

Synthesis and electrochemical performance of cobalt disulfide

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Abstract The anode material cobalt disulfide for lithium-ion batteries was synthesized using the hydrothermal method at a lower temperature. The microstructure and surface morphology of the powders were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrochemical tests showed that this sample had superior electrochemical properties. The first discharge capacity is up to 1313.9 mAh/g in the voltage range of 3.00–0.02 V at a current density of 50 mA/g. Adjusting the voltage range to 3.00–0.50 V, the first discharge capacity decreases, but the 20th discharge capacity is 435.5 mAh/g, which is better than what has been reported in the literature.

Keywords Lithium-ion battery · Anode · Cobalt disulfide · Hydrothermal method

Introduction

Carbon materials as anode materials are widely used in commercial Li-ion batteries, but they are insufficient to meet the high-energy density, high capacity, and safety standards that will be required intensively in future development. (Its theoretical maximum capacity is only 372 mAh/g [1].) In recent years, research has been undertaken to search for new anode materials in place of carbon materials. The compounds investigated include: transition metal oxides [2, 3], metal-based composite oxides [4, 5], lithium alloy [6, 7], silicon alloy [8, 9], metal

nitrides, metal sulfides, metal phosphates, and metal fluorides [10–13], as well as some improved carbon materials. Among these various candidate active materials for secondary lithium batteries, metal sulfides are known to be promising materials because of their high theoretical capacity. A wide variety of metal sulfides such as ZnS [14], MoS₂ [15], and CoS₂ [16] have been considered for anode materials in lithium batteries.

Cobalt disulfide has normally been synthesized by the polymer matrix method [17] or by the solvent-thermal method [18] or by the traditional solid-state method [16]. This paper reports cobalt disulfide powders synthesized by a one-step simple chemical reaction method at a lower temperature and its electrochemical properties are also discussed.

Experimental

CoCl₂·6H₂O (analytically pure), Na₂S₂O₃ (analytically pure), and sulfur were supplied by the Shanghai Chemical Reagent Company, China. CoCl₂·6H₂O, Na₂S₂O₃, and S were added to a Teflon-lined stainless steel autoclave of 20-ml capacity in a 2:2:1 mole ratio. The autoclave was filled with distilled water to 80% of the total volume, then tightly sealed and maintained at 140 °C for 24 h. After heating, the autoclave was cooled to room temperature. The black powders were collected after being filtered and successively washed several times with distilled water, ethanol, and carbon disulfide. At last the powders were dried at 80 °C in vacuum.

The X-ray diffraction (XRD) measurements were carried out with a Shimadzu XRD-6000 diffractometer with Cu K α radiation and a power of 40 kV×30 mA. Data were collected in the 20–80° range using a constant scan method at 4°/min. The scanning electron microscope (SEM) images

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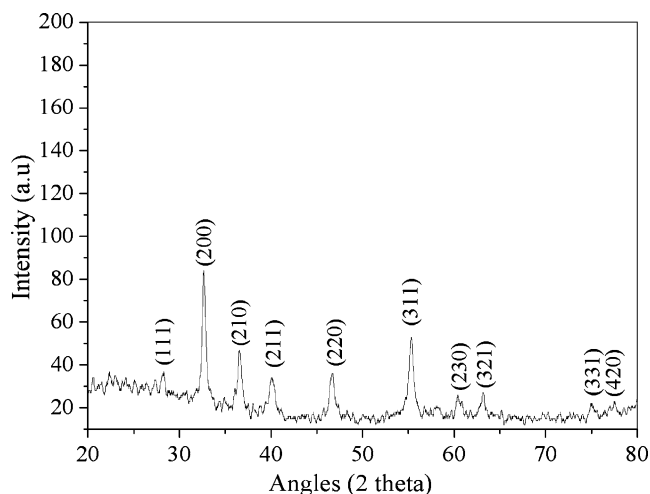


