

Short communication

Carbon-coated Ni₂₀Si₈₀ alloy–graphite composite as an anode material for lithium-ion batteries

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Received 18 June 2004; accepted 19 August 2004

Available online 14 October 2004

Abstract

A carbon-coated Ni₂₀Si₈₀ alloy–graphite composite has been studied as the anode for lithium-ion batteries. The composite is prepared by simple heat-treatment of a mixture of coal tar pitch and a Ni₂₀Si₈₀–graphite composite at 900 °C and under argon. The Ni₂₀Si₈₀ alloy powders are synthesized by mechanical alloying. The composite demonstrates promising electrochemical properties such as high reversible capacity, excellent cycle performance, and sufficiently high initial charge–discharge coulombic efficiency. This suggests buffering and conductive actions on the main active material, viz., Ni₂₀Si₈₀ alloy, of the graphite. These two effects are strongly enhanced by the carbon coating treatment.

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Keywords: Lithium-ion battery; Anode materials; Carbon-coated composite; Ni–Si alloy; Mechanical alloying

1. Introduction

In recent years, intensive studies have been conducted on Si-based anode materials to increase the specific energy of lithium-ion batteries [1–8]. The major problem with Si-based materials is the large volume changes associated with lithium insertion and extraction, that lead to drastic capacity fading on cycling. It has been reported [4,5] that this problem of Si-based anode materials can be effectively circumvented by applying a carbon coating. Although a carbon coating significantly improves the electrochemical performance of Si, the formation of alloy phases with high lithium-content, which cause structural damage and degrade cycling performance, has still to be overcome.

Previous investigations [3,7,9–11] have shown that the alloying of Si with an inactive metal element (e.g., Zr, Ni, Fe and Cr) limits alloying of lithium with Si to form high lithium-content alloys, and that the metal silicide phases act

as a buffering matrix for the formation of Li_xSi. Moreover, composites of metal silicide alloys and graphite, prepared by ball-milling a mixture of metal–silicon alloy and graphite powders have exhibited good cycleability and a high reversible capacity of about 600 mAh g⁻¹ [11]. Nevertheless, the first irreversible capacity loss, which is mainly caused by electrolyte decomposition and the formation of a passivation film on the graphite particles, limits the applicability of metal silicide alloy–graphite composite materials. This irreversible capacity can be reduced through a surface modification that is based on coating the graphite with carbon [12]. Therefore, it is expected that the combined effects of mixing graphite with metal silicide alloys and carbon coating will lead to a highly optimized composite structure for Si-based anode materials. Carbon has been successfully coated on graphite powder by simple heat-treatment of mixtures of graphite and carbon precursors, such as polyvinyl chloride and coal tar pitch, in which carbonization takes place via a liquid phase [12,13]. It was found that the carbon coating can reduce significantly the initial irreversible capacity of the graphite, even in propylene carbonate-based electrolyte [13–16].

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In the study, an attempt has been made to improve the electrochemical performance of silicon-based alloy–graphite composites, especially in terms of the initial charge–discharge coulombic efficiency, by coating with disordered carbon. This has been achieved by mechanically mixing the composite and coal tar pitch, followed by heat-treatment under an argon flow for pyrolysis of the coal tar pitch. The excellent electrochemical performance of the resultant product as an anode material for lithium-ion batteries is demonstrated.

2. Experimental

Metal silicide alloy powders of $\text{Ni}_{20}\text{Si}_{80}$ composition were prepared by milling in a high-energy ball-mill (SPEX Mixer/Mill 8000). The metal silicide alloy–graphite (Timrex SFG6; 1:1, w/w) composites were obtained by ball-milling in a planetary mill (Pulverisette 7, Fritsch) at a rotation rate of 1600 rpm in an argon atmosphere. Carbon-coated composites were prepared by mechanically mixing the composite powders in a mortar with 70 wt.% coal tar pitch and heating the mixture in an alumina boat to 900 °C for 1 h under an argon flow. The phases present in the as-milled and carbon-coated composite powders were analyzed by means of X-ray diffraction (XRD) with a Cu $K\alpha$ source.

