FeS₂ microsphere as cathode material for rechargeable lithium batteries

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Abstract

The spherical pyrite FeS₂ was synthesized through a green and simple method with the addition of the polyvinylpyrrolidone (PVP) dispersant. The as-prepared FeS₂ displays a good electrochemical performance with an initial specific capacity over 80% of the theoretical value and a very low decay rate of 0.33% per cycle (calculated from 2nd to 50th at 0.1C). Rate capability testing exhibits a discharge capacities of around 371.6 mAh/g (0.1C), 343 mAh/g (0.2C), 294.9 mAh/g (0.5C), 239 mAh/g (1C) and 161.8 mAh/g (2C) respectively. Besides, coulombic efficiency close to 100% at various rates can also be obtained. We calculate Li⁺ diffusion coefficient and multi-electron feature of the pyrite FeS₂ during charge/discharge process. It shows that smaller potential window is beneficial for cyclability, which was in good agreement with experimental results.

Keywords: Electrode materials; FeS₂; lithium battery; PVP

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1. Introduction

In the past few decades lithium batteries have been widely used in portable electronic devices, electric vehicles, etc. Due to the rapid development of electric cars and hybrid vehicles, research on batteries with high energy density and excellent cyclability is imperative[1]. High specific capacity transition metal sulfides have drawn growing attention from researchers as cathode material for lithium batteries due to their high specific capacity. Pyrite FeS_2 , as a natural abundant, low-cost, high theoretical capacity material (890 mAh/g) is being used in the commercial primary lithium batteries (Li- FeS_2)[2-6]. Moreover, in recent years, studies have shown that FeS_2 with conversion reaction mechanism can also be utilized in the secondary lithium batteries and shown to have many advantages[7]. First of all, since FeS_2 produces lithium sulfide and metal iron during the discharge process, lithium sulfide tends to grow on iron, which improves the utilization of lithium sulfide, and enhances cyclability of FeS_2 cathode. More importantly, there is no direct formation of lithium polysulfide upon cycling which inhibits the shuttle effect and thus a high coulombic efficiency can be delivered[7].

Despite all the above merits, many issues have been attributed to the poor cyclability of FeS_2 [8],[9]. Firstly, most commercial Li- FeS_2 batteries use natural FeS_2 which has impurity[10]. Secondly, electrode material can be converted to $\text{Fe}_{(1-x)}\text{S}$ causing loss of S during delithiation processes[7]. The sulfur gives rise to the formation of lithium polysulfides which is soluble in electrolyte solutions and thus leading to the shuttle effect[8].

To date, many attempts have been made to overcome the challenges mentioned above and improve the electrochemical performance of FeS_2 cathode. With nanostructured active materials, not only does the reaction kinetics improve, but also the instabilities caused by the effects of large volume

changes might be mitigated[11]. To avoid dissolution of lithium polysulfides, different electrolytes have been chosen such as fluoroethylene carbonate (FEC)[11], ionic liquid[12] and diglyme (DGM)[13]. Conductive phases such as carbon nanotube (CNT)[14], polyacrylonitrile (PAN)[15] and reduced graphene oxide (RGO)[16] have also been compounded with FeS_2 to enhance conductivity and reduce the volume effect.

Despite extensive research on pyrite FeS_2 , its formation mechanism has scarcely been studied. In the past years, Polyvinylpyrrolidone (PVP) has been applied as an important surfactant for morphology control, and various nanomaterials were successfully fabricated with the assistance of PVP[17]. It is found that PVP in the reaction mixture can prevent the randomly aggregation of nanocrystal and promote the assembly of these crystal into 3D microspheres[18]. In this study, spherical pure pyrite FeS_2 has been prepared via a green and simple hydrothermal method using PVP as the surfactant. The as-prepared pristine FeS_2 with smaller size and pure pyrite phase shows good cyclability in lithium batteries. The FeS_2 cathode was not fully charged to avoid loss of S and a very low capacity fading (0.33%) was achieved compared to previous reports (1.09%[19]).

