Hydrothermal Synthesis of SnO₂ Embedded MoO_{3-x} Nanocomposites and Their Synergistic Effects on Lithium Storage

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ABSTRACT: We demonstrate a facile hydrothermal synthesis of SnO₂/MoO_{3-x} nanocomposites with ultrafine SnO₂ crystallites uniformly embedded into an amorphous MoO_{3-x} matrix, which demonstrate superior electrochemical performance as anodes for lithium ion batteries, including long-term cycling stability (953 mA h/g after 100 cycles at 200 mA/g), high rate capability (668.0 mA h/g after 1000 cycles at 1000 mA/g) and high initial Coulombic efficiency (81.3% at 200 mA/g). Synergistic effects of the both components SnO₂ and MoO_{3-x} on the lithium storage are revealed by electrochemical characterization and supported by TEM and XPS analysis performed at the different discharge/charge states of the respective electrodes. SnO₂ nanocrystallites confined within the amorphous MoO_{3-x} matrix efficiently buffer the volume changes of Li-Sn alloying-dealloying upon cycling, while the metallic Mo *in situ* generated by a conversion reaction of MoO_{3-x} promotes the reversible reaction $\text{SnO}_2 + \text{Li}^+ \leftrightarrow \text{Sn} + \text{Li}_2\text{O}$. In addition, the amorphous MoO_{3-x} with bulk or surface defects allows for a better lithium insertion and thus enhanced capacity.

KEYWORDS: SnO₂/MoO_{3-x} nanocomposites; electrochemical performance; synergistic effect; lithium storage mechanism

INTRODUCTION

Rechargeable lithium ion batteries (LIBs) have been widely used in portable electronics because of their high energy density and long cycle life.[1-4] For a lot of emerging large-scale applications such as electric vehicles and electric grid storage, further improvements of LIBs are necessary, in particular in terms of higher energy and power densities, long-term cycle stability, safety and cost.[5-7] In an effort to improve the LIB performance, various potentially suitable anode materials with higher lithium storage capacity and better cycle/rate performance have been explored, in an attempt to replace the commercial graphite anode material with its rather low theoretical capacity (~ 372 mA h/g). Among various candidate anode materials, metal oxides such as SnO_2 and MoO_3 have received considerable attention owing to their high theoretical capacities, easy fabrication, abundance, low cost, and eco-friendliness. Nanostructured composites based on these metal oxides have demonstrated attractive electrochemical properties in this respect, owing to synergistic effects between multiple metal species.[8-14] As a representative alloy-type metal oxide, SnO_2 has a theoretical capacity of ~ 780 mA h/g based on the reversible alloying-dealloying reaction[4, 15-20]

which involves large ($\sim 300\%$) volume changes. This results in the severe electrochemical pulverization of electrodes and eventually leads to the fast capacity fading upon cycling.[1, 17, 21] Moreover, SnO_2 has to be reduced by lithium metal in the first discharge process according to the reaction:

which is also accompanied with structure destruction and amorphization. The formation of amorphous Li_2O was suggested to be irreversible or only partially reversible, which results in a large capacity loss and thus low initial Coulombic efficiency.[12] Therefore, making the formation of Li_2O reversible would improve the overall electrochemical properties of tin-based anode materials.

MoO_3 is a typical conversion-type anode material which exhibits a high theoretical capacity of 1117 mA h/g based on the reversible conversion reaction:[22, 23]

where the formation-decomposition of Li_2O is electrochemically reversible, which is different from the irreversible formation of Li_2O in the case of the SnO_2 anode (Eq. 2). During the first lithium insertion process (Eq. 3), MoO_3 irreversibly converts into amorphous state, followed by a conversion reaction to form metal Mo and Li_2O . [24, 25] Previous work demonstrated that the small size effect of Mo nanoparticles can greatly enhance the electrochemical reactivity and make the conversion between Li^+ and Li_2O reversible. [24, 26] This has been suggested to be applicable for the reversible decomposition of Li_2O associated with SnO_2 . [27, 28]

For MoO_3 anodes, both the poor conductivity and the large volume changes limit their industrial application in LIBs. SnO_2 on the other hand is a semiconducting oxide with a good conductivity determined by electron mobility ($100\text{-}200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), [6] which further converts into conductive metallic Sn or Li_xSn alloy during cycling. Moreover, as the lithiation-delithiation of MoO_3 and SnO_2 happens at different potential ranges, the volume changes of electrodes occur in a stepwise manner, namely, the unreacted components can accommodate the strain yielded by the reacted phase. Thus a stable cycling performance with high capacity can be realized. Therefore, it is fundamentally interesting and practically important to realize electrochemically active $\text{SnO}_2/\text{MoO}_3$ composites. Xue *et al.* reported a two-step hydrothermal synthesis of $\text{SnO}_2/\alpha\text{-MoO}_3$ core-shell nanobelts with SnO_2 nanoparticle shells grown on $\alpha\text{-MoO}_3$ nanobelt cores, which showed a high reversible capacity of 2214 mAh/g at C/10 and maintained 1895 mA h/g after 50 cycles. [9] Si *et al.* fabricated one-dimensional $\text{SnO}_2/\text{MoO}_3$ nanocomposites with SnO_2 nanosheets densely grown on amorphous MoO_3 nanobelts by one-pot hydrothermal method, which delivered a reversible discharge capacity of ~560 mA h/g after 120 cycles at 200 mA/g. [10] Guo *et al.* prepared $\text{MoO}_3/\text{SnO}_2$ hollow spheres composed of mixed nanocrystallites by a solvothermal method and subsequent calcination, exhibiting a reversible capacity of 807 mA h/g after 200 cycles at 200 mA/g. [29] Despite of these encouraging reports, the initial Coulombic efficiency and the cycle and rate performance of $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposites are still far from satisfactory, and the synergic effects of the single components on lithium storage mechanisms require further investigations.

