Effect of Morphology on Electrochemical Performance of Chalcopyrite Cathode

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Abstract. Chalcopyrite was synthesized with various reaction precursors and solvents, and plate-, rod-, and sphere-like chalcopyrite can be obtained. Our results show that rod-like chalcopyrite has higher discharge capacity, better rate capacity and cycle performance than others.

1. Introduction
The successful development of a lithium/sulfide battery which has been regarded as one of the candidates for next generation battery requires extensive research on the electrochemical behaviors of positive electrode. Among lots of candidates of cathode materials, FeS₂ has attached a lot of attentions because of its high capacity, low weight, low cost and low toxicity [1-3]. Recently, our research group has synthesized the plate-like transition metal sulfide CuFeS₂ with solvothermal method and investigated its electrochemical performance as cathode for lithium battery [4]. Several of researchers reported that the morphology of cathode material has greatly impact on electrochemical performance for lithium battery. Lai [5] reported the difference in electrochemical performance of Cu₂S cathode with different morphologies and pronounced rod-like Cu₂S was more suitable for cathode material. However, the difference in electrochemical performance of CuFeS₂ cathode with different morphology has not been reported.

In this paper, chalcopyrite CuFeS₂ was prepared solvothermally using variation of reaction precursor and solvent. It was found that by changing precursors and solvents several morphologies such as plate-like, rod-like and sphere-like CuFeS₂ were obtained and the electrochemical performance of these CuFeS₂ as cathode active species for lithium batteries was investigated.

2. Experimental

2.1. Synthesis of CuFeS₂
All reaction reagents were of analytical grade, and used without further purification. Appropriate amount of Iron sources and Copper sources and Sulfur sources Thiourea (Tu) with molar ratio 1:1:5 were used as starting materials, shown as Table 1. They were added to PPL (polyphenylene)-lined stainless steel autoclave filled with anhydrous Ethylenediamine (En) or anhydrous Ethanol (EtOH) up to 90% of the capacity (130ml). The autoclave was maintained at 230°C for 24h and then naturally
cooled to room temperature. After filtering, the precipitate was washed with CS₂, anhydrous ethanol, dilute-sulfuric acid (0.1mol/l), and distilled water several times, and then dried at 130℃ for 15h in vacuum. The obtained product was chalcopyrite CuFeS₂.

X-ray diffraction (XRD) measurements on powdered CuFeS₂ samples were performed on a Philips X'pert MPD X-ray diffractometer using CuKα radiation. Morphology of the powder CuFeS₂ was determined by field emission scanning electron microscopy (Hitachi, S-4800).

Table 1. Reaction precursor, solvent and Morphology

| Solvent | Iron Sources | Copper sources | Sulfur Source | Morphology |
|---------|--------------|----------------|---------------|------------|
| En      | Fe(NO₃)₃·9H₂O | Cu(NO₃)₂·3H₂O | Tu            | (a) Plate-like |
|         | 1g           | 0.65g          | 0.95g         |            |
| En      | FeCl₃·4H₂O   | CuCl₂·2H₂O     | Tu            | (b) Rod-like |
|         | 1g           | 0.6307g        | 1.408         |            |
| EtOH    | FeSO₄·7H₂O   | Cu(NO₃)₂·3H₂O | Tu            | (c) Sphere-like |
|         | 1g           | 0.87g          | 1.37g         |            |

2.2. Preparation of the cathodes

The prepared CuFeS₂ was used as cathode active species, carbon nanotube (Nachen Chemical, Beijing) and conducting graphite (Fuchen Chemical, Tianjin) the conducting species. Desired amounts of the CuFeS₂, the carbon nanotube, and conducting graphite were weighed in a weight ratio of 4:1:1, and placed in a stainless-steel vessel with 10 zirconic balls (10mm in diameter). Then the vessel was sealed with an O-ring in dry Ar atmosphere. Total amount of the mixture was 2g and the ball to sample ratio was 10:1. All manipulations were carried out in a glove box filled with dry Ar. Mechanical milling process was conducted by use of a planetary ball-milling apparatus (Fritsch, P-7) at a rate of 250rpm for 2h.

Polytetrafluoroethylene (PTFE) binder was added into the ball-milled mixture in 40wt% and some ethanol was introduced to produce more homogeneous paste by ultrasonic mixing for 30min. The paste was pressed into a film of about 100μm in thickness. The obtained film was dried at 130℃ for 15h in vacuum and then cut into a disc with a diameter of 10mm. The disc was used as cathode. Stainless steel collector, cathode, polypropylene separator (Celgard 2400), lithium anode and Stainless steel collector were sandwiched in a stainless steel battery holder. The battery was assembled in an argon filled glove box, and electrolyte was 1M LiPF₆ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (2:2:1 in volume). The assembled Li/CuFeS₂ batteries were held at 80℃ for 2h before discharging.

