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A Novel synthesis of MgS and its application as electrode material for lithium-ion batteries



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ABSTRACT

MgS was firstly investigated as an anode material for lithium-ion batteries (LIBs). A novel method for the synthesis of nano-sized MgS was conducted, i.e., by means of a reaction of MgH₂ of S via ball milling. Acetylene black (AB) was used as electron conductive agent and introduced by two approaches to the MgS anode material: the one is ball milling AB with the as-prepared MgS derived from MgH₂ and S; the other is pre-milling AB with S and then further milling the mixture with MgH₂. X-ray diffraction, scanning electron microscopy, transmission electron microscopy (TEM) and high resolution TEM analyses show that MgS/AB composites with MgS nanocrystallites embedded in the AB matrix are formed via either of the approaches. The MgS anode derived from MgH₂ and the pre-milled S/AB mixture shows high capacity. Capacity fading occurs mainly in the initial several cycles. A capacity of 630 mA h/g is retained after 80 cycles. The electrochemical property is much better than that of the MgS/AB derived from MgS and AB, due to the much homogenous microstructure of the former. The mechanism of the lithium insertion and extraction process of MgS is primarily discussed. The work is considered helpful in developing new synthesis method for MgS and new electrode material for LIBs.

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1. Introduction

As one of the chemical power sources, lithium-ion batteries (LIBs) have been widely used in cellular phones, laptop computers, cameras, etc., because of their advantages of high energy density, long cycle life and environmental benignity, and so on. However, the power density and capacity of actual commercial LIBs cannot meet fully the demands for the next generation LIBs, which are highly desired in the use in electronic vehicles, hybrid electronic vehicles and energy storage systems for wind and solar energies, as the ever-growing need for energy coupled with the cumulative depletion of fossil fuel and the rapid increase in greenhouse gases. Therefore, a great many of alternative electrode materials have been studied [1–4]. Among different candidates, metal sulfides are promising electrode materials due to their low cost and high theoretical capacities [5,6]. The use of metal sulfides as cathode or anode materials depends on their potential properties for lithium insertion and extraction, and the applied cut-off potential range vs. Li⁺/Li. For examples, TiS₂ [6], Co₉S₈ [7] and NiS [8] have been investigated as cathode materials for LIBs. Whereas, some other sulfides, such as MnS [5], WS₂ [9], MoS₂ [10] Al₂S₃ [11], Ag₂S [12] and SnS₂ [13,14] have been investigated as anode materials. In addition, some metal sulfides have been investigated as both anode and cathode materials, such as FeS₂ [15,16]. The theoretical capacities of some metal sulfides are extremely high. For instance, the theoretical capacity of SnS₂ anode material is 1494 mA h/g [13], which is *ca.* 4 times higher than 372 mA h/g of the commercial anode material of graphite. Metal sulfides have aroused much attention on the basis of their novel electrochemical properties and important technological applications. Therefore, exploiting other metal sulfides by novel synthesis and of novel electrochemical property as electrode materials for LIBs is still necessary.

Mg (magnesium) and S (sulfur) are abundant elements in the earth. MgS is a wide bandgap barrier material providing excellent confinement in the family of II–VI sulfide compounds [17]. It is an important host material of phosphors of high quantum efficiency. Normally, MgS can crystallize in rock-salt (*B*1), zinc blende (*B*3) and wurtzite (*B*4) structures [18]. Metastable zinc blende MgS thin film used for laser diode devices synthesized by molecular beam epitaxy was reported [19]. Rocksalt MgS nanotubes were synthesized via a thermal reaction process, and were investigated as a hydrogen storage material [20]. However, to the best of our knowledge, there is no report on the feasibility of MgS as electrode material for LIBs. If MgS reacts with lithium as other metal sulfide



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electrode materials aforementioned or not mentioned yet in the present paper, the capacity of MgS is expected to be high. It is suggested meaningful to study the electrochemical properties of MgS as electrode material for LIBs.

In the present work, MgS with nanocrystalline structure are synthesized via a novel solid state reaction of MgH₂ with S via ball-milling. The electrochemical properties of the MgS as anode material for LIBs are investigated and the mechanism of lithium reaction is primarily discussed. It is found that MgS shows favorable lithium insertion and extraction properties as electrode material for LIBs. The present work is considered not only helpful for the further study of MgS as a high-capacity electrode material for LIBs, but also provides new synthesis method for MgS for other scientific study and industrial use.

2. Experimental

As-received MgH₂ (Alladdin, 98%, 100-200 meshes) was initially ball-milled for 96 h at 500 rpm under 80 MPa H_2 with a ball-to-powder ratio of 20:1 in order to reduce the particle size. The use of H₂ atmosphere is to avoid the decomposition of MgH2 during the milling. The pre-milled MgH2 was then milled with S (Alladdin, 99%) in a molar ratio of 1:1 for 24 h at 500 rpm in a stainless steel jar on a planetary ball mill (QM-3SP4, Nanjing, China) with a ball-to-powder ratio of 60:1 to form MgS. Acetylene black (AB, ca. 50 nm, Shanghai Haohua Chemical Co., China) is adopted as electron conductive agent for the MgS anode. Therefore, the synthesized MgS was further ball milled with 35 wt.% AB for 12 h at 350 rpm. The so-formed MgS/AB electrode material is denoted as MgS-MC. Alternatively, S and AB powders were ball-milled firstly for 96 h at 500 rpm with a ball-to-powder ratio of 20:1 and then further milled with the pre-milled MgH_2 for 24 h at 500 rpm with a ballto-powder ratio of 120:1, in which the AB introduced in the final product was also designed to be 35 wt.% and a mole ratio of 1:1 for MgH₂ to S is also adopted. This soformed MgS/AB electrode material is denoted as MgS-MSC. Ar milling atmosphere were used for these milling processes. As MgS is a wide band-gap semiconductor, its electronic conductivity is poor. Therefore, a comparatively high content of AB is applied to offer a sufficient electronic contact of the MgS particles. In addition, AB can also act as a buffer to alleviate the volume change of MgS during lithium insertion and extraction, and hence improves the cycle stability. The transfer of the samples during the synthesis process was conducted in an Ar-filled glove box (MBRANV, Germany) considering the high reactivity of MgH₂ and MgS in air. To determine the gaseous composition released from the reaction of MgH₂ and S to assess the reaction, the gases after the milling was analyzed by mass spectrometry (MS, OIC-20, HIDEN).