Herein, we demonstrate a facile one-pot hydrothermal synthesis of $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposites, with ultrafine (~ 5nm) SnO_2 nanocrystallites uniformly distributed within the amorphous MoO_{3-x} matrix. When used as anode materials for LIBs, $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposites demonstrate an excellent electrochemical performance, such as high specific capacity, good cycle stability and rate capability. Synergistic effects between SnO_2 and MoO_{3-x} components are illustrated by TEM and XPS measurements.

EXPERIMENTAL SECTION

Materials synthesis. All chemicals including tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and sodium molybdate (VI) dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) were used as received without further purification. In a typical synthesis of $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposites, equimolar amounts of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (2 mmol) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2 mmol) were dissolved in 15 mL distilled water forming transparent Sn- and Mo-precursor solutions. Both precursor solutions were mixed together under magnetic stirring, immediately forming milky suspension. After stirring for 15 min, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, followed by a hydrothermal reaction at 185°C for 24 h. After cooling down to room temperature, the light green precipitate was collected by centrifugation and rinsed with distilled water and ethanol for 3-5 times. The product was dried in the oven at 80°C overnight. Bare SnO_2 nanoparticles were prepared by hydrothermal treatment of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (4 mmol) aqueous solution at 185°C for 24 h.

Materials characterization. Powder X-ray diffraction (XRD) patterns of the products were obtained on a Bruker D2 PHASER X-ray diffractometer using Cu K α radiation ($\lambda=1.5418$ Å) with an operating voltage of 30 kV and a current of 10 mA. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) and the corresponding selected-area electron diffraction (SAED) pattern were obtained on a JEOL JEM2100 TEM operated at 200 kV. High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was performed by using an aberration-corrected JEOL ARM200F instrument with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis. Scanning electron microscopy (SEM) was performed on a FEI Quanta 250 SEM. Raman spectra were measured using a Renishaw Raman RE01 spectrometer with a 514 nm excitation argon laser. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250Xi instrument.

Electrochemical measurements. Electrochemical measurements were performed on CR2016 coin-type cells assembled in an Ar-filled glove box with H_2O and O_2 content less than 1.0 ppm. The working electrode was prepared by casting an aqueous slurry consisted of active material, acetylene black, and poly acrylic acid binder with a weight ratio of 70:20:10, followed by drying at 120°C under vacuum overnight. Lithium foil was used as the counter electrode, and Celgard 2400 microporous membrane was used as a separator. An electrolyte contained 1 M LiPF_6 dissolved in a mixture of ethylene carbonate/dimethyl carbonate with a volume ratio 1:1. Galvanostatic discharge/charge tests of the cells were carried out on a battery test system (NEWARE BTS, Neware Technology Co., Ltd., China) in the range of 0.01-3.0 V (vs. Li/Li^+) at room temperature (25°C). Cyclic voltammetry (CV) was carried out on an electrochemical station

(Autolab PGSTAT 302N) in the range of 0.01-3 V at a scan rate of 0.2 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out with a voltage amplitude of 10 mV in the frequency range of 10 MHz to 0.01 Hz.

RESULTS AND DISCUSSION

SnO₂/MoO_{3-x} nanocomposites were synthesized by a hydrothermal treatment of SnCl₄ / Na₂MoO₄ aqueous precursor solution. For comparison, bare SnO₂ nanoparticles were prepared by hydrothermal treatment of SnCl₄ aqueous solution. It was impossible to obtain bare MoO₃ nanoparticles at the similar reaction conditions using Na₂MoO₄ precursor, indicating that the presence of SnCl₄ (or SnO₂ seeds) is vital for precipitation of MoO₃. [30] Moreover, the molar ratio of Mo/Sn ($R_{\text{Mo/Sn}}$) can be easily controlled by adjusting the relative content of SnCl₄ and Na₂MoO₄ and the maximum $R_{\text{Mo/Sn}}$ value is ~1.0. Further increasing the amount of Na₂MoO₄ will not reverse the relative content, indicating SnCl₄ can maximally precipitate equimolar Na₂MoO₄ (Table S1.). Figure 1a compares XRD patterns of the SnO₂/MoO_{3-x} nanocomposite and the SnO₂ nanoparticles. All diffraction peaks in the bare SnO₂ can be indexed to crystalline tetragonal (rutile) SnO₂ phase (JCPDS No. 41-1445; space group: P4₂/mm; a=4.738 Å, c=3.187 Å), while the main diffraction peaks at 26.6°, 33.8°, 37.9° and 51.8° in the SnO₂/MoO_{3-x} composite can be indexed to (110), (101), (200) and (211) planes of tetragonal SnO₂ phase. No diffraction peaks belonging to MoO_{3-x} could be detected, indicating its amorphous nature in the composite. Diffraction peaks of (101) and (211) planes become broader and their relative intensity decreases, indicating that the presence of MoO_{3-x} resulted in the random growth orientation of SnO₂ crystallites, as compared with bare SnO₂ nanoparticles.

