ORIGINAL ARTICLE

Production of highly pure iron disulfide nanoparticles using hydrothermal synthesis method

Asieh Akhoondi · Mahmoud Aghaziarati · Nahid Khandan

Abstract Hydrothermal synthesis of nanopyrite was investigated in a stirred reactor. The product was characterized by X-ray diffraction (XRD). The result indicated that the synthesized powder was a mixture of pyrite and elemental sulfur. Purification of pyrite was studied via various methods including; solvent extraction, reaction with Na_2SO_3 and thermal treatment. Before and after purification the synthetic powder was characterized by XRD and scanning electron microscopy. Finally, it was concluded that thermal treatment at temperature 300 °C for 2.5 h was the most appropriate condition to purify pyrite.

Keywords Hydrothermal synthesis · Nanopyrite · Sulfur · Solvent · Thermal treatment

Introduction

Because of environmental issues and high oil price, many countries are extensively developing hybrid electric vehicles. The success of these electric vehicles depends primarily on the performance of the battery. Due to the material low cost, many researchers have been performed on electrochemical properties of various metal sulfides such as FeS_2 (Kim et al. 2007). Iron disulfide has been used in commercial lithium primary cells (Montoro et al. 2004)

to power cameras, computers and watches; it has also been studied for applications in solar cells and electric vehicle batteries (Montoro and Rosolen 2003; Rezig et al. 1992; Siyu et al. 2009). Nanostructured FeS_2 used as the cathode material in thermal batteries resulted in improved electrochemical performance (Masset and Guidotti 2008; Strauss et al. 2003; Shao-Horn et al. 2002). It was found that the performance of nanoFeS_2 electrodes was superior to that of microFeS_2 electrodes (Shao-Horn et al. 2002). In addition to size, purity of pyrite influences Performance of battery, too. Presence of impurity such as sulfur decreases efficiency. Briefly, a thermal battery has a solid electrolyte which is converted to liquid phase in operational mode. In this situation, electrodes must have good resistance against heat and mustn't be decomposed or transformed to liquid phase. Sulfur decreases heat resistance of cathode. Also, evaporation of sulfur causes some problem and decreases electricity efficiency (Shao-Horn and Horn 2001). It is concluded that purification of pyrite is an important issue and must be studied extensively.

Many techniques of preparation were investigated in order to obtain nano pyrite. One of them is wet chemical synthesis. There are basically two pathways to produce pyrite in aqueous solution, i.e. (a) solvothermal and (b) hydrothermal production (Xuefeng et al. 2001; Kar and Chaudhuri 2004; Kar et al. 2004). Zheng et al. reported that they have prepared pyrite using $FeSO_4$, $Na_2S_2O_3$ and sulfur by a single stage hydrothermal method in the temperature range 90–280 °C for 24 h with average grain size of about 500 nm (Wu et al. 2004).

In this paper, nano pyrite was produced via hydrothermal process in a new way, using $FeSO_4$ and $Na_2S_2O_3$ without adding sulfur in a stirred reactor. Applying a stirred reactor is another innovation of this paper. In previous studies, a stainless-steel cylindrical impeller-free chamber

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was used to produce pyrite. Finally, the most appropriate method to purify pyrite was chosen.

Experiments

Materials

Iron sulfate ($FeSO_4$, E-Merck) and sodium thiosulfate ($Na_2S_2O_3$, E-Merck) were used as iron and sulfur sources without further purification. Carbon disulfide (CS_2, E-Merck) was used as sulfur-extracting solvent. Other solvents were purchased from Merck Company and were used without further purification. The distilled water was prepared in double water distiller.

