Journal of Alloys and Compounds 762 (2018) 109–114

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Preparation and electrochemical properties of a new $Fe_{0.5}Co_{0.5}S_2$ cathode material for thermal batteries

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ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form
8 May 2018
Accepted 9 May 2018
Available online 20 May 2018

Keywords:
Thermal batteries
$Fe_{0.5}Co_{0.5}S_2$ cathode material
Solid-state method
Liquid phase method
Electrochemical performances

ABSTRACT

Composite sulfide $Fe_{0.5}Co_{0.5}S_2$ used as cathode material in thermal batteries can be prepared through traditional high-temperature solid-state method and liquid phase method, which combines precipitation and high temperature sulfuration. The single cells with S-$Fe_{0.5}Co_{0.5}S_2$ and L-$Fe_{0.5}Co_{0.5}S_2$ exhibit discharge capacities of 1547.17 A s g^{-1} and 1872.89 A s g^{-1} with the cut-off voltage of 1.25 V. For comparison, the single cell with FeS_2 also discharged, demonstrating a discharge capacity of 1221.45 A s g^{-1}. Moreover, the physical properties and electrochemical behaviors of L-$Fe_{0.5}Co_{0.5}S_2$ are obviously superior to that of S-$Fe_{0.5}Co_{0.5}S_2$. Due to its excellent electrochemical properties, $Fe_{0.5}Co_{0.5}S_2$ compound, especially synthesized by liquid phase method, can be used as cathode material instead of FeS_2 for thermal batteries.

1. Introduction

Thermal batteries are pyrotechnically initiated primary reserve batteries employing inorganic salt electrolytes [1,2], which are solid and non-conducting at ambient temperatures. The complete thermal battery is totally inert and non-reactive until the electrolyte becomes molten. Due to the high inherent ionic conductivity of molten salts, once activated, thermal batteries can transmit energy at very high rates. In view of its significantly inherent advantages, thermal batteries are mainly used for many military applications as primary power sources [3–5]. The primary electrochemical system used in today's thermal batteries is the Li-alloy/FeS_2 couple [6,7]. Almost universally, the FeS_2 obtained from natural pyrite is inexpensive and abundant [8,9]. Moreover, the open-circuit voltage of the Li/FeS_2 couple is high, about nominal 2 V [1]. However, there are several inherent limitations of the FeS_2-based system. First, the thermal stability of FeS_2 is much poor, beginning to decompose at 550 °C [4], which can greatly reduce the efficiency of cathode material and the life of thermal batteries. Second, the FeS_2 cathode has the high internal resistance issue which finally results in serious ohmic polarization in the discharge process. For special high-power application, the FeS_2 is replaced by CoS_2, which possesses lower resistivity (about 0.002 Ω cm) and higher thermal stability (starting to decompose above 650 °C) [10]. The carbon based material can be used as a functional material to improve conductivity in battery field [11,12], but the proportion of active substances in cathode material can also be reduced, leading to reduction of specific capacity for thermal battery. However, the initial discharge voltage and electrochemical capacity of Li/CoS_2 battery is relatively lower, in contrast to Li/FeS_2 system. More importantly, it needs to be synthetically made, wherein the cobalt is part of strategic scarce resources [13]. In addition, CoS_2 more easily reacts with moisture in the air to deteriorate. In order to improve the discharge performance of FeS_2 and save scarce cobalt supply, some works have been done in transition-metal disulfides cathode material. Guidotti RA et al. [14] reported that the various first-row transition-metal disulfides nanoparticulate materials were prepared by hydrothermal method and discharged in single cells

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https://doi.org/10.1016/j.jallcom.2018.05.118
0925-8388/

at temperatures of 400–550 °C. Awano A et al. [15] reported that the composite disulfide $Fe_{1-x}Co_xS_2$ was synthesized by high temperature solid state reaction to replace the traditional FeS_2 cathode material, which exhibited higher discharge utilization and excellent plateau.

In this study, we prepared $Fe_{0.5}Co_{0.5}S_2$ using traditional high-temperature solid-state method and liquid phase method which combines with precipitation and high temperature sulfuration. In addition, a series of performances of $Fe_{0.5}Co_{0.5}S_2$ synthesized by two different methods were characterized and analyzed, including structure, thermal properties and surface morphologies. More importantly, the electrochemical properties of FeS_2, S-$Fe_{0.5}Co_{0.5}S_2$ (synthesized by high-temperature solid-state method) and L-$Fe_{0.5}Co_{0.5}S_2$ (synthesized by liquid phase method) as battery active materials were analyzed and compared.

2. Experimental

2.1. High-temperature solid–state synthesis of $Fe_{0.5}Co_{0.5}S_2$ powders

In order to prepare S-$Fe_{0.5}Co_{0.5}S_2$, pure iron powders (99.9%, 5 μm), cobalt powders (99.9%, 5 μm) and sulfur powders (99.5%, 8 μm), were dried in a vacuum oven at 70 °C f or 12 h. According to the chemical formula for $Fe_{0.5}Co_{0.5}S_2$, the atomic percent of iron, cobalt and sulfur was set at 1:1: (4–6). The raw materials mixed uniformly by mechanical ball-milling method and reacted for 4–8 h at 600–700 °C under argon atmosphere.

