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Ether based electrolyte improves the performance of CuFeS₂ spike-like nanorods as a novel anode for lithium storage



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ABSTRACT

This paper firstly reports a facile hydrothermal method to prepare CuFeS₂ spike-like nanorods as a promising anode material for lithium ion batteries. When being evaluated as an anode material in traditional carbonate-based (EC/DEC/DMC) and ether-based (DOL/DME) electrolytes, it's found that the type of the electrolytes plays a key role in contribution to the electrochemical performance. The CuFeS₂ binary mental sulfide material has initial discharge capacities of 632.6 mAh/g in the carbonate-based electrolyte and 674.9 mAh/g in the other at the rate of 0.2 C. After 50 circles, the discharge capacity decays severely, down to 64.3 mAh/g while the one performed in the ether-based electrolyte still possesses a capacity of 425.3 mAh/g, whose capacity retention is far more higher. Besides, an outstanding rate capability (~190 mAh/g) can be obtained at a high rate of 10 C in the ether-based electrolyte, which is indicative of becoming promising anode materials for high-rate lithium batteries.

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1. Introduction

Nowadays, increasing the energy density of battery has become one of the most urgent issues due to the huge demand of grid scale application and vehicle electrification [1–4]. As a new class of anode electrode material, metal sulfides have many advantages such as high capacity and energy density. Therefore, large scale of researches has been done on different kinds of metal sulfides as electrode material for the energy storage system [5–11]. Among these metal sulfides, CuFeS₂ as hopeful electrode material has a high theoretical capacity (the specific capacity is 587 mAh/g, the specific energy is 881 Wh/kg) and a good electrical conductivity (10^3 S/cm at 100 K) [12]. As we know, LTO is a commercial anode material with discharge voltage plateau (1.55 V). Compared with it (the specific capacity is 175 mAh/g and specific energy is 266 Wh/kg [13-16]), CuFeS₂ has the similar discharge plateau with higher specific capacity and energy. Besides, the plateau at around 1.5 V (vs. Li⁺/Li) is higher than the operating voltage of graphitic anodes so the formation of SEI layers and the electroplating of lithium can be avoided, which could improve the safety in LIBs. Therefore, CuFeS₂ material could be a promising electrode material for high-rate lithium storage material due to its good electrical conductivity and considerable specific

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capacity. Moreover, to the best of our knowledge, there are very few reports about the electrochemical studies of $CuFeS_2$ as anode material in Li ion battery fields. Mostly, it's regard as a kind of additive [17,18] or the cathode for lithium ion batteries [19] without stable cycle performance. How to improve the cycle stability of $CuFeS_2$ electrode has become a pivotal concern.

In this study, a facile hydrothermal method was presented to synthesized $CuFeS_2$ material. Meanwhile, the components of electrolyte are found to play a very important role in the cyclic stability of the $CuFeS_2$ material fabricated as anode, which means a great deal to the practical application of such kind material. When being evaluated in electrolytes of EC/DEC/DMC and DOL/DME, the capacity of the $CuFeS_2$ electrode fades quickly in the carbonate-based electrolytes, but shows a much better electrochemical performance in the ether-based electrolytes.

2. Experimental

2.1. Material Synthesis

All reagents were used without further purification and of analytical grade. In a typical process, $CuSO_4$ ·5H₂O (0.01 mol), $FeSO_4$ ·7H₂O (0.02 mol), $Na_2S_2O_3$ ·5H₂O (0.02 mol) and S powder (0.005 mol) were measured into the PTFE-line stainless steel autoclave with a volume of 100 mL, which was then filled with 50 mL deionized water. The autoclave was sealed and maintained at 210 °C for 24 h, then was took out and cooled down to room

temperature naturally. The precipitates were filtered off and washed with deionized water and anhydrous alcohol sequentially to remove the residual impurities. Then the product was transferred to oven to dry at $60 \,^{\circ}$ C for 8 h before further processing.

2.2. Structure characterization

The dried products were characterized by X-ray diffraction (XRD, Rigagu/mini Flex 600) with a Cu K_{α} radiation with scanning step of 2°/min. The operating voltage and current were 40 KV and 15 mA, respectively. And the morphologies were characterized with scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100).

2.3. Preparations of electrode and electrochemical measurement

The working electrode consisted of the active material (70%), acetylene black (15%) as the conductive agent and PVDF (15%) with N-methyl pyrrolidone as the solvent. Then the slurry was coated onto a 20 μ m aluminum foil. A lithium metal was used as the counter electrode in the cell.