Figure 1b displays Raman spectra of bare SnO₂ nanoparticles and the SnO₂/MoO_{3-x} nanocomposite, while the Raman spectrum of the bulk MoO₃ is also presented for comparison. In the bare SnO₂, the peaks at 630 and 772 cm⁻¹ can be indexed to the A_{1g} mode and B_{2g} mode of the rutile SnO₂ structure with tetragonal symmetry, both related to the expansion and contraction vibration mode of Sn-O bonds. [31] The peak at 567 cm⁻¹ is related to the surface defects in SnO₂. All these peaks are not present in SnO₂/MoO_{3-x}, which may be due to the embedding of SnO₂ nanoparticles into MoO_{3-x} matrix and also maybe the too weak intensity of SnO₂ bands as compared with that of MoO_{3-x} matrix. [32] Instead, two peaks centered at 870 and 965 cm⁻¹ emerge, which can be related to MoO_{3-x}. In the bulk crystalline MoO₃, the highest Raman band at 994 cm⁻¹ is due to the vibration of the shortest Mo=O bonds, whereas the next highest band at 818 cm⁻¹ is related to the intermediate bridging Mo-O-Mo bond. [33] Therefore, the broad bands at around 870 and 965 cm⁻¹ which are shifted in SnO₂/MoO_{3-x} may indicate the amorphous nature of MoO_{3-x} in

this nanocomposite, with the short-range order and long-range disorder. In addition, the mutual doping, namely Sn-doping in MoO_{3-x} and Mo-doping in SnO_2 , may happen during the synthesis owing to the atomic mixing of Sn^{4+} and Mo^{6+} during the synthesis, which may also resulted in the disappearance or weakening or shifting of symmetric bond vibration in bare SnO_2 or MoO_3 .

Figure 1. (a) XRD patterns and (b) Raman spectra of the bare SnO_2 nanoparticles and the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite. Inset in (a) illustrates the corresponding powdered samples. Raman spectrum of bulk MoO_3 is also shown for comparison in (b). (c) Sn 3d and (d) Mo 3d XPS spectra of the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite.

X-ray photoelectron spectroscopy (XPS) was applied to analyze the chemical states of Sn and Mo in the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite (Figure S2). Peaks located at 495.6 eV and 487.1 eV can be indexed to $\text{Sn } 3d_{5/2}$ and $\text{Sn } 3d_{3/2}$ which belong to the tin with the highest oxidation state (Sn^{4+}) (Figure 1c).[34] In the Mo XPS spectrum (Figure 1d), the binding energies of $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ peaks located at 233.1 eV and 236.1 eV, respectively, correspond to Mo in its highest oxidation state (Mo^{6+}), while the peaks at 234.9 eV and 231.9 eV are ascribed to the Mo^{5+} , [35] indicating the nonstoichiometric nature of the molybdenum oxide, which was previously suggested to correlate with the pH value of the reaction system.[30]

Figure 2. (a) SEM, (b) TEM and (c) HRTEM images of bare SnO_2 nanoparticles. (d) SEM image, (e) TEM image with an inset showing the selected area electron diffraction (SAED) pattern, and (f) HRTEM image of the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite. (g) High-angle annular dark-field (HAADF) STEM images of a fragment of $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite, with the corresponding EDS maps of (h) Sn, (i) Mo and (j) O elements.

Figures 2 a-b show the SEM and TEM images of bare SnO_2 , indicating the presence of elongated nanoparticles with sizes of 5-15 nm. The lattice spacing of 0.33 nm can be indexed to the (110) planes of tetragonal SnO_2 phase (Figure 2c). $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite is composed of larger aggregates (Figure 2d, e). Inset of Figure 2e shows its SAED pattern, which can be indexed to crystalline tetragonal SnO_2 (inset of Figure 2e). HRTEM image (Figure 2f) reveals that the $\text{SnO}_2/\text{MoO}_{3-x}$ composite includes multiple nanocrystallites with the size of around 5 nm, which are dispersed within an amorphous matrix. The spacing of the lattice fringes in the crystallites is 0.33 nm, which can be assigned to the (110) plane of the tetragonal SnO_2 phase. Figure 2g shows the HAADF image of a $\text{SnO}_2/\text{MoO}_{3-x}$ fragment, within which Sn, Mo and O elements are uniformly distributed, indicating the presence of MoO_{3-x} alongside with SnO_2 . The Sn/Mo molar ratio was estimated to be 1, according to the EDS analyses (Figure S2).

Electrochemical properties of the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite have been investigated and

compared with those of the bare SnO₂ nanoparticles. Figure 3a shows cyclic voltammetry (CV) curves of bare SnO₂ electrodes in the initial several cycles, providing similar profiles such as reported in literature previously for SnO₂.^[36-38] In the first cathodic scan, the peak at 0.8 V is attributed to the reduction of SnO₂ into metallic Sn and Li₂O, accompanied by the formation of solid electrolyte interphase (SEI), which further evolves into peaks at around 1.0 V in the following CV cycles. The broad cathodic peak at around 0.07 V and the broad anodic peak at around 0.6 V are ascribed to the reversible Li-Sn alloying and dealloying processes (Eq. 1),^[39, 40] respectively. A reversible peak at around 1.0 V emerges in the 2nd cathodic scan, ascribed to the re-reduction of oxidized SnO_x formed in the anodic scan (Eq. 2).^[41] Correspondingly, two reversible anodic peaks at 1.3 and 1.8 V appear, which correspond to the partial conversion of Sn into SnO₂ and SnO, respectively.^[42] This was further confirmed by TEM and XPS analyses, as will be discussed below in relation to Figures 5 and 6. The CV curves for the SnO₂/MoO_{3-x} electrode are substantially different (Figure 3b), as both SnO₂ and MoO_{3-x} are electrochemically active with similar Li-insertion potentials below 0.7 V. The broader peak in the range of 0.01-0.7 V in the cathodic scans, which further separates into two peaks at ~0.14 and ~0.47 V, is a consequence of the synergistic interaction between the reversible Li-Sn alloying and the reversible conversion of MoO_{3-x} into metallic Mo and Li₂O.^[42-44] In the anodic scans, broad peaks at around 0.6 V are attributed to the Li-Sn dealloying, similar to the bare SnO₂. Broad peaks at around 1.42 and 1.90 V show higher current intensity than the peak at around 0.6 V, which can be attributed to the re-oxidation of freshly generated metallic Sn and Mo reacting with Li₂O. The presence of the *in situ* generated transition metal Mo clusters can promote the decomposition of the Li₂O associated with the electrochemical reduction of SnO₂ by lithium metal. A broad peak at around 0.98 V in the first cathodic scan may correspond to the reduction of SnO₂, Li-insertion into the MoO_{3-x} and formation of SEI, which further shifts to around 1.25 V, ascribing to the conversion of SnO_x into Sn and amorphous Li₂O, as well as the Li-insertion into the MoO_{3-x} according to the reaction:^{39, 42}