2. Experimental procedure

2.1 Preparation of FeS_2

In a typical experimental procedure, 5 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10 mmol $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 1 mmol PVP were added into 40 ml distilled water followed by continuous stirring for 30 min to form a clear solution. Then the mixture was transferred to a teflon-lined stainless autoclave (100 ml) with the addition of another 40 ml distilled water under stirring for 15 min. The autoclave was sealed and maintained at 180 °C for 24 h. After cooling to room temperature naturally, the resulting black solid products were collected by vacuum filtration, washed with distilled water and alcohol several times to

remove the sodium and sulfur, and finally dried at 60 °C and utilized for further characterization.

2.2 Material characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer operating with Cu K α radiation (2 θ from 10° to 85°, with steps of 0.02°, and a counting time of 0.2 s per step). Scanning electron microscopy (SEM) images were taken on a scanning electron microscope (HITACHI S-3400) to further characterize the morphology and structure of the products.

2.3 Electrochemical characterization

Test coin cells were assembled in a dry argon-filled glove box with the working electrode consisted of FeS₂ (70%), acetylene black (15%), and PVDF (Polyvinylidene Fluoride, 15%) on the Al foil. Pure metallic lithium foil was used as a counter electrode. One layer of a glass fiber membrane with thickness of about 120 μ m was employed as a separator. The electrolyte was 1 M Lithium bis(trifluoromethane sulfonimide) (LiTFSI) dissolved in an ethylene carbonate (EC)/dimethyl carbonate (DMC) mixture (1:1, by volume). A normal battery has about 1 mg active materials on a 14 mm Al electrode. The batteries were tested by galvanostatic cycling in the voltage range of 1.0-2.4 V vs. Li/Li⁺ using a LAND CT2001A battery test system (Wuhan, China). Specific capacities were calculated based on FeS₂ mass. Electrochemical impedance measurements of the cell were performed on an Autolab PGSTAT302N Electrochemical Workstation (ECO CHEMIE B.V, Netherlands) with a Frequency Response Analyzer (FRA), and a small perturbation voltage of 10 mV in the frequency range from 0.1 Hz to 1 MHz was applied. All electrochemical tests were conducted at room temperature.

3. Results and discussion

The phase of the as-synthesized materials was characterized by XRD measurements as shown in

Fig. 1. Impurities of marcasite peaks can be found in sample a, which is a low temperature phase of FeS_2 without electrochemical activity. After the addition of PVP, phase purity improved a lot (sample b), all the diffraction peaks of the sample c and d could be indexed to pure pyrite phase FeS_2 . No impurity peaks were detected, indicating the successful preparation of highly pure FeS_2 . Moreover, the strong and sharp diffraction peaks hinted their high crystallinity.

Fig. 2a shows the influence of reaction time on the phase evolution of FeS_2 . Controlled experiments were carried out with specific reagents concentration ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}:\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}=1:2$) and a fixed amount of PVP (1 mmol) at 180°C . When the reaction time was kept as 3 h, decomposition of $\text{Na}_2\text{S}_2\text{O}_3$ and hydroxylation of FeSO_4 took place, yielding mixed products containing S, Fe_2O_3 , marcasite and pyrite, as was indicated by the XRD results. When the reaction time was further increased to 12 h, almost all the reactants were transformed into the pyrite phase, leaving only a few Fe_2O_3 detected in XRD. With further prolongation of the reaction time to 24 h, no impurity peaks were detected in XRD pattern. Fig. 2b shows XRD results for the samples without PVP at different reaction times. When the reaction time was kept as 3 h, the similar results can be obtained as the case with PVP. However, no obvious phase changes can be observed with the prolongation of the reaction to 12 h and even 24 h. Therefore, conclusions can be drawn that both proper amount of PVP dispersant and suitable reaction time were necessary for the synthesis of the pure pyrite FeS_2 .

SEM images of as-prepared FeS_2 with different amounts of PVP have been presented in Fig. 3 to further evaluate the role of PVP in FeS_2 formation. Inhomogeneous spheres assembled by nanosheets can be observed for the product without the use of PVP, as shown in Fig. 3a and 3b. Upon the addition of PVP (0.5 mmol), nanosheets vanished and microspheres with diameters ranging from $5\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$ appeared in Fig. 3c and 3d. When the amount of PVP was further increased, uniformly distributed FeS_2

microspheres displayed an average diameter of 10 μm , as can be seen in Fig. 3e and 3f.

