

Microwave-assisted synthesis and characterization of Co_3S_4 nanoparticles

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Cobalt sulfide (Co_3S_4) nanoparticles of 17.0 nm in crystal size have been successfully synthesized by the reaction of cobaltous acetate ($\text{Co}(\text{H}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and TAA (CH_3CSNH_2) under microwave irradiation. The samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). SEM image of the as-prepared Co_3S_4 shows the sphere-like structure. The electrochemical tests were conducted using CR2302 cointype cell, which consists of a cathode and a lithium metal anode, separated by a porous polyethylene film (Cellgard 2500). The microwave synthesis of Co_3S_4 and possible electrochemical reaction mechanisms were primarily analyzed. The results indicate that the $\text{Li}/\text{Co}_3\text{S}_4$ cell system has first discharge capacity of 336mAh/g, indicating that the Co_3S_4 sample shows potential application as anode in lithium-ion battery.

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1. Introduction

Metal chalcogenides have attracted considerable attention due to their proven and potential applications in electronic, optical and superconductor devices [1]. Cobalt sulfide (Co_3S_4) has been prominently emphasized due to its unique catalytic, electric and magnetic properties [2]. Poizot et al. studied $\text{CoS}_{0.89}$ as anode material, and found that the overpotential is lower than oxides in the lithium ion intercalation [3]. Co_3S_4 has a normal spinel structure (space group $\text{Fd}\bar{3}\text{m}$), in which Co atoms occupy both the tetrahedral (A) and the octahedral (B) sites [4]. However, very few researches have been done on the preparation and electrochemical behaviors of Co_3S_4 . Miyazaki et al. researched the electronic band structure of Co_3S_4 and indicated that spinel Co_3S_4 is an antiferromagnetic metal [4].

Microwave is electromagnetic radiation with frequency range of 0.3 to 300 GHz. Due to the properties of internal and volumetric heating, thermal gradients during microwave processing are avoided, providing a uniform environment for reaction [5-7]. This method has been successfully applied for the organic synthesis and the preparation of a variety of nanosized inorganic materials [8-10]. Compared with conventional heating, microwave heating has an advantage of high-efficiency and rapid formation of nanoparticles with a narrow size distribution. In this work, we developed this method to synthesize Co_3S_4 nanoparticles under aqueous conditions.

2. Experimental

All reagents were analytical grade and directly used without further purification. Distilled water was used throughout the experiments. 50 ml aqueous solution of 0.05 M TAA was added dropwise into a 250 ml round-bottom flask filled with 50 ml, 0.05 M cobaltous

acetate solution. 1 g PVP was dissolved into the solution. Simultaneously, the mixture was stirred and ultrasonicated. Then this round-bottom flask connected with a refluxing system was placed in a modified domestic Galanz WP900 microwave oven (A water-cooled condenser outside the microwave oven cavity was connected by a glass joint to the round-bottomed flask stably set inside). The reaction was carried out under microwave irradiation (2450 MHz) for 10 min. After cooling to room temperature, the white precipitate was centrifuged and washed for several times with distilled water, and dried in a vacuum at 60 °C for about 10 h to form the product.

The phases of the product was identified by means of X-ray diffraction (XRD) at a scanning rate of 4 °/min in the 2θ range from 10 ° to 80 °, with graphite monochromatic $\text{Cu K}\alpha$ -radiation ($\lambda=0.154056$ nm). The morphology of the sample was observed by using a FEI Sirion 200 scanning electron microscope (SEM). The electrochemical tests were conducted using CR2302 cointype cell, which consists of a cathode and a lithium metal anode, separated by a porous polyethylene film (Cellgard 2500).

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared Co_3S_4 powders. The three diffraction peaks corresponded to the (311), (400), (440) planes indicating a spinel crystal structure (JCPDS42-1448, $a=0.9437$ nm) without impurities. The calculated lattice constants of $a=0.9446$ nm base on the (311) planes at the $2\theta=28.657$ ° is consistent with standard literature value within error range. The peaks are obviously wide and the crystal size of the Co_3S_4 particle calculated by Scherrer's formula is ca. 17.0 nm.

