fig. 2(i)) is the Li$_3$V(MoO$_4$)$_3$ crystal with homogeneous elemental (V, Mo, O) distribution and that the surfaces of Li$_3$V(MoO$_4$)$_3$ particles are surrounded by carbon film. The carbon is derived from the extra oxalic acid, and may improve the electronic conductivity of Li$_3$V(MoO$_4$)$_3$ [42–45]. As a result, the carbon-coated Li$_3$V(MoO$_4$)$_3$ exhibits good electrochemical performance.

3.2. Electrochemical performance

The electrochemical performance of Li$_3$V(MoO$_4$)$_3$ as an anode material was investigated in the potential range of 0.01–3.0 V vs. Li$^+$/Li at room temperature. Fig. 3(a) presents the galvanostatic charge–discharge profiles of Li$_3$V(MoO$_4$)$_3$ at 50, 200 and 500 mA g$^{-1}$. The first discharge cycling curve exhibits a working lithiation plateau at about 1.65 V, which is related to the reaction of V(+3) to V(+2) during the cycling process. The capacity at this plateau is about 100 mAh g$^{-1}$. Encouragingly, there are long plateaus at around 0.6 and 0.3 V, which can be assigned to a typical conversion-reaction-based lithium storage process. The capacity fading. In particular, the reversible capacities of Li$_3$V(MoO$_4$)$_3$ are 931 and 890 mAh g$^{-1}$ at 200 and 500 mA g$^{-1}$, respectively. In Fig. 3(b), it can be seen that the Li$_3$V(MoO$_4$)$_3$ electrode shows good cycle performance, with ~100% and 92.0% of capacity retention after 75 cycles at 200 and 500 mA g$^{-1}$, respectively.

After the first cycle, the curves in the following cycles overlap, indicating good cycle repeatability for the Li$_3$V(MoO$_4$)$_3$ electrode. The charge–discharge profiles at 200 and 500 mA g$^{-1}$ maintain a similar shape as that at 50 mA g$^{-1}$, but exhibit some potential polarization and capacity fading. In particular, the reversible capacities of Li$_3$V(MoO$_4$)$_3$ are 931 and 890 mAh g$^{-1}$ at 200 and 500 mA g$^{-1}$, respectively. In Fig. 3(b), it can be seen that the Li$_3$V(MoO$_4$)$_3$ electrode shows good cycle performance, with ~100% and 92.0% of capacity retention after 40 and 75 cycles at 200 and 500 mA g$^{-1}$, respectively. As presented in Fig. 3(b), Li$_3$V(MoO$_4$)$_3$ can deliver a reversible capacity of ~350 mAh g$^{-1}$ even under the high current density of 1600 mA g$^{-1}$, which is higher than that of the commercial graphite anode. In addition, the electrochemical performance of Li$_3$V(MoO$_4$)$_3$ is expected to be further improved by appropriate approaches such as structural optimization and conductive agent modification. Fig. 3(c) shows the Nyquist plot of the Li$_3$V(MoO$_4$)$_3$ electrode at 3.0 V after cycling 2 times; specifically, two semi-circles in the high-to-medium frequency region and a straight line of inductance at low frequency are observed.

