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Zinc tetrathiomolybdate as novel anodes for rechargeable lithium batteries

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Abstract An ever first attempt has been made to investigate the anode performance characteristics of zinc tetrathiomolybdate. The poor crystallized zinc tetrathiomolybdate was prepared by precipitation method from Na_2MoO_4 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and CH_3CSNH_2 as starting materials. Galvanostatic data in the voltage range of 0.01–2.0 V up to 20 cycles at a rate of 100 mA g^{-1} revealed that the material gave high reversible capacities and good performance.

Keywords ZnMoS_4 · Precipitation · Anode materials · Rechargeable lithium-ion batteries

Introduction

Lithium-ion batteries have attracted special attention in recent years because they have a high-energy density and are environmentally friendly. Generally, commercially available lithium-ion batteries consist of two Li-intercalation materials as both cathode and anode materials. Commonly, lithiated transitional metal oxides are used as the cathode, and graphite is used as the anode. However, a conventional anode material, graphite, which can intercalate one Li per six C, has a limited maximum capacity of 372 mA h g^{-1} [1]. It is not always sufficient to meet all demands. Therefore, much research has been aimed at finding new materials with high capacities and excellent cycle performance. Recently, molybdenum-based compounds, such as MoS_2 [2], MnMoO_4 [3], MoO_2 [4], $\text{Mo}_y\text{Sn}_x\text{O}_2$ [5], etc., received attention as possible anode

electrode material to replace the graphite presently being used in the Li-ion batteries.

Zinc tetrathiomolybdate once identified as a potential high-temperature lubricant [6]. The present investigation was aimed at the exploration and exploitation of zinc tetrathiomolybdate as anode for rechargeable lithium batteries, which is an ever first attempt of this kind. Towards this intriguing interest, the compound zinc tetrathiomolybdate was synthesized via precipitation method and subjected further to physical as well as electrochemical anode performance characterization studies.

Experimental

Synthesis of the material

ZnMoS_4 was prepared by precipitation. The preparation procedure we developed is as follows. The starting materials were normally stoichiometric mixtures of Na_2MoO_4 (AR) and CH_3CSNH_2 (AR). The mixtures were put into a three-necked flask, and then some water was added into it. The flasks were heated by water bath at a constant temperature of 75°C while being stirred. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (AR) was added after the solution turned red, and then the precipitate appeared. After having been cooled naturally, the liquid in the three-necked flask was removed by decanting, and the precipitate was washed with water until SO_4^{2-} did not exist, followed by washing with anhydrous ethanol and acetone, respectively. ZnMoS_4 was obtained after the final dark brown powder had been vacuum-dried in an oven at 60°C for 3 h.

Structure determination

A Shimadzu XRD 6000 diffractometer with Cu-K α radiation was used to define the structure of ZnMoS_4 . Mo X-ray photoelectron spectrometer (XPS) measurements for the synthesized ZnMoS_4 were carried out by an X SAM800 XPS. The Mg K α achromatic X-ray source

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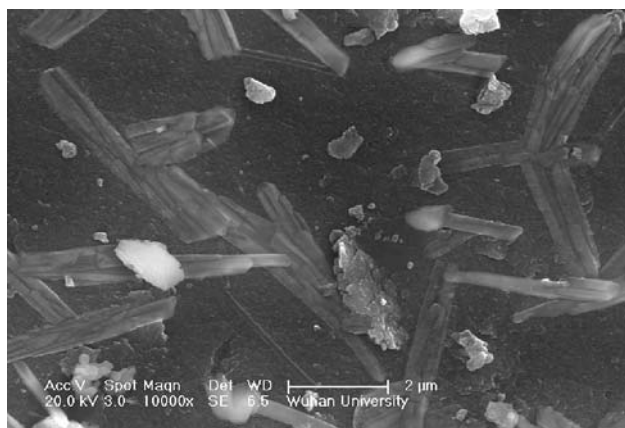


Fig. 1 Scanning electron micrographs for the sample ZnMoS₄

(1,235.6 eV) was operated at 192 W (12 kV, 16 mA), the pressure inside the analysis chamber being kept below 2×10^{-9} Torr during the measurements. The sample holder was oriented at 90° with respect to the analyzer. The analyzer is with medium resolution scans. Linear lines