On the basis of the above results, the growth process of the pyrite FeS_2 microspheres could be speculated including following three steps: an initial nucleation stage, a transformation stage and a crystal growth stage, which involved a fast nucleation of the S and Fe_2O_3 , followed by a slow transformation to main phase, then growth of the crystals. Firstly, lots of S can be produced by the facile decomposition of $\text{Na}_2\text{S}_2\text{O}_3$. At the same time, Fe_2O_3 nuclei are generated due to the hydrolysis of FeSO_4 . Potential nucleation and growth of Fe_2O_3 on the surface of S shall further give rise to the formation of assembly of nanosheets. With the addition of PVP surfactant, complete transformation of the mixed precursor into pyrite FeS_2 is favored, which is confirmed by the XRD results. Moreover, the important role of PVP as a capping agent should be taken into account, resulting in efficient constrain of nuclei growth [20-22]. Thus, well-dispersed FeS_2 microspheres can be eventually obtained with suitable amount of PVP. A summary of the synthetic route involving the possible role of PVP is illustrated in Fig. 4.

The electrochemical performance of FeS_2 as cathode for rechargeable lithium batteries has been investigated. In Fig. 5a, only one discharge plateau in all cycle can be observed, and the capacity of the second cycle was close to half of the first one, indicating FeS_2 was not fully charged. On the basis of previous studies by Strauss[7] and Yang[23], at room temperature and high discharge rate (more than 3 mA/g), Li^+ diffusion rate is so low that only Li_2S and Fe can be generated on the surface, resulting in one discharge plateau.

When partially charged to 1.8 V, the charge process can be schematically described by the following equation:

If fully charged to 2.6 V the charge process can be expressed by the following equations:

So different charge-discharge potential windows could bring about different electrochemical reactions in the Li-FeS₂ battery. According to Eq. (4), elemental sulfur would be generated when charged over 2.6 V, which would grow in following charge-discharge cycles, causing problems such as: loss of active substance, shuttle effect and inhibition of electrode reaction with lithium.

The influence of potential windows on the cyclability of FeS₂ can be observed in Fig. 5b.

Although higher discharge capacity in the first five cycles has been obtained with a larger potential window (1-3 V), worse cyclability can be observed since the capacity decayed faster. The electrode only has a capacity of 274.3 mAh/g after 50 cycles. On the contrary, when charged within a **smaller** potential range (1-2.4 V), a capacity of 371.5 mAh/g can be retained after 50 cycles, with a coulombic efficiency of almost 100% throughout the cycling process. Herein, the main reason of poor cyclability with higher charging cut-off voltage can be attributed to the incomplete conversion of Li₂FeS₂ to FeS₂ in delithiation process, generating more and more sulfur in the battery, along with reduced utilization of active material[25]. What's worse, shuttle effect would also be caused by elemental sulfur [26].

AC impedance in Fig. 5c spectroscopy showed that the impedance didn't change a lot even after 100 cycles within a potential range of 1 to 2.4 V (Equivalent circuit simulation showed in Table 1). Otherwise, the impedance increased rapidly once complete charged. It can be speculated that S hindered good contacts of electrodes and Li⁺, resulting in the increase of charge transfer resistance corresponding to poor electronic conductivity. Fig. 5d shows the plot of the imaginary resistance as a

function of the inverse square root of the angular frequency for FeS₂. A linear behavior was observed for frequency values ranging from 0.3 Hz to 0.1 Hz. The electrode after 100 cycles corresponded to the linear with a slope of 33.4 $\Omega s^{1/2}$, and the electrode after one complete charge and discharge corresponded to 11.4 $\Omega s^{1/2}$. Electron transfer number n could be calculated by the charge-discharge curve for these two electrodes, which was 1.66 for 100 cycles and 3.47 for the first cycle of one complete charge and discharge (n is calculated by the discharge capacity 371/775.7 mAh/g of two electrodes), respectively. As the diffusion coefficient of Li⁺ for FeS₂ can be calculated by using Eq. (5).

$$D_{Li} = 1/2 \times [RT/n^2 F^2 A C A_w]^{-2} \quad (5) [27]$$

Where R is gas constant, T is the temperature, A is the contact area between electrolyte and sample, F is the Faraday constant, and A_w is the slope of the linear function mentioned above. D_{Li} of these two electrode are calculated as 1.79×10^{-12} and 8.04×10^{-13} cm²/s, respectively, indicating that the lithium ion conductivity decreases with the larger potential window for discharge-charge process. As a consequence, a smaller potential window (1-2.4 V) was chosen for electrochemical measurements.