Electrochemical performances were investigated in CR2016 coin-type cells which were assembled in an argon-filled glove box. With the Celgard 2400 as the separator, the material was tested using 1 M LiPF₆ dissolved in ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC/DEC/DMC in the 1:1:1 volume ratio) and 1 M bistrifluoromethanesulfonimide lithium salt



Fig. 1. SEM images of the synthetic CuFeS₂ (a, b) and elemental mapping of Cu(c), Fe(d), S(e) & superposed one (f), (g) EDX analysis of CuFeS₂.

(LiTFSI) dissolved in 1, 3-dioxolane and dimethyl ether (DOL/DME in the 1:1 volume ratio), respectively. The charge-discharge tests were conducted on Land battery program-control system at different rates in the voltage range between 1.0 V and 3.0 V. Cyclic voltammetry (CV) was carried out on CHI 1030 C electrochemical workstation and recorded at a scan rate of 0.2 mV/s from 1.0 V to 3.0 V. All the electrochemical performance tests were conducted at room-temperature.

3. Results and Discussion

SEM structural study of the prepared CuFeS₂ is shown in Fig. 1. From the figure, the CuFeS₂ synthesized by hydrothermal method is in spike-like nanord shape and composed of micron-sized secondary particles stacked with nanometer-size primary particles, which is optimal for practical usage as electrode materials. The formation process sketch map of spike-like nanorods is shown in Fig. S1. Firstly, the crystal nucleus was formed and grew up into grains. Secondly, the grains accumulated together and formed the spike-like nanorods. From Fig. 1c-e, it could be observed that the Cu, Fe and S elements are uniformly distributed, and the superposed one shown in Fig. 1f can demonstrates more clearly. Fig. 1g shows that the atomic ratio of Cu/Fe/S is 1:1.15:1.85, which is close to the stoichiometry of CuFeS₂.

The XRD patterns of the CuFeS₂ powders are shown in Fig. 2a. Sharp diffraction peaks of the sample signify good crystallization and all can be indexed to the CuFeS₂ standard card (PDF card No.065-1573), except the two little peaks (31.9°, 33.1°) which are ascribed to CuS (PDF card No.065-3931). In order to prove that the nanorods are not hollow-structure and show more clearly the morphology of spike-like nanorods, TEM test was employed which is showed in Fig. 3. As can be seen, the structure is solid structure and spike-like, which is consistent with the results shown in Fig. 1. The high resolution TEM (HRTEM) image in Fig. 3b reveals that the morphology of nanorod is well-defined with good crystallization and the lattice spacing is 0.3 nm, corresponding to the (112) crystal plane of CuFeS₂.

It's reported that the ion valence state of Cu and Fe in CuFeS₂ are +1 and +3, respectively [20]. And it's understandable that the Cu²⁺ was reduced due to the reducibility of Na₂S₂O₃ and Fe²⁺. The formation process could be summarized as follow [21,22]:

 $FeSO_4 + CuSO_4 + Na_2S_2O_3 + H_2O \rightarrow CuFeS_2 + Na_2SO_4 + H_2SO_4$

In traditional preparations, Cu^+ , $(NH_4)_2S$ are usually used as the raw material [23,24] or organics as the solvents [19,24,25]. As we know, Cu^+ is more unstable than Fe^{2+} within the same system and the cost of production of thiourea is higher than $Na_2S_2O_3$, so taking

advantage of Fe^{2+} salt and thiosulfate as raw material is more attractive in consideration of cost. Usually, the reducing atmosphere could be provided by solvents like ethylenediamine [19]. Although it is an effective way to synthesize such kind material, it is not a desirable way because the organic solvents are unfriendly to the environment. Compared with the methods mentioned above, it is more attractive and environment-friendly to use the Cu^{2+} , Fe^{2+} and deionized water as the raw material and solvent, respectively.

