

Short communication

Synthesis and characterization of nanosize cobalt sulfide for rechargeable lithium batteries

J. Wang^{a,*}, S.H. Ng^{a,c}, G.X. Wang^{a,c}, J. Chen^{b,c}, L. Zhao^a, Y. Chen^a, H.K. Liu^{a,c}

^a Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

^b Intelligent Polymer Research Institute, University of Wollongong, NSW 2522, Australia

^c ARC Centre for Nanostructured Electromaterials, University of Wollongong, NSW 2522, Australia

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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.

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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 Co₃O₄ with SO₂ 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 syn-

thesized 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, FeCl₃ solution,

* Corresponding author. Tel.: +61 2 4221 5722; fax: +61 2 4221 5731.
E-mail address: jjazhao@uow.edu.au (J. Wang).

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 $\text{Cu K}\alpha$ 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 $1\text{ cm} \times 1\text{ cm}$ 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 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 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 aver-

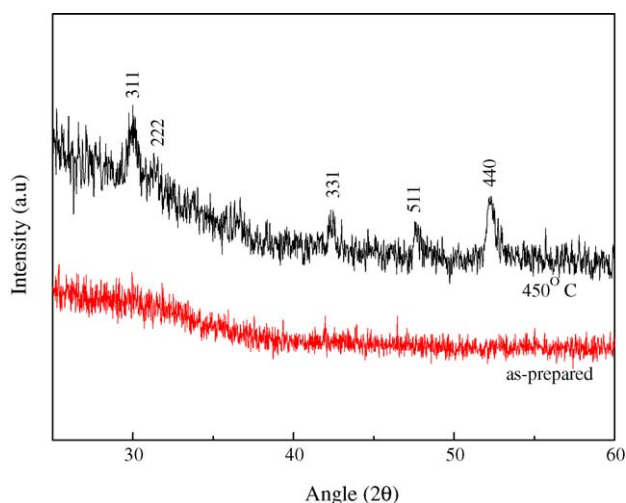


Fig. 1. X-ray diffraction patterns of cobalt sulfide powders.

age 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.: $Fm\bar{3}m$) 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.

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 $\text{Li}/\text{Co}_9\text{S}_8$ 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

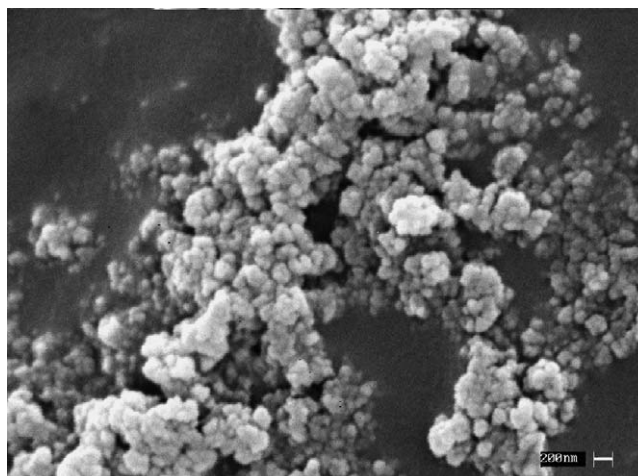


Fig. 2. SEM image of as prepared cobalt sulfide powder.

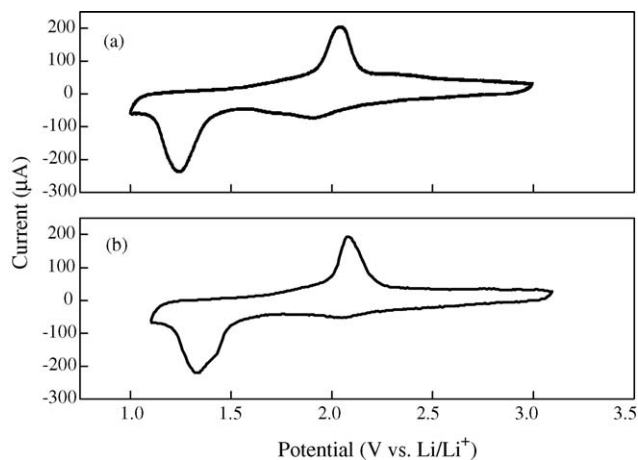
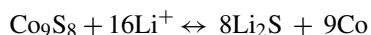


Fig. 3. Cyclic voltammograms of cobalt sulfides electrodes: (a) as prepared sample and (b) annealed sample.

