



## Short communication

# Cycleable graphite/FeSi<sub>6</sub> alloy composite as a high capacity anode material for Li-ion batteries

T. Li, Y.L. Cao, X.P. Ai, H.X. Yang\*

Department of Chemistry, Wuhan University, Wuhan 430072, PR China

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## ABSTRACT

FeSi<sub>6</sub>/graphite composite was prepared by mechanical ball milling. The FeSi<sub>6</sub> alloy particles consist of an electrochemically active silicon phase and inactive phases FeSi<sub>2</sub>, distributed uniformly in the graphite matrix. The composite anode offers a large reversible capacity (about 800 mAh g<sup>-1</sup>) and good cycleability, due to the buffering effect of the inactive FeSi<sub>2</sub> phase and graphite layers on the volumetric changes of Si phase during lithium–Si alloying reaction. Since FeSi<sub>6</sub> alloy is a low-cost industrial material, this alloy compound provides a possible alternative for development of high capacity lithium-ion batteries.

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## 1. Introduction

Silicon and silicides have received considerable research attention in recent years as high capacity anode materials for Li-ion batteries [1–5]. However, there are two main problems of these materials for lithium battery applications. One is the severe volumetric change of these materials during charge and discharge cycles [6], which result in cracking and pulverization of the electrode, leading to a rapid capacity fading [7,8]. The other is their high irreversible capacity at the first cycle due to the phase transformation of the silicon phase alloyed with lithium and the electrochemical reduction of electrolyte solvent on the anode surface [9,10].

Several approaches have been suggested to overcome these problems. A commonly used method is to reduce the size of Si particle to nanosize [11,12]. It is revealed the capacity fade of smaller Si particles was much lower than that of larger Si granules because the volumetric expansion and contraction of the alloy particles become alleviated with decreasing particle size. Since the nanoparticles would aggregate to form inactive dense blocks during charge–discharge cycling, a simple size reduction of the Si particles cannot effectively eliminate its capacity degradation. Another approach is the use of dual-phase composite materials that consist of an inactive host matrix and well-dispersed active materials [13–17]. The homogeneous inactive phase acts

as a buffer to suppress the volumetric changes of the alloy electrodes.

In recent reports [14–16,18], composites of silicon (or silicides) and graphite have been prepared by mechanical milling and found to be a feasible way for improving the cycleability of Si anodes. In this work, we report a cycleable FeSi<sub>6</sub>/C composite prepared by mechanical ball milling and describe the structural and electrochemical properties of the composite as an anode material for lithium ion batteries.

## 2. Experimental

FeSi<sub>6</sub> alloy was an industrial product (99% purity, Wuhan Hongda Materials Co., Ltd., China), composed of ~25 wt.% Fe and ~75 wt.% Si. Graphite powder was a commercial product of chemical grade (99% purity). For experimental use, the FeSi<sub>6</sub> alloy was firstly pulverized into fine powders of several tens of micrometers by high-energy ball milling (8000 M Mixer/Mill, SPEX, USA) for 7 h and then milled with graphite by a planetary mill (QM-1SP04, Nanjing, China) with the rotation speed of 240 rpm for 6 h both in Ar atmosphere. The weigh ratio of FeSi<sub>6</sub> alloy and graphite powder was 60:40. The weight ratio of milling balls to the powder materials was maintained as 20 to 1.

The structural and surface morphology of the as-prepared FeSi<sub>6</sub>/C composite were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000) using Cu K $\alpha$  radiation and scanning electron microscopy (SEM, Quanta 200, FEI, Netherlands).

To evaluate the electrochemical characteristics of the FeSi<sub>6</sub>/C composite anode, the electrode was prepared by mixing 70 wt.%

\* Corresponding author. Tel.: +86 27 68754526; fax: +86 27 87884476.  
E-mail address: [ece@whu.edu.cn](mailto:ece@whu.edu.cn) (H.X. Yang).