**Table 2** Comparison on capacity, initial coulombic efficiency, and average charging voltage (the voltage of half charging capacity) of typical TMOs and as-prepared Li$_3$V(MoO$_4$)$_3$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacity (mAh g$^{-1}$)</th>
<th>Initial coulombic efficiency (%)</th>
<th>Average charging voltage (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>950/50</td>
<td>76.2</td>
<td>2.0</td>
<td>[51]</td>
</tr>
<tr>
<td>NiO</td>
<td>700/156</td>
<td>70.6</td>
<td>1.9</td>
<td>[52]</td>
</tr>
<tr>
<td>CoO</td>
<td>650/100</td>
<td>61.5</td>
<td>1.95</td>
<td>[53]</td>
</tr>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td>1104/100</td>
<td>71.5</td>
<td>1.7</td>
<td>[25]</td>
</tr>
<tr>
<td>CoMoO$_4$</td>
<td>1035/100</td>
<td>76.4</td>
<td>1.6</td>
<td>[54]</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>1123/223</td>
<td>48.0</td>
<td>1.6</td>
<td>[55]</td>
</tr>
<tr>
<td>Ni-Co oxides</td>
<td>1194/200</td>
<td>54.9</td>
<td>1.9</td>
<td>[17]</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>855/100</td>
<td>65.7</td>
<td>1.8</td>
<td>[18]</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>950/50</td>
<td>82.6</td>
<td>1.4</td>
<td>This work</td>
</tr>
<tr>
<td>Li$_3$V(MoO$_4$)$_3$</td>
<td>999/50</td>
<td>~</td>
<td>~</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. (a) Selected galvanostatic charge-discharge curves in the potential range of 0.01–3.0 V at 50, 200 and 500 mA g$^{-1}$; (b) Profiles of specific capacity vs. cycle number at 200 and 500 mA g$^{-1}$; (c) Nyquist plot of as-prepared Li$_3$V(MoO$_4$)$_3$ obtained after two cycles under open circuit voltage; Inset is the equivalent circuit diagram used to fit the as-obtained Nyquist plot. (d) GITT curves of Li$_3$V(MoO$_4$)$_3$ anode as a function of time in the voltage range of 3–0.01 V during both discharge and charge processes; The condition is controlled by repeatedly applying 100 mA g$^{-1}$ for 10 min followed by an open-circuit stand for 100 min; (e) Scheme for a single titration step of GITT curves; Inset is the linear fit of the cell voltage (E) as a function of the square root of time ($t^{1/2}$); (f) $D_{Li^+}$ values in the Li$_3$V(MoO$_4$)$_3$ anode as a function of open-circuit voltage.
line in the low-frequency region. The intercept at the Z' axis in the high frequency refers to the ohmic resistance of the cell (R0), and the value of R0 is only several ohms. One semicircle at high frequency corresponds to surface film impedance (Rf/CPEf) and the other at middle frequency is indexed with charge transfer impedance (Rct/CPEct). The sloping line in the low frequency region refers to the semi-infinite diffusion of lithium-ion (Warburg impedance, W0). The impedance spectra are fitted by the equivalent electrical circuit as shown in the inset of Fig. 3(c). The values of Rct and Rf for Li3V(MoO4)3 are only 3 and 8 Ω, respectively, indicating that Li3V(MoO4)3 has a preeminent and stable interface that is beneficial for charge mobility and electrochemical reactions. This might be one reason why Li3V(MoO4)3 exhibits good electrochemical performance as an anode material. It is well known that Li+ diffusion within the compounds (Dli+) is one of the factors affecting the kinetics of the electrochemical reaction in LIBs. Fig. 3(d) shows the GITT curves of Li3V(MoO4)3 as a function of time. To obtain such continuous curves, the activated cell repeatedly experiences 100 mA g \(^{-1}\) for 10 min, followed by an open-circuit stand for 100 min. Fig. 3(e) demonstrates a typical amplified single titration, schematically presenting the meanings of \(\Delta E_a\), \(\Delta E_c\), \(\Delta E_d\) and \(\Delta E_f\). Assuming that the voltage can reach a new steady state at the end of each titration, the Dli+ can be determined by applying Fick's second law of diffusion and be calculated using the following equation (Eq. (1)) [47]:

\[
D_{li^+} = \frac{4 \pi \left( m_{li^+} V_{li^+} \right)^2}{\pi E_{li^+} \left( \tau_{ee/d,d/e} \right)} \left( \tau \frac{E}{D_{li^+}} \right)
\]

where \(m_{li^+}, V_{li^+}\) and \(E_{li^+}\) are the molecular weight, volume and mass of the material, respectively. Given the linear relationship between E and \(t^{1/2}\) [Inset of Fig. 3(e)], Eq. (1) can be simplified as:

\[
D_{li^+} = \frac{4 \pi \left( m_{li^+} V_{li^+} \right)^2}{\pi E_{li^+} \left( \Delta E_{c} \right)} \left( \Delta E_{c} \right)^2
\]

Based on Eq. (2), the calculated Dli+ as a function of voltage is shown in Fig. 3(f). It can be seen that the Dli+ values range from \(10^{-10}\) to \(10^{-10}\) cm\(^2\) s\(^{-1}\) during discharging and from \(10^{-10}\) to \(5 \times 10^{-12}\) cm\(^2\) s\(^{-1}\) during charging. Overall, the Dli+ values present a decreasing trend during both discharging (from 3 to 0.01 V) and charging (from 0.03 V to 3). During most of the voltage range, the Dli+ values show only a little difference (\(10^{-10}\) to \(10^{-11}\) cm\(^2\) s\(^{-1}\)). However, the Dli+ values decrease rapidly near the end of the discharge process, indicating largely increased Li+ diffusion resistance due to high Li+ concentration in Li3V(MoO4)3 at the end of discharging. Notably, calculated Dli+ values of Li3V(MoO4)3 exhibit levels similar to those of the Li1/3V2(PO4)3 and LiVPO4F anodes [48,49], which are more preponderant compared to that of nano-Si [50]. As such, Li3V(MoO4)3 can also be used as a promising anode material with good lithium ion mobility.