versus Li/Li^+ . It is suggested that the $\text{Li/Co}_9\text{S}_8$ cell discharges in a two-step process [12]. Firstly, Co_9S_8 is transformed to an intermediate phase at 1.9 V, and then this phase is converted to Co at 1.25 V. The overall charge–discharge reaction of Co_9S_8 may be explained in following way:



From the CV results, it can be seen that the cathodic and anodic peaks appeared in the range of 1.0–3.0 V versus Li/Li^+ , so the potential range of 1.0–3.0 V versus Li/Li^+ is enough for charge–discharge cycling. Fig. 4 shows the charge and discharge curves for Co_9S_8 electrode made from as prepared and annealed materials. The discharge curves show two plateaus, which may be related to the two different reactions between cobalt sulfides, as the CV measurement has demonstrated.

Fig. 5 shows the discharge capacity versus the cycle number for cells made from as prepared and annealed samples with 10 wt.% carbon black. It can be seen that the discharge capacity of the cell made from the as prepared material is higher than with the annealed sample. However, the initial discharge capacities of the two samples are not high, being approximately 350 and

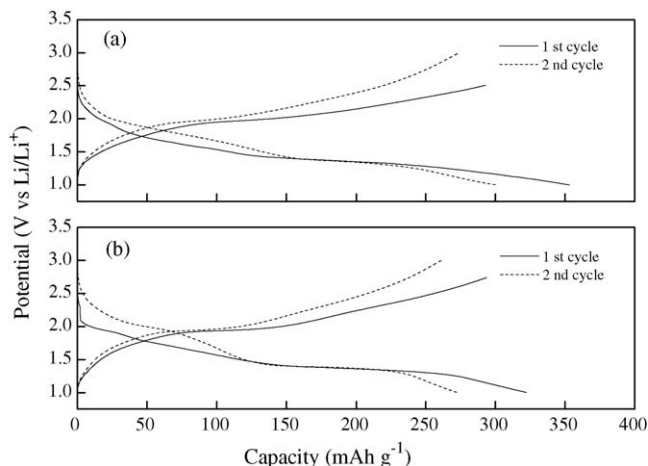


Fig. 4. The charge/discharge profiles of cobalt sulfide electrodes: (a) as prepared sample and (b) annealed sample.

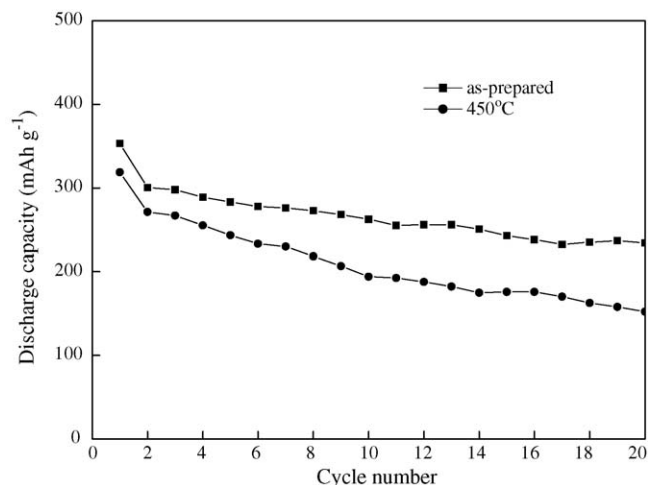


Fig. 5. Discharge capacities of cobalt sulfide electrodes with 10 wt.% carbon black vs. cycle number.

310 mAh g^{-1} for the as prepared and annealed samples, respectively. The capacity declined rapidly to about 230 mAh g^{-1} , that is 65% of the initial capacity after 20 cycles for the as prepared sample. For the sample annealed at 450 °C, the capacity decreased to about 50% after 20 cycles. The discharge capacities of these cobalt sulfides are quite low compared with the theoretical capacity (539 mAh g^{-1}). This may be due to the fact that cobalt sulfide is a semiconductor, with the conductivity just $1.63 \times 10^{-5} \text{ S cm}^{-1}$. Therefore, using 10 wt.% carbon black as an electronic conductor is not enough to get good results. In order to improve the electrochemical performance, the electronic conductor content in the electrode active materials was increased by the following methods:

- (i) Increase carbon black (electronic conductor) content from 10 to 20 wt.%.
- (ii) Firstly, 10 wt.% PPy powder was mixed with as prepared Co_9S_8 powder to form cobalt sulfide–polypyrrole composite. Then 10 wt.% of carbon black was added into the composite.

