



Carbon-Coated FeS as an Anode for Lithium Ion Batteries

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Carbon sourced from thermal decomposition of sucrose is coated on FeS particles prepared by precipitating Fe^{2+} and S^{2-} under atmospheric conditions. The effects of carbon content on the electrochemical performance of FeS anodes for use as lithium ion batteries are investigated. The cycling stability of the FeS anode is improved by the presence of a carbon coating. The FeS/C composite containing 10 wt. % carbon heat treated at 600 °C shows the better performance than that of pristine FeS, with an initial capacity of 472.9 and 348.9 mAh/g after 20 charge/discharge cycles. The improved capacity stability of the carbon-coated FeS electrode is explained by the improvement of electronic conductivity.

Key Words: Lithium ion batteries, Anode, FeS.

INTRODUCTION

Graphite is the most commonly used active material for anodes in lithium ion batteries. However, the theoretical capacity of graphite (372 mAh/g) restrains further improvement of the energy density of lithium ion batteries. Surface modification by oxidization¹, sulfidization² or fluorination³ has improved the performance of graphite in lithium ion batteries to some extent, but the drive for new multifunctional communication devices such as smart phones and clean energy vehicles sparks further exploration towards new active material systems. Among these potential anode materials, Sn-based⁴⁻⁶ and Si-based⁷⁻⁹ anodes have been intensively investigated. The Nexlion hybrid lithium ion batteries produced by Sony contain an anode made of Sn-Co-C alloy and display an increased capacity of 18650, which is 30 % than that of the graphite-based battery¹⁰. Transition metal sulphides such as CoS_x , NiS and $\text{FeS}^{11,12}$ have a high theoretical capacity, high tap density and are easy to prepare, making them potential anode materials for lithium ion batteries. Iron(II) sulfide has a theoretical capacity of 609 mAh/g¹³ and a charge potential that is relatively low for a transition metal sulphide, making it suitable for an anode in lithium ion batteries with high energy density. However due to the formation of Li_2S during lithium intercalation process, FeS exhibits relatively rapid cycle degradation¹⁴. In this paper, a FeS anode was coated with carbon under an ambient atmosphere to increase the electronic conductivity of FeS. The effect of the carbon coating on the electrochemical performance of the FeS anode was investigated.

EXPERIMENTAL

Iron(II) sulfide was prepared by mixing aqueous solutions of Na_2S (0.5 mol/L) and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mol/L). The resulting precipitate was filtered and then dried under vacuum. Carbon-coated FeS was prepared by mixing sucrose and FeS powder in water containing an adequate amount of poly(ethylene glycol). The resulting solution was volatilized at 40-50 °C under vacuum to produce a gel which was placed in a tube furnace heated at 600 °C for 3 h under argon. The content of carbon in the resulting material was estimated by a yield of 25 %.

The structure of the samples was measured by X-ray diffraction (XRD) (X'pert PRO, PANalytical, Netherlands). The morphologies of the samples were observed with a scanning electron microscope (SEM) (S4800, Hitachi, Japan).

A FeS slurry was prepared by ball-milling a mixture of carbon-coated FeS (85 wt. %), polyvinylidene fluoride (PVDF, 10 wt. %) and Super P carbon (5 wt. %) in adequate amount of N-methyl-2-pyrrolidone (NMP) for 2 h. The resulting slurry was coated onto copper foil with an area of 1 cm². The slurry coating was dried at 100 °C under vacuum for at least 10 h to obtain the carbon-coated FeS electrode. For electrochemical measurement, the cells (CR2025 coin-type) were assembled in an argon-filled glove box (Etekex 2000, China), where both moisture and oxygen levels were kept at less than 1 ppm. The electrolyte used was LiPF_6 (1 mol/L) in ethylene carbonate and dimethyl carbonate (EC-DMC, 1:1 v/v) and lithium foil was used as the counter electrode. Charge/discharge cycles were performed using a Neware® instrument.

