Facile One-Pot Hydrothermal Synthesis of Hierarchical MoS$_2$/α-MnS Nanocomposites with Good Cycling Performance as Anode Materials for Lithium-Ion Batteries

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Abstract: The design of nanoscale composites with a hierarchical structure can improve the poor cycling performances of transition metal sulfides such as anode materials. The hierarchical MoS$_2$/α-MnS nanocomposites were synthesized by a facile one-pot hydrothermal method in this study, aiming to improve the cycling performance. As an anode material, hierarchical MoS$_2$/α-MnS nanocomposites deliver a high reversible capacity, of 1498 mAh g$^{-1}$ at a current density of 50 mA g$^{-1}$; a capacity of ~800 mAh g$^{-1}$ is maintained over 100 cycles at 300 mA g$^{-1}$, and a capacity of 907 mAh g$^{-1}$ is obtained at 1200 mA g$^{-1}$. Moreover, these capacities increase with the number of cycles, which is mainly owed to the occurring metallic nanoparticles that catalyze the developing polymeric film and enhance the conductivity of the active materials during the electrochemical reactions. The good cycling performances are attributed to the synergistic effects between MoS$_2$ and α-MnS.

Keywords: lithium-ion batteries; α-MnS; molybdenum disulfide; capacity increase

1. Introduction

Electric vehicles (EVs) have become increasingly popular due to their environmental advantages. However, the relatively low energy density of the lithium-ion batteries (LIBs) used as power sources for the EVs in today’s market leads to range anxiety, to some extent, which results in many people having difficulty adopting EVs [1–3]. Developing high-performance LIBs with high energy density, low cost, long cycle life, and environmental friendliness is urgent. Transition metal sulfides are promising electrode materials because of their high theoretical lithium storage capacity, low cost, and nontoxicity to the environment [4–7]. The reaction mechanism between transition metal sulfides and lithium generally consists of two processes: insertion followed by conversion reaction. The insertion mechanism is the reaction of nLi+$\alpha$MnS $\leftrightarrow$ Li$_n$M$_x$S$_y$; the conversion mechanism can be described as Li$_n$M$_x$S$_y$ $\leftrightarrow$ Li$_n$M$_x$S$_{y'}$; the conversion mechanism can be described as Li$_n$M$_x$S$_y$ $\leftrightarrow$ Li$_n$M$_x$S$_{y'}$; the conversion mechanism can be described as Li$_n$M$_x$S$_y$ $\leftrightarrow$ Li$_n$M$_x$S$_{y'}$ [8–21]. The transition metal sulfides used as the anode materials suffer from the poor cycling performances due to the high solubility of the intermediates (lithium polysulfides) and the huge volume change during the charging/discharging process. The strategies, compositing and nanometerization, are widely applied to address these issues. The composites, which are comprised of conductive carbon, polymer, and transition metal sulfides, have been synthesized and deliver good electrochemical performances, especially in the first tens of charge/discharge cycles [14,22–31]. However, the improved electrochemical performances of these composites fade away during cycling because the coatings of carbon or polymer fall off quickly under the erosion of the electrolyte due to the weak coupling between the metal sulfides and carbonaceous matrix.

Nanomaterials possessing unique advantages have been applied widely in sensors, capacitors, solar cells, and especially LIBs. MnS can theoretically deliver a high lithium storage capacity of 616 mAh g$^{-1}$, as an anode material, while exhibiting a poor cycling performance due to its low electrical conductivity [32]. Some MnS-based composite materials have...
been synthesized, aiming to improve conductivity, which exhibited better electrochemical performance than pristine MnS, while their long-term cycling performances were still poor [33–36]. Moreover, the multistep and complicated procedures of synthesizing these composites limit their large-scale production. Developing a simple, scalable method to prepare transition metal sulfide based nanocomposites is still beneficial.