Figure 3. Electrochemical properties of SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes. (a, b) Cyclic voltammogram (CV) curves of (a) SnO_2 and (b) $\text{SnO}_2/\text{MoO}_{3-x}$ at a scan rate of 0.2 mV/s in the range of 0.01-3.0 V. (c) Comparison of galvanostatic discharge-charge profiles of the SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$ at 200 mA/g in the range of 0.01-3.0 V. (d) Comparison of the cycle performances of SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$ at 200 and 500 mA/g in the range of 0.01-3.0 V. (e) Long-term cycling performance of $\text{SnO}_2/\text{MoO}_{3-x}$ at 1000 mA/g in the range of 0.01-3.0 V.

Figure 3c compares the first two cycle galvanostatic discharge-charge profiles of SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$, at 200 mA/g in the range of 0.01-3.0 V. Initial discharge/charge capacities for SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$ are approximately 1482/833 and 1311/1066 mA h/g, respectively, and initial

Coulombic efficiencies are 51.4% for SnO₂ and 81.3% for SnO₂/MoO_{3-x}. SnO₂ shows a well-defined plateau at around 0.9 V in the first discharge process, corresponding to the reduction of SnO₂ into Sn and the formation of Li₂O, which is consistent with the CV data (Figure 3a). This plateau disappears in the following discharge cycles, similar to SnO₂/MoO_{3-x}. However, the charge profiles are largely different, owing to the delithiation from Li₂O matrix and simultaneous oxidation of both metallic Sn and Mo at potentials above 1.0 V. The enhanced release of Li⁺ ions from the Li₂O matrix is attributed to the improved initial Coulombic efficiency of SnO₂/MoO_{3-x}, as further discussed in relation to the TEM and XPS analysis.

Figure 3d compares the cycling performances of SnO₂ and SnO₂/MoO_{3-x} in the range of 0.01-3.0 V. SnO₂/MoO_{3-x} electrodes deliver higher capacities of about 953 and 802 mA h/g, while SnO₂ electrodes exhibit continuously decreasing capacities with only 449 and 367 mA h/g after 100 cycles at 200 and 500 mA/g, respectively. The corresponding capacity retentions for SnO₂/MoO_{3-x} are 89.3% and 81.1%, much higher than that of SnO₂ (49.5% and 46%), indicating the better cycle performance of SnO₂/MoO_{3-x}. The long-term cycling performance of SnO₂/MoO_{3-x} at a higher current density of 1000 mA/g is presented in Figure 3e, delivering a discharge capacity of 668.0 mA h/g even after 1000 cycles with an initial Coulombic efficiency of 78.2% and subsequent Coulombic efficiencies over 99% in the following discharge-charge cycles. The capacity increases with increasing cycle number, giving a maximum capacity of 1028 mA h/g after 380 cycles, and then decreases gradually to ~700 mA h/g and remains stable in the following cycles. Such a capacity increase with cycling has been previously observed for nanostructured metal oxide electrodes,[45] and was ascribed to formation of a gel-like film resulting from decomposition of the electrolyte at low voltages.[46] Partial crystallinity degradation towards amorphous-like structure during initial cycling may also contribute to the capacity increase in metal oxide electrodes.[47] The superior cycling stability of SnO₂/MoO_{3-x} electrodes can be related to the following advantageous characteristics of the nanocomposite: i) ultra-small SnO₂ crystallites facilitate the insertion/extraction of Li⁺ ions and alleviate the severe volume changes upon cycling;[39] ii) the presence of amorphous MoO_{3-x} matrix with bulk (vacancies and void spaces) or surface defects contributes to the increase in capacity;[30] iii) SnO₂ nanocrystallites are homogeneously distributed within the amorphous MoO_{3-x} matrix and are linked together by the matrix, which prevents their aggregation, tolerates the volume changes and prevents pulverization of the SnO₂/MoO_{3-x} electrodes upon long-term cycling.

To further elucidate the electrochemical performance of SnO₂/MoO_{3-x} electrodes, electrochemical impedance spectroscopy (EIS) has been performed. From the Nyquist plots presented in Figure 4, freshly prepared SnO₂/MoO_{3-x} electrode exhibits a much smaller semicircle diameter (40 Ω), indicating the small charge-transfer resistance (R_{ct}) and fast electron transfer.

The R_{ct} of the electrode only increases to 118 Ω even after cycling at higher current density of 1000 mA/g for 1000 cycles, indicating the electrode integrity with the existence of efficient charge transfer channels.