RESULTS AND DISCUSSION

XRD patterns of FeS and FeS/C containing 10 wt. % carbon samples are shown in Fig. 1. Peaks typical of FeS appeared at $2\theta = 29, 33, 43$ and 53° , corresponding to the (110), (112), (114) and (300) phases of a hexagonal structure, respectively¹⁵, which means that the structure of FeS is not affected by the formation of carbon during pyrolysis process.

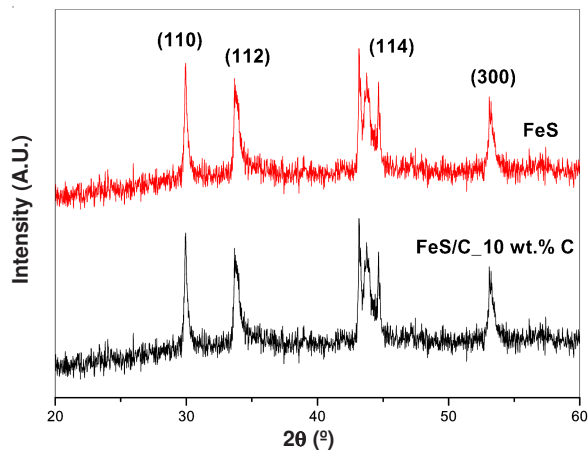


Fig. 1. X-Ray diffraction patterns of FeS and FeS/C with 10 wt. % carbon

The SEM images of FeS and FeS/C with 10 wt. % carbon shown in Fig. 2 reveal the presence of smaller particles partially coating the surface of the FeS particles, which are mainly carbon resulting from the pyrolysis of sucrose. The SEM images also showed that the carbon does not totally cover the surface of the FeS samples by thermal decomposition of sucrose.

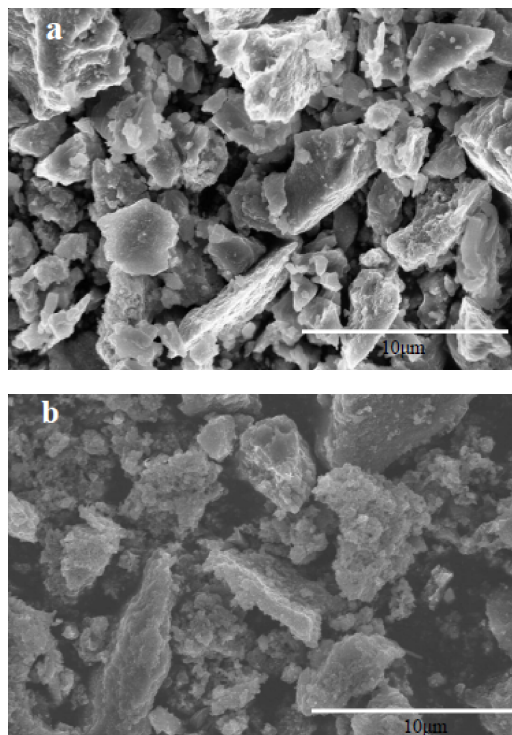


Fig. 2. SEM images of FeS and FeS/C with 10 wt. % carbon

Fig. 3 shows the cycle performance and the initial charge-discharge curves of pristine FeS and FeS/C with 10 wt. % carbon between 1.0-2.5 V at 0.2 C. The cycling performance