In this study, the hierarchical MoS$_2$/α-MnS nanocomposites have been synthesized through a one-pot hydrothermal method. These hierarchical MoS$_2$/α-MnS nanocomposites, when being tested as the anode material in LIBs, exhibit a reversible capacity of 1498 mAh g$^{-1}$ at 50 mA g$^{-1}$ and deliver a rate capability of 907 mAh g$^{-1}$ at 1200 mA g$^{-1}$. The high capacity, 800 mAh g$^{-1}$, is maintained for over 80 cycles at 300 mA g$^{-1}$. Moreover, the capacity increase occurs during discharging/charging cycles, which is owed to the metallic nanoparticles that can catalyze the developing polymeric film and enhance conductivity. The excellent electrochemical performances have been discussed in detail and are attributed to the synergistic effect.

2. Materials and Methods

2.1. Materials

All chemicals were used as received without any purification and were analytical grade. Na$_2$MoO$_4$·H$_2$O, ethanol, CH$_3$CSNH$_2$, KMnO$_4$, H$_2$C$_2$O$_4$, and NaBH$_4$ were supplied by China National Pharmaceutical Group Corporation (SINOPHARM).

2.2. Preparation of MoS$_2$/α-MnS

Hierarchical MoS$_2$/α-MnS nanocomposites were synthesized via a modified hydrothermal route [16]. In a typical synthesis, first 4.7 mmol Na$_2$MoO$_4$·H$_2$O, 16.7 mmol CH$_3$CSNH$_2$, and 4.6 mmol H$_2$C$_2$O$_4$ were added to 100 mL of DI water; then, a homogeneous, purple solution formed after 2.97 mmol KMnO$_4$ were added under magnetic stirring. The purple solution was transferred to two 50 mL Teflon-lined stainless-steel autoclaves, which were heated at 200 °C for 24 h. Finally, the resultants were naturally cooled with oven, centrifuged, and washed with DI water/ethanol several times. The products were obtained after the washed resultants dried at 60 °C in vacuum for 6 h.

2.3. Electrochemical Measurements

For preparing the working electrodes, active material, conductive graphite, and carboxymethyl celluloses (CMC) were mixed in a weight ratio of 70:20:10; after being ground for 30 min, the mixture was added to deionized water to make homogeneous slurries under stirring; the slurries were cast on copper foils. The coated copper foils were dried under vacuum at 105 °C for 12 h and then transferred to an argon-filled glove box. In this box, CR2016-type coin cells were fabricated, with polyethylene film as separator, pure lithium metal foils as counter electrode, and 1 M LiPF$_6$ dissolved in a mixed solvent containing ethylene carbonate and dimethyl carbonate (1:1 vol%) as electrolyte. Galvanostatic discharge/charge measurements were performed on a Neware battery tester within a voltage window of 3–0.01 V versus Li$^+$/Li. Cyclic voltammetry (CV) test was investigated on an electrochemical workstation (CHI600E, China) in the voltage window of 0.01–2.8 V at a scan rate of 0.1 mV S$^{-1}$.

2.4. Materials Characterization

The microstructure and morphology of hierarchical MoS$_2$/α-MnS nanocomposites were characterized by scanning electron microscopy (SEM; Hitachi S4800) equipped with an energy dispersive X-ray spectrometer (EDX) and transmission electron microscopy (TEM; JEOL JEM-2010). The crystalline structure was obtained by X-ray powder diffraction (XRD; D/max 2550V, Cu K$_\alpha$ radiation).
3. Results and Discussion

Figure 1 shows the XRD patterns of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites. The diffraction peaks located at 14.5°, 32.6°, 39.5°, and 58.2° correspond to the (002), (100), (103), and (110) crystal planes of 2H-MoS$_2$ (JCPDS No. 37-1492) [14–16]; The peak at 14.5° corresponds to the (002) plane, indicating 2H-MoS$_2$ has a layered structure [18]. The diffraction peaks at 29.6°, 34.6°, 49.5°, 58.8°, and 61.6° can be assigned to the (111), (200), (220), (311), and (222) crystal planes of $\alpha$-MnS (JCPDS No. 06-0518), respectively [22,33–36]. The intensive peaks indicate the good crystal structure of $\alpha$-MnS.

Figure 1. XRD of hierarchical MoS$_2$/$\alpha$-MnS nanocomposites.