Figure 4. Nyquist plots of the $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes before and after different discharge/charge cycles in the charged state.

TEM and XPS analysis has been carried out to investigate the underlying lithium storage mechanism in SnO_2 and $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes. Figure 5a,b shows TEM and HRTEM images of the SnO_2 electrode in the charged state after 100 cycles at 200 mA/g, clearly demonstrating the presence of metallic Sn nanospheres with size of ~ 20 nm. They form due to the gradual migration and aggregation of metallic Sn nanocrystallites formed during the dealloying processes, as spherical shape is usually thermodynamically stable with minimum surface energy. Spheres observed in the TEM have lattice fringes with spacing of 0.29 nm, which can be indexed to the (200) plane of tetragonal Sn (JCPDS No. 04-0673). In addition, a shell layer is conformably coated around metallic Sn spheres, whose lattice spacing of 0.21 nm can be indexed to the (210) plane of the tetragonal SnO_2 phase. This is consistent with the CV measurements, correlating the oxidation of the metallic Sn in the charging process. The fast capacity fading of bare SnO_2 can be explained by the gradual aggregation and growth of Sn particle upon cycling, which cause volume changes and thus severe internal stress, finally resulting in the pulverization of the electrode.[48]

On the contrary, no Sn metal particles were detected within the charged $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes after 100 cycles at 200 mA/g (Figure 5c), and their SAED patterns reveal the presence of SnO_2 . From the HRTEM image in Figure 5d, ultrafine crystalline nanoparticles with a lattice

spacing of 0.21 nm belonging to tetragonal SnO_2 are clearly observed, which are well distributed within the amorphous $\text{Li}_2\text{O-MoO}_x$ matrix, indicating the complete conversion of metallic Sn into SnO_2 after the introduction of MoO_{3-x} in the $\text{SnO}_2/\text{MoO}_{3-x}$ electrode. XPS measurements confirmed the formation of metallic Mo in the discharged $\text{SnO}_2/\text{MoO}_{3-x}$ electrode (Figure 6b), which can promote the decomposition of Li_2O by reacting with metallic Sn, thus contributing to the improved lithium storage capacity. Figure 5e shows the $\text{SnO}_2/\text{MoO}_{3-x}$ electrode at discharged state after 1000 cycles at 1000 mA/g, which is polycrystalline with its diffraction rings ascribed to $\text{Li}_{22}\text{Sn}_5$. HRTEM image (Figure 5f) shows many crystalline domains with random orientation, embedded within an amorphous matrix. The lattice spacing of 0.24 nm of these crystalline domains can be ascribed to the (733) plane of cubic $\text{Li}_{22}\text{Sn}_5$ (JCPDS No. 18-0753), while the lattice spacing of 0.28 nm can be ascribed to the (015) plane of rhombohedral Li_5Sn_2 (JCPDS No. 65-2121), indicating the formation of various Li_xSn alloys in the discharge process. Both Li_xSn alloy nanoparticles with irregular shapes and random alignment in the discharge state and the ultrafine SnO_2 nanocrystallites in the charge state are well distributed within the MoO_{3-x} amorphous matrix (Figure 5f vs. Figure 5d), indicating the robust structural integrity of the $\text{SnO}_2/\text{MoO}_{3-x}$ electrode upon long-term and high rate cycling.

Figure 5. TEM analysis of (a, b) SnO_2 and (c, d) $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes at the charge states (to 3.0 V) after 100 cycles at 200 mA/g. Inset in (b) shows the spacing variations of lattice fringes in the square area. (e) TEM and (f) HRTEM images of $\text{SnO}_2/\text{MoO}_{3-x}$ electrode at the discharge states (to 0.01 V) after 1000 cycles at 1000 mA/g. Insets in (c) and (e) show the corresponding SAED patterns.

XPS measurements were performed to investigate the reaction mechanisms from the aspect of the valence evolutions of Sn and Mo elements at different discharge/charge states. Figure 6 shows XPS spectra of Sn 3d and Mo 3d core level region of the $\text{SnO}_2/\text{MoO}_{3-x}$ electrode at discharge and charge states in the first cycle, respectively. Table S2 summarizes the binding energy (E_B)

positions and the relative atomic content of Sn and Mo elements with different valence states. When the electrode was firstly discharged to 0.01 V, Sn 3d XPS spectrum (Figure 6a) revealed the presence of metallic Sn^0 and oxidized Sn^{2+} , indicating the reduction of SnO_2 , while in the Mo 3d XPS spectrum (Figure 6b), both Mo^0 and Mo^{4+} emerged at the discharge state, and the relative content of Mo^{5+} increased, indicating the additional lithium storage via conversion of MoO_{3-x} into metallic Mo^0 and Li_2O . As the Li^+ ions can be inserted into both the amorphous MoO_{3-x} and the defect sites,[30] the appearance of Mo^{4+} and the increased Mo^{5+} content may be attributed to the formation of LiMoO_{3-x} via intercalation mechanism (Eq. 4). When further charged to 3.0 V, the lower oxidation states of Sn disappeared, and only Sn^{4+} in the form of SnO_2 exist (Figure 6c), indicating that Sn produced from the dealloying of Li_xSn further reacts with Li_2O and converts into SnO_2 . This is consistent with the CV and TEM data (Figure 3b and Figure 5d, respectively). The metallic Mo^0 disappeared in the charge state (Figure 6d), indicating its oxidation by reacting with Li_2O . Thus the Li^+ ions stored in the Li_2O matrix can be released, which consequently improved the initial Coulombic efficiency and the reversible specific capacity of $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes. The atomic ratio of $\text{Mo}^{6+}/\text{Mo}^{5+}$ was estimated from the Mo 3d_{5/2} peak areas at the different states (Table S2), which changed from 82/18 in the pristine $\text{SnO}_2/\text{MoO}_{3-x}$ to 49/51 at charged states (to 3 V) in the first discharge-charge cycle. This may indicate that the amorphous MoO_{3-x} undergoes partially irreversible reaction with lithium ions in the first charge/discharge cycle,[49] which contributes to the irreversible capacity loss in the first cycle.

