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Short communication

Synthesis and characterization of nanosize cobalt sulfide for rechargeable lithium batteries

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Abstract

Nanosize cobalt sulfides were synthesized through a one step chemical reaction method at room temperature. The cobalt sulfide nanopowders were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy and electrochemical testing. The results revealed that the cobalt sulfide is a semiconductor; the reversible capacity is increased with increasing content of electronic conductors in the active material of electrodes. The as prepared sample with 10 wt.% carbon black and 10 wt.% polypyrrole (PPy) powder as electronic conductors shows the best electrochemical properties, with a reversible capacity of over 300 mAh g^{-1} based on the total mass of the electrode. Cobalt sulfide nanopowders show promise as cathode active materials for lithium-rechargeable batteries.

Keywords: Lithium-rechargeable battery; Cobalt sulfide; Nanoparticles; Polypyrrole additive

1. Introduction

Among the 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 have been considered for cathode material in lithium battery [1–5], including those of W, Ni, Pb, Ti, Mo, V and Cu. However, nanosize cobalt sulfide has not been explored.

Normally, cobalt sulfide powders were synthesized by traditional solid-state methods. For example, cobalt sulfide could be formed by the reaction of cobalt with sulfur [6] or hydrogen sulfide [7] or by reaction of cobalt monoxide with hydrogen sulfide [8]. Cobalt sulfide has also been synthesized by the reaction of Co_3O_4 with SO_2 in the presence of carbon [9]. With these methods, high-temperature (600–800 °C) quenching was needed to form crystalline cobalt sulfide [10]. Recently, cobalt sulfide has been synthesized by a hydrazine-assisted low-temperature hydrothermal preparation method [11]. To the best of our knowledge, the room temperature chemical solution route has never been reported as a way to synthesize nanocrystalline cobalt sulfide. In this paper, cobalt sulfide nanosize powders were synthesized by a one-step simple chemical reaction method at room temperature. The possibility of using cobalt sulfide nanopowders as cathode materials for lithium-rechargeable batteries has been examined.

2. Experimental

Nanoparticles of cobalt sulfide were prepared at room temperature by simultaneously dropping 20 ml of 1 M cobalt sulfate (99.9%, Aldrich) solution and 20 ml of 1 M sodium sulfide (99.9%, Aldrich) solution into 160 ml of distilled water containing 20 ml 0.1 M solution of ethylene diamine tetra acetic acid (EDTA, Aldrich). The mixture solution was vigorously stirred using a magnetic stirrer. Insoluble black cobalt sulfide was formed. The suspension was centrifuged at 4000 rpm for 15 min, and the precipitate was washed using deionized water with the assistance of an ultrasonic disintegrator. This procedure was repeated three times to remove any adsorbed ions. The precipitate was finally dried at 100 °C in a vacuum oven for 10 h.

Polypyrrole powder was used as the electronic conductor and was synthesized by a chemical polymerization method. First, an active material, paratoluene sulfonic acid (PTSA) (0.1 M) was added to the 0.1 M pyrrole/distilled water solution. Then, the mixture was stirred while the oxidation agent, $FeCl_3$ solution,

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was slowly added to the aqueous solution. The black aqueous solution was washed thoroughly until free of $FeCl_3$ by the method described above. Finally, the black mass was dried at 50 °C for 4 h under vacuum to yield a very fine black PPy powder.

The morphology and structure of the products have been examined by X-ray diffraction (XRD, PW1010 diffractometer with Cu Kα radiation), scanning electron microscopy (SEM, Leica Model Stereoscan 440), and energy dispersive X-ray spectroscopy (EDS). Resistance measurements of the as prepared Co_9S_8 powders were performed on the pellets using the ASTM four-probe technique with a Jandel Resistivity Test Unit (model RM2). A dc current of 5 mA was applied across the probes and the resistivity test unit measured the corresponding voltage drop across the probes.

The cobalt sulfide electrodes were made by dispersing the active materials, electronic conductors, and polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidinone (NMP) solvent to form homogeneous slurries. The slurries were spread on copper foil substrates. The coated electrodes were dried in a vacuum oven at 100 °C for 20 h and then pressed. After drying, the cobalt sulfide electrodes were cut into a 1 cm × 1 cm size. The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged in the range of 1.0–3.0 V at a current density of $0.05\ \mathrm{mA\ cm^{-2}}$. The specific capacities were calculated based on the total weight of electrode materials. Cyclic voltammetry (CV) measurements were performed using a potentiostat (model M362, EG&G Princeton Applied Research, USA) at a scanning rate of $0.1\ \mathrm{mV\ s^{-1}}$. The ac impedance measurements were carried out using an EG&G Princeton Applied Electrochemical Impedance Analyser (model 6310). The ac amplitude was 5 mV. The frequency range was 100 kHz–10 mHz.

