



# Electrochemical characteristics of pyrrhotine as anode material for lithium-ion batteries



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## ABSTRACT

Micron-sized pyrrhotine particles with a standard hexagonal structure were prepared by simple precipitation and subsequent heat treatment and were investigated as anode material for lithium-ion batteries. The as-prepared Fe<sub>7</sub>S<sub>8</sub> electrode delivered a highly reversible capacity of 604.1 mAh/g with a voltage range of 2.5–0.05 V. X-ray diffraction, scanning electronic microscopy and X-ray photoelectron spectroscopy were employed to characterize the reaction products at different stages, and a possible two-step reaction mechanism was proposed. The electrochemical test results demonstrated that the discharge/charge voltage range had a remarkable influence on the capacity retention and coulombic efficiency, which could be associated with the decomposability of lithiation products and volume change. Additionally, the dissolution of Li<sub>2</sub>S<sub>x</sub> (2 < x < 8) in electrolyte was found to cause severe capacity loss as well. Thus a proper coating layer and cycling voltage range were essential for this kind of electrode material to achieve practical application in lithium-ion batteries.

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## 1. Introduction

Recently, various kinds of alternative materials for lithium-ion battery anodes have been extensively studied because of the low specific capacity and poor high-rate performance of graphite which is seriously falling behind the demand for some applications, such as electric vehicles and hybrid electric vehicles. As new-generation anode materials, several transitional metal compounds (i.e., M<sub>n</sub>X<sub>m</sub>, where M = transitional metal; X = O, S, F or P) based on the conversion reaction mechanism have gained considerable attention because of their much higher theoretical capacity and energy densities than graphite electrode. Among them, iron monosulphide has recently been considered to be a promising anode material for lithium-ion batteries and has attracted much attention because of its excellent electrochemical attributes, low environmental effect, and natural abundance [1–3]. However like other transitional metal compounds, iron monosulphide (denoted as FeS) exhibits poor capacity retention and low coulombic efficiency. The chemical reaction process proceeds as follows:



According to previous studies [4–6], the key to realize the reversibility of the conversion reaction is the nanosized transition metal particles, Fe<sup>0</sup>, which has been verified to be electrochemically active in decomposing the Li<sub>2</sub>S matrix. However, given the drastic volume expansion after lithiation and poor electron conductivity of Li<sub>2</sub>S, the reverse reaction can be inhibited, thereby resulting in rapid capacity degradation [3,7,8]. Furthermore, the lithiation process of metal sulfides tends to generate the polysulfides Li<sub>2</sub>S<sub>x</sub> (2 < x < 8), which can easily dissolve into organic electrolyte and result in poor capacity retention [1,9–11]. To improve the electrochemical performance of the FeS material, many effective methods have been proposed, most of which focus on the synthesis of nanosized particles with different structures [12–14] or nanocomposites with high-conductivity materials [15–17]. Nanosized materials can better accommodate strains caused by volume change and reduce the lithium-ion diffusion path. The coating layer of conductive carbon or metals can enhance the conductivity of the electrode, thereby improving coulombic efficiency and reversible capacity.

As a main natural form of iron monosulphide, pyrrhotine powder has a broad size distribution and is often referred to as Fe<sub>7</sub>S<sub>8</sub> because of the deficient part of Fe<sup>2+</sup>. Nanosized pyrrhotine/

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carbon composite has been reported to exhibit almost the same electrochemical properties as FeS; the reversible reaction mainly occurs in a voltage range of 2.5–0.9 V [18]. However, studies on other similar anode materials (e.g., hematite) have identified particle size and morphology as important factors that influence their electrochemical performance, even the electrochemical reaction process [19–23]. To the best of our knowledge, no report exists on micron-sized pyrrhotine particles that account for most of the natural powder. For this purpose, we synthesized micron-scale pyrrhotine particles without any modification and investigated the electrochemical properties as anode materials for lithium-ion batteries. The results reveal that micron-sized pyrrhotine particles exhibit a reaction process that differs from the reported reaction process of nano or submicron-sized particles, and can deliver an initial reversible capacity as high as the theoretical capacity when discharged/charged in the voltage range of 2.5–0.05 V.

## 2. Experimental

### 2.1. Preparation of sample

In the experiment, an aqueous solution of  $\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.44 mol/l) was added dropwise in equimolar  $\text{Na}_2\text{S}$  (0.50 mol/l) solution while stirring at room temperature. The resulting precipitate was repeatedly rinsed in distilled water to remove inorganic ions and was rinsed with ethanol for drying. After drying under vacuum at 80 °C, the product was heat-treated at 600 °C for 3 h under a constant flow of argon to obtain the final  $\text{Fe}_7\text{S}_8$  powder with a hexagonal lattice structure.

### 2.2. Characterization

The crystalline structure of the electrodes was measured by X-ray diffraction (XRD) (X'pert PRO, Panalytical) at a scanning rate of 10°/min. The morphology of the samples was observed with a scanning electron microscope (SEM) (S4800, Hitachi). The surface functional groups were measured with X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 Scanning ESCA Microprobe with monochromatic Al K $\alpha$  radiation (1486.6 eV).