Figure 6. XPS analyses of the $\text{SnO}_2/\text{MoO}_{3-x}$ electrodes at different states. (a, c) Sn 3d and (b, d) Mo 3d XPS spectra of the $\text{SnO}_2/\text{MoO}_{3-x}$ electrode at (a, b) discharge (to 0.01 V) and (c, d) charge (to 3.0V) states.

CONCLUSIONS

In summary, $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposites comprising ultrafine SnO_2 nanocrystallites embedded in an amorphous MoO_{3-x} matrix were successfully prepared via a facile hydrothermal route. When used as anode materials for lithium ion batteries, these nanocomposites showed excellent cycle stability and rate capability, delivering discharge capacities of 953 and 802 mA h/g after 100 cycles at 200 and 500 mA/g, respectively, and 668.0 mA h/g after 1000 cycles at 1000 mA/g, which was attributed to the synergistic enhancement effects of the electrochemically active SnO_2 and MoO_{3-x} components. The amorphous MoO_{3-x} matrix which contains either bulk or surface defects allows for a more efficient lithium insertion and thus results in an enhanced capacity based on the conversion- and intercalation-type lithium storage mechanism (namely, formation of $\text{Mo}+\text{Li}_2\text{O}$ and LiMoO_{3-x}). Ultrafine SnO_2 nanocrystallites confined within the amorphous MoO_{3-x} matrix can efficiently buffer the volume changes of the Li-Sn alloying-dealloying upon cycling, maintaining the structural integrity of the electrodes and thus improving the long-term cycle stability. Moreover, the *in situ* generated ultrafine Sn nanodots confined within the amorphous $\text{Li}_2\text{O}-\text{MoO}_x$ matrix react with Li_2O under the catalytic effect of the metallic Mo, making the conversion reaction between SnO_2 and Li_xSn indirectly reversible, which brought enhanced lithium storage capacity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Survey XPS spectrum of the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite; SEM image of the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite with the corresponding EDS maps; Binding energy positions and the relative atomic content of Sn and Mo in the $\text{SnO}_2/\text{MoO}_{3-x}$ nanocomposite (PDF)

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REFERENCES

- [1] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature*, 414 (2001) 359-367.
- [2] C.K. Chan, H.L. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, High-performance lithium battery anodes using silicon nanowires, *Nat. Nanotechnol.*, 3 (2008) 31-35.
- [3] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, Tin-Based Amorphous Oxide: A High-Capacity Lithium-Ion-Storage Material, *Science*, 276 (1997) 1395-1397.
- [4] J.S. Chen, X.W. Lou, SnO₂-Based Nanomaterials: Synthesis and Application in Lithium-Ion Batteries, *Small*, 9 (2013) 1877-1893.
- [5] H. Wang, L. Xi, J. Tucek, C. Ma, G. Yang, M.K.H. Leung, R. Zboril, C. Niu, A.L. Rogach, Synthesis and Characterization of Tin Titanate Nanotubes: Precursors for Nanoparticulate Sn-Doped TiO₂ Anodes with Synergistically Improved Electrochemical Performance, *ChemElectroChem*, 1 (2014) 1563-1569.
- [6] H. Wang, A.L. Rogach, Hierarchical SnO₂ Nanostructures: Recent Advances in Design, Synthesis, and Applications, *Chem. Mater.*, 26 (2014) 123-133.
- [7] H. Wang, H. Huang, C. Niu, A.L. Rogach, Ternary Sn–Ti–O Based Nanostructures as Anodes for Lithium Ion Batteries, *Small*, 11 (2015) 1364-1383.
- [8] F. Wu, S. Xiong, Y. Qian, S.-H. Yu, Hydrothermal Synthesis of Unique Hollow Hexagonal Prismatic Pencils of Co₃V₂O₈ · nH₂O: A New Anode Material for Lithium-Ion Batteries, *Angewandte Chemie*, 127 (2015) 10937-10941.
- [9] X.Y. Xue, Z.H. Chen, L.L. Xing, S. Yuan, Y.J. Chen, SnO₂/α-MoO₃ core-shell nanobelts and their extraordinarily high reversible capacity as lithium-ion battery anodes, *Chem. Commun.*, 47 (2011) 5205-5207.
- [10] L.L. Si, Z.Q. Yuan, J.W. Liang, L. Hu, Y.C. Zhu, Y.T. Qian, Fabrication of one-dimensional SnO₂/MoO₃/C nanostructure assembled of stacking SnO₂ nanosheets from its heterostructure precursor and its application in lithium-ion batteries, *J Mater Chem A*, 2 (2014) 9784-9791.
- [11] W.Q. Zeng, F.P. Zheng, R.Z. Li, Y. Zhan, Y.Y. Li, J.P. Liu, Template synthesis of SnO₂/α-Fe₂O₃ nanotube array for 3D lithium ion battery anode with large areal capacity, *Nanoscale*, 4 (2012) 2760-2765.
- [12] M.V. Reddy, G.V. Subba Rao, B.V.R. Chowdari, Metal Oxides and Oxysalts as Anode Materials for Li Ion Batteries, *Chem. Rev.*, 113 (2013) 5364-5457.
- [13] X. Zhou, L. Yu, X.W. Lou, Formation of Uniform N-doped Carbon-Coated SnO₂ Submicroboxes with Enhanced Lithium Storage Properties, *Advanced Energy Materials*, 6 (2016) 1600451.
- [14] J.S. Chen, C.M. Li, W.W. Zhou, Q.Y. Yan, L.A. Archer, X.W. Lou, One-pot formation of SnO₂ hollow nanospheres and α-Fe₂O₃@SnO₂ nanorattles with large void space and their lithium storage properties, *Nanoscale*, 1 (2009) 280-285.
- [15] Z. Wang, D. Luan, F.Y. Boey, X.W. Lou, Fast formation of SnO₂ nanoboxes with enhanced lithium storage capability, *J. Am. Chem. Soc.*, 133 (2011) 4738-4741.
- [16] Y.H. Xu, Q. Liu, Y.J. Zhu, Y.H. Liu, A. Langrock, M.R. Zachariah, C.S. Wang, Uniform Nano-Sn/C Composite Anodes for Lithium Ion Batteries, *Nano Lett.*, 13 (2013) 470-474.
- [17] S. Ding, D. Luan, F.Y.C. Boey, J.S. Chen, X.W. Lou, SnO₂ nanosheets grown on