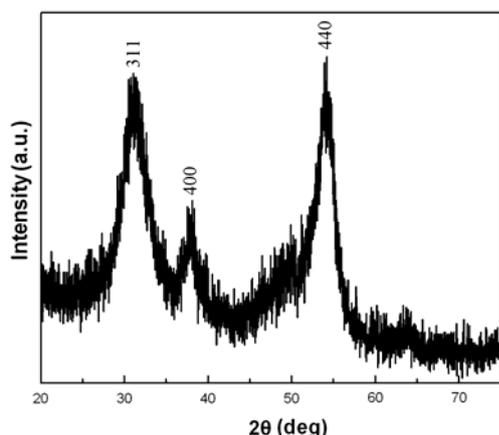


Fig. 1. XRD pattern of the Co_3S_4 particles synthesized by microwave irradiation for 10 min.

Fig. 2 shows the SEM morphology of the Co_3S_4 particles. The particles are mostly spherical with about 100 nm in particle size, but moderate agglomeration can be found. Contact conditions among particles are clearly observed. Spherical morphology of the Co_3S_4 particles is possibly associated with the addition of PVP as a kind of long-chain organic dispersant, which can protect nanocrystallite from growing on the surface of particles by the help of position resistance.

TAA (CH_3CSNH_2) acts as sulphur source in this experiment, chemical reactions for Co_3S_4 formation under microwave irradiation are as following:

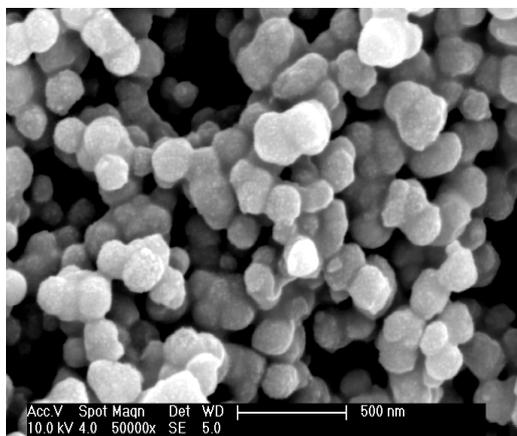
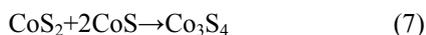
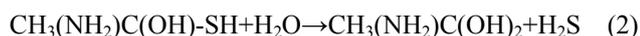
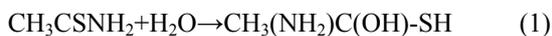


Fig. 2. SEM image of the Co_3S_4 particles synthesized by microwave irradiation for 10 min.

Fig. 3 shows the cyclic voltammogram (CV) curves of $\text{Li}/\text{Co}_3\text{S}_4$ cell. A pair of redox reaction peaks appear in the CV curves. When scanning potential is from 4.6 V to 1.5 V, lithium ions can insert into the Co_3S_4 structure. The corresponding reduction peaks is observed at 2.1 V. For the scanning potential is from 1.5 V to 4.6 V, the lithium ions were extracted from the Co_3S_4 structure. The corresponding oxidation peak forms at 2.5 V. The oxidation and reduction peaks in the CV curves indicated that lithium intercalation and de-intercalation reactions occurred for the Co_3S_4 electrode. In the anodic sweep, another peak forms at 2.0 V. The irreversible peak strongly affected the capacity and the cycle stability of the cell. The evidence can be seen from the charge/discharge tests.

Poizot et al. reported that the reaction mechanism of sulfides with Li^+ as same as that of oxides [3], which can be written as follows:



According to above reaction equation, the electrochemical reaction happened in the Co_3S_4 electrode may be written as follows:

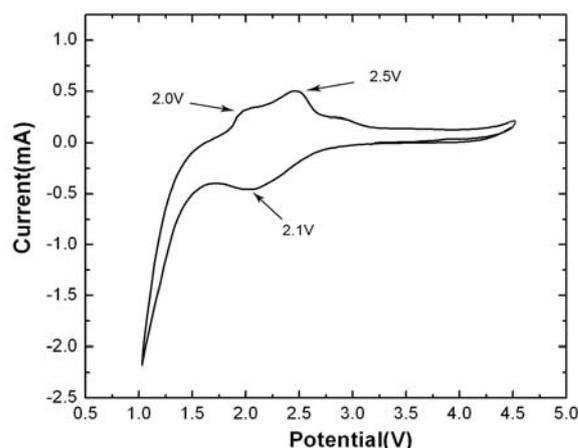


Fig. 3. CV curves of the Co_3S_4 electrode.