Fig. 1 The XRD pattern of cobalt disulfide powders

were collected by means of a Hitachi X-650 microscope. Cyclic voltammetry (CV) measurements were collected using a three-electrode system CHI605A potentiostat/galvanostat system (ShanghaiChenhua, China). A Li foil served as the counter and reference electrode. The scan potential range was chosen to be 3.00–0.50 V and the potential scanning rate was 0.5 mV/s. The electrochemical properties were examined using a Land cell test system (Wuhan, China). The cells were fabricated using lithium as the counter electrode, with cobalt disulfide powders, acetylene black, and polytetrafluoroethylene (PTFE) binder (weight ratio of 60:30:10) pressed onto a nickel net as working electrode, Celgard 2400 film as the separator, and ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) containing 1 M LiPF_6 as the electrolyte. The cells were assembled in an argon-filled glove box and were discharged and charged in the voltage range of 3.00–0.02 V and 3.00–0.50 V at a current density of 50 mA/g.

Results and discussion

The XRD pattern of CoS_2 powders is shown in Fig. 1. The CoS_2 is a cubic phase with space group $Pa\bar{3}$. The lattice constant is $a=5.518 \text{ \AA}$, which approximately agrees with the literature data (JCPDS card No.41-1471).

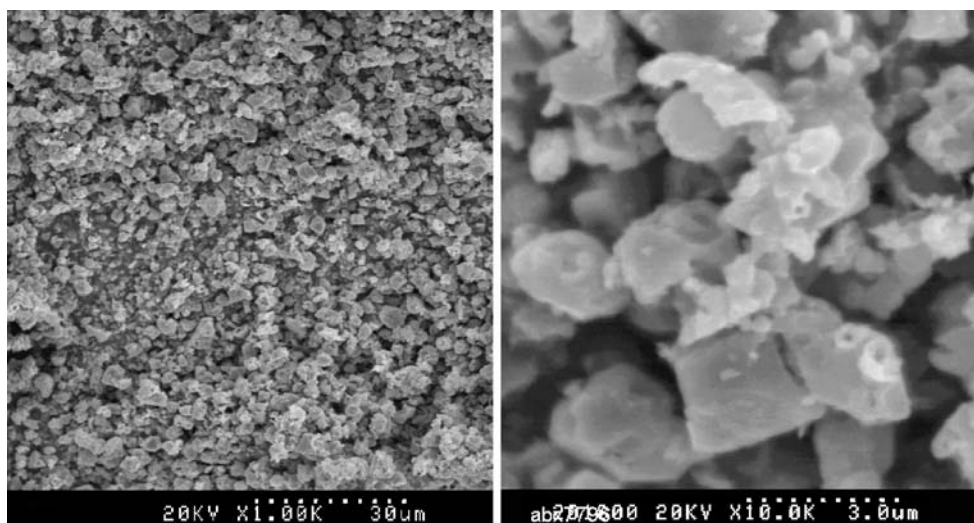
Chemical analysis was used to detect the sulfur content of the as-prepared sulfide. The sample was heated to constant weight in a stream of oxygen, and the sulfide was converted to CoO . To prevent overoxidation of CoO , the heating temperature should not exceed $900 \text{ }^\circ\text{C}$ [19]. This sample prepared by the above procedure corresponded to the formula $\text{CoS}_{1.95}$.

Figure 2 shows SEM images of the cobalt disulfide powders. The average grain size is approximately $2 \mu\text{m}$. Particles tend to agglomerate and uniformly distribute themselves in terms of shape, size, and texture. This specific particle size and morphology explain some of the superior cycle stability of this sample synthesized via the hydrothermal method.

Figure 3 illustrates some charge–discharge curves of the sample. In the voltage range of 3.00–0.50 V, the potential rapidly drops to reach a large plateau at 1.10 V, then slowly drops to a lower plateau at 0.70 V, and then drops continuously to 0.50 V during the first discharge curve. From the second cycle on, there is only one plateau at 1.25 V. The plateau potential of the charge curve was about 2.0 V. While in the voltage range of 3.00–0.02 V, the first discharge curve is also different from the subsequent curves, but the capacity retention decreased in the following cycles. These plateaus involve a series of different reactions, as the CV measurement demonstrates.

