



# The influence of treatment in a sulfur environment on the electrochemical performance of $\text{LiFePO}_4$ as a cathode material for lithium-ion batteries

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## ABSTRACT

$\text{LiFePO}_4$  is considered as one of efficient cathode materials for lithium-ion batteries due to its high specific capacity, long cycle life, low cost and good safety. As a result, its electrochemical performance has been extensively researched. In this paper, commercial pure  $\text{LiFePO}_4$  is treated in a sulfur environment by sintering at 155 °C for 10 h, followed by sintering at 300 °C for 2 h. Through XRD tests, the chemical compositions are determined as  $\text{LiFePO}_4$  before and after treatment in a sulfur environment. Through SEM observation and Raman measurements, the  $\text{LiFePO}_4$  particles treated in the sulfur environment become more dispersed, and the samples appear to be polycrystalline. The electrochemical test results show that the specific capacities of the  $\text{LiFePO}_4$  treated in the sulfur environment at 1C, 2C and 5C discharge current rates can reach 146.73  $\text{mAh.g}^{-1}$ , 120.73  $\text{mAh.g}^{-1}$  and 104.97  $\text{mAh.g}^{-1}$ , respectively. In addition, with the increase in the current density, the discharge voltage platform shows no obvious decrease. Most importantly, the discharge specific capacities do not show a downward trend after 1100 charge and discharge cycles.

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## 1. Introduction

The lithium-ion battery is an excellent energy storage system due to its high specific capacity, low self-discharge and long cycle life [1–10]. It is regarded as the most promising power system for electric vehicles. The cathode material usually determines the capacity and working voltage of the cell, and so, researching these materials is important.  $\text{LiFePO}_4$  is considered an ideal cathode material for the lithium-ion battery system because of its high specific capacity, long cycle life, low cost and good safety. However, its low conductivity has limited its application and causes electrode polarization, which seriously affects the specific capacity, rate performance and cycle life [11–15]. At present, the main solution to improving the conductivity is through carbon coating or loading on

the surface using high conductivity materials, such as graphene, carbon black and so on. Bao et al. [16] synthesized a type of  $\text{LiFePO}_4$ @C core-shell [001] nanorods, and the new  $\text{LiFePO}_4$  exhibited an excellent rate capacity and stable cycle performance. The specific capacity at 5C and 10C was over 120  $\text{mAh.g}^{-1}$  and 110  $\text{mAh.g}^{-1}$ . Yang et al. [17] described the use of unfolded graphene as the three-dimensional (3D) conduction network for  $\text{LiFePO}_4$  nanoparticle growth. The specific capacity was 166.2  $\text{mAh.g}^{-1}$  in the first cycle, which is 98% of the theoretical capacity, and after 100 cycles, it continued to exhibit a stable discharge capacity. Huang et al. [18] introduced  $\text{Mg}^{2+}$  to a  $\text{LiFePO}_4$ /reduced graphene oxide composite via mechanical mixing and annealing, showing great improvements in its rate performance. The specific capacity at 20C was as high as 78  $\text{mAh.g}^{-1}$ .

Elemental sulfur is inexpensive and nontoxic. Most importantly, sulfur exhibits a very high theoretical energy density (2600  $\text{Wh kg}^{-1}$ ) and volumetric energy density (2800  $\text{Wh dm}^{-3}$ ) and can be used as a positive material [19,20]. However, sulfur must be loaded into the porous and conductive carbon material by melting method [21–23] due to its low conductivity and

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polysulfide dissolution [24,25]. In the melting process, sulfur at 155 °C is a liquid and has a low viscosity, and it is easy to load it into porous carbon to form a S@C composite material. However, sulfur will be gasified above 300 °C [26–28].

In this paper, commercial pure LiFePO<sub>4</sub> was treated in a sulfur environment and used as an electrode material for lithium-ion batteries. Then, the microstructure and electrochemical properties of the modified pure LiFePO<sub>4</sub> were examined using physical characterization techniques and electrochemical analyses.

## 2. Experimental

### 2.1. Treatment of LiFePO<sub>4</sub> in a sulfur environment

In this research, pure LiFePO<sub>4</sub> was treated in a sulfur environment by the heat melt method. First, sublimated sulfur and LiFePO<sub>4</sub> according to the mass ratio 1:9 were fully ground to allow for even blending. Second, the mixture was loaded into a tube furnace. The powder was first sintered at 155 °C for 10 h and then sintered at 300 °C for 2 h. The sintering process was carried out in Ar gas to prevent the oxidation of sulfur. After cooling and grinding, the desired material was obtained.

### 2.2. Physical characterization of LiFePO<sub>4</sub> treated in a sulfur environment

The physical properties of the LiFePO<sub>4</sub> treated by sulfur at different conditions (two sintering stages, 155 °C for 10 h and a second stage at 300 °C for 2 h) were characterized by SEM, XRD and Raman spectroscopy. The XRD test was carried out with a Rigaku Ultima IV using a D Max-RD12 Kw diffractometer with Cu K $\alpha$  radiation. The scan data were collected in the 2 $\theta$  range from 10 to 90° at a scan rate of 2°min<sup>-1</sup>. The phase-structural composition of the material can be established from analysis of the XRD diffraction pattern. The micromorphology of the LiFePO<sub>4</sub> treated in the sulfur environment was studied using an SEM with S-4800 FESEM. The changes in the grain size and morphology of the modified LiFePO<sub>4</sub> were analyzed. The modified LiFePO<sub>4</sub> was characterized by Raman spectroscopy using Horiba LabRAM HR Evolution. The wavelength of the light source was 532 nm. The wave number range during the Raman spectroscopy measurements was 50 cm<sup>-1</sup> to 3000 cm<sup>-1</sup>.