active material (Si:FeSi<sub>2</sub>:graphite = 30:30:40 by wt.), 10 wt.% acetylene black and 20 wt.% PTFE into paste, then rolling the pasted mixture into ca. ~0.1 mm thick electrode sheet, and finally pressing the electrode sheet onto a copper net. The charge–discharge experiments were carried out on the test cells of a three–electrode design with reference to Li counter electrode. The separator was Celgard 2400 microporous membrane. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1:1:1 by wt., Shines-tar Battery Materials Co., Ltd., China). The cells were assembled in an argon-filled glove box and galvanostatically charged and discharged over a voltage range of 0.02–1.5 V at a current density of 100 mA g<sup>-1</sup> by battery tester (BTS-55 Neware Battery Testing System, Shenzhen, China). Cyclic voltammetry (CV) measurements were performed using an electrochemical workstation (CHI660a, Shanghai, China) in a voltage range of 0.01–1.5 V at a scanning rate of 0.05 mV s<sup>-1</sup>.

### 3. Results and discussion

The XRD patterns of FeSi<sub>6</sub> alloy and its composite with graphite are shown in Fig. 1. Compared with standard X-ray diffraction data of silicon and silicides, FeSi<sub>2</sub> and Si phases are clearly seen in the XRD patterns of original FeSi<sub>6</sub> alloy and no any XRD signals of elemental Fe were detected, indicating that the FeSi<sub>6</sub> alloy purely consisted of FeSi<sub>2</sub> and Si phases. Thus, FeSi<sub>6</sub> alloy can be expressed as FeSi<sub>2</sub> + 4Si, and the weight ratio of active Si and inactive FeSi<sub>2</sub> is very close to 1:1. When the alloy powder was further ground by high-energy ball milling, all the XRD lines became broadened and the intensities of Si phase decreased drastically, suggesting that the surface layer of alloy particles were mainly composed of FeSi<sub>2</sub> phase. When the fine alloy powder was milled with graphite, the XRD pattern of the FeSi<sub>6</sub>/C composite (Fig. 1c) did not exhibit much changes except for the appearance of graphite peaks at 2θ = 26.5°, 43.7°, 44.6°, indicating that no new phase was formed in mechanical milling treatment.

Fig. 2 shows the SEM images of FeSi<sub>6</sub> alloy powder and FeSi<sub>6</sub>/C composite. It can be seen from the figures that the FeSi<sub>6</sub> alloy particles have an average size of 200–300 nm after high-energy ball milling and disperse uniformly on the graphite surface. Since the graphite particles are flexible and conductive, it is expected that such a composite structure of the electrode can accommodate the large volumetric changes of Si during cycling.

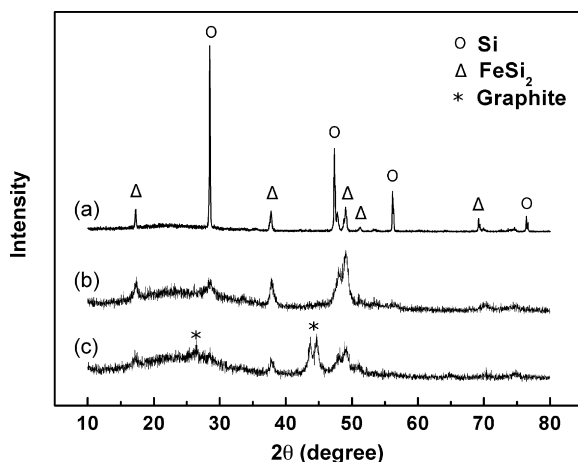


Fig. 1. XRD patterns of FeSi<sub>6</sub> alloy: (a) original powder, (b) ball-milled, (c) milled with graphite.