Figure 2 presents the morphology and microstructure of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites. The SEM image (Figure 2a) demonstrates that MoS$_2$/$\alpha$-MnS has a rose-like hierarchical micromorphology. The TEM images in Figure 2b,c, reveal the microstructure of MoS$_2$/$\alpha$-MnS, showing MoS$_2$ nanosheets wrapped by $\alpha$-MnS nanoparticles. The high-resolution TEM image (HRTEM) further provides information about the microstructure (Figure 2d). An interlayer distance of 0.61 nm, corresponding to the (002) crystal plane, indicates the multi-layer nanostructure of MoS$_2$ [37]; a distance of 0.26 nm corresponds to the (200) crystal plane of $\alpha$-MnS [22,33]. The bright concentric rings and broad diffused halos (shown in the inset of Figure 2d) demonstrate both MoS$_2$ and $\alpha$-MnS polycrystalline nanostructures. The images of the elemental mapping by energy dispersive spectroscopy (EDS), as shown in Figure 2e, indicate that the elements of Mo, S, and Mn are uniformly distributed. The EDS spectrum of MoS$_2$/$\alpha$-MnS is depicted in Figure 2f, which confirms that the sample contains elements of Mn, S, and Mo as well as Si from the substrate.
Figure 2. (a) SEM; (b) and (c) TEM at different magnifications; (d) HRTEM; (e) EDS mapping for elements of Mn, S, and Mo; (f) EDS spectrum of hierarchical MoS$_2$/$\alpha$-MnS nanocomposites.

The electrochemical performances of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites were utilized as the anode materials (Figure 3). The discharging/charging tests performed at a current density of 200 mA g$^{-1}$ (Figure 3a). Well-defined plateaus, located at about 2.1, 1.6, and 0.5 V, are observed; the 1st, 2nd, 10th, 50th, 100th, and 150th discharge/charge cycles deliver discharge/charge capacities of 743/580, 587/567, 616/607, 710/700, 889/869, and 959/939 mAh g$^{-1}$, respectively, and the coulombic efficiencies are 78.1%, 96.6%, 98.5%, 98.6%, 97.8%, and 97.9%, respectively. Note that the capacity of the 150th discharge cycle is nearly 200 mAh g$^{-1}$ more than that of the 1st discharge cycle, and the capacity keeps rising from the 2nd discharge/charge cycle on until the 150th cycle.
resulting in the reduction of Mn2+ to Mn [19,22]; and the peak around 0.16 V corresponds to the developing of a polymeric film [38–40]. During the anodic process, three oxidation peaks at 1.3, 1.9, and 2.3 V are observed. The peak at 1.3 V corresponds to the Li+ ions extracted from Li\textsubscript{x}MoS\textsubscript{2}; the peak at 1.9 V indicates that Li\textsubscript{2}S reacted with Mn; the peak at 2.3 V denotes that Li\textsubscript{2}S was oxidized [14–18,37]. Based on the above analysis, the metallic nanoparticles of Mo and Mn that occurred during the charging/discharging process improve the conductivity, which can enhance the high-rate ability of active materials [14,17,19,22]. Moreover, the polymeric film may facilitate hindrance of the dissolution of the polysulfides from the electrode [17,40]. Therefore, for the half cell made of MoS\textsubscript{2}/\alpha-MnS and Li foil, the possible electrochemical reactions during the discharging/charging process can be described as follows [14–17,21,33,36,41]:

\begin{align*}
\text{MnS} + x\text{Li}^+ + xe^- & \leftrightarrow LixMnS \quad (1) \\
\text{Li}_2- x \text{MnS} + 2\text{Li}^+ + 2e^- & \rightarrow \text{Mn} + \text{Li}_2\text{S} \quad (2) \\
\text{MoS}_2 + x\text{Li}^+ + xe^- & \leftrightarrow \text{LixMoS}_2 \quad (3) \\
\text{LixMoS}_2 + (4-x)(\text{Li}^+ + e^-) & \rightarrow \text{Mo} + 2\text{Li}_2\text{S} \quad (4) \\
\text{S} + 2(\text{Li}^+ + e^-) & \leftrightarrow \text{Li}_2\text{S} \quad (5)
\end{align*}