Pyrite production

Experiments were carried out in 2,000 ml stainless steel stirred reactor equipped with a temperature controller and a barometer (Fig. 1). Iron sulfate (11 g) and sodium thiosulfate (45 g) were dissolved separately in 500 ml distilled water, and were mixed in the reactor. In all experiment molar ratio of $Na_2S_2O_3$ to $FeSO_4$ was 4:1. The solution volume into reactor was kept constant at 1.00 ± 0.02 l. The Teflon-lined reactor was sealed and maintained at 180 ± 1 °C. All reactions were carried out in 4 h and agitation speed 1,000 rpm. After finishing the reaction, products which included pyrite (6 g) and sulfur (1.05 g) were filtered, washed two times with boiling distilled water, and then dried in oven for 4 h at 60 °C. Finally, the sample was purified by considered purification method.
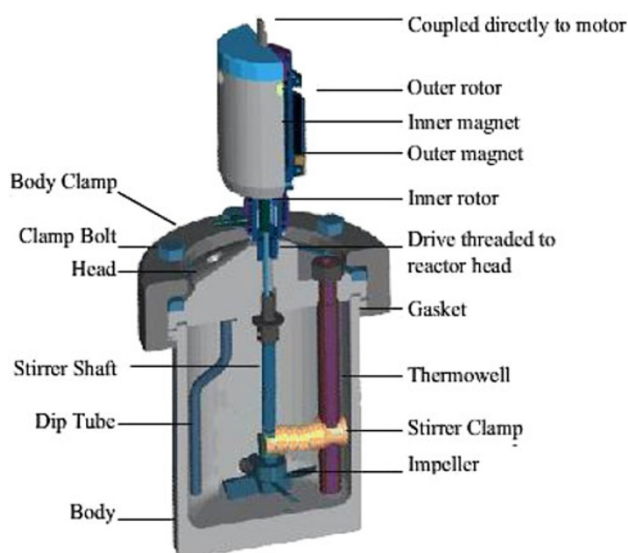

Fig. 1 A schematic of the reactor set-up constructed and utilized in this research. Inner diameter of reactor (D) = 10 cm, height of reactor (H) = 25 cm, impeller diameter (d) = 4.5 cm, distance between impeller and reactor bottom (t) = 4 cm, width of impeller (w) = 0.5 cm

Purification of the produced pyrite

Solvent extraction

Several polar and non polar organic solvents were investigated for sulfur removal. The extraction was conducted at room temperature and sulfur was added to solvent slowly until the sulfur deposition was observed. Ultimately, solubilities of sulfur in different solvents were obtained. Results are given in Table 1.

Reaction with sodium sulfite

It was reported that sodium thiosulfate can be produced by reaction between sulfur and sodium sulfite (Howard 1930):

$$Na_2SO_3(s) + S(s) \rightarrow Na_2S_2O_3 \tag{1}$$
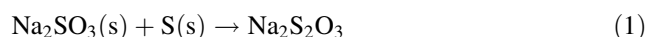
In other words, an alternative route to purify pyrite is the addition of sodium sulfite into reactor after finishing pyrite production process. This way was examined. Typically, 24 g sodium sulfite (Na_2SO_3) was dissolved in 500 ml hot water. After that, 12 g of sulfur was added to the solution. The suspension was maintained in room temperature and moderate agitation for 2 h. Then solid product was filtered, dried and weighted. In this process, 6 g of sulfur was consumed. Also, the reaction between Na_2SO_3 and $FeSO_4$ was investigated in a separate experiment to find out effect of Na_2SO_3 on main reaction (reaction between $Na_2S_2O_3$ and $FeSO_4$).

After initial tests, the purification process was optimized to find out the required amount of Na_2SO_3 and optimum temperature. For this purpose, in each experiment, after finishing main reaction (reaction between $Na_2S_2O_3$ and $FeSO_4$), effluent was filtered and washed with distilled water. Next, solid product and sodium sulfite were taken into the reactor with 1,000 ml distilled water. The reaction was carried out at temperature range of 50–100 °C and stirred rate of 1,000 rpm. After that, effluent was filtered and extracted with 100 ml of CS_2 for 15 min under magnetic stirring at room temperature. Finally, the mixture was filtered and solvent was evaporated to measure the quantity of unreacted sulfur. Operation conditions and results are given in Table 2.

Thermal treatment

The powder obtained in main reaction was thermally treated in a furnace to remove sulfur. Treatment program was; heating from ambient temperature to defined temperature with heating rate of 10 °C/min under air atmosphere. After treatment, the amount of unreacted sulfur was measured by solvent extraction method. Results are presented in Table 3.