### 2.3. Electrode preparation and experimental battery assembly

The treated by sulfur LiFePO<sub>4</sub> cathodes were prepared from the active material (LiFePO<sub>4</sub>), Super-p and PVDF binder (11 wt% in the NMP) which were mixed in a weight ratio 8:1:1. After intensive mixing in the NMP, the obtained mixture was coated on an aluminum collector and dried at 50 °C for over 20 h in a vacuum oven.

The experimental battery was assembled into a 2025-type button battery cell consisting of a lithium electrode, electrolyte, separator and a working positive electrode. The separator was the Celgard® 2325. The electrolyte was a 1 mol solution of LiPF<sub>6</sub> in EC/EMC/DMC (1:1:1 v/v/v). The working electrodes were discs with a diameter of 10 mm. The loading of the active material per electrode was approximately 1 mg. The experimental battery was purged continuously in a glove box filled with a high-purity Ar gas.

### 2.4. Electrochemical characterization of an electrode made from LiFePO<sub>4</sub> treated by sulfur

The electrochemical properties of LiFePO<sub>4</sub> treated by sulfur were analyzed by charge and discharge studies, cyclic voltammetry (CV) and AC impedance (EIS) tests. The charge and discharge tests were

performed using multi-channel battery testers (BTS 5 V, 1 mA, Neware, Shenzhen, China) at room temperature. The charge/discharge voltage range was from 1.5 V to 4.2 V. The current density was 1C, 2C and 5C.

CV and EIS tests were performed using LK2005A and CHI 660E electrochemical workstations, respectively. The potential range during the CV measurements was from 1.5 to 4.2 V. Sweep speeds were selected as 0.1 mV/s, 0.2 mV/s and 0.5 mV/s. The frequency range of the EIS measures was from 100 kHz to 10 mHz with amplitude of 5 mV.

## 3. Results and discussion

### 3.1. Physical properties of LiFePO<sub>4</sub> treated in sulfur environment

Fig. 1 shows the XRD diffraction pattern of LiFePO<sub>4</sub> before and after treatment in sulfur environment. By comparing with LiFePO<sub>4</sub> standard XRD data (PDF#40-1499), we conclude that phase compositions of the samples are all consistent with presence of LiFePO<sub>4</sub>. Furthermore, it can be found that the sample modified at 155 °C has an obvious diffraction peak at 23°. However, when the temperature is 300 °C this diffraction peak disappears. These changes are consistent with the fact that sulfur has a strongest diffraction peak at 23° based on the standard data for sulfur (PDF #08-0247). It is believed that sulfur is in liquid form at 155 °C while some free solid crystalline sulfur may still remain in the sample. However, when the sintering temperature becomes 300 °C, free sulfur is vapourised. Therefore, the diffraction peak at 23° disappears.

SEM images of LiFePO<sub>4</sub> before and after treatment by sulfur at variable temperatures are presented in Fig. 2. From the figure, it can be found that the LiFePO<sub>4</sub> before and after the treatment by sulfur exhibits a granular structure. By comparison we can find that when the LiFePO<sub>4</sub> is treated by liquid sulfur at 155 °C for 10 h, LiFePO<sub>4</sub> particles agglomerate clearly. However, the particle aggregation phenomenon of the LiFePO<sub>4</sub> treated by sulfur at 155 °C for 10 h and then sintered at 300 °C for 2 h is obviously suppressed. This means that a portion of the sulfur is vapourised at the sintering temperature of 300 °C and the LiFePO<sub>4</sub> particles start to gradually disperse.

Raman spectroscopy of LiFePO<sub>4</sub> before and after treatment by sulfur is shown in Fig. 3. It shows that the Raman peaks of the pure LiFePO<sub>4</sub> and LiFePO<sub>4</sub> treated by liquid sulfur at 155 °C for 10 h are similar and very sharp. This confirms that LiFePO<sub>4</sub> is a single phase

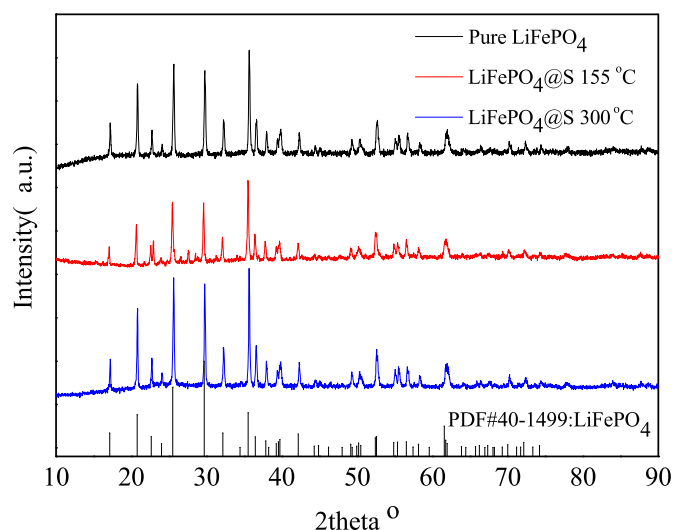


Fig. 1. XRD diffraction peaks for LiFePO<sub>4</sub> before and after treatment by sulfur.

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