Figure 3. The galvanostatic measurements tested in the voltage range of 0.01–3.0 V for hierarchical MoS\textsubscript{2}/\alpha-MnS nanocomposites. (a) Discharge–charge profiles at 200 mA g\textsuperscript{-1}. (b) CV curves tested in the voltage window of 0.01–2.8 V (versus Li\textsuperscript{+}/Li) at a scan rate of 0.1 mV s\textsuperscript{-1}. (c) Cycling–performance profiles at 300 mA g\textsuperscript{-1}. (d) Rate–capability profiles at different rates. (e,f) SEM image electrode after 1 cycle and 150 cycles, respectively.

Figure 3b exhibits the cyclic voltammetry (CV) curves of the hierarchical MoS\textsubscript{2}/\alpha-MnS nanocomposites, further revealing electrochemical reactions during the lithiation/delithiation process. Reduction peaks appear at 2.1, 1.2, 0.6, 0.45, and 0.16 V in the first cycle during the cathodic process. The peak around 2.1 V corresponds to the occurrence of lithium polysulfides [15–17,21]; the peak around 1.2 V is assigned to the formation of Li\textsubscript{i}MoS\textsubscript{2} through Li\textsuperscript{+} ions insertion into MoS\textsubscript{2}; the peak around 0.6 V suggests a part of Li\textsubscript{i}MoS\textsubscript{2} further converts into Li\textsubscript{2}S and metallic Mo nanoparticles [14–18,37]; the peak around 0.45 V can be associated with the further reduction of Li\textsubscript{i}MnS, with Li\textsuperscript{+} ions resulting in the reduction of Mn\textsuperscript{2+} to Mn [19,22]; and the peak around 0.16 V corresponds to the developing of a polymeric film [38–40]. During the anodic process, three oxidation peaks at 1.3, 1.9, and 2.3 V are observed. The peak at 1.3 V corresponds to the Li\textsuperscript{+} ions extracted from Li\textsubscript{i}MoS\textsubscript{2}; the peak at 1.9 V indicates that Li\textsubscript{2}S reacted with Mn; the peak at 2.3 V denotes that Li\textsubscript{2}S was oxidized [14–18,37]. Based on the above analysis, the metallic nanoparticles of Mo and Mn that occurred during the charging/discharging process improve the conductivity, which can enhance the high-rate ability of active materials [14,17,19,22]. Moreover, the
polymeric film may facilitate hindrance of the dissolution of the polysulfides from the electrode [17,40]. Therefore, for the half cell made of MoS$_2$/$\alpha$-MnS and Li foil, the possible electrochemical reactions during the discharging/charging process can be described as follows [14–17,21,33,36,41]:

$$\text{MnS} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{MnS}$$ (1)

$$\text{Li}_2\text{MnS} + 2\text{Li}^+ + 2e^- \rightarrow \text{Mn} + \text{Li}_2\text{S}$$ (2)

$$\text{MoS}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{MoS}_2$$ (3)

$$\text{Li}_x\text{MoS}_2 + (4 - x)(\text{Li}^+ + e^-) \rightarrow \text{Mo} + 2\text{Li}_2\text{S}$$ (4)

$$\text{S} + 2(\text{Li}^+ + e^-) \leftrightarrow 2\text{Li}_2\text{S}$$ (5)