3.3. Lithium storage mechanism and in-situ XRD measurement

The CV curves of the Li3V(MoO4)3 electrode for the first three cycles are presented in Fig. 4(a). In the first negative scan, the Li3V(MoO4)3 electrode displays an intensive peak located at around 1.615 V (R11), which is associated with the insertion of Li+ into the channel of Li3+xV(m) (MoO4)3 [Eq. (3)] due to its half-filled characteristic. This phenomenon can also be observed in another lithium-containing metal molybdate, LiFe(MoO4)2 [30]. After that, the subsequent peaks at around 0.49 (R12) and 0.12 V (R13) correspond to the conversion of Mo(+6) to Mo0 (and V(+3) to V(0)) [Eq. (4)], accompanied by the decomposition of the electrolyte and SEI film [57]. During the first positive scan, the O11 peak located at 1.29 V is indexed with the transformation of metallic Mo to MoO2 [Eq. (5)]; the broad O12 peak located at 1.79 V reflects the overlap of the conversions of MoO2 to Mo3O7 [Eq. (6)] and V to V2O5 [Eq. (7)] [54,58-61]. The O3 peak at 2.38 V is associated with the oxidation of V2O5 to VO2 [Eq. (8)]. [The XPS spectrum after one cycle in Fig. 54 indicates the high oxidative state \((+4)\) of V]. After the first cycle, the cathodic R22, R23 peaks are the reflection of lithium inserting into Li4V(VO)4 [Eq. (9)] and LiVMO3 [Eq. (10)], respectively; R24, R25 peaks correspond to the reduction of Li4+xVO4 and Li4+xMoO3 to metallic V [Eq. (11)] and Mo [Eq. (12)], respectively. Note that, during the first cycle, the electrode stores 21 mol Li+ and releases 22 mol Li+ per mol Li3V(MoO4)3. As a result, the Li3V(MoO4)3 can be regarded as a "pre-lithiated" anode material and its initial coulombic efficiency may be higher than traditional TMOs [Table 2]. In addition, the CV curves after the first cycle overlap, indicating good reversibility and repeatability during cycling. In-situ XRD characterization [Fig. 4(b, c, d)] is conducted to better understand the reaction mechanism and structural change of Li3V(MoO4)3 during the first cycle. Fig. 4(b) and (d) show the three-dimensional in-situ XRD pattern of intensity and selected diffraction peaks of (122), (104), (026) and (200) for Li3V(MoO4)3 during cycling. In the first discharging, above 0.55 V, the peaks almost maintain the principle intensity and peak (104) merges into peak (122). After that, the characteristic peaks for Li3V(MoO4)3 decrease gradually and finally disappear at the end of the last plateau (~0.25 V). This indicates that during the first discharging, the initial structure of Li3V(MoO4)3 is damaged and an amorphous phase is formed. In this state, the amorphous Mo0 will be rearranged and leading to many lattice defects in structure, which is benefit for the transfer of lithium ions [62,63]. When recharging to 3.0 V, there is still no peak observed in the XRD curves, indicating that the subsequent lithium storage reaction occurs in the amorphous material without re-crystallization. It is a typical reflection of the conversion-type of Li3V(MoO4)3 during the first cycling [30,60]. As shown in Fig. 55, after the first cycle, the material presents both amorphous and crystal phases. Moreover, many nano crystals are homogeneously distributed in the amorphous media. These results prove the structural recombination of the Li3V(MoO4)3 during the first cycles.
for LIBs and opened up innovations in the design of novel, high-performance electrode materials for energy storage and conversion.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 51704332, 51574287), the National Postdoctoral Program for Innovative Talents (BX201700290), and the T21-711/16R and 17212015 from the Research Grants Council (RGC) of the Government of Hong Kong SAR. We also thank the Advanced Research Center of CSU for performing the HRTEM examination.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at https://dx.doi.org/10.1016/j.nanoen.2017.11.079.

References

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