graphene sheets with enhanced lithium storage properties, *Chem. Commun.* , 47 (2011) 7155-7157.

[18] X. Wang, Z. Li, L. Yin, Nanocomposites of SnO₂@ordered mesoporous carbon (OMC) as anode materials for lithium-ion batteries with improved electrochemical performance, *Crystengcomm*, 15 (2013) 7589-7597.

[19] J. Ning, T. Jiang, K. Men, Q. Dai, D. Li, Y. Wei, B. Liu, G. Chen, B. Zou, G. Zou, Syntheses, Characterizations, and Applications in Lithium Ion Batteries of Hierarchical SnO Nanocrystals, *J. Phys. Chem. C* 113 (2009) 14140-14144.

[20] L. Zhang, G. Zhang, H.B. Wu, L. Yu, X.W. Lou, Hierarchical Tubular Structures Constructed by Carbon-Coated SnO₂ Nanoplates for Highly Reversible Lithium Storage, *Adv. Mater.* , 25 (2013) 2589-2593.

[21] C. Wang, Y. Zhou, M. Ge, X. Xu, Z. Zhang, J.Z. Jiang, Large-Scale Synthesis of SnO₂ Nanosheets with High Lithium Storage Capacity, *J. Am. Chem. Soc.* , 132 (2009) 46-47.

[22] F. Ma, A. Yuan, J. Xu, P. Hu, Porous α -MoO₃/MWCNT Nanocomposite Synthesized via a Surfactant-Assisted Solvothermal Route as a Lithium-Ion-Battery High-Capacity Anode Material with Excellent Rate Capability and Cyclability, *ACS Appl. Mat. Interfaces* 7(2015) 15531-15541.

[23] C. Wang, L.X. Wu, H. Wang, W.H. Zuo, Y.Y. Li, J.P. Liu, Fabrication and Shell Optimization of Synergistic TiO₂-MoO₃ Core-Shell Nanowire Array Anode for High Energy and Power Density Lithium-Ion Batteries, *Adv. Funct. Mater.* , 25 (2015) 3524-3533.

[24] L.A. Riley, S.-H. Lee, L. Gedvilas, A.C. Dillon, Optimization of MoO₃ nanoparticles as negative-electrode material in high-energy lithium ion batteries, *Journal of Power Sources*, 195 (2010) 588-592.

[25] T. Tsumura, M. Inagaki, Lithium insertion/extraction reaction on crystalline MoO₃, *Solid State Ionics*, 104 (1997) 183-189.

[26] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, *Nature*, 407 (2000) 496-499.

[27] H.-X. Zhang, C. Feng, Y.-C. Zhai, K.-L. Jiang, Q.-Q. Li, S.-S. Fan, Cross-Stacked Carbon Nanotube Sheets Uniformly Loaded with SnO₂ Nanoparticles: A Novel Binder-Free and High-Capacity Anode Material for Lithium-Ion Batteries, *Advanced Materials*, 21 (2009) 2299-2304.

[28] F. Han, W.-C. Li, M.-R. Li, A.-H. Lu, Fabrication of superior-performance SnO₂@C composites for lithium-ion anodes using tubular mesoporous carbon with thin carbon walls and high pore volume, *J Mater Chem*, 22 (2012) 9645-9651.

[29] H. Guo, L.X. Liu, T.T. Li, W.W. Chen, Y.P. Wang, W. Wang, Hierarchical synthesis of Mo-Sn oxide cage-bell hybrid structures with superior lithium storage, *Chem. Commun.* , 50 (2014) 673-675.

[30] J. Jang, S.M. Kim, Y. Kim, K.H. Park, J.H. Ku, J.H. Ryu, S.M. Oh, Electrode Performances of Amorphous Molybdenum Oxides of Different Molybdenum Valence for Lithium-ion Batteries, *Isr. J. Chem.* , 55 (2015) 604-610.

[31] H. Wang, S. Kalytchuk, H. Yang, L. He, C. Hu, W.Y. Teoh, A.L. Rogach, Hierarchical growth of SnO₂ nanostructured films on FTO substrates: structural defects induced by Sn(ii) self-doping and their effects on optical and photoelectrochemical properties, *Nanoscale*, 6 (2014) 6084-6091.

