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Short communication

Flower-like CoS with nanostructures as a new cathode-active material for rechargeable magnesium batteries

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HIGHLIGHTS

- Flower-like CoS composed of nanoplates was synthesized by a solvothermal method.
- CoS was proved possible to be used as the cathode-active material for Mg^{2+} batteries.
- The mechanism of charge–discharge reactions was discussed.
- Flower-like CoS with nanostructures shows superior electrochemical properties.

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ABSTRACT

Cobalt sulfides have become promising electrode materials for lithium ion batteries while their applications in rechargeable magnesium batteries are rarely reported. In this paper, we have done some research on the electrochemical properties of cobalt sulfide (CoS) as the cathode-active material for rechargeable magnesium batteries. Flower-like CoS with nanostructures is synthesized by a facile solvothermal route. The obvious redox peaks on the cyclic voltammetric curves confirm the possibility of applications. The galvanostatic charge–discharge tests display excellent cycle stability and high coulomb efficiency. Meanwhile, the possible mechanism of charge–discharge reactions is proposed and discussed. These results show that flower-like CoS is a promising candidate as cathode-active material for rechargeable magnesium batteries.

1. Introduction

Although rechargeable lithium batteries are widely used in the portable electronics, the high cost ($64,800/t) and low safety factor of the Li metal limit their applications in the electric vehicles or the large scale energy storage systems. On the contrary, rechargeable magnesium batteries are regarded as promising power supplies in these fields owing to their better optional safety and the lower price of the magnesium metal ($2700/t). Besides, the volumetric energy density of Mg is almost 2 times as large as that of Li [1]. Thus many scientists have shown their interests in developing the rechargeable magnesium battery systems [2]. Nevertheless, several obstacles influence their commercial application. One of the major problems is the high charge density of magnesium ions. Compared with Li^+, Mg^{2+} has a similar ion radius but two electric charges, which cause serious polarization of the electrolyte and make it difficult for magnesium ions to insert or extract general matrix materials reversibly [3]. Most of the lithium battery materials cannot be applied to the rechargeable magnesium batteries because Mg^{2+} diffuses slowly and is easier to be trapped in these cathodes [4].

According to the previous literature, several compounds have been proposed as the suitable cathode-active materials for Mg^{2+} intercalation, including $MxMo_6T_8$ (M = Metal, T = S, Se) system [5–8], $Mg_{1.03}Mn_{0.97}SiO_4$ [9–11], TiS_2 [12], MnO_2 [13], V_2O_5 [14] and MoS_2 [15–17]. However, these materials either have a poor electrochemical performance or have a complex synthesis method. For instance, the discharge capacity of Mo_6S_8 is 100 mAh g^{-1} and remains more than 85% after 2000 charge–discharge cycles while the compound has to be synthesized in the absence of oxygen at really high temperature [2]. Liang et al. [16] reported graphene-like MoS

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cathode has a discharge capacity of about 170 mAh g^{-1} with the ultrasmall Mg nanoparticle anode while its capacity drops to less than 90 mAh g^{-1} with the bulk Mg anode. The discharge capacity of the first cycle for acid-treated MnO_2 can reach to more than 200 mAh g^{-1} while the cycle stability is so poor that it is less than half after only 5 cycles [13]. Chevrel-phase cathode materials $Cu_xMo_6S_8$ ($x \geq 1$) [8] have reversible capacities not better than 112 mAh g^{-1}. In short, the lack of suitable cathode materials is a drawback of rechargeable magnesium batteries. Therefore, it is urgent to search for the new promising candidate for this system [4].

At present, metal sulfides and metal oxides have been studied most commonly. The crystal architecture of metal sulfides is less easy to trap magnesium ions compared to that of metal oxides [14,18]. So the cycle performance of metal sulfides is usually better. Currently, much attention has been paid to the cobalt sulfides due to their advanced electronic properties. They are widely applied in energy storage, lithium-ion batteries, solar cells and so on [19–25].

As a member of cobalt sulfides, CoS, especially nanostructural CoS, has been studied in many fields due to its advantages. In detail, CoS nanoplates prepared by Lin show excellent behavior as the dye-sensitized material [24]. CoS microspheres was also performed as negative electrode for alkaline secondary batteries [25]. Nanowires and nanospheres of CoS were used as low-cost replacements for RuO_2 in electrochemical capacitors [26,27]. However, to the best of our knowledge, there are no reports on the electrochemical study of cobalt sulfides in the rechargeable magnesium battery field [28,29]. In this communication, CoS, which has a high theoretical capacity, was tested for the first time as a cathode-active material for magnesium rechargeable batteries. On the other hand, it is well-known that the properties of materials are sensitive to their sizes and morphologies. So well-shaped nanostructured CoS should be more suitable compared to Bulk CoS for rechargeable magnesium batteries. Herein, in this work, a facile solvothermal method was adopted to prepare flower-like CoS with nanostructures. Their electrochemical properties as the cathode-active material for rechargeable magnesium batteries were performed using LAND battery test instrument. The results show that the batteries have superior cycle performance and high efficiency, which may be attributed to the special nanostructure of the cathode-active material CoS.