Cycling performances of the commercial as well as the as-prepared FeS₂ electrodes, at a rate of 0.1C between 1 to 2.4 V are presented in Fig. 5b, respectively. In the initial lithiation process, both the FeS₂ electrodes exhibited a high capacity of 859.3 and 741.1 mAh/g, over 80% of the theoretical value (890 mAh/g). After 20 cycles, the capacity of the natural FeS₂ electrodes faded rapidly which is less than 150 mAh/g. In contrast, the as-prepared spherical FeS₂ electrode showed much better cyclability, with a capacity of 396.6 mAh/g at the 20th cycle, and 371.5 mAh/g at the 50th cycle. The capacity retention of 85.2% (from 436 to 371.5 mAh/g, calculated from 2nd cycle because of incomplete charging) is obtained, with the decay rate as low as 0.33% per cycle.

Rate performance of the as-prepared spherical FeS₂ which completed 50 cycles at 0.1C was

studied. As can be seen in Fig. 5e, fifth-cycle discharge capacities of around 371.6 mAh/g (0.1C), 343 mAh/g (0.2C), 294.9 mAh/g (0.5C), 239 mAh/g (1C) and 161.8 mAh/g (2C) respectively, are found. Moreover, the discharge capacity of the FeS₂ electrodes returned to 373.2 mAh/g when the rate recovered from 2C to 0.1C. Besides, an excellent coulombic efficiency (close to 100%) at various rates can also be obtained. In brief, excellent cycling performance and rate capability of the FeS₂ cathode well demonstrated the stability of the structure and good conductivity of the spherical FeS₂.

4. Conclusions

In summary, this study showed the nucleation and growth of FeS₂ in a hydrothermal process and enhanced performance of the FeS₂ cathodes for lithium batteries. The spherical pyrite FeS₂ was synthesized using Na₂S₂O₃ and FeSO₄. With the addition of the PVP dispersant, the size of sulfur has been limited at the initial stage of the hydrothermal reaction and pure pyrite FeS₂ microspheres with smaller grain size has been obtained within a shorter reaction time. The as-prepared FeS₂ displayed good electrochemical performance with an initial specific capacity over 80% of the theoretical value and 371.5 mAh/g after 50 cycles at 0.1C rate. Calculation for Li⁺ diffusion coefficient of the pyrite FeS₂ in different potential window showed that smaller potential window is benefit for cyclability.

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Figure captions:

Fig. 1 XRD patterns of as-prepared powders obtained under different conditions a) without PVP, b) 0.5 mmol PVP, c) 1 mmol PVP, d) 2 mmol PVP

Fig. 2 XRD patterns of as-prepared powders obtained at different reaction time: a) using 1 mmol PVP; b) without PVP

Fig. 3 SEM images of FeS₂ obtained under different concentrations of PVP: a, b) 0 mmol; c, d) 0.5mmol; e, f) 1 mmol

Fig. 4 Schematics depicting the possible role of PVP in the synthesis of FeS₂ microspheres.

Fig. 5 a) Charge-discharge curves of FeS₂ electrode; b) Cycling performances of the commercial and the as-prepared FeS₂ electrodes at a rate of 0.1C; c) AC impedance spectroscopy of the FeS₂ electrode in different state; d) The plot of the imaginary resistance as a function of the inverse square root of the angular frequency for FeS₂ (Data obtained From Fig. 5c); e) Rate performance of the as-prepared FeS₂ electrode

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1 Equivalent Circuit Simulation for AC impedance spectroscopy of the FeS₂ electrodes in different state

	R1(Ω)	R2(Ω)	CPE1-Y0(μ Mho)	CPE1-N	R3(Ω)	CPE2-Y0(μ Mho)	CPE2-N	Zw-Y0(mMho)
Complete discharge	3.14	65.4	7.23	0.85	48.3	795	0.708	31.6
Charge to 2.4V	2.04	66.4	6.71	0.862	56.3	549	0.71	54.3
Complete charge	1.87	84	7.08	0.853	125	241	0.705	32.9
after 100 cycles	4.02	62.4	8.19	0.86	60.9	713	0.658	22.4