- [32] J. Jia, H. Wang, S. Ji, H. Yang, X. Li, R. Wang, SnO₂-embedded worm-like carbon nanofibers supported Pt nanoparticles for oxygen reduction reaction, *Electrochim. Acta* 141 (2014) 13-19.
- [33] A.M. Hashem, H. Groult, A. Mauger, K. Zaghib, C.M. Julien, Electrochemical properties of nanofibers alpha-MoO₃ as cathode materials for Li batteries, *J. Power Sources* 219 (2012) 126-132.
- [34] H. Wang, K. Dou, W.Y. Teoh, Y. Zhan, T.F. Hung, F. Zhang, J. Xu, R. Zhang, A.L. Rogach, Engineering of Facets, Band Structure, and Gas-Sensing Properties of Hierarchical Sn²⁺-Doped SnO₂ Nanostructures, *Adv. Funct. Mater.*, 23 (2013) 4847-4853.
- [35] B. Ahmed, M. Shahid, D.H. Nagaraju, D.H. Anjum, M.N. Hedhili, H.N. Alshareef, Surface Passivation of MoO₃ Nanorods by Atomic Layer Deposition toward High Rate Durable Li Ion Battery Anodes, *ACS Applied Materials & Interfaces*, 7 (2015) 13154-13163.
- [36] Y. Li, X. Lu, H. Wang, C. Xie, G. Yang, C. Niu, Growth of Ultrafine SnO₂ Nanoparticles within Multiwall Carbon Nanotube Networks: Non-Solution Synthesis and Excellent Electrochemical Properties as Anodes for Lithium Ion Batteries, *Electrochim. Acta* 178 (2015) 778-785.
- [37] H. Wang, M. Wang, B. Li, X. Yang, K. Safarova, R. Zboril, A.L. Rogach, M.K.H. Leung, Hydrothermal synthesis and electrochemical properties of tin titanate nanowires coupled with SnO₂ nanoparticles for Li-ion batteries, *Crystengcomm*, 16 (2014) 7529-7535.
- [38] H. Wang, X. Lu, L. Li, B. Li, D. Cao, Q. Wu, Z. Li, G. Yang, B. Guo, C. Niu, Synthesis of SnO₂ versus Sn crystals within N-doped porous carbon nanofibers via electrospinning towards high-performance lithium ion batteries, *Nanoscale*, 8 (2016) 7595-7603.
- [39] L. Liu, M. An, P. Yang, J. Zhang, Superior cycle performance and high reversible capacity of SnO(2)/graphene composite as an anode material for lithium-ion batteries, *Sci Rep-Uk*, 5 (2015) 9055.
- [40] X. Zhu, Y. Zhu, S. Murali, M.D. Stoller, R.S. Ruoff, Reduced graphene oxide/tin oxide composite as an enhanced anode material for lithium ion batteries prepared by homogenous coprecipitation, *Journal of Power Sources*, 196 (2011) 6473-6477.
- [41] X. Wang, X. Zhou, K. Yao, J. Zhang, Z. Liu, A SnO₂/graphene composite as a high stability electrode for lithium ion batteries, *Carbon*, 49 (2011) 133-139.
- [42] A.M. Tripathi, S. Mitra, Ecofriendly Approach to Making Graphene-Tin/Tin Oxide Nanocomposite Electrodes for Energy Storage, *ChemElectroChem*, 1 (2014) 1327-1337.
- [43] J. Zhou, N. Lin, L. Wang, K. Zhang, Y. Zhu, Y. Qian, Synthesis of hexagonal MoO₃ nanorods and a study of their electrochemical performance as anode materials for lithium-ion batteries, *Journal of Materials Chemistry A*, 3 (2015) 7463-7468.
- [44] M. Mohamedi, S.-J. Lee, D. Takahashi, M. Nishizawa, T. Itoh, I. Uchida, Amorphous tin oxide films: preparation and characterization as an anode active material for lithium ion batteries, *Electrochimica Acta*, 46 (2001) 1161-1168.
- [45] Z. Wang, D. Luan, S. Madhavi, Y. Hu, X.W. Lou, Assembling carbon-coated [small alpha]-Fe₂O₃ hollow nanohorns on the CNT backbone for superior lithium storage capability, *Energy Environ Sci*, 5 (2012) 5252-5256.
- [46] S. Laruelle, S. Grugeon, P. Poizot, M. Dollé, L. Dupont, J.-M. Tarascon, On the Origin of the Extra Electrochemical Capacity Displayed by MO/Li Cells at Low Potential, *Journal of The Electrochemical Society*, 149 (2002) A627-A634.

- [47] Z. Wang, J.S. Chen, T. Zhu, S. Madhavi, X.W. Lou, One-pot synthesis of uniform carbon-coated MoO₂ nanospheres for high-rate reversible lithium storage, *Chemical Communications*, 46 (2010) 6906-6908.
- [48] Y. Deng, C. Fang, G. Chen, The developments of SnO₂/graphene nanocomposites as anode materials for high performance lithium ion batteries: A review, *Journal of Power Sources*, 304 (2016) 81-101.
- [49] J. Światowska-Mrowiecka, S. de Diesbach, V. Maurice, S. Zanna, L. Klein, E. Briand, I. Vickridge, P. Marcus, Li-Ion Intercalation in Thermal Oxide Thin Films of MoO₃ as Studied by XPS, RBS, and NRA, *The Journal of Physical Chemistry C*, 112 (2008) 11050-11058.