Figure 3c depicts the cyclic performance of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites tested within 0.01–3 V at 300 mA g$^{-1}$. As shown in Figure 3c, the capacities evidently increase from the 2nd cycle to the 100th cycle, with a capacity increase of 0.32% per cycle, a slight increase from the 101st cycle to the 160th cycle, and a slow decrease from the 170th cycle onward. The capacity increasing with cycles has been observed in other cycling performance tests (Figure S1). This capacity-increase behavior during cycling has been largely attributed to the conductivity being enhanced by the metallic nanoparticles of Mo [15]. The coulombic efficiency in the initial cycle is 79.4%, which then arrives to ~97%, indicating high structural stabilization. Figure 3d shows that the rate capability of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites has been evaluated at different current densities within 0.01–3.0 V. The average discharge capacities are around 942, 957, 963, 969, 977, 998, and 907 mAh g$^{-1}$ at current densities (for 10 cycles each) of 100, 200, 300, 400, 500, 800, and 1200 mA g$^{-1}$, respectively. When the current density goes back stepwise to 250 and 50 mA g$^{-1}$, the average discharge capacity arrives to 1136 and 1498 mAh g$^{-1}$, respectively. The capacity increase also occurs with a stepwise increment of the current density (except for 1200 mA g$^{-1}$) during rate-capability testing. Some metal oxide based or transition metal sulfide based composites also exhibit similar behavior, owing to interfacial Li storage, pseudo-capacitive behavior, or the electrochemical milling effect [19,22,40,42–44]. Another view argues that the metallic nanoparticles occurring in the reactions should account for this capacity increase [38,45]. According to the analysis above, we presume that the metallic Mn and Mo nanoparticles account for the capacity increase in the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites. Figure 3e,f reveal the morphologies of MoS$_2$/$\alpha$-MnS nanocomposites after being cycled for 1 cycle and 150 cycles, respectively. As shown in these SEM images, the structure of the electrode maintains its integrity on the whole, even after experiencing over 150 cycles, despite cracking, which is in accordance with its good cycling performances.

To verify the presumption above, the electrochemical performances of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites have been evaluated by preventing the Mn and Mo nanoparticles from influencing the electrochemical reactions. According to Figure 3b, for the MoS$_2$/$\alpha$-MnS nanocomposites, the occurrence of the metallic Mn and Mo nanoparticles is inhibited when the testing voltage window is 0.5–2.5 V [40,43]. Figure 4a–c present the galvanostatic electrochemical performances of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites tested at 200 mA g$^{-1}$ within 0.5–2.5 V. Figure 4a displays the specific capacity versus the voltage curves, showing that the specific capacity fades with the number of cycles in the absence of metallic Mn and Mo nanoparticles. Figure 4b presents the differential capacity curves corresponding to the curves of Figure 4a, providing information about the electrochemical reactions within 0.5–2.5 V. Obviously, the curve of Figure 4b resembles that of Figure 3b within 0.5–2.5 V, indicating that they present the same electrochemical behaviors within 0.5–2.5 V. Figure 4c shows the cyclic performance of the hierarchical MoS$_2$/$\alpha$-MnS nanocomposites tested at 200 mA g$^{-1}$ within 0.5–2.5 V, indicating that the capacity fades with the number of cycles. Figure 4d shows the discharge capacity versus the voltage curves of Figure 3a within 0.5–2.5 V, which indicates the capacity increases with...
the cycles in the presence of metallic Mn and Mo nanoparticles (after being discharged to 0.01 V in the first discharging process, Mo nanoparticles occur in the active materials). Therefore, the capacity increase disappears within 0.5–2.5 V, indicating that the metallic Mn and Mo nanoparticles mainly account for the capacity increase during cycling.

![Figure 4](image-url)

**Figure 4.** The galvanostatic measurements tested in the voltage range of 0.5–2.5 V for hierarchical MoS$_2$/α–MnS nanocomposites. (a) Discharge–charge profiles at 200 mA g$^{-1}$. (b) The corresponding derivative relation of the galvanostatic voltage versus the capacity. (c) Cycling performance profiles at 200 mA g$^{-1}$. (d) Discharge capacity versus voltage curves of Figure 3a within 0.5–2.5 V.