When the CoS_2/Li test cells were discharged and charged between 3.00 V and 0.02 V, the first discharge capacity was 1313.9 mAh/g, but the discharge capacity

Fig. 2 SEM images of cobalt disulfide powders



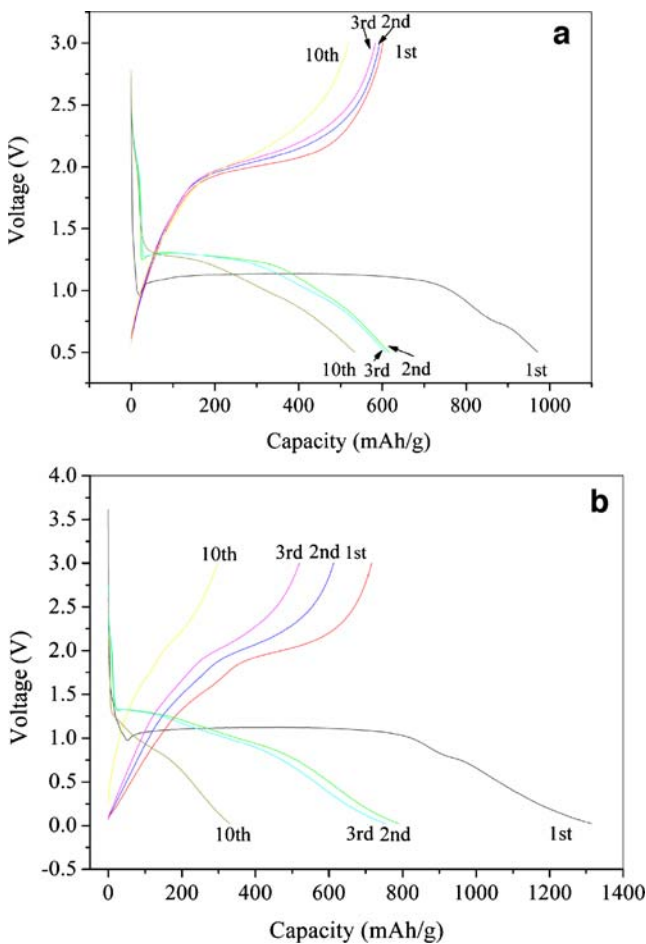


Fig. 3 Charge and discharge capacity against voltage curves of CoS₂/Li test cells. The charge–discharge voltage range: **a** 3.00–0.50 V and **b** 3.00–0.02 V

rapidly dropped to 330.8 mAh/g in the 10th cycle. To improve the cycle stability, in accordance with the CV experiment, we adjusted the voltage range to 3.00–0.50 V.

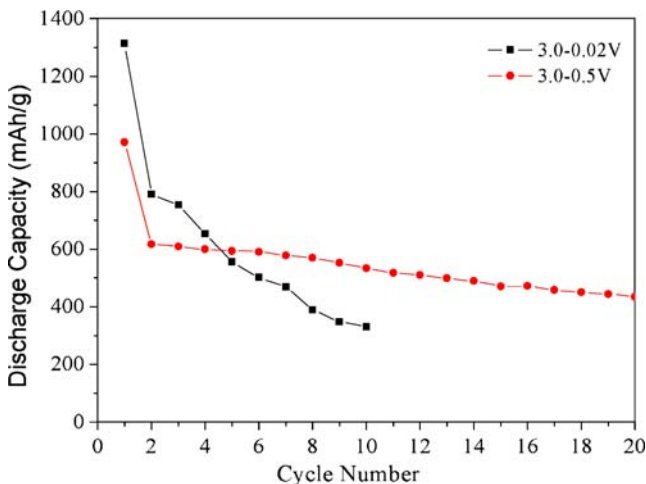


Fig. 4 The curves of discharge capacity with cycle number of CoS₂/Li test cells in the different voltage range of 3.00–0.02 V and 3.00–0.50 V