2. Experimental method

2.1. Preparation of cathode-active materials CoS and characterization methods

In this paper, all the chemical reagents were analytically pure and used without further purification. The cobalt sulfide (CoS) was synthesized by solvothermal method. The cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was used as cobalt source, and the thiocarbamide (CN_2H_4S) was used as sulfur source. The typical solution was prepared by dissolving 7.5 mmol $CoCl_2 \cdot 6H_2O$ and 30 mmol thiourea into a mixed solvent of 60 mL ultrapure water and 15 mL ethylene glycol. After agitation, the pink solution was then transferred into 100 mL Teflon-lined stainless steel autoclave, and kept at 180 °C for 15h to react fully. Finally the autoclave was naturally cooled inside the furnace to room temperature. The resulting products were collected by centrifugation and subsequently washed three times with ultrapure water and ethanol respectively to get rid of impurities attached on the surface of CoS. At last, the powder of CoS was dried at 50 °C under vacuum condition.

Structure characterizations of as-prepared samples were performed by X-ray diffraction (XRD) using an apparatus (D/max 2550VL/PCX) equipped with a Cu Kα radiation. The 2θ range in the measurement was from 20° to 80°. The morphology and microstructure were examined using a scanning electron microscopy (SEM) on a field-emission microscope (JSM 7600F) and a high resolution field-emission transmission electron microscopy (TEM, JOEL 2100F). The contents of metallic elements in the cathode material were analyzed by the inductive coupled plasma emission spectrometer (ICP) using the Agilent 7500a ICP-MS system.

2.2. Electrochemical measurements

The cathode material was made by mixing 80wt% active material, 10%wt carbon black and 10wt% binder (polyvinylidene fluoride (PVDF) dissolved in N-methyl-2- pyrrolidinone). The electrodes were fabricated by coating the mixture onto copper foil, and vacuum dried at 60 °C for 6 h. Pure magnesium (99%) was cut into wafer with diameter of 15 mm to be the counter electrode. The CR2032 coin cells were assembled in the argon-filled glove box, with 0.25 mol L^{-1} $Mg(AlCl_2EtBu)_2$/THF as an electrolyte, and a Celgard 2400 separator. To measure the electrochemical properties of the cathode, a two-electrode setup was used with magnesium metal as the counter and reference electrodes. Galvanostatic charge–discharge tests were run on a Land Battery Measurement System at the ambient temperature; the voltage range was between 0.1 V and 2.0 V (vs. Mg/Mg^{2+}) and the current density was 50 mA g^{-1}. Cyclic voltammograms experiments were performed on a CHI660C Electrochemical Workstation; the scanning voltage was also in the range from 0.1 V to 2.0 V (vs. Mg/Mg^{2+}).

3. Results and discussion

The typical XRD pattern of as-prepared CoS is shown in Fig. 1. The main diffraction peaks (2θ) at 30.60°, 35.30°, 46.96°, 54.40° and 74.70° are accord with standard diffraction patterns of the hexagonal phase CoS with a space group of P63/mmc(194) (JCPDS No.65–3418). All the peaks fit well and no impure ones are observed, which demonstrates the good crystallinity and the high purity of the product. However, it is easy to find that the relative intensity of these peaks has changed. This shows that the material has a preferred orientation hinting at the possible special morphology of as-prepared CoS.

Fig. 2 shows the SEM and TEM images of the CoS particles synthesized in mixed solvent of H_2O and EG (volume ratio is 4:1),

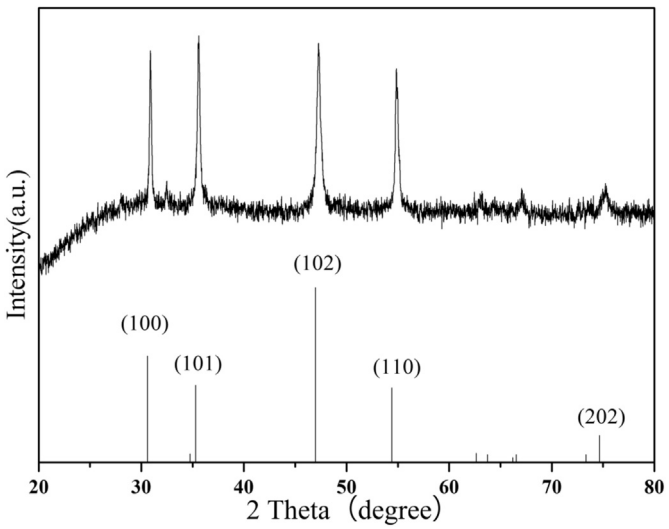

Fig. 1. XRD pattern of the flower-like CoS with nanostructures.