Fig. 4 exhibited the discharge curves of $\text{Li}/\text{Co}_3\text{S}_4$ cell. As shown in Fig. 4, the first discharge capacity is 336mAh/g, but the discharge capacity decreases rapidly within several cycles. The major source of capacity fading is due to some irreversibility of reaction occurred in the charging procedure, which corresponds to the irreversible oxidation peak shown in CV curves. Brousse et al. investigated SnS_2 as anode in lithium-ion battery. SnS_2 powder exhibits similar irreversible capacity on the first cycle [11]. Chuang et al. also reported the similar phenomenon that the cell, using CuS as a positive electrode shows some irreversible reaction in the electrochemical tests [12]. Many factors can result in the capacity fading. But the irreversible reaction occurred in the charging procedure is the main barrier. So, controlling the irreversibility of reaction may obtain the improvement of the electrochemical behaviors.

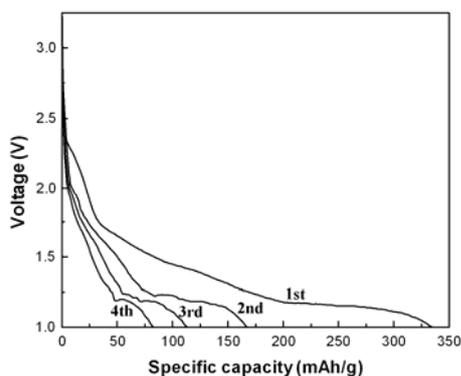


Fig. 4. Discharge curves of the Co_3S_4 electrode in the 1st to 4th cycle from 1.0 V to 3.3 V at room temperature.

Fig. 5 is the 1st-4th charge curves. An obvious plateau occurred at 2.0-2.5V during the oxidation processes, which indicates the lithium ions deinserting from Co_3S_4 . The large irreversible capacity at the cycles indicates that a lot of lithium keeps stabilized in the electrode. The charge/discharge capacities of the electrode are listed in Table 1. To our knowledge, there are still no reports about the electrochemical research of Co_3S_4 in Li-ion battery field.

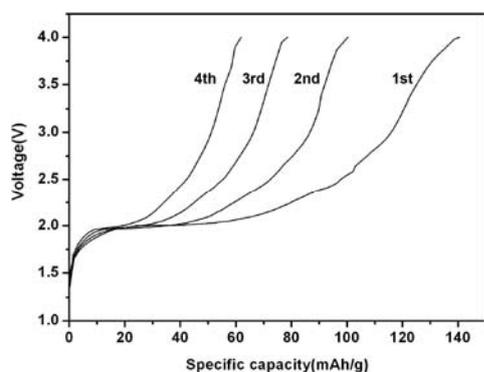


Fig. 5. Charge curves of Co_3S_4 electrode (the 1st-4th charge, charge voltage range: 3.3V-1V, at room temperature).

Table 1. The discharge and charge capacities (mAh/g) of Co_3S_4 cathode in the cycles.

Cycle number	Discharge	Charge
1	336.09	140.50
2	168.42	100.28
3	113.26	78.57
4	82.65	61.91

4. Conclusions

Spherical Co_3S_4 nanoparticles of 17.0 nm in crystal size have been successfully synthesized via a simple microwave-assisted heating process. It has been found that the electrochemical behaviors of Co_3S_4 powder are prominently affected by the irreversible reaction. The cell system has first discharge capacity (336mAh/g), indicating that this kind of material shows possible application as electrode materials.

Acknowledgements

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