In order to get insight into the electrochemistry, the cyclic voltammetry test of CuFeS₂ electrode was conducted as shown in Fig. 4. A sequence of peaks, linked with electrochemical processes involving with the formation of intermediate by lithium insertion and conversion reaction are observed. In the first cathodic scan tested in the carbonate-based electrolyte, four peaks at 2.01 V, 1.73 V, 1.65 V and 1.29 V are observed in Fig. 4a. The peaks at 2.01 V and 1.65 V are associated with the electrochemical reaction of residue CuS [26], which is in good accordance with the XRD result discussed above. The peak at 1.73 V represents the formation of intermediates, Li_xCuFeS₂ [27]. And the cathodic peak at 1.29 V would be ascribed to the conversion reaction: $Li_xCuFeS_2 + xLi \rightarrow$ $Cu + Fe + xLi_2S$ [17,19]. In the successive cycles (10 cycles), the cathodic peaks at 1.73 V and 1.65 V disappear while the peak at 2.01 V still exists. The cathodic peak at 1.29 V shifts to 1.39 V, which is consistent with the result reported by W Ding et al. [19]. For the process of oxidation, three anodic peaks at 1.90 V, 2.40 V and 2.52 V are observed apparently. The peak at 1.9 V is corresponding to the reverse cathodic reaction at 1.29 V peak and the peaks at 2.40 V and 2.52 V are related with the formation of intermediates by lithium insertion mentioned above.

In Fig. 4b, the electrochemical behavior of the first cycle is similar. The difference appears in subsequent scanning. The cathodic peak located at 1.98 V becomes a broad peak but does not disappear completely. The cathodic peak at 1.70 V shifts towards lower voltage to 1.62 V while the peak at 1.29 V shifts higher voltage to 1.44 V. It is noteworthy that in carbonate-based electrolyte, the peak in the same location just shifts to the peak at 1.39 V, which illustrates that the polarization is larger than that in the ether-based electrolyte. During the anodic sweep, there are corresponding anodic peaks at 1.84 V and 2.11 V, while the peaks at 2.42 V and 2.52 V have disappeared in the successive scanning. Taken together, it is notly observed that the cathodic and anodic current peaks decrease more in the carbonate-based electrolyte than that in the ether-based electrolyte after subsequent scanning of 10 cycles. It is indicated the electrochemical performance in ether-based electrolyte is better than that in carbonate electrolyte and more details would be shown later.



Fig. 2. (a, b) XRD pattern of synthetic CuFeS₂ compared with the corresponding standard material card.



Fig. 3. (a)TEM images and (b) the HRTEM image of CuFeS₂.

The charge–discharge voltage profiles of Li/CuFeS₂ cells were tested in the voltage range of 1.0 V-3.0 V at the rate of 0.2 C (1C=587 mA/g), as shown in Fig. 4c, 4d. During the discharge process of the initial cycle, both curves show four voltage plateaus at 2.05 V, 1.76 V, 1.65 V and 1.51 V. There are three voltage plateaus at 1.78 V, 2.32 V and 2.45 V in the charge process of the 1st cycle. As mentioned above, the plateaus at 2.05 V and 1.65 V of the initial discharge process correspond to the reduction of CuS [26].

 ${S_2}^{2-} + 2e^- \mathop{\rightarrow} 2\,S^{2-}\,\,2.05\,V$

 $Cu^+ + e^- \rightarrow Cu \ 1.65 V$

The plateaus at 1.76 V and 1.51 V are related with the electrochemical reactions as follows [17,19,27]:

 $CuFeS_2 + xLi \rightarrow Li_xCuFeS_2$ 1.76 V

 $Li_xCuFeS_2 + xLi \rightarrow Cu + Fe + xLi_2S$ 1.52 V

While in the charge process, the electrochemical reactions are not completely reversible. There are just three voltage platforms (1.78 V, 2.32 V and 2.45 V) in both ether and carbonate based electrolytes. The mechanism related with the charge process is rarely mentioned except for the Fong R's group [27], which still needs more studies and explorations.

In the DOL/DME electrolyte, the charge voltage plateaus (2.32 V, 2.45 V) of Li/CuFeS₂ cell almost disappear in the third cycle and the initial discharge specific capacity is 674.7 mAh/g, which is higher than that in EC/DEC/DMC with the initial discharge specific capacity of 632.6 mAh/g, as shown in Table 1. The extra capacity may be due to the intercalation mechanism as below. Take the 1st discharge curve for example, the platform at around 1.8 V is associated with the formation of intermediate, Li_xCuFeS₂, a kind of intercalation compound which contributes more than 60 mAh/g of capacity, which is relevant to the charge-discharge current density and working temperature [28–30]. In EC/DEC/DMC electrolyte, the discharge specific capacity of CuFeS₂ is 527.9 mAh/g, but 558.8 mAh/g in DME/DOL electrolyte in the third cycle. From data



Fig. 4. Cyclic voltammetry profile of CuFeS₂ electrodes cycling in: a) EC/DEC/DMC. b) DOL/DME electrolyte and the charge-discharge curves performed in: c) EC/DEC/DMC. d) DOL/DME at a rate of 0.2 C in the voltage range of 1.0-3.0 V.