In order to remove excess sulfur, the synthesized products were calcined at 480 °C in the tube furnace for 4 h under Ar. Finally, after cooling, the reaction product was taken out, followed by grinding (mechanical ball-milling method) and sieving (mechanical vibration sieve method).

2.2. High-temperature solid–state synthesis of FeS_2 powders

The raw material and preparation process of FeS_2 is the same as that of S-$Fe_{0.5}Co_{0.5}S_2$. According to the chemical formula for FeS_2, the atomic percent of iron and sulfur was set at 1: (2–3).

2.3. Liquid phase synthesis of $Fe_{0.5}Co_{0.5}S_2$ powders

Synthesis of precursor by liquid-phase precipitation: here, $CoSO_4 \cdot 7H_2O$ (99.9%), $FeSO_4 \cdot 7H_2O$ (99.9%) and $Na_2S \cdot 9H_2O$ (99.9%) were used as cobalt source, iron source and precipitant, respectively. All of the chemicals above are of analytical grade and used with further purification. First, the raw materials were completely dissolved in deionized water, wherein the atomic ratio of iron and cobalt was set at 1:1. Then Na_2S aqueous solution was slowly added into the mixed solution of $CoSO_4$ and $FeSO_4$ with continuous stirring. To ensure that Co^{2+} and Fe^{2+} are completely precipitated, the amount of sulfur is excessive and the proportion of Co^{2+}, Fe^{2+} and S^{2-} is 1:1:(3–4). Next, the reactive sediment was filtered and washed with distilled water for many times, until there was no sulfate ion in filtrate. In order to avoid the sediment oxidation, it was dried in a vacuum environment at 120 °C for 10 h.

Synthesis of $Fe_{0.5}Co_{0.5}S_2$ by high-temperature sulfuration: first, synthesized precursor and sulfur powder were mixed uniformly by mechanical ball-milling method with mass ratio of 2: (1–1.5), then, the mixture was fully reacted for 4–8 h at 600–700 °C under argon atmosphere. In order to remove excess sulfur, the synthesized products were calcined at 480 °C in the tube furnace for 4 h under argon atmosphere. At last, the product was stored in vacuum conditions after grinding (mechanical ball-milling method) and sieving (mechanical vibration sieve method).

2.4. Preparation of thin film cathode by screen printing

The appropriate amount of specific binder (PVDF) was added into the cathode active material to obtain uniform viscous paste. Then the positive electrode material was printed to the substrate using the printing machine through 100 mesh nylon net under 0.4 MPa pressure. Finally, the prepared films were dried at 300 °C for 2 h under vacuum conditions.

2.5. Preparation of thermal batteries

The single cells were prepared as shown in Fig. 1. It was constructed using $Fe_{0.5}Co_{0.5}S_2$ cathode, Li-Si alloy anode and separator based on LiCl-LiBr-LiF eutectic wherein anode and electrolyte were made by cold pressing of powder. The conventional Li-Si alloy anode was a mixture of 80 wt % Li-Si alloy (Li content of 44 wt %) and 20 wt % LiCl-KCl eutectic salts. The anode was prepared by melting the mixture, followed by grinding and pressing. As a separator, LiCl-LiBr-LiF eutectic salt was mixed with 50 wt % MgO binder (purity of over 99%) and then melted and ground.

2.6. Assessment and measurement

The powder X-ray diffraction (XRD) patterns were measured on a Panalytical X'Pert PRO system within the range of scattering angle 2θ of 5–90°. The morphology and microstructures were recorded on a scanning electron microscope (SEM, JEOL JSM-6700F, Japan) and transmission electron microscope (TEM, JEOL JEM-2010F, Japan). The surface areas were test by BET specific surface area analyzer (SSA-7300, China). The contents of Fe, Co, S in $Fe_{0.5}Co_{0.5}S_2$ were measured by using X Ray Fluorescence (XRF, AXIOS-MAX, China). In addition, the thermal stability of the products were characterized by thermogravimetry (TG) and differential thermal analysis (DTA) using a simultaneous thermal analyzer (TG-DTA6300, Japan), with a heating rate of 10 °C·min^{-1} in N_2 atmosphere.

2.7. Discharge test

Discharge test of single cell was conducted by Land battery test system. In order to simulate real discharge condition, the single cell was activated by heater source pellets (Fe/$KClO_4$) to melt electrolyte.

Constant current discharge: the single cell was discharged with a constant current density of 300 mA cm^{-2} with the cut-off voltage of 1.25 V.

Pulse discharge: the single cell was discharged with a constant

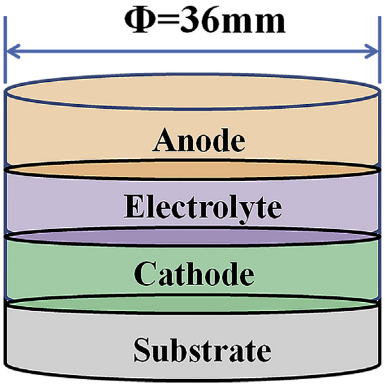

Fig. 1. Schematic diagram of single cell.