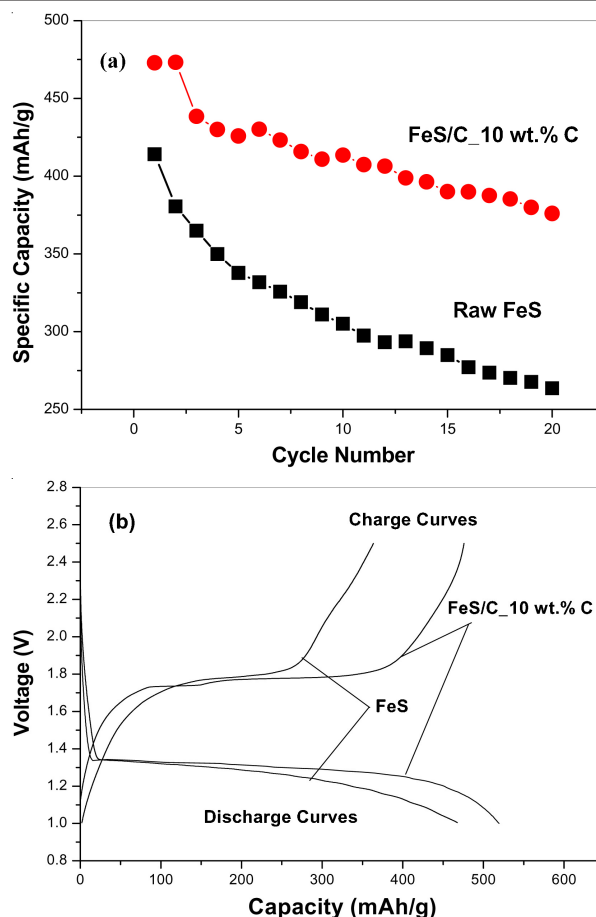


Fig. 3. (a) cyclic performance of FeS and FeS/C with 10 wt. % carbon and (b) initial charge-discharge curves of FeS and FeS/C with 10 wt. % carbon

was greatly increased by the carbon coating. The FeS sample containing 10 wt. % carbon showed the better cycling performance, with an initial reversible capacity of 472.9 and 348.9 mAh/g after 20 charge/discharge cycles. In contrast, the uncoated FeS sample displayed an initial reversible capacity of 349.5 mAh/g, which decreased to just 137.4 mAh/g after 20 cycles. The capacity retention rate after 20 cycles is 79.5 % for the FeS electrode containing 10 wt. % carbon but only 39.3 % for the plain FeS electrode. As shown in Fig. 3 (b), FeS/C with 10 wt. % carbon exhibits obviously better potential plateau than that of pristine FeS, which indicating that the pyrolytic carbon coating on the surface of FeS particles can improve the electronic conductivity.

The difference in the cycling performance of the electrodes was further analyzed by electrochemical impedance spectroscopy. The electrochemical impedance spectroscopy data for electrodes containing uncoated FeS and FeS coated with 10 wt. % carbon as the active material after one discharge are shown in Fig. 4. The impedance of the electrode containing uncoated FeS is much larger than that of the carbon-coated one. The larger impedance can be attributed to the poor conductivity of the uncoated FeS sample.

Conclusion

The cycling performance of electrodes containing FeS was improved by introducing a carbon coating. The sample containing 10 wt. % carbon that was heat treated at 600 °C

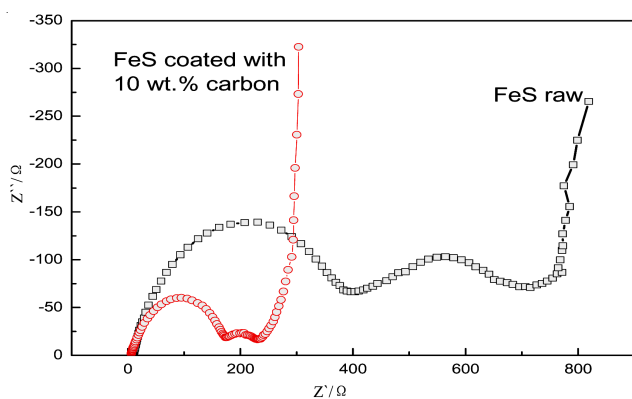


Fig. 4. Electrochemical impedance spectroscopic graph of electrodes containing uncoated FeS and FeS/C with 10 wt. % carbon

exhibited an initial reversible capacity of 472.9 and 348.9 mAh/g after 20 charge/discharge cycles. The electronic conductivity of FeS electrode was increased by the presence of the carbon coating, which decreased the impedance during charge/discharge cycles.

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