

Fe K-edge XAFS spectra for FeS₂ and Li₂S-FeS₂ composite materials

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Abstract

Fe K-edge XAFS measurements were carried out for FeS₂ and Li₂S-FeS₂ composite positive electrode materials. The measured EXAFS profiles after charge and discharge became similar each other after 10 cycles for the FeS₂ electrodes, while they were rather distinguishable for the Li₂S-FeS₂ electrodes. This difference indicates that the structural reversibility of Li₂S-FeS₂ was improved as compared with FeS₂, which would be responsible for the improved cycle capability of the cells.

1. Introduction

Iron disulfide (FeS₂) is one of the promising cathode materials for high-energy rechargeable lithium batteries because of its high theoretical capacity (*ca.* 890 mAh/g) and relatively low cost. Although FeS₂ shows a complete structural reversibility during charge/discharge redox reactions at high temperature and with an alkali molten salt, such structural reversibility cannot be observed at room temperature, which explains partly why the ambient temperature Li/FeS₂ cells show capacity degradation with cycling [1,2]. One of the methods to overcome this problem is to prepare a lithiated FeS₂, that is Li₂S-FeS₂ composites, by which the structural changes during the Li insertion/extraction reactions would be reduced, resulting in the improvement of cycle capability.

In the present work, we measured the Fe K-edge XAFS spectra for FeS₂ and Li₂S-FeS₂ composite positive electrode materials, and compared them in an attempt to investigate the mechanism of the cycle capability for these sample cells.

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2. Experimental Procedure

Li_2S - FeS_2 composites were prepared by mixing FeS_2 and Li_2S with a molar ratio of 1 : 1, followed by the spark-plasma-sintering treatment [3] at 1200°C . Electrochemical lithium insertion / extraction reactions were carried out using lithium coin-type cells with 1M LiPF_6 / (EC + DMC) electrolytes at a current density of 46.7 mA/g initially with charging. After the electrochemical cycling, the electrodes were characterized by Fe K-edge XAFS (BL-4, SR Center, Ritsumeikan University) measurements.

3. Results and Discussion

The electrochemical measurements showed that the cycle capability of the Li_2S - FeS_2 composite cells was much improved as compared with that of the FeS_2 cells; the discharge capacity after 20 cycles was *ca.* 350 mAh/g (capacity retention, *ca.* 48%), which was much higher than that of the FeS_2 cells (*ca.* 140 mAh/g, *ca.* 18%).

Figure 1 shows the k^3 -weighted EXAFS oscillations for FeS_2 and Li_2S - FeS_2 composite electrodes before and after the electrochemical cycling. The profiles after charge and discharge became similar each other after 10 cycles for the FeS_2 electrodes, while they were rather distinguishable for the Li_2S - FeS_2 electrodes. This result indicates that the structural reversibility of FeS_2 - Li_2S was improved as compared with FeS_2 , which would be responsible for the improved cycle capability of the cells.

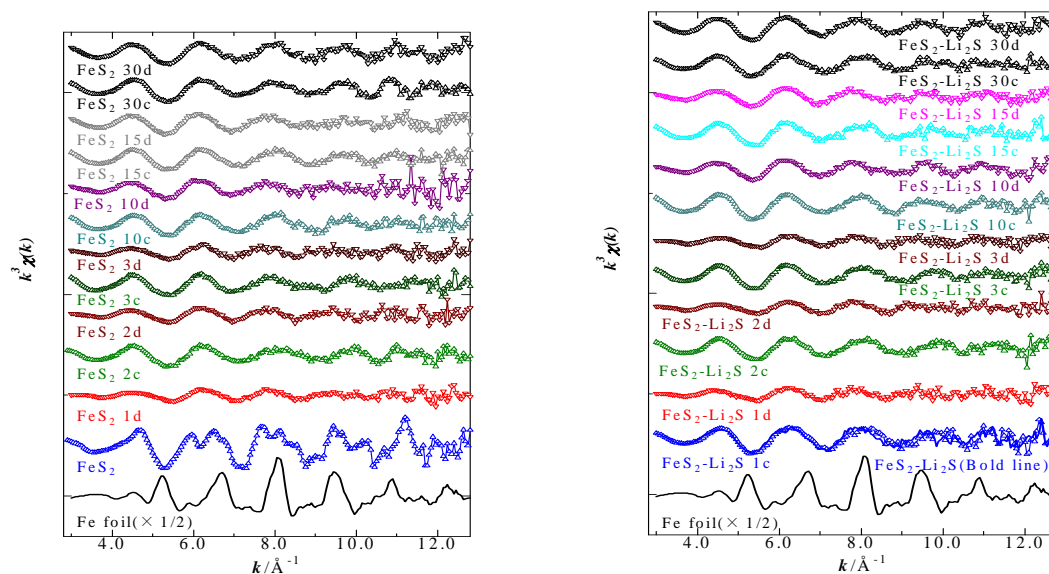


Fig. 1 k^3 -weighted Fe K-edge EXAFS oscillations for FeS_2 and Li_2S - FeS_2 composite electrodes.

References

- [1] R. Fong et al., *J. Electrochem. Soc.*, **136**, 3206 (1989).
- [2] D. Golodnitsky and E. Peled, *Electrochim. Acta*, **45**, 335 (1999).
- [3] T. Takeuchi et al., *J. Electrochem. Soc.*, **155**, A679 (2008).