Facile synthesis of CoS$_2$/CNTs composite and its exploitation in thermal battery fabrication

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ABSTRACT

CoS$_2$/CNTs composites were prepared by a facile and simple hydrothermal growth of CoS$_2$ in the presence of carbon nanotubes (CNTs), as a novel approach of synthesizing cathode composites for thermal battery fabrication. The incorporation of CNTs in the CoS$_2$ cathode materials thus synthesized effectively improved the electrical conductivity and discharge performance of the resultant cathode, without significantly compromising its thermal stability. The thermal battery cell fabricated with such a composite cathode and with a common Li–Si anode showed all functional features of a proper thermal battery cell. The specific discharge capacity at a cut-off voltage of 1.7 V was 219.8 mA h g^{-1}, and the corresponding energy density was 387.2 W h kg^{-1}. With a pulse current density of 500 mA cm^{-2}, the battery delivered a pulse power of 2.45 W, and maintained 64% of this power after 30 pulses. Regarding thermal stability, the CoS$_2$/CNTs cathode was stable at least at 625 °C.

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1. Introduction

Due to their high level of reliability, excellent energy and power density, and long shelf-life, thermally activated (thermal) batteries are extensively used as power sources for weapon systems and other engineering systems requiring such special battery properties [1–3]. Similar to other batteries, thermal batteries comprised of an anode, a cathode and an electrolyte. However, thermal batteries are unique in that the electrolyte in such a battery is a solid with virtually no electrical conductivity at room temperature but changes into a highly conductive ionic liquid when it melts at elevated temperature [4]. A binder with a high melting point and thermal stability, such as MgO, is typically added to hold the electrolyte in place and to prevent leaking when the electrolyte melts into a liquid [4]. In this case, the physics of "binding" is electrolyte-wetting of MgO capillary channels in the electrolyte-MgO matrix.

As for electrodes, Li–Si is typically adopted as anode materials and pyrite (FeS$_2$) as cathode materials. In this combination, the thermal instability of pyrite beyond 500 °C is the most critical limitation; hence, applications requiring high temperature operation demand research on cathode alternatives. Despite of this limitation, pyrite is commonly used in thermal battery fabrication because of its high natural abundance, applicability of mined pyrite with no purification in electrode fabrication, good compatibility with molten electrolytes, and stable discharge performance [5–7]. Among all alternatives, cobalt sulfide (CoS$_2$) is the most promising replacement of pyrite due to its attractive electrical conductivity, thermal stability and discharge performance [7–11]. The research group of Preto et al. [8] pioneered the basic research of comparative electrochemistry of CoS$_2$ and FeS$_2$ electrodes in molten electrolyte. Although little works [10,11] have been known since the seminal review by Masset and Guidotti [9] in 2008, the research on battery applications of Co–S compounds is by no means diminishing. Indeed, compounds such as CoS, CoS$_2$, and Co$_9$S$_8$ have been synthesized by various means [10–20]; interestingly, all of them show promising properties for applications in lithium-ion batteries [13–16], and supercapacitors [17–20]. Advance in thermal batteries can benefit from these promising recent developments by renewing and intensifying the research on electrochemistry of Co–S compounds, particularly CoS$_2$.

Herein, we report on a facile hydrothermal route for the synthesis of composites of CoS$_2$ and carbon nanotubes (CNTs), as novel cathode materials for thermal battery fabrication. By incorporating CNTs to CoS$_2$, we intend to further reduce the cathode resistivity and to explore other advantages of such a composite approach. To

show the effectiveness of this approach, we report on the performance of thermal batteries fabricated with such CoS$_2$/CNTs composites, and compare the performance with that of thermal batteries having bare CoS$_2$ as cathode materials.

2. Experimental

2.1. Materials preparation

All chemical reagents in this work were of analytical grade and used without further purification. Commercial carbon nanotubes (CNTs) were purchased from the Nanjing XFNANO Materials Tech Co., Ltd and were functionalized by refluxing them in 6 M HNO$_3$ at 80 °C for 3 h before use. Both CoS$_2$ and CoS$_2$/CNTs were prepared by a facile hydrothermal synthesis method. For the preparation of CoS$_2$/CNTs with 5% of CNTs by weight, 0.05 g sodium dodecyl benzene sulfonate (SDBS) was dissolved into 80 mL deionized water. After this, 0.01 g CNTs, 0.43 g cobalt acetate and 1 g sodium thiosulfate were added into the solution successively. After 30 min of stirring and 30 min of ultrasonic shaking, the solution was transferred to a Teflon-lined stainless steel autoclave and then subjected to hydrothermal heating at a temperature of 180 °C for 30 h. After the autoclave was cooled naturally to room temperature, the precipitate in the autoclave was collected by filtration and then washed repetitively with absolute ethanol and then carbon disulfide. Finally, the precipitate was dried in a vacuum drying oven at 70 °C for 6 h. The reaction product is referred therein as CoS$_2$/CNTs. For the preparation of bare CoS$_2$ with no CNTs, all the procedures were the same except no addition of CNTs.