2.3. Characterization

Discharging curves was galvanostatically tested at a current density of 14 to 1172mA/g versus Li/Li⁺ using a Land CT-2001A instrument (Wuhan, China). The discharging cut-off voltage was 1.0V. Cycle performance was test at a current density of 1172mA/g, and the charging cut-off voltage was 2.5V. Cyclic voltammetry (CV) was carried out in a potential range of 1.0 to 2.8V versus Li/Li⁺ at a scanning rate of 0.1mV/s on Zahner IM6 electrochemical work station. All the tests were conducted at room temperature.

3. Results and discussion

The XRD patterns of samples synthesized with various reaction precursors and solvents are shown in Fig.1. All the diffraction peaks can be perfectly indexed as chalcopyrite CuFeS₂ ((JCPDS No. 65-1573)). No other peaks were found in XRD patterns, which indicating that pure CuFeS₂ can be obtained at 230℃ for 24h. Another important characteristic of the XRD patterns is peak intensity and full width at half maximum (FWHM). It should be noted that strong and sharp diffraction peaks appeared with En solvent and weak and broaden one obtained when EtOH was used as solvent. Strong
and sharp diffraction peaks indicate that the obtained products are well crystallized. According to Scherrer’s formula, the average grain size of rod-like and plate-like samples are 100nm and 108nm and only 18nm for that of sphere-like CuFeS2, respectively. The characteristics in crystallization degree should be resulted from the polarity of solvent [6, 7].

Figure 1. XRD patterns and SEM images of CuFeS2 with different morphologies

The SEM images of CuFeS2 with different morphologies are shown in Fig.2. On the one hand, using En as solvent, plate-like and rod-like CuFeS2 can be obtained with different iron precursors and copper precursors, as shown in Table 1 (Experimental section). The CuFeS2 with a hexagonal plate-like morphology has a thickness of about 200nm and a diameter of about 1.5μm (Fig.2a) and rod-like CuFeS2 has a length of about 0.5μm and a diameter of about 40nm (Fig.2b). On the other hand, using ethanol as solvent, sphere-like CuFeS2 was obtained with the diameter about 2.5μm (Fig.2c).

When En was used as solvent blue solutions were obtained as soon as the solvents were added into the autoclaves which indicated that the complexes were formed through the reaction between metal ions and solvent. It is believed that En plays a critical role in the formation of rod- and plate-like CuFeS2 particles. CuFeS2 prepared in ethanol in composed of uniform spherical particles, which were caused by the interface action between ethanol and the reactions. The reason behind the morphological change of the CuFeS2 particles might be due to the difference of the solubility of the metal salts in the solvent and the polarity of solvent [6-8].

It is interesting note that rod-like CuFeS2 aggregated by top connection and formed a hollow tube or hollow sphere as shown in Fig.2b, which is expected to provide sufficient electron transfer paths and enhance electrochemical performance of lithium battery.

Figure 2. SEM images of CuFeS2 with different morphologies

The discharge curves of CuFeS2 cathode with different morphologies are shown in Fig. 3. All the batteries show two discharge plateaus at 1.75V and 1.5V, respectively, which is coincident with our
previous report. The initial discharge capacity of rod-like CuFeS$_2$ cathode is higher than those of other cathodes with plate or spherical morphologies, which is up to 1300mAh/g. Moreover, rod-like CuFeS$_2$ cathode has the significant and flat discharge plateaus at both voltages, while such characterization was not observed for plate- or sphere-like CuFeS$_2$ cathode whose plateaus are slight slope at 1.75V.

![Figure 3. Discharge curves of Li/CuFeS$_2$ battery with different morphologies at 14mA/g](image)

Fig. 3. Discharge curves of Li/CuFeS$_2$ battery with different morphologies at 14mA/g

Fig. 4 shows the discharge curves of Li/CuFeS$_2$ batteries at various current densities. The curves indicated that rod-like CuFeS$_2$ has better rate capability than other two cathodes. Even at the current density of 586mA/g, the special capacity is still up to 565mAh/g. In order to identify the difference in electrochemical performance of these cathodes, we investigated the impedance of the batteries with plate-, rod- and sphere-like CuFeS$_2$ as cathode active material before discharge (Fig.5). Rod-like CuFeS$_2$ cathode has the lowest resistance of 90 Ω at 20°C lower than that of sphere-like CuFeS$_2$ cathode (247Ω). Lower resistance results from the short diffusion length of and high contact area between active materials and electrolyte. Li ion diffusion is highly dependent on the transport length and accessible sites on the surface of active materials. Thus, the cathode shows low resistance usually shows high Li ion storage capacities, especially at high current rates [9]. Rod-like CuFeS$_2$ aggregated into hollow tube or sphere by end to end, which results in a large contact area and much more electron transfer paths. Thus, rod-like CuFeS$_2$ active materials have a lower resistance than other two CuFeS$_2$ which results in a larger discharge capacity and rate capability.