Table 1 Solubility of sulfur in different solvents

Solvent	Volume of solvent (cc)	Mass of solved sulfur (g)	Melting point of solvent (°C)	Boiling point of solvent (°C)	Auto ignition temperature (°C)
Carbon disulfide	200	65	−110	46	90
Cyclohexane	400	4	6	80	245
Benzene	200	5.5	5.5	80	497
Paraxylene	200	4.5	12	138	527
THF	200	1.5	−108	65	321
Chlorobenzene	400	6.1	−45	132	638
Toluene	400	4	−95	110	480
Diethyl ether	200	0.2	−116	34	170
Fluorobenzene	100	0	−40	84	–
Ethanol	400	0	−40	78	363
Methanol	400	0	−114	64	464
2-Propanol	400	0	64	82	65
Acetone	200	0	−97	56	465
Diethylene-triamine	100	Reacted	−39	200	399

Table 2 Operation conditions and results of reaction between Na_2SO_3 and sulfur in various conditions

No.	Na_2SO_3 (mole)	Temperature (°C)	Time (min)	Sulfur (g)
1[a]	0	180	240	1.05
2	0.05	50	60	0.1
3	0.05	70	60	0.05
4	0.05	80	60	Trace
5	0.05	95	60	0
6	0.05	95	30	0
7	0.05	95	15	0
8	0.05	95	12	0
9	0.05	95	6	Trace

[a] Main reaction

Characterization

The products were analyzed by XRD and SEM analysis. SEM images were collected on a Leica/Cambridge Instruments S360 SEM. XRD analysis was carried out using a Philips PW170 based diffractometer (CuK_α radiation, 35 kV, 40 mA). XRD patterns, in the range of 3–90° 2θ, were collected under air using the following settings: 0.1 mm receiving slit, 0.4 s/0.02° 2θ counting time.

Results and discussion

Characterization of product obtained in hydrothermal synthesis step

The related X-ray diffraction pattern of the powder produced in main reaction is shown in Fig. 2. This figure shows that the powder consists of pyrite (FeS_2) with a large amount of sulfur.

Solvent extraction process

Abilities of some solvents were investigated to remove sulfur existed in solid product. A summary of the results is shown in Table 1. It can be seen from that carbon disulfide (CS_2) has the highest ability to solve sulfur. X-ray diffraction pattern of solid product after extraction is given in Fig. 3. A comparison between Figs. 2 and 3, it was found that sulfur has completely removed by CS_2 extraction. However, because of low miscibility of CS_2 in water (0.29 g/100 g at 20 °C), a pasty product was formed during washing with CS_2 and consequently sulfur removal wasn't performed well. For this reason, the product must be dried before CS_2 extraction. In other words, CS_2 extraction adds an extra drying step to the process.

Table 3 Results of thermal treatment process at different temperature (initial mass of pyrite: 4 g)

Temperature (°C)	S (g) after 12 min	S (g) after 24 min	S (g) after 1 h	S (g) after 2 h	S (g) after 2.5 h	S (g) after 3 h
200	0.9	0.87	0.7	0.05	Trace	0
250	0.9	0.85	0.65	0.03	Trace	0
300	0.85	0.8	0.5	Trace	0	0

Fig. 2 X-ray diffraction pattern of the product before washing with solvent (*P* pyrite, *S* sulfur)
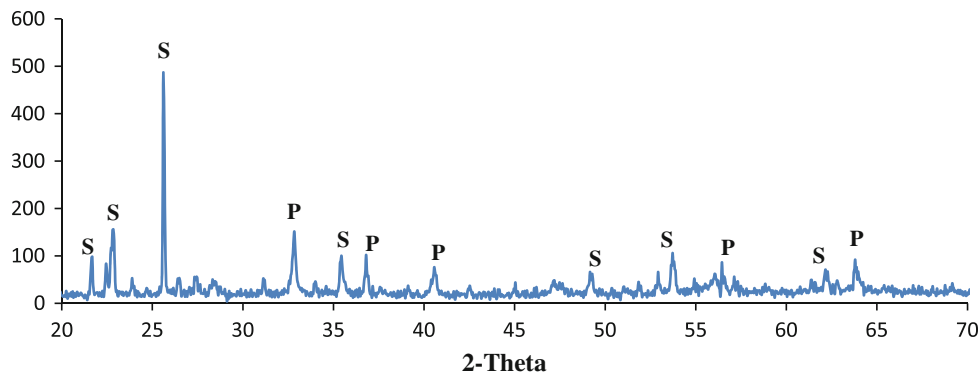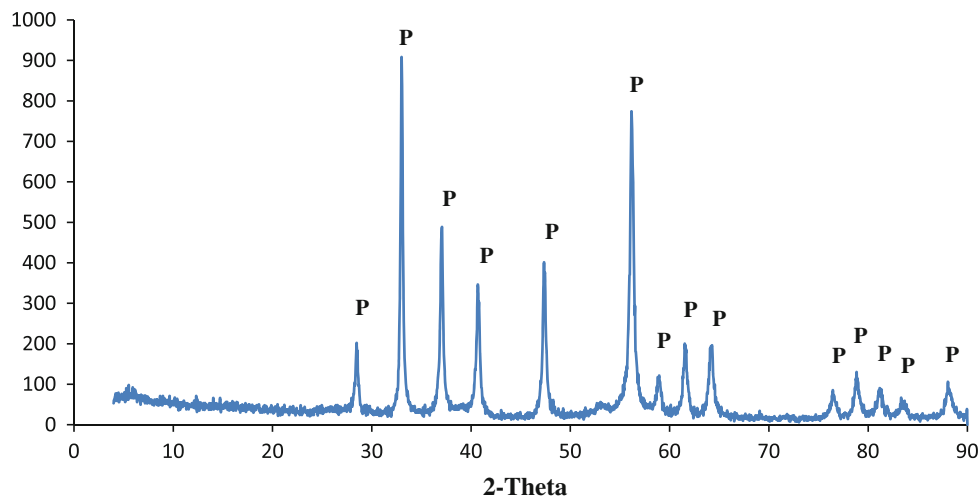
Fig. 3 X-ray diffraction pattern of the powder after washing with CS_2 (*P* pyrite)