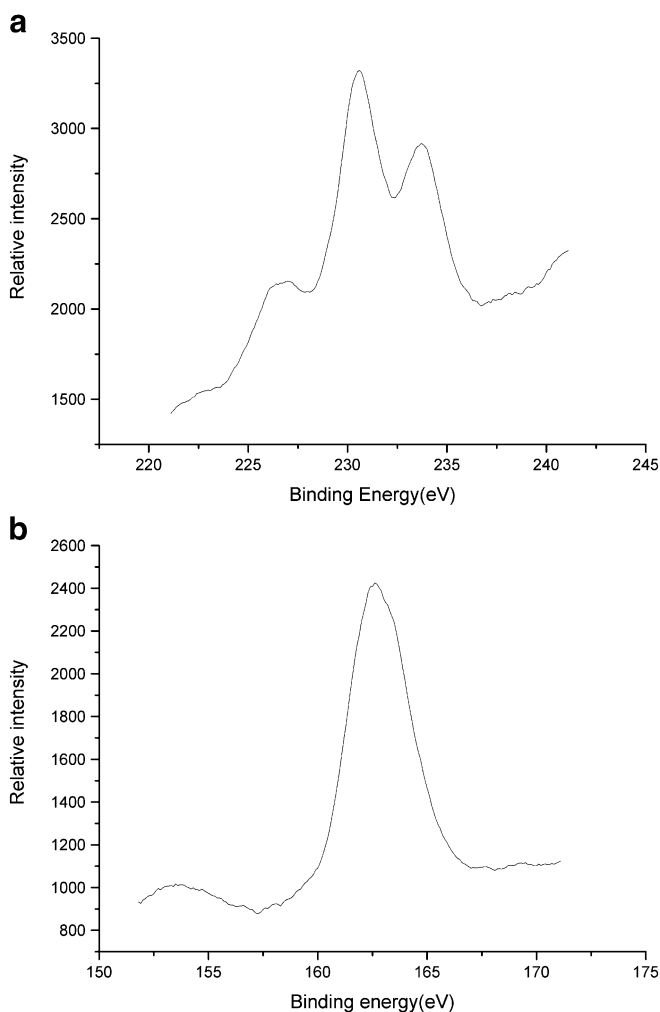


Fig. 2 Mo3d, S2p XPS spectra of ZnMoS₄

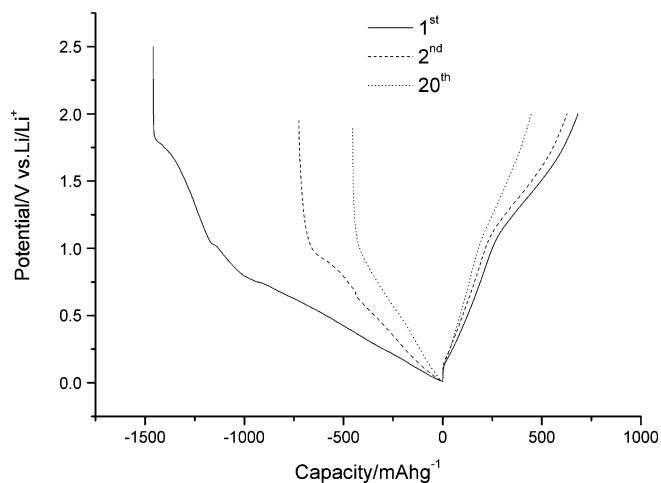


Fig. 3 The discharge-charge potential profiles and capacity of ZnMoS₄

were used for the background subtraction of the XPS spectra. The XPS binding energies were referenced to the graphite C_{1s} peak at 284.8 eV. Moreover, a Sirion FEG SEM was employed for morphological observation and the size of the active materials.