2.2. Materials characterization

The crystalline phases of the precipitates from the hydrothermal processes were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (Model D/max 2200PC/RB of Rigaku). Raman spectra were recorded on a LabRAM HR800 Laser Confocal Micro-Raman Spectroscopy with 532 nm laser excitation. The morphologies of the precipitates were observed by a scanning electron microscope (Hitachi S-5200 SEM) and by a high-resolution transmission electron microscope (JEOL JEM-2010 HRTEM). The specific surface areas of them were determined by the standard Brunauer−Emmett−Teller (BET) nitrogen adsorption−desorption method (Autosorb-iQ). Thermogravimetric (TG) results were obtained by a thermal analysis system (Model SDT Q600 of TA Instruments-Waters), with a heating rate of 10 °C min^{-1} in N$_2$ atmosphere.

2.3. Separator and electrode preparation

Separator: 60 wt.% LiCl−KCl eutectic salts (LiCl 45−KCl 55 wt.%) and 40 wt.% MgO binder.
Anode: 75 wt.% Li−Si (Li 44−Si 56 wt.%) and 25 wt.% LiCl−KCl eutectic salts.
Cathode: 60 wt.% CoS$_2$/CNTs (or CoS$_2$) and 40 wt.% separator.
Typically, a single-cell thermal battery was made by spreading the anode (0.2 g), separator (0.2 g) and cathode (0.35 g) powders layer by layer in a die and pressing the multiple layers to a pellet with a diameter of 20 mm under a static pressure of 6 MPa.

2.4. Electrochemical measurements

Single cell discharge properties were measured by placing the fabricated thermal battery cell between heated copper platens in a glovebox. The copper platens were heated from room temperature to 500 °C at a rate of 25 °C min^{-1}, and the temperature was maintained until the end of discharge. An electrochemical test instrument (Model CT2001A of the Wuhan Land Electronic Co. Ltd., China) was employed to measure discharge properties. With these measurements, total polarization (η_{total}), which is equivalent to effective cell resistance (R_{cell}), is calculated by the following equation: [1,4,5]

$$\eta_{total} = R_{cell} = \left(delta\ V_{pulse} \right) / \left(delta\ I_{pulse} \right)$$

3. Results and discussion

The processes of preparing CoS$_2$/CNTs composites and electrodes are depicted in Scheme 1. The composite formation basically comprises the following steps: (a) dispersion of CNTs in an SDBS solution; and (b) hydrothermal growth of CoS$_2$ with cobaltous acetate (Co(CH$_3$COO)$_2$) and sodium thiosulfate (Na$_2$S$_2$O$_3$) as reactants, in the presence of CNTs. XRD analysis of the reaction products (for both CoS$_2$/CNTs and bare CoS$_2$), as shown in Fig. 1, gave diffraction peaks which can be assigned to the planes of cubic CoS$_2$ (JCPDS, No. 65-3322). On the other hand, the diffraction peak of CoS$_2$/CNTs at $2\theta = 26.3°$ can be assigned to the (002) plane of the graphite-like structure of multi-walled carbon nanotubes. The intensity of this peak due to the presence of CNTs is very weak because the concentration of CNTs in the CoS$_2$/CNTs composite is merely 5% by weight. This characteristic is consistent with previous studies on nanocomposites comprising CNTs, Ni, and SiC [21]. It is also important to note that for all cathode samples prepared with the present processes showed no measurable diffraction peaks other than those derived from CoS$_2$ and CNTs. This observation implies that there are neither any chemical impurities nor any Co−S compounds other than CoS$_2$ in the cathode samples studied in this work.

In order to better verify the presence of cubic CoS$_2$ and CNTs in the nominal CoS$_2$/CNTs samples, these samples were further examined by Raman spectroscopy. The Raman results, as shown in Fig. 2, confirm that bare CoS$_2$ prepared in this work indeed gave Raman peaks at 287, 314, 389, 414 cm^{-1} and these are the respective reference positions for the E$_g$, T$_g$(1), A$_g$, and T$_g$(2) modes of cubic CoS$_2$ [22,23]. All CoS$_2$/CNTs composite samples prepared in this work also gave these Raman features. Hence, these Raman and XRD analyses consistently confirm that all cathode materials prepared in this work comprise no Co−S compounds other than cubic CoS$_2$. For the CoS$_2$/CNTs composite samples, Raman spectroscopy also confirmed the presence of a pair of Raman peaks at 1350 and 1590 cm^{-1} – characteristics of nano-carbon materials such as nano-diamond, nano-graphite, and CNTs. The relative intensity ratio of these two peaks (I_D/I_G) was always close to 1.14, and this ratio matches the reported value of multi-walled carbon nanotubes [24].

Regarding thermal stability of the cathode materials prepared in this work, the thermogravimetric analysis results of such cathode samples, as shown in Fig. 3, give evidence that the bare CoS$_2$ samples typically decomposed at 640 °C and the CoS$_2$/CNTs composite samples decomposed at 625 °C. The results are consistent with the decomposition properties of CoS$_2$ reported earlier by Guidotti et al. [7] It is worth mentioning that these decomposition temperatures are about 100 °C higher than that of FeS$_2$ [6], and about 200 °C higher than that of CoS$_2$ nanocrystals [19]. Such a comparison first confirms that using the cathode materials of CoS$_2$ or CoS$_2$/CNTs prepared in this work to replace FeS$_2$ can indeed raise the high-temperature operation range of thermal batteries from 500 °C to about 620 °C; in addition, the comparison also suggests that decreasing the crystal size of CoS$_2$