![Figure 4. Discharge performance of Li/CuFeS$_2$ battery at different current density](image)

Figure 4. Discharge performance of Li/CuFeS$_2$ battery at different current density
Figure 5. Impedance spectra of CuFeS$_2$ Cathode with different CuFeS$_2$ as cathode active species before discharge

Fig.6 shows the cyclic voltammograms obtained for the Li/CuFeS$_2$ battery at room temperature. With rod-like CuFeS$_2$ as active material, battery has three reduction peaks at 2.0V, 1.6V and 1.2V, respectively and an apparent oxidation peak at 1.9V. The reduction peak at 2.0V is associated with oxidation of some residual S ($S^2-/S_0$ or $S_2-/S_2^{2-}$) in as-prepared CuFeS$_2$ sample or some impurities such as oxide on the surface of Cathode [10] and the peaks at 1.6V and 1.2V correspond to the discharge plateaus in Fig.1. The battery with plate-like CuFeS$_2$ as cathode material has the same reduction/oxidation peaks voltages as those of rod-like battery, but the current decrease, which result from the higher resistance of plate-like CuFeS$_2$ species. As for sphere-like CuFeS$_2$ as cathode material, the current is lower than that of other two batteries because of its highest resistance, moreover the position of reduction/oxidation peaks are different from other two batteries. This result indicated that reaction mechanism between cathode and electrolyte change greatly. Further researches on reaction mechanism of the Li/CuFeS$_2$ battery with sphere-like CuFeS$_2$ as cathode active species are in study and will be reported later.

Above results indicated that among the three types of CuFeS$_2$ powder, the rod-like CuFeS$_2$ was found to be better for lithium battery cathode because of its lower resistance and larger contact area. So cycle performance of rod-like CuFeS$_2$ cathode was also investigated as shown in Fig.7. During cycling, the current density was enhanced to 1172mA/g and the initial discharge capacity was 517mAh/g and two discharge plateaus at 1.5V and 1.2V appeared (Fig.7a). Comparing with the discharge curve in Fig.1, the plateau voltage decreased with current density increasing, which results from polarization of electrode because of aggregation of Lithium ion on the surface of Cathode.

Figure 6. CV curves of Li/CuFeS$_2$ battery at room temperature
As the cycle number increases, the capacity of the battery decreases. After 25 cycles the capacity remains 150mAh/g, which indicates that Li/CuFeS2 battery has certain reversibility at room temperature. However, it is noting that the degenerate rate of Li/CuFeS2 is high. The rapid degeneration of Li/CuFeS2 battery results from several reasons. Firstly, during cycle processing, volume of cathode changed dramatically, which deteriorate electrical contact of cathode and cut-off the electron transfer paths. As a result, the internal resistance of cathode raised and capacity decreased [11, 12]. The SEM images of cathode before and after discharge at current density of 1172mA/g are shown in Fig. 7. Before discharging, the cathode is compactly (Fig. 7a) and then become loosely (Fig. 7b) after several cycles. Secondly, lithium reacts with sulfide to form dissolvable polysulfide, which not only expense the active material in battery but also enhance the resistance of electrolyte [13-15]. In present study, the electrolyte became nepheloid after several cycles. Moreover, quite different from the intercalation of Li+/e− in a host structure such as LiCoO2 and LiFePO4 cathode, reduction of transition metal sulfides forms another material. The inversed reaction usually required a large amount of energy, as the reversible of Li/FeS2 battery at high temperature [16]. Perhaps, the stable cycle performance of Li/CuFeS2 battery will be obtained at high temperature.

4. Conclusion
Chalcopyrite CuFeS2 with different morphologies was synthesized by solvothermal process. The morphology is strongly dependent on reaction precursors and solvent polarity. The rod-like CuFeS2 was used as a cathodic active material has two apparent discharge plateaus and its room-temperature specific discharging capacity was 1300mAh/g at a current density of 14mAh/g in a cut-off voltage of 1.0V. Though increase in current density caused a decrease in discharging capacity, it was more than 565mAh/g at a current density of 586mA/g. Battery with rod-like CuFeS2 as active species shows certain reversibility at current density of 1172mA/g, after 25 cycles the capacity remain 150mAh/g. The mainly reasons for degenerate of battery are volume change of cathode, dissolvable polysulfide and required inversed reaction energy.
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