3. Results and discussion

Nanoparticles of cobalt sulfide were synthesized using a conventional precipitation method in an aqueous solution at room temperature. The insolubility of the cobalt sulfide formed from the chemical reaction caused the formation of a number of new nuclei while preventing the growth of already existing ones, thus limiting the size of the particles. EDTA was used as stabilizing agent. The role of EDTA was to stabilize the particles against aggregation, which may lead to an increase in the size of the particles. The X-ray diffraction patterns of the as prepared cobalt sulfide and annealed powders are shown in Fig. 1. The X-ray diffraction pattern demonstrated that the cobalt sulfide powder prepared via the chemical reaction method was amorphous. The EDS spectra revealed that the powder consists of Co and S, and the atomic ratio of Co to S is close to 9:8. The chemical formula should be Co_9S_8. After annealing the as prepared cobalt sulfide powder at 450 °C for 3 h in flowing argon gas, cobalt sulfide with disorder construction converted to nanocrystalline cobalt sulfide, which was indicated by the broad peaks. The average crystal size of the cobalt sulfide powder was determined by using the Traces Program and the Scherrer formula. The average crystal size is about 10 nm. All diffraction lines are indexed to a cubic phase (S.G.: *Fm*3*m*) and the peaks positions agree with JCPDS 03–0631. The micromorphology of as prepared Co_9S_8 powders is shown in Fig. 2. The Co_9S_8 powders are agglomerates with an average particle size of 50–100 nm and consist of cotton-like structures. The morphology of the annealed sample is similar to that of the as prepared sample.

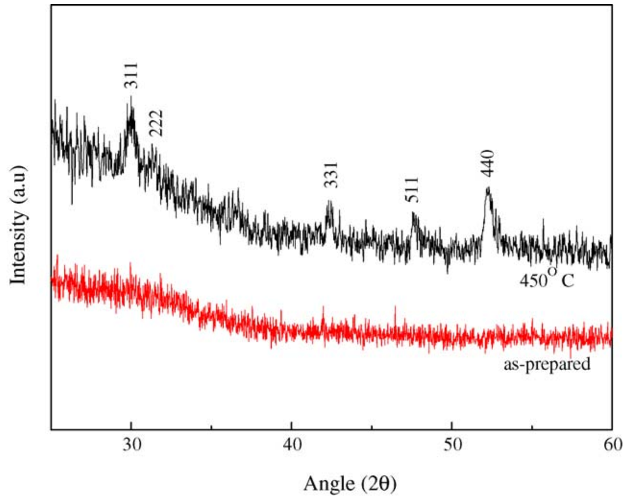

Fig. 1. X-ray diffraction patterns of cobalt sulfide powders.

The electrochemical properties of cobalt sulfide were measured at room temperature. The cobalt sulfide electrodes were made by first dispersing 80 wt.% active materials, 10 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder, by a method described in a previous publication on the preparation of metal sulfide electrodes [2]. Fig. 3 shows the cyclic voltammetry (CV) curves for the Li/Co_9S_8 cells with the electrodes containing powders from the as prepared and annealed samples. A small peak exists at around 1.9 V and a large current peak at around 1.25 V during discharging. Also, we can find a large charging current peak at 2.0 V and a small peak at 2.4 V

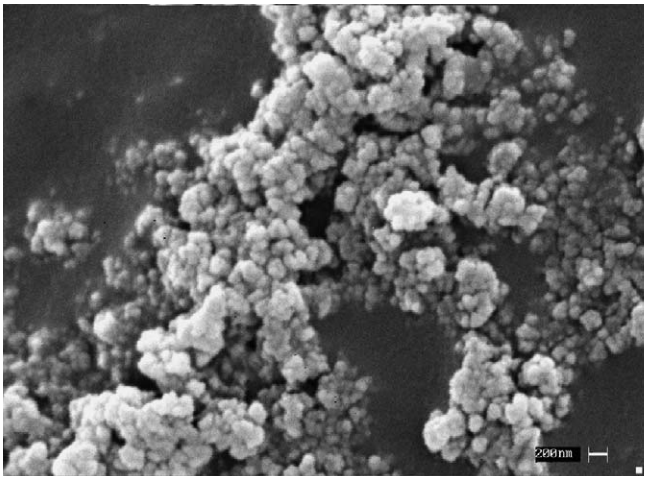

Fig. 2. SEM image of as prepared cobalt sulfide powder.