The superior electrochemical performances of the hierarchical MoS$_2$/α–MnS nanocomposites is owed to their synergistic effects (Scheme 1). First, the metallic nanoparticles occurring in the electrochemical reactions not only increase the number of paths for electrons and Li$^+$ ions transport but also catalyze the developing polymeric film that lessens the dissolution of the lithium polysulfides, accommodates the massive Li$^+$ ions, and hinders the agglomeration of the metallic nanoparticles [17,19,22,37,40]. Second, the hybrid nanostructure can shorten the diffusion length of the Li$^+$ ions and active materials have been flooded largely by the electrolyte [6,7,9]. Third, the rose-like morphology possesses plenty of void space, which is beneficial in accommodating the Li$^+$ ions [16,46]. Last, the polymeric film and the SEI along with the Mn and Mo metallic nanoparticles can prevent lithium polysulfides from coming out of the electrode, which can enhance the cyclic performance.
Scheme 1. The lithiation/delithiation of MoS$_2$/α-MnS nanocomposites.

4. Conclusions

In summary, a simple, scalable one-pot hydrothermal method has been developed for preparing hierarchical MoS$_2$/α-MnS nanocomposites. As an anode material in LIBs, the hierarchical MoS$_2$/α-MnS nanocomposites deliver a high reversible capacity, a superior cyclic performance, and a high-rate capability. The high reversible capacity is $\sim$1500 mAh g$^{-1}$ at a current density of 50 mA g$^{-1}$; the reversible capacity of $\sim$800 mAh g$^{-1}$ is maintained for over 100 cycles at 300 mA g$^{-1}$. The superior performances are mainly ascribed to the synergistic effect between MoS$_2$ and α-MnS. Moreover, metallic nanoparticles occur in the electrochemical reactions and lead to the capacity increase during the cycling process. All in all, although the electrochemical mechanism of the hierarchical MoS$_2$/α-MnS nanocomposites needs to be further developed theoretically and experimentally, compared with other widely used strategies, this study proposes a novelty method to improve the electrochemical performances of the anodes in LIBs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12121763/s1, Figure S1: Cycling performances of different MoS$_2$/α-MnS nanocomposites tested at different density current: S1 1500, S2 1000, S3 800, S4 600, S5 200 mA g$^{-1}$.


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References


5. Yan, J.M.; Huang, H.Z.; Zhang, J.; Liu, Z.J.; Yang, Y. A study of novel anode material CoS$_2$ for lithium ion battery. J. Power Sources 2005, 146, 264–269. [CrossRef]


24. Feng, Y.; Zhang, Y.L.; Wei, Y.Z.; Song, X.Y.; Fub, Y.B.; Battaglia, V.S. A ZnS nanocrystal/reduced graphene oxide composite anode with enhanced electrochemical performances for lithium-ion batteries. J. Power Sources 2015, 283, 352–359. [CrossRef]

25. Ramon, J.; Yang, J.L.; Yu, L.; Zhao, Y.; Pan, F. Core-shell nano-FeS$_2$@N-doped graphene as an advanced electrode material for rechargeable Li-ion batteries. Chem. Commun. 2015, 52, 986–989. [CrossRef]

37. Chang, K.; Chen, W. In situ synthesis of MoS$_2$/graphene nanosheet composites with extraordinarily high electrochemical performance for lithium-ion batteries. Chem. Commun. 2011, 47, 4252–4254. [CrossRef]
39. Kilibarda, G.; Szabó, D.V.; Schlabach, S.; Winkler, V.; Bruns, M.; Hanemann, T. Investigation of the degradation of SnO$_2$ electrodes for use in Li-ion cells. J. Power Sources 2013, 233, 139–147. [CrossRef]
41. Sen, U.K.; Mitra, S. High-rate and high-energy-density lithium-ion battery anode containing 2D MoS$_2$ nanowall and cellulose binder. ACS Appl. Mater. Interfaces 2013, 5, 1240–1247. [CrossRef]
45. Hassan, M.F.; Guo, Z.P.; Chen, Z.X.; Liu, H.K. α-Fe$_2$O$_3$ as an anode material with capacity rise and high rate capability for lithium-ion batteries. Mater. Res. Bull. 2011, 46, 858–864. [CrossRef]
46. Xing, L.L.; He, B.; Nie, Y.X.; Deng, P.; Cui, C.X.; Xue, X.Y. SnO$_2$–MnO$_2$–SnO$_2$ sandwich-structured nanotubes as high-performance anodes of lithium ion battery. Mater. Lett. 2013, 105, 169–172. [CrossRef]