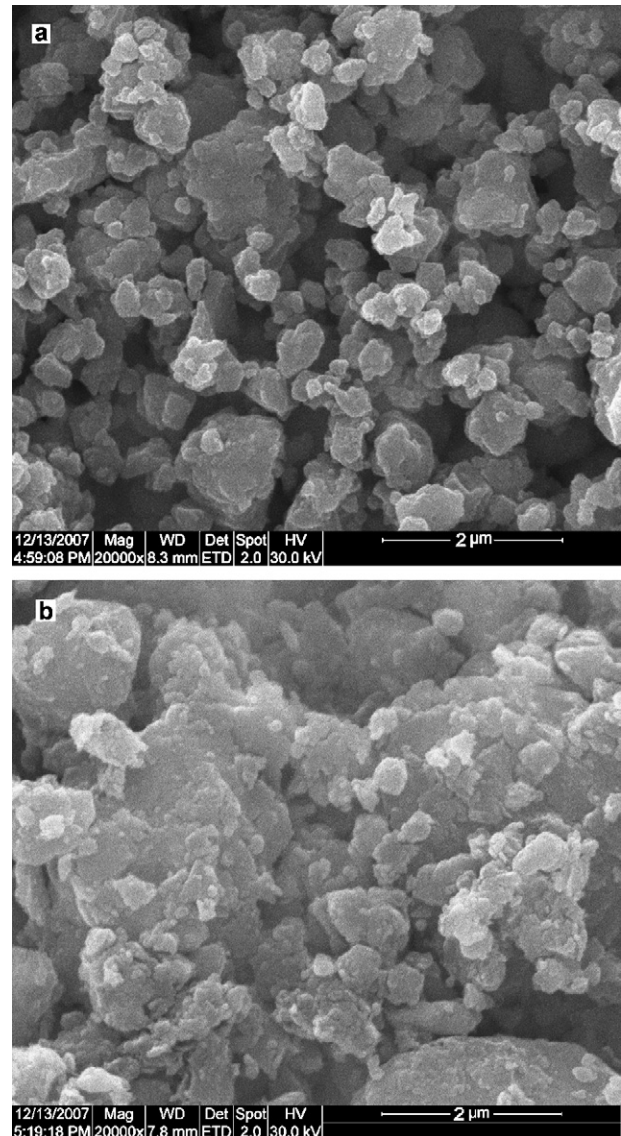


Fig. 2. SEM images of (a) FeSi<sub>6</sub> alloy, (b) FeSi<sub>6</sub>/C composite.

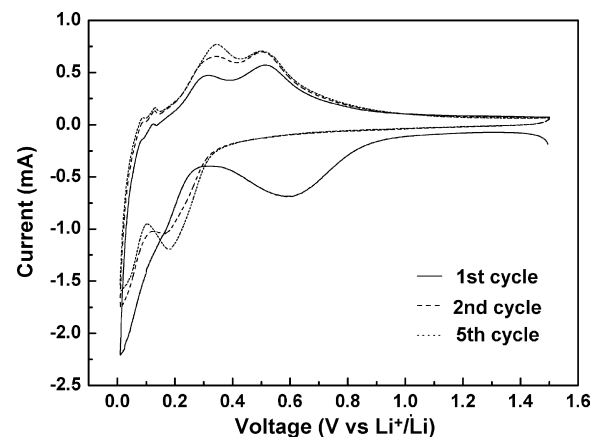


Fig. 3. CV curves of the FeSi<sub>6</sub>/C composite electrode in 1 M LiPF<sub>6</sub> in EC–DMC–EMC (1:1:1 by wt.).

Fig. 3 shows the cyclic voltammograms of the  $\text{FeSi}_6/\text{C}$  electrode in 1 M  $\text{LiPF}_6 + \text{EC} + \text{DMC} + \text{EMC}$  electrolyte. In the first cathodic scan, there are three reduction peaks appearing at 0.6 V, 0.15 V and 0.08 V featuring the Li-insertion process. The first broad peak at 0.6 V appeared only in the initial scan and disappeared from the second and subsequent scans, implying that this current peak is caused by the electrochemical reduction of electrolyte solvent for the formation of SEI film on the composite anode [19]. The latter two cathodic peaks are located right at the formation potential of lithium intercalating compounds and therefore can be assigned to Li-insertion into silicon and graphite, respectively. Once the potential was reversed in positive scan, two anodic peaks appeared at 0.51 V and 0.30 V, corresponding to the deintercalation of lithium ions from the silicon and graphite. Obviously, the pair of the redox peaks at 0.15 V and 0.51 V should be attributed to the reversible alloying and dealloying reactions of lithium in the Si phase [20].