Electrochemical testing

The samples for the electrochemical measurement were prepared by mixing active material, acetylene black as conductive agent, and polytetrafluoroethylene (PTFE) binder (80, 15, and 5 wt%, respectively) in an agate mortar and were made in the form of film (0.2–0.3 mm thickness). The film was then cut into a disk with area of appropriately 1 cm². Cells were fabricated by coupling this disk with fresh lithium foil with the same area as counter-electrode using micropylene film (Celgard 2400) as separator. One molar of LiPF₆ dissolved in ethylene carbonate (EC)/diethylene carbonate (DEC) with a volume ratio of 1:1 was used as the electrolyte. All the cell assembling (Li|1 M LiPF₆ in EC/DEC|ZnMoS₄) was performed in a glove box filled with argon gas. The electrochemical measurement was carried out galvanostatically at a constant current of 100 mA g⁻¹. The cutoff voltage was set at 0.01 and 2.0 V vs Li/Li⁺.

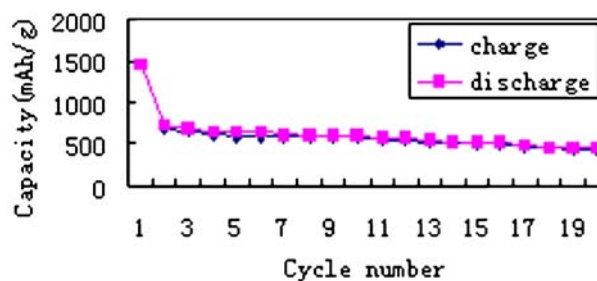


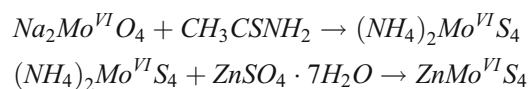
Fig. 4 The discharge-charge capacity variation ZnMoS₄ with cycle number

Results and discussion

The X-ray diffraction (XRD) pattern of the as-prepared ZnMoS₄ sample revealed that the powder so prepared showed very broad diffraction lines, indicating poor crystallinity. There are three main diffraction lines at 28.67°, 47.70°, 56.38°, with *d* values of 3.111, 1.905, 1.631, respectively. The SEM photographs of ZnMoS₄ with different magnifications are shown in Fig. 1. In sample ZnMoS₄, most of the particles have a long-stick shape with average of about 5 μm, with average width of 300 nm. Some irregular particles can also be seen from the SEM of the material.

Figure 2 shows the Mo 3d_{5/2}, S 2p XPS spectra of ZnMoS₄. The binding energy of Mo 3d_{5/2} for ZnMoS₄ is 230.5 eV; we think that molybdenum oxidation state in ZnMoS₄ is +6. For the existence of S²⁻, the S 2p binding energy of ZnMoS₄ is 162.6 eV, which can be clearly seen in Fig. 2. The S (2p) and Mo (3d) peak intensities of ZnMoS₄ yield an S/Mo atom ratio of 3.87:1.00.

From the results above, the presumed reaction mechanism of forming ZnMoS₄ is as follows:



First, Na₂MoO₄ reacted with CH₃CSNH₂ to form (NH₄)₂MoS₄ [7], and then ZnMoS₄ was obtained when ZnSO₄·7H₂O was added.

To obtain the discharge–charge profile (Li|1 M LiPF₆ in EC/DEC|ZnMoS₄) cell, the cell was subjected to 20 cycles in a constant mode. Figure 3 shows the discharge–charge profiles of the cell for the 1st, 2nd, and 20th cycles. The profiles are similar, probably because they correspond with the same de-lithiation mechanism. There is large irreversible capacity loss during the first cycle. The initial dis-

charge capacity is 1,460 mA h g⁻¹, while the subsequent charge capacity is 682 mA h g⁻¹. The reversible capacity of 682 mA h g⁻¹ is nearly two times as large as that of graphite (350 mA h g⁻¹) which is used as anode material for commercial Li-ion secondary battery. The discharge and charge capacities variation of ZnMoS₄ vs cycle number is shown in Fig. 4. It demonstrates good cycle performance, and even after 20 cycles, the charge capacity still remains 446 mA h g⁻¹. The irreversible charge capacity loss of the formal 20 cycles is only 2.21%. More elaborated work is needed to understand the underlying reaction mechanisms so as to make it a commercially available material.

Conclusions

With a view of our findings, zinc tetrathiomolybdate as anode material for lithium-ion batteries, synthesized by precipitation method, shows an unassumingly high specific capacity value and good cycle performance. The zinc tetrathiomolybdate anodes qualify themselves as potential lithium battery anode candidate to be considered for practical lithium battery application.

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