Recently, polypyrrole has been studied as an additive to improve the performances of cathode and anode materials in lithium-ion batteries [13–16], but using PPy powder as an additive for a cathode material in lithium-rechargeable batteries has not been explored. Therefore, the PPy electrode was cycled in the range of 1.0–3.0 V versus Li/Li^+ . The PPy electrode demonstrated an initial discharge capacity of 22 mAh g^{-1} ; the capacity declined with cycling, but remained stable after 10 cycles with the capacity at about 16 mAh g^{-1} .

Electrochemical impedance spectroscopy (EIS) was performed on the electrodes using as prepared Co_9S_8 with 10 and 20 wt.% carbon black, respectively. Impedance measurements were also conducted on the sample with 10 wt.% carbon + 10 wt.% polypyrrole powder as the electronic conductor. Fig. 6 shows the impedances results obtained for the cells of the three samples. The results indicate that the electrical impedance of the cell with 10 wt.% carbon black is much higher

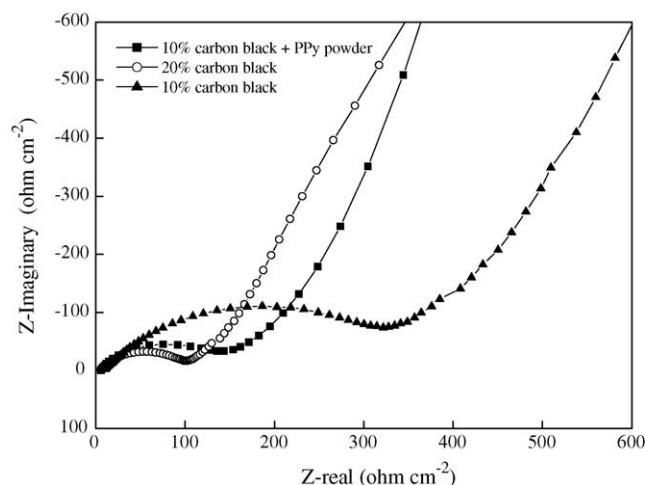


Fig. 6. ac impedance spectra of the samples with different electronic conductors.

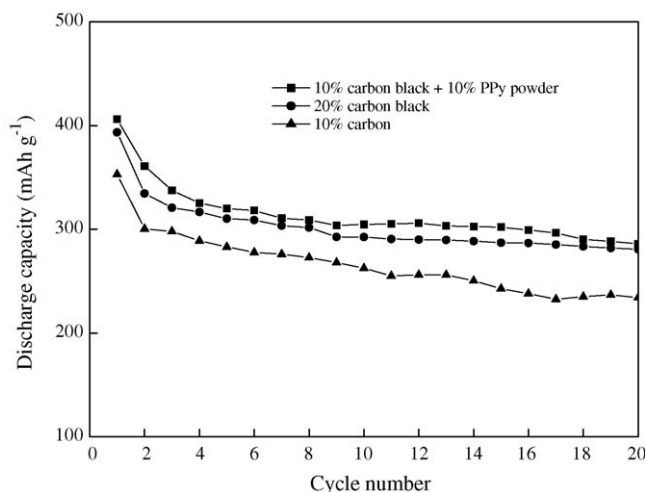


Fig. 7. Discharge capacities of cobalt sulfide electrodes with different electronic conductors.

than that of the cells with 20 wt.% carbon and 10 wt.% carbon black + 10 wt.% PPy powder. The impedance of the cells with 20 wt.% carbon black and 10 wt.% carbon black + 10 wt.% PPy are similar. It is obvious that the conductivities of these cells were improved by increasing the electronic conductors in the electrodes.

Fig. 7 shows the discharge capacity versus the cycle number for cells with different electronic conductors. The discharge capacities were improved with increasing carbon content in the electrode. This may be because the electrical impedance of the cells decreased with increased carbon content. Although the two kinds of electrodes contain the same content of electronic

conductors, the capacity of the electrode with 10 wt.% carbon black + 10 wt.% PPy is slightly higher than that of the electrode with 20 wt.% carbon black. This may be because the PPy powders can contribute some capacity in the electrode while it is used as an electronic conductor.

4. Conclusions

Nanosize cobalt sulfide powders were prepared by a simple chemical reaction method at room temperature. The possibility of using cobalt sulfide powder as a cathode material in lithium-rechargeable batteries was explored through electrochemical testing. Cyclic voltammetry measurements revealed that the Li/Co₉S₈ cell discharges in a two-step process. The discharge capacities were improved with increasing contents of electronic conductors in the electrodes.

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