The specific capacity and cycleability of  $\text{FeSi}_6/\text{C}$  composite electrodes were measured by constant current discharge/charge. Fig. 4 gives the charge–discharge profiles of the  $\text{FeSi}_6/\text{C}$  electrode. In the first cycle, the  $\text{FeSi}_6/\text{C}$  anode showed a large charge capacity of  $1758 \text{ mAh g}^{-1}$  and delivered a discharge capacity of  $795 \text{ mAh g}^{-1}$ , in which quite a few of the charging capacity ( $\sim 600 \text{ mAh g}^{-1}$ ) was consumed at the potential  $\geq 0.4 \text{ V}$ . The charging plateau at high voltage of 0.8–0.5 V was only observable in the first charging curve and disappeared since the second cycle, suggesting that this charging capacity was consumed by electrolyte reduction for the SEI formation on the alloy surface. This observation is in good agreement with CV measurement. Once the SEI layer is formed, the composite anode showed quite high charge–discharge efficiency. From the third cycle and afterwards, the  $\text{FeSi}_6/\text{C}$  electrode displayed a reversible charge and discharge capacity of  $800\text{--}700 \text{ mAh g}^{-1}$  with a coulombic efficiency  $>90\%$ . The initial discharge capacity ( $795 \text{ mAh g}^{-1}$ ) of the  $\text{FeSi}_6/\text{C}$  composite is possibly contributed by both active Si and graphite. Since the discharge capacity of graphite is about  $250 \text{ mAh g}^{-1}$  in our experiments, the active Si in the composite should give a discharge capacity of  $\sim 2320 \text{ mAh g}^{-1}$  ( $(795 - 250 \times 0.4) / 0.3$ ), which corresponds to the formation of  $\text{Li}_x\text{Si}$  alloy with  $x = 2.4$  during the alloying process. Compared to the theoretical value of  $\text{Li}_x\text{Si}$  alloy ( $x = 4.4$ ), the discharge capacity of the  $\text{FeSi}_6/\text{C}$  composite could be improved in future works.

Fig. 5 shows the cycling performance of  $\text{FeSi}_6/\text{C}$  composite electrode. As it shown, the  $\text{FeSi}_6/\text{C}$  composite electrode displays good capacity retention and gives a reversible capacity

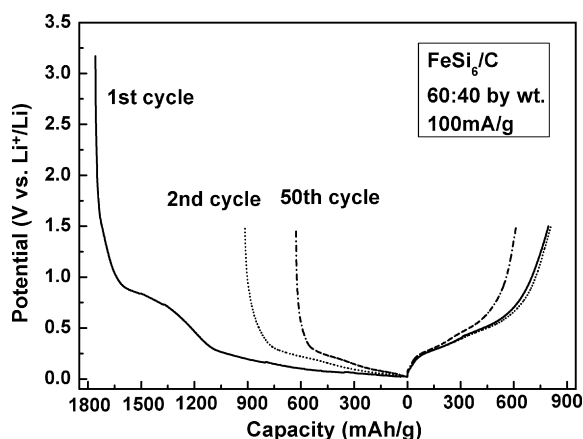


Fig. 4. The discharge–charge profiles of the  $\text{FeSi}_6/\text{C}$  composite electrode in 1 M  $\text{LiPF}_6$  in EC–DMC–EMC (1:1:1 by wt.).

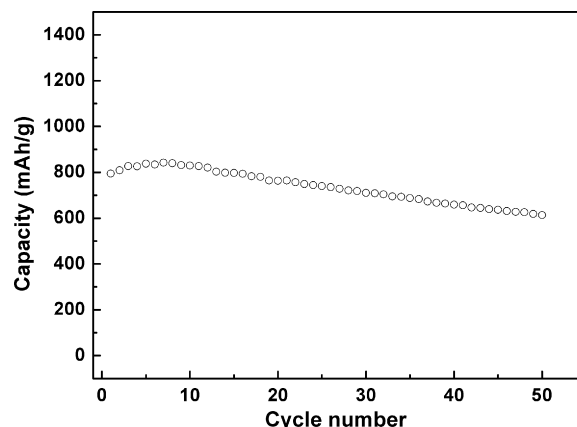


Fig. 5. The cycling performance of  $\text{FeSi}_6/\text{C}$  composite electrode.

of ca.  $615 \text{ mAh g}^{-1}$  after 50 cycles. This improved cycleability may be attributed to the buffering effect of the inactive  $\text{FeSi}_2$  phase and graphite layers, which serve as an inert and conductive matrix to alleviate the volumetric change of Si phase [14–16].

