



Review article

Binary iron sulfides as anode materials for rechargeable batteries: Crystal structures, syntheses, and electrochemical performance



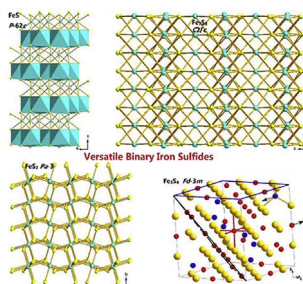
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HIGHLIGHTS

- The structures of iron sulfides are systematically summarized.
- The synthetic methods of iron sulfides are discussed.
- Recent progress on various binary iron sulfides' electrochemical applications is overviewed.
- More attention should be paid on their applications for post-lithium types of batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective utilization of energy requires the storage and conversion device with high ability. For well-developed lithium ion batteries (LIBs) and highly developing sodium ion batteries (SIBs), this ability especially denotes to high energy and power densities. It's believed that the capacity of a full cell is mainly contributed by anode materials. So, to develop inexpensive anode materials with high capacity are meaningful for various rechargeable batteries' better applications. Iron is a productive element in the crust, and its oxides, sulfides, fluorides, and oxygen acid salts are extensively investigated as electrode materials for batteries. In view of the importance of electrode materials containing iron, this review summarizes the recent achievements on various binary iron sulfides (FeS, FeS₂, Fe₃S₄, and Fe₇S₈)-type electrodes for batteries. The contents are mainly focused on their crystal structures, synthetic methods, and electrochemical performance. Moreover, the challenges and some improvement strategies are also discussed.

1. Introduction

With the rapid development of society, nonrenewable natural resources are becoming scarcer and scarcer, such as coal, petroleum and natural gas. It is urgent to explore green and renewable energy resources, or effective utilization and storage of energy, as the remnant nonrenewable resources can hardly meet the requirements of our life in the future. Effective utilization and storage of energy require high effective energy storage and conversion devices. To date, there are many types of such devices have been developed well, including various

rechargeable batteries, super capacitors, solar cells, and so on. For energy storage devices, Li ion batteries (LIBs) show their great potential in various portable electronic products in view of their ideal energy densities [1–4]. A promising type of batteries needs electrodes with high capacities, low cost and safety. Among the main battery components, anode materials have received great attention as they are the main contributors for the batteries' capacities.

Researchers wish to find a series of anode materials with much higher theoretical capacity than the commercial graphite electrode (theoretical capacity: 372mAh/g). In the search of potential anode

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materials, Si, Ge, Sn, SnO₂, alloys, Li₄Ti₅O₁₂, Li_xV₃O₈, transition-metal oxides, sulfides, and fluorides, have been extensively developed [5–8]. Among so many types of anode materials, iron-based materials are specifically studied in view of iron's abundance, low price, and non-toxicity. The most successful iron-based electrode material is olivine type LiFePO₄ cathode, which has been commercialized [9,10]. It is well known that sulfides usually have much higher conductivities and smaller volume expansions during cycling than those of oxides, which means that sulfides have better ion transport mobilities than oxides [11,12]. In addition, the chemical bond between metal and sulfur is weaker than that of metal oxides, which can be advantageous to the conversion reactions. Moreover, metal sulfides usually have better mechanical and thermal stabilities than metal oxides [11]. Combining the advantages of iron and sulfides, it is valuable to develop iron sulfides as anode materials for rechargeable batteries. In fact, there are a large number of reports concerning with binary iron sulfides-type anodes. In view of the success of iron sulfides in the field of LIBs, more and more exploration of them in the field of sodium-ion batteries (SIBs) have been carried out in recent years. Apart from the well-known advantages, iron sulfides also demonstrate several disadvantages to restrict their practical applications, these including relatively large volume changes during cycling induced poor cyclability, and relatively difficult syntheses. To solve these issues and get valuable metal sulfide anode materials, a huge number of efforts are being made to explore and develop metal sulfide-based anode materials for rechargeable batteries via modified synthetic methods, and various morphology control and material composite techniques. Intrigued by iron sulfides' potential in the fields of LIBs and SIBs, it is necessary to present a summary on their crystal structures, syntheses, electrochemical properties, and future studies. To date, there are only limited review papers about nanostructures transition metal sulfides for LIBs and another review about metal sulfides/selenides for SIBs summarized, respectively [13–15]. As far as we know, there is not a specific review focusing on the applications of iron sulfides in LIBs and SIBs.