### 2.3. Electrochemical characterization

The electrochemical performance was measured with CR2025 coin-type cells. A slurry was first prepared by ball-milling a mixture of active materials (80 wt.%), conductive carbon black (Super-P, 10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) in an adequate amount of N-methyl-2-pyrrolidone (NMP) for 2 h. The resulting slurry was used as coating for a copper foil with an area of 1 cm<sup>2</sup>. The coated copper foil was dried at 100 °C under vacuum for at least 10 h to obtain an electrode for electrochemical measurement. The cells were assembled in an argon-filled glove box (Etelux 2000, China), where both moisture and oxygen levels were kept at less than 1 ppm. The electrolyte used was  $\text{LiPF}_6$  (1 mol/L) in ethylene carbonate and dimethyl carbonate (EC-DMC, 1:1 v/v), and the lithium foil was used as the counter electrode. The charge/discharge cycles were performed using a battery test instrument (Neware<sup>®</sup>, China).

## 3. Results and discussion

The XRD pattern of the as-prepared  $\text{Fe}_7\text{S}_8$  sample is presented in Fig. 1. The reflection of the sample has sharp diffraction peaks at 29.9°, 33.7°, 43.6° and 53.0°, corresponding to the (200), (203), (206), and (220) faces, respectively, which are in good agreement with the standard hexagonal structure of  $\text{Fe}_7\text{S}_8$  (JCPDS reference

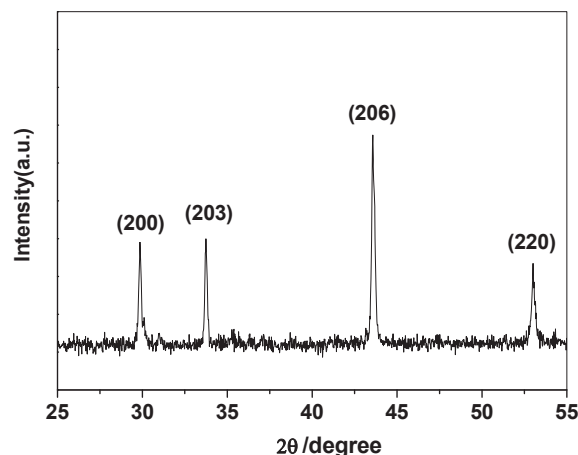
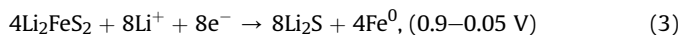
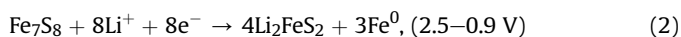


Fig. 1. X-ray diffraction pattern of as-prepared pyrrhotine sample.

code 00-025-0411). Additionally, no other obvious peaks are found in the pattern indicating the high purity of the product.

Fig. 2(a) shows the first discharge/charge voltage profiles of  $\text{Fe}_7\text{S}_8$  electrode at a 0.1C rate (1C = 660 mA/g) in the potential range of 2.5–0.9 V, which is the region of the as-known lithiation/delithiation reaction of iron monosulphide. The initial discharge-charge curve exhibits a typical discharge plateau at 1.32 V and charge plateau at 1.78 V, which are consistent with the behavior of FeS or nanosized  $\text{Fe}_7\text{S}_8$  [12–14,16,18]. Nevertheless, the initial discharge and charge capacities are only 416.7 and 361.2 mAh/g, respectively, which are far below the theoretical capacity (660 mAh/g for  $\text{Fe}_7\text{S}_8$ ). When the discharge cut-off voltage extends to 0.05 V (Fig. 2(b)), another discharge plateau at approximately 0.7 V is found. Similar anomalous electrochemical activities have also been reported in the literature on FeS [12,13], and these activities are generally attributed to the formation of a solid electrolyte interlayer (SEI) film because of the extremely low corresponding reversible capacity. Obviously, the discharge plateau found in our test results cannot be simply ascribed to the formation of the SEI film because in the voltage range the discharge and charge capacities remarkably increases to 793.2 and 604.1 mAh/g, respectively. This phenomenon indicates that the lithiation process can involve a two-step mechanism to actualize the formation of  $\text{Fe}^0$  and  $\text{Li}_2\text{S}$ , which is quite different from the reported single-step reaction process of FeS or nanosized  $\text{Fe}_7\text{S}_8$ . The reason for this phenomenon may be due to the formation of the intermediate,  $\text{Li}_2\text{FeS}_2$  [24,25]. During the lithiation process at 1.3 V, the conversion reaction first occurs on the surface of the particles. Given the relatively longer diffusion path of  $\text{Li}^+$ , the pristine pyrrhotine inside the particles cannot undergo full lithiation, thereby resulting in the formation of  $\text{Li}_2\text{FeS}_2$ . The proposed reaction mechanism is shown below:



During the subsequent de-lithiation process, the charge curve in Fig. 2(a) is much more steady with a potential plateau observed at around 1.8 V than that in Fig. 2(b), and the latter exhibits a steep slope before a potential plateau appears, indicating a different de-lithiation process. For a clear understanding of the reaction, the differential capacities versus potential ( $dQ/dV$  versus V) curves are provided (Fig. 2(c) and (d), respectively), which are considered to provide information similar to that of cyclic voltammograms. In

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