The major problem of the  $\text{FeSi}_6$  material is its low charge/discharge efficiency, approximately 45%, at the first cycle. This large irreversible capacity ( $\sim 650 \text{ mAh g}^{-1}$ ) of the  $\text{FeSi}_6/\text{C}$  composite may be brought about by a large increase in the grain boundaries and active sites of the surface of the composite material, which were produced during mechanical ball milling. To solve this problem, we are now trying to use surface modifications [19] and electrolyte additives [21] to improve the initial charge–discharge efficiency.

#### 4. Conclusions

A  $\text{FeSi}_6/\text{C}$  composite anode material was prepared by mechanical ball milling. The  $\text{FeSi}_6$  alloy particles are comprised of an electrochemically active Si phase and inactive phases  $\text{FeSi}_2$ , which are dispersed uniformly in graphite layers. A reversible capacity of  $800 \text{ mAh g}^{-1}$  for  $\text{FeSi}_6/\text{C}$  composite electrodes was achieved with considerable cycling stability. Since  $\text{FeSi}_6$  alloy is a very low-cost industrial material, this alloy compound provides a possible alternative for development of high capacity lithium-ion batteries.

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#### References

- [1] H. Kim, J. Choi, H.J. Sohn, T. Kang, J. Electrochem. Soc. 146 (1999) 4401.
- [2] Y. Liu, K. Hanai, T. Matsumura, N. Imanishi, A. Hirano, Y. Takeda, Electrochem. Solid-State Lett. 7 (2004) A492.
- [3] I.-S. Kim, P.N. Kumta, G.E. Blomgren, Electrochem. Solid-State Lett. 3 (2000) 493.
- [4] H.Y. Lee, S.M. Lee, J. Power Sources 112 (2002) 649.
- [5] H. Jung, M. Park, Y.G. Yoon, G.B. Kim, S.K. Joo, J. Power Sources 115 (2003) 346.
- [6] B.A. Boukamp, G.C. Lesh, R.A. Huggins, J. Electrochem. Soc. 128 (1981) 725.
- [7] J. Yang, M. Winter, J.O. Besenhard, Solid State Ionics 90 (1996) 281–287.
- [8] A. Netz, R.A. Huggins, W. Weppner, J. Power Sources 119–121 (2003) 95–100.
- [9] J.W. Kim, J.H. Ryu, K.T. Lee, S.M. Oh, J. Power Sources 147 (2005) 227.
- [10] J.H. Ryu, J.W. Kim, Y.-E. Sung, S.M. Oh, Electrochem. Solid-State Lett. 7 (2004) A306.
- [11] Z.P. Guo, J.Z. Wang, H.K. Liu, S.X. Dou, J. Power Sources 146 (2005) 448.
- [12] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, Electrochem. Solid-State Lett. 2 (1999) 547.

- [13] G.X. Wang, L. Sun, D.H. Bradhurst, S. Zhong, S.X. Dou, H.K. Liu, J. Power Sources 88 (2000) 278.
- [14] H. Dong, R.X. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, Electrochim. Acta 49 (2004) 5217.
- [15] H. Dong, X.P. Ai, H.X. Yang, Electrochem. Commun. 5 (2003) 952.
- [16] M.S. Park, Y.J. Lee, S. Rajendran, M.S. Song, H.S. Kim, J.Y. Lee, Electrochim. Acta 50 (2005) 5561.
- [17] H.Y. Lee, Y.L. Kim, M.K. Hong, S.M. Lee, J. Power Sources 141 (2005) 159.
- [18] C.S. Wang, G.T. Wu, X.B. Zhang, Z.F. Qi, W.Z. Li, J. Electrochem. Soc. 145 (1998) 2751.
- [19] Y.L. Cao, L.F. Xiao, X.P. Ai, H.X. Yang, Electrochem. Solid-State Lett. 6 (2003) A30.
- [20] S. Bourderau, T. Brousse, D.M. Schleich, J. Power Sources 81–82 (1999) 233.
- [21] Y. Ein-Eli, S.R. Thomas, V.R. Koch, J. Electrochem. Soc. 143 (1996) L195.