Reaction with sodium sulfite

Effect of sodium sulfite on main reaction

As said in "Reaction with sodium sulfite", an experiment was performed to find out whether sodium sulfite can be added to main reaction. In this experiment an orange-brown precipitate was obtained. The powder was investigated by XRD analysis (Fig. 4). The XRD pattern shows that the powder includes $Fe_2NaOH(SO_3)_2 \cdot H_2O$ and goethite (FeO(OH)). Therefore, this method must be performed after filtration of products obtained in main reaction.

Optimization of the purification process

Sulfur removal by reaction with sodium sulfite was investigated in various conditions. Results were summarized in Table 2. As seen in this table, sulfur was completely removed at 95 °C after 12 min. Therefore, sulfur can be removed by reaction with sodium sulfite. However,

Fig. 4 XRD pattern of the product obtained in reaction between Na_2SO_3 and $FeSO_4$ (*F* $Fe_2NaOH(SO_3)_2 \cdot H_2O$, *G* goethite)
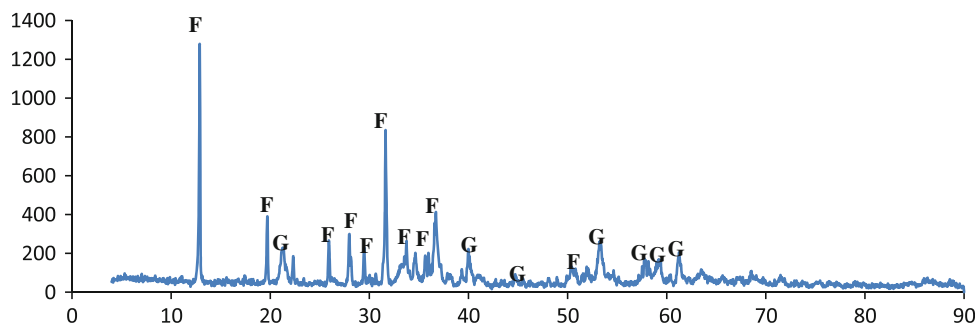
Fig. 5 Mineral phases detected (through XRD analysis) after thermal treatment of pyrite for 1 h at various temperatures up to 1000 °C (Boyabat et al. 2003)
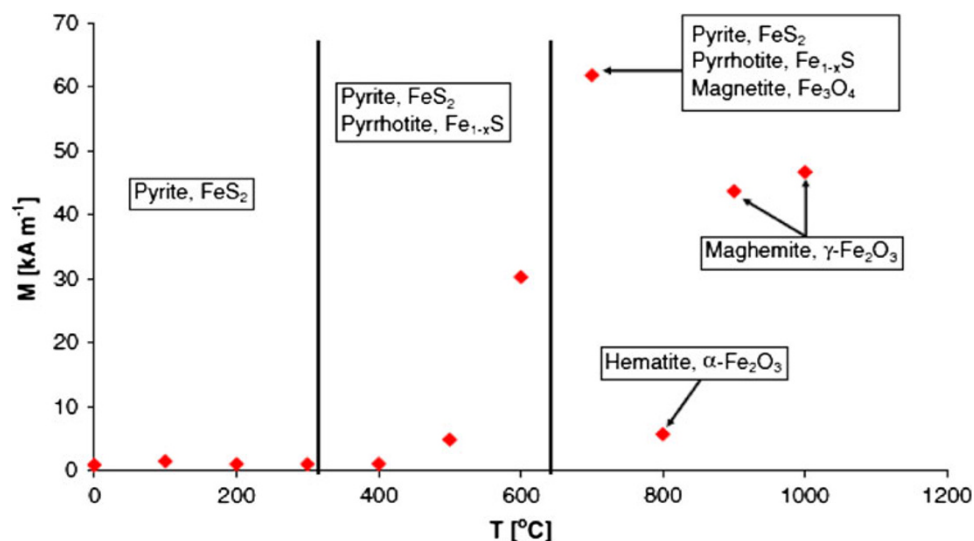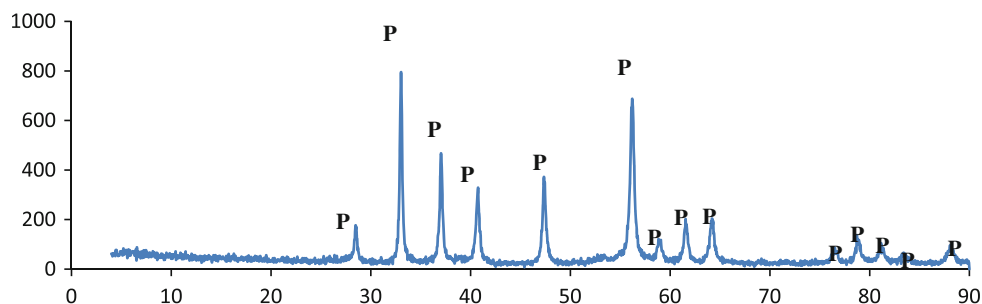