Crystal structures of the ball milled products were characterized by X-ray diffraction (XRD, PANalytical) with Cu K α radiation (λ = 1.5418 Å) in a step scanning model with a step interval of 0.02° and a count time of 1 s per step. Microstructures of the obtained products were investigated by scanning electron microscopy (SEM, Hitachi-S-2800), transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN), high-resolution TEM (HRTEM) and energy dispersive spectroscopy (EDS).

Electrochemical properties of the obtained MgS as anode material for LIBs were tested using CR2025 coin-type cells assembled in the Ar-filled glovebox. The working electrode was prepared by cold pressing the above two types of MgS/AB electrode materials directly onto a nickel foam at 20 MPa. There is no extra conductive agent added in the electrode preparation. Considering the sensitivity of MgS to moisture, which is difficult to obviate completely from the common binders used for LIBs, no binder was used in the anode preparation. This is another reason for the choice of the comparatively high content of AB in order to get a sufficiently electronic contact of the MgS particles. The loading of MgS in each electrode was ca. 2 mg/cm². Lithium foil was served as counter electrode, and a Celgard 2400 membrane was used as separator. A solution of 1M LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (1:1 by volume) was used as electrolyte. Galvanostatical discharge/charge measurements were conducted in a potential range of 0.005-3 V (vs. Li⁺/Li) at a current of 50 mA/g using a Neware battery teat system (Shenzhen, China). Rate capability of the MgS/AB electrode derived from MgH₂ and S/AB mixture was performed in a current range of 50-500 mA/g in the same potential range. Cyclic voltammetry (CV) measurement was performed in a potential range of 0.005-3 V (vs. Li⁺/Li) at a scan rate of 0.1 mV/s using a multi-channel electrochemical testing system (MATAT, Arbin Instrument). All electrochemical tests were performed at 25 °C.

In order to reveal the phase transition of the lithiation and delithiation processes, electrodes discharged and charged to different potentials in the first and second cycles were disassembled in the glove box and analyzed by XRD in the step scanning model also. To further clarify the structure of the charge product, the initially charged one is also analyzed by TEM, HRTEM and selected-area electron diffraction (SAED). The electrodes were rinsed with dimethyl carbonate prior to the above analyses.

3. Results and discussion

3.1. Structural characterization

XRD patterns of the milled product of MgH₂ (pre-milled) with S, the one further milled with AB (MgS-MC), the pre-milled S/AB and its further milling with MgH₂ (MgS-MSC) are shown in Fig.1. For comparison, those of the pre-milled MgH₂ and the as-received S are also shown. It is seen that the pre-milled MgH₂ shows broad diffraction peaks, indicating a poor crystallinity. However, after milling with S, rock-salt MgS (JCPD-65-5548) forms. The comparatively sharp diffraction peaks indicates a good crystallinity of MgS. There is no other diffraction peak appearing in the pattern, indicating an almost full reaction of MgH₂ and S without detectable residual reactants. The diffraction peaks of the MgS-MC sample do not show visible difference from those of the as-prepared MgS. Calculation of the crystallite size of the as-prepared MgS ((200) facet) by the Scherrer equation using the XRD data shows a value of 15 nm, and that of the MgS in the MgS-MC composite is 14 nm, which is very close to the former.

The diffraction peaks of S are still evidently seen in the milled S/AB, indicating that the crystal structure of S maintains mostly after the milling. The broad hump at the low diffraction angle around 25° is from AB. Similar as in the MgS-MC composites, MgS is the only crystal phase detected in the MgS-MSC composite. There is no residual MgH₂ or S detected. The result indicates that MgH₂ also reacted fully with the S in the S/AB mixture during the milling, forming MgS/AB composite. However, the diffraction peaks of MgS in the MgS-MSC composite are broader than those of either the as-prepared MgS or those of the MgS-MC composite, indicating a smaller crystallite size of the former. Calculation of the crystallite size of the MgS in the MgS-MSC composite by the Scherrer equation also shows a smaller value of 11 nm.

Mass spectrum measurement of the gases after the milling of MgH_2 with either the individual S or the S/AB mixture showed that there was only H_2 detected in addition to the Ar milling gas. There was no S-containing gas such as H_2S generated during the milling process. This further demonstrates a stoichiometric reaction between MgH_2 and S, forming MgS and H_2 .

Fig. 2a and b shows the SEM images of the starting materials of the pre-milled MgH₂ and as-received S, respectively. The pre-milled MgH₂ shows particle size of *ca.* $1-2 \mu m$, which is considerably reduced compared with the as-received one



Fig. 1. XRD patterns of the milled products of MgH₂ and S and the one further with AB, the MgH₂ with S/AB, as well as the pre-milled MgH₂, S/AB mixture and the asreceived S.

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