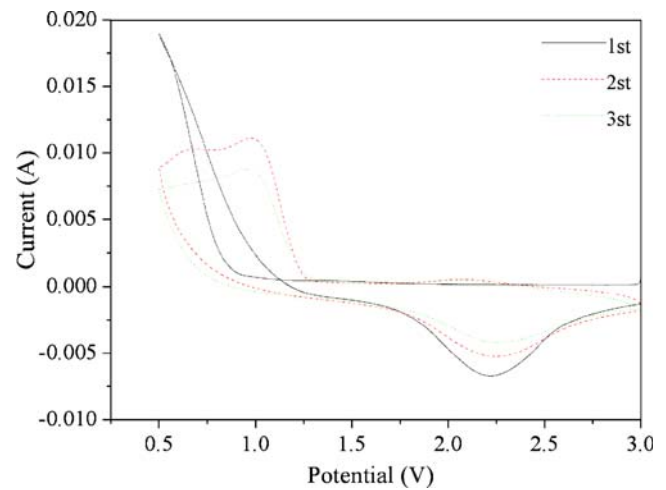


Fig. 5 The CV of cobalt disulfide electrode composed of 10% PTFE and 30% acetylene black

The discharge capacity of lithium insertion in the first discharge is 971.9 mAh/g and the first charge capacity is 601.2 mAh/g, even in the 20th cycle, the discharge capacity is still 435.5 mAh/g (Fig. 4). The first cycle irreversible loss was 38%, which is less than that in some metal-based composites, such as ZnCo₂O₄ [20] and MnV₂O₆ [21]. The irreversible capacity loss may be because of the formation of solid electrolyte interphase (SEI). This result indicates the different insertion mechanism of Li ions into CoS₂ between the first and the following cycles.

The CV of the cobalt disulfide electrode is shown in Fig. 5. In the first potential scanning cycle, more and more cobalt is precipitated along with the deoxidizing reaction. It improves the conductivity and enhances the current density, so that the curves cross. In the following scanning cycles, the oxidation peak current decreased but the peak potential did not change; two reduction peaks appeared at 1.00 and 0.65 V. It suggested that the CoS₂/Li cell discharges in a two-step process. First, CoS₂ is transformed to Li_xCoS₂ at 1.00 V, and then Li_xCoS₂ is gradually converted to Co and Li₂S at 0.65 V. Poizot et al. [11] studied CoS_{0.89} anode material and confirmed that the reaction mechanism is similar to that in transition-metal oxides (MO + 2Li ↔ M + Li₂O, M: Co Ni Cu Fe). According to this and the CV experiment, we think that the possible reaction mechanism is 4Li⁺ + 4e⁻ + CoS₂ ↔ Co + 2Li₂S. When the voltage range was adjusted to 3.00–0.50 V, there was relatively less cobalt precipitation, and the structure recovered more easily, so the cycle stability is better.

Conclusions

Cobalt disulfide was synthesized using the hydrothermal method at a lower temperature. The compound cobalt

disulfide shows better electrochemical properties than that of carbon materials and some metal-based composites. When the cells were discharged and charged between 3.00 and 0.02 V, the first discharge capacity is up to 1313.9 mAh/g. After adjusting the voltage to 3.00–0.50 V, the discharge capacity is 971.9 mAh/g in the first cycle, but even in the 20th cycle the discharge capacity is still 435.5 mAh/g. The CV measurements suggest that the possible reaction mechanism is $4\text{Li}^+ + 4\text{e}^- + \text{CoS}_2 \leftrightarrow \text{Co} + 2\text{Li}_2\text{S}$.

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