Fig. 6 The XRD pattern of the powder after thermal treatment at 300 °C for 2.5 h

this method increases steps of pyrite production process. In other words, number of steps becomes twice.

Thermal treatment

Performance of thermal treatment method was investigated. For this purpose, the powder produced in hydrothermal synthesis process was heated in a furnace at different temperatures. Results are given in Table 3. The initial and final mass of all samples were measured. Figure 5 shows importance of the treatment temperature (Waters et al. 2008). At temperatures higher than 300 °C, pyrite is decomposed. This reaction can be represented as following (Boyabat et al. 2003):

$$FeS_2(s) \rightarrow FeS_{1-x}(s) + (1-x)/2\ S_2(g) \quad (2)$$
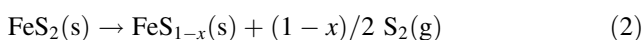
Therefore, to prevent pyrite decomposition, it is necessary to keep treatment temperature below 300 °C.

During thermal treatment, sulfur is oxidized to sulfur dioxide and leaves pyrite:

$$S + O_2 \rightarrow SO_2 \quad (3)$$

According to Table 3, it seems that thermal treatment at temperature 300 °C for 2.5 h is the most appropriate condition to purify pyrite (Fig. 6).

Investigation of the product morphology after purification

Scanning electron microscopy (SEM) analysis was carried out on the product after each treatment (Fig. 7). This figure shows fine and spherical particles in all treatments. Also, particles have nano structures.