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The first 3 cycles of charge-discharge in two kinds of electrolytes at 0.2 C rate.





Fig. 5. The cycling performance of Li/CuFeS₂ cells performed in: a) EC/DEC/DMC. b) DOL/DME current rate of 0.2 C in the voltage range of 1.0–3.0 V and c) rate capabilities of CuFeS₂ at various current rates from 0.2 C to 10 C.

above, it could be noted that the capacity decays more severely in the EC/DEC/DMC electrolyte than that in the DOL/DME electrolyte and the result fits reasonably well with results shown in cyclic voltammetry measurement.

Fig. 5a and b demonstrate the cycle performance of the Li/ CuFeS₂ cells at the current rate of 0.2 C. In Fig. 5a, the dramatic capacity decay is observed and the capacity retention falls to 10.1% after 50 cycles (as shown in Table 2). However, although a slight decay in capacity occurs upon cycling in the DOL/DME electrolyte, no sign of severe capacity failure is observed. The capacity retention is 63.0% after 50 cycles, which shows much better cyclic stability compared with that in the carbonate-based electrolytes. In order to compare more clearly in two cases, the cycle performance data are listed in Table 2. The capacity fades quickly in the first 20 cycles and the coulombic efficiency can hardly achieves 100% in the carbonate-based electrolyte, while the much better result can be obtained in the ether-based electrolyte. Although the charge and discharge process of CuFeS₂ isn't involved in high order polysulfides species, one of discharge products- Li₂S, is incompatible with carbonate-based solvent as well, which could cause severe capacity fading [31,32]. Besides, the properties of CuFeS₂ are similar with copper sulfides, for which the ether-based electrolytes are more appropriate than the carbonate-based electrolytes [33]. When being tested as electrodes in EC/DMC (LiPF₆) and DOL/DME (LiTFSI), rapid capacity fading is observed in cells containing carbonate-based electrolytes in the first several circles, while an excellent electrochemical reversibility can be obtained in ether-based can greatly improve the cycle stability of CuFeS₂ material fabricated as an electrode. The results, combined with the data from CV measurement and charge–discharge test, are good indications that the DOL/DME electrolyte is more suitable for CuFeS₂ electrode.

Fig. 5c shows the outstanding rate performance for the Li/ CuFeS₂ cell. When the applied C rate is progressively increased from 0.2 C to 10 C rate (1C = 587 mA/g), the data shows no dramatic

Table 2

The	cvcling	performance	of Li/CuFeS	cells at 0.2 C	performed in: a) EC/DEC	/DMC and b) DOL/DME
	-,	P			P	/ /		/ /

Electrolyte	Discharge capacity of 1st cycle $(mAh g^{-1})$	Discharge capacity of 20th cycle $(mAhg^{-1})$	Discharge capacity of 50th cycle $(mAh g^{-1})$	Capacity retention (%)
EC/DEC/DMC	632.6	161.8	63.4	10.1
DOL/DME	674.9	483.8	425.3	63.0

capacity fade when the rate is restored to 0.2 C after 40 circles of rate testing. As be seen, the discharge capacity of the first cycle at 0.2 C is 585.3 mAh/g. Capacities maintain at around 415, 380, 320, 260 and 190 mAh/g as the rate increases from 0.5 C to 10 C, respectively. The capacity returns to around 420 mAh/g under a small rate of 0.2 C, suggesting the rate performance is excellent and could be a promising electrode material for high-rate lithium storage material.

4. Conclusions

In summary, the CuFeS₂ spike-like nanorods were successfully prepared by a simple hydrothermal method with relatively lowcost raw material. In traditional carbonate electrolytes (EC/DEC/ DMC), the capacity of the spike-like nanorods CuFeS₂ electrode fades quickly, but shows a much better electrochemical performance in the ether-based electrolytes (DOL/DME). The capacity retention cycling in EC/DEC/DMC at 0.2 C is 10.1% after 50 cycles, while the ether is 63.0% in the same condition. And the material shows excellent rate capability and the discharge specific capacity still remains about 190 mAh/g at 10 C. Thus, we believe that the binary metal sulfide CuFeS₂ could be promising anode materials for high-rate lithium batteries by making use of ether-based electrolytes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2015.01.141.

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