In this review, the contents are addressed to firstly give the crystal structures of iron sulfides (FeS, FeS₂, Fe₃S₄, and Fe₇S₈). It is well known that crystal structure is the decisive factor to influence a material's properties. Secondly, various synthetic methods for iron sulfides are discussed, mainly focused on the normally employed ones. Thirdly, the electrochemical properties for each type of iron sulfide are discussed, respectively. Relatively, FeS and FeS₂ are extensively investigated, while Fe₃S₄ and Fe₇S₈ are rarely studied. Finally, the possible future of these iron sulfides is expected. This summary should give researchers not only a systematic summary of known iron sulfide-type anodes, but also make a discussion on their future.

Table 1
Known polymorphs of FeS.^a

Crystal system	Space group	Unit cell parameters	Prototype	Modification
hexagonal	<i>P6₃/mmc</i>	3.445 × 3.445 × 5.763	NiAs, hP4	pyrrhotite
tetragonal	<i>P4/nmm</i>	3.674 × 3.674 × 5.033	PbO, tP4	mackinawite
hexagonal	<i>P6̄2c</i>	5.965 × 5.965 × 11.759	FeS, hP24	troilite
orthorhombic	<i>Pnma</i>	5.739 × 3.377 × 5.807	FeAs, oP8	HT ^b
orthorhombic	<i>F222</i>	5.195 × 5.487 × 5.540	FeS, oF8	LT ^b
cubic	<i>F4̄3m</i>	5.42 × 5.42 × 5.42	ZnS, cF8	RT ^b blende
monoclinic	<i>P2₁/c</i>	8.110 × 5.667 × 6.483, β = 93.05	FeS, mP24	- ^b
hexagonal	<i>P6̄3mc</i>	6.588 × 6.588 × 5.400	Nb _{0.92} S, hP16	HT ^b

^a All the data from Pearson's Crystal Data (PCD) or Inorganic Crystal Structure Database (ICSD). Eight polymorphs have been identified via carefully checking their unit cell parameters and powder X-ray diffraction patterns.

^b HT, LT, RT denote high-, low-, and room temperature phases, respectively. “-” indicates no data available.

2. Crystal structures

2.1. FeS

To date, there are totally eight polymorphs of FeS discovered as listed in Table 1. FeS can crystallize in the cubic, monoclinic, orthorhombic, tetrahedral, and hexagonal space groups, respectively. Their structures can be classified into pyrrhotite, troilite, mackinawite, and their modifications. Some polymorphs are rarely studied as they are high temperature stable phases. When carefully check the literature on the electrochemical application of FeS, it can be found that most of them crystallize in the hexagonal space group *P6̄2c* (troilite) (Fig. 1a). This structure can be simply described as distorted FeS₆ octahedra constructed a 3D structure, in which each FeS₆ unit shares edges with its neighboring FeS₆ units along on either *a* or *c* direction [16]. Apart from troilite one, pyrrhotite (hexagonal *P6₃/mmc*) and mackinawite (tetragonal *P4/nmm*) FeS materials also have been studied as anode materials for LIBs [17]. Pyrrhotite FeS demonstrates a 3D structure also built by FeS₆ octahedra, in which these octahedra are also linked together via sharing edges (Fig. 1b). While for mackinawite FeS, it shows a layered structure parallel to the *ab* plane, in which intralayer FeS₄ tetrahedra link their neighbors by sharing corners or edges (Fig. 1c).

2.2. FeS₂

There are two polymorphs for FeS₂, pyrite and marcasite, respectively. For the former, it crystallizes in the cubic space group *Pa3̄*, and its 3D structure contains FeS₆ octahedra and S–S dimers. The distorted FeS₆ octahedron has six identical Fe–S bond distances. Each S atoms have neighboring three Fe and one S atoms, and each FeS₆ octahedron connects with the nearest twelve FeS₆ octahedra via sharing corners (Fig. 2a). For marcasite FeS₂, it crystallizes in the orthorhombic space group *Pnmm*, and also contains the structure building units FeS₆ octahedron and S–S dimers (Fig. 2b). Different from pyrite one, the distorted FeS₆ octahedra in marcasite FeS₂ contains two groups of Fe–S bond lengths. Each FeS₆ octahedron has ten neighboring FeS₆ units, linked via sharing corners (eight) or edges (two). Compared with pyrite, marcasite has shorter Fe–S and longer S–S distances. It is interesting to find that almost all the studied FeS₂ anode materials for batteries are pyrite.

2.3. Fe₃S₄

There are two polymorphs for Fe₃S₄, namely, cubic greigite (*Fd3̄m*, Pearson code: cF56) and trigonal smythite (*R3̄m*, Pearson code: hR21). The former with spinel structure has been extensively studied as electrode materials for batteries, while the latter has attracted little attention. For the cubic phase, the S atoms construct a face-centered cubic lattice, in which 1/8 of the tetrahedral cavities are occupied by Fe³⁺ ions, and 1/2 of the octahedral cavities are co-occupied by 1: 1 Fe²⁺

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