Conclusion

In this study, purification of pyrite was investigated via three routes. It was found that carbon disulfide is the most appropriate solvent to extract sulfur. However, this method had some disadvantages such as safety. Second route, reaction with Na_2SO_3, was a complicated method and
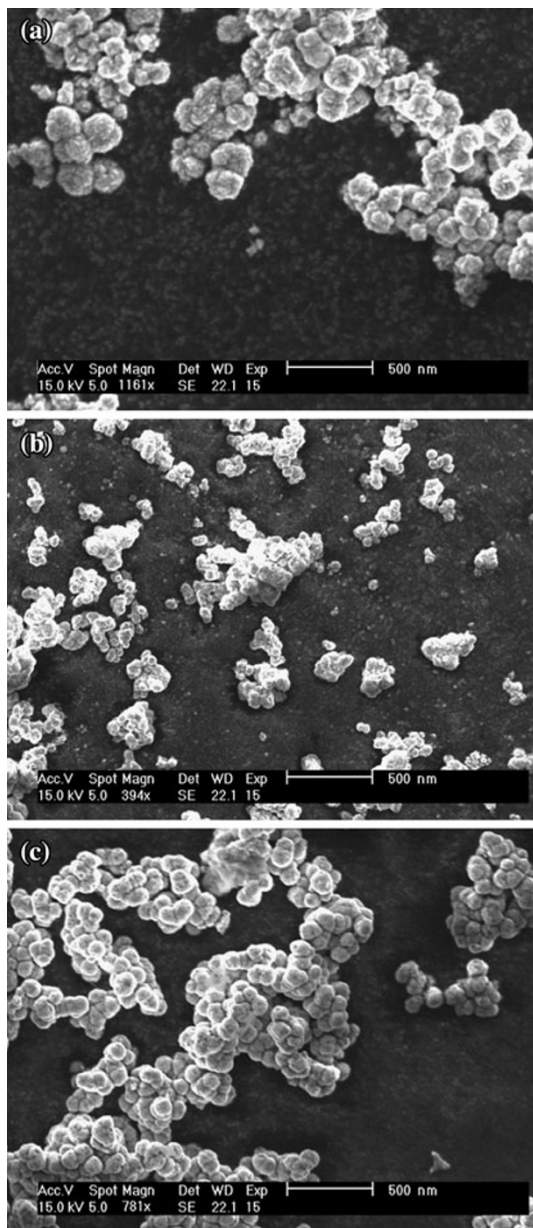
Fig. 7 The SEM images of FeS$_2$ produced at 180 °C after **a** solvent extraction with CS$_2$, **b** reaction with Na$_2$SO$_3$ and **c** thermal treatment

increased steps of pyrite production process. Ultimately, it was suggested Thermal treatment as the best purification method.

References

Boyabat N, Ozer AK, Bayrakceken S, Gulaboglu MS (2003) Thermal decomposition of pyrite in the nitrogen atmosphere. Fuel Process Technol 85:179

Howard H (1930) Process for the production of sodium thiosulfate, United States Patent, No.1760137

Kar S, Chaudhuri S (2004) Solvothermal synthesis of FeS$_2$ nanocrystalline with different morphologies. Chem Phys Lett 398:22

Kar S, Mandal SK, Das D, Chaudhuri S (2004) Wet chemical synthesis of iron pyrite and characterization by Mössbauer spectroscopy. Mater Lett 58:2886

Kim TB, Choi JW, Ryu HS, Cho GB, Kim KW, Ahn JH, Cho KK, Ahn HJ (2007) Electrochemical properties of sodium/pyrite battery at room temperature. Power Sources 174:1275

Masset PJ, Guidotti RA (2008) Thermal activated ("thermal") battery technology Part IIIa: feS$_2$ cathode material. J Power Sources 177:595

Montoro LA, Rosolen JM (2003) Gelatin/DMSO: a new approach to enhancing the performance of a pyrite electrode in a lithium battery. Solid State Ionics 159:233

Montoro LA, Rosolen JM, Shin JH, Passerini S (2004) Investigations of natural pyrite in solvent-free polymer electrolyte, lithium metal batteries. Electrochim Acta 49:3419

Rezig B, Dahman H, Kenzari M (1992) Iron pyrite FeS$_2$ for flexible solar cells. Renew Energy 2:125

Shao-Horn Y, Horn QC (2001) Chemical, structural and electrochemical composition of natural and synthetic FeS$_2$ pyrite in lithium cells. Electrochim Acta 46:2613

Shao-Horn Y, Osmialowski S, Horn QC (2002) Nano-FeS$_2$ for commercial Li/FeS$_2$ primary batteries. Electrochem Soc 149:1499

Siyu H, Xinyu L, Yu LQ, Jun C (2009) Pyrite film synthesized for lithium-ion batteries. J Alloy Compd 472:9

Strauss E, Golodnitsky D, Freedman K, Milner A, Peled E (2003) To the electrochemistry of pyrite in Li/solid composite-polymer-electrolyte battery. J Power Sources 115:323

Waters KE, Rowson NA, Greenwood RW, Williams AJ (2008) The effect of heat treatment on the magnetic properties of pyrite. Miner Eng 21:679

Wu R, Zheng YF, Zang XG, Sun YF, Xu JB, Jian JK (2004) Hydrothermal synthesis and crystal structure of pyrite. J Cryst Growth 266:523

Xuefeng Q, Yi X, Yitai Q (2001) Solventothermal synthesis and morphological control of nanocrystalline FeS$_2$. Mater Lett 48:109