Coin cells (type 2016) were fabricated to evaluate the electrochemical properties. The electrodes were made by dispersing 90 wt.% active materials and 10 wt.% poly(vinylidene fluoride) (PVDF) binder in a *N*-methyl-2-pyrrolidone (NMP) solvent. The resultant slurries were spread on a copper mesh, dried at 120 °C under vacuum overnight to remove the NMP, and then pressed into a sheet. The electrolyte was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v, provided by Cheil Industries Inc., South Korea). Half-cells were assembled in an argon-filled glove-box. The cells were galvanostatically charged and discharged in the voltage range 0–1.2 V versus Li/Li^+ at a current density of 0.2 mA cm^{-2} .

3. Results and discussion

Carbon-coated $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composites were prepared by means of three processes, as described in Section 2, namely: (i) $\text{Ni}_{20}\text{Si}_{80}$ alloy formation by mechanical alloying; (ii) uniform mixing of the $\text{Ni}_{20}\text{Si}_{80}$ alloy and graphite particles; (iii) carbon coating treatment of the $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite.

The XRD patterns of the products obtained in each stage are presented in Fig. 1. The mechanically alloyed $\text{Ni}_{20}\text{Si}_{80}$ powders exhibit the broadened peaks of the NiSi_2 and silicon phases (Fig. 1(a)). These peaks are caused by grain refinement and lattice internal strain. It should be noted that the reflection line positions of the crystalline NiSi_2 and silicon phases nearly overlap each other. Note, since the starting mixture

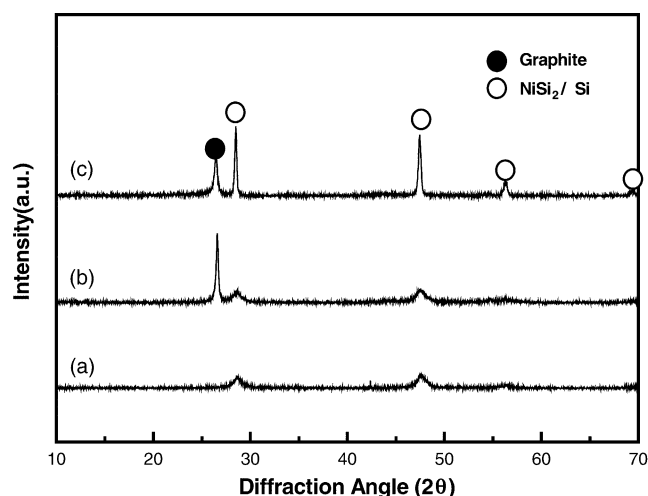


Fig. 1. X-ray diffraction patterns of: (a) ball-milled $\text{Ni}_{20}\text{Si}_{80}$ powder; (b) ball-milled $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite; (c) carbon-coated $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite.

for mechanical alloying contains an excess of silicon compared with NiSi_2 , it is assumed that the mechanical alloyed powders consists of the two phases. The XRD pattern of a carbon-coated composite powder is shown in Fig. 1(c); the powder was prepared by heating a mixture of the composite material and coal tar pitch (70 wt.%) at 900 °C in an argon flow. After carbon coating, the diffraction peaks become narrow and increase in their intensities, which, indicates that the crystallinity of both the NiSi_2 and Si phases has been enhanced.

A comparison of the charge (lithium insertion)–discharge (lithium extraction) curves is given in Fig. 2 for the first two cycles of the products corresponding to each stage in Fig. 1. The carbon-coated composite experiences the lowest irreversible capacity on the first cycle, although the capacity is decreased to some extent. The polarization, as measured by the voltage drop at the cut-off voltage (i.e., 1.2 V) for the discharge reaction, decreases significantly with carbon coating treatment, as shown in Fig. 2(c). These results demonstrate that carbon coating treatment improves the conductive connection between the $\text{Ni}_{20}\text{Si}_{80}$ alloy and the graphite particles with the addition of surface modification that decreases the first irreversible capacity associated with the surfaces of graphite particles. For the carbon-coated sample, it is found that a single plateau around 0.1 V is observed during the first lithium insertion. During the second lithium insertion, however, the curve gradually approaches the cut-off voltage without a plateau. On the other hand, during the extraction reaction, the carbon-coated sample shows a distinct plateau at around 0.45 V. This behaviour is attributed to the enhanced crystallinity of the Si phase after carbon coating treatment, which is supported by the XRD data presented in Fig. 1.

The specific capacity of the carbon-coated composite as a function of cycle number is given in Fig. 3, together with data from $\text{Ni}_{20}\text{Si}_{80}$ alloy and $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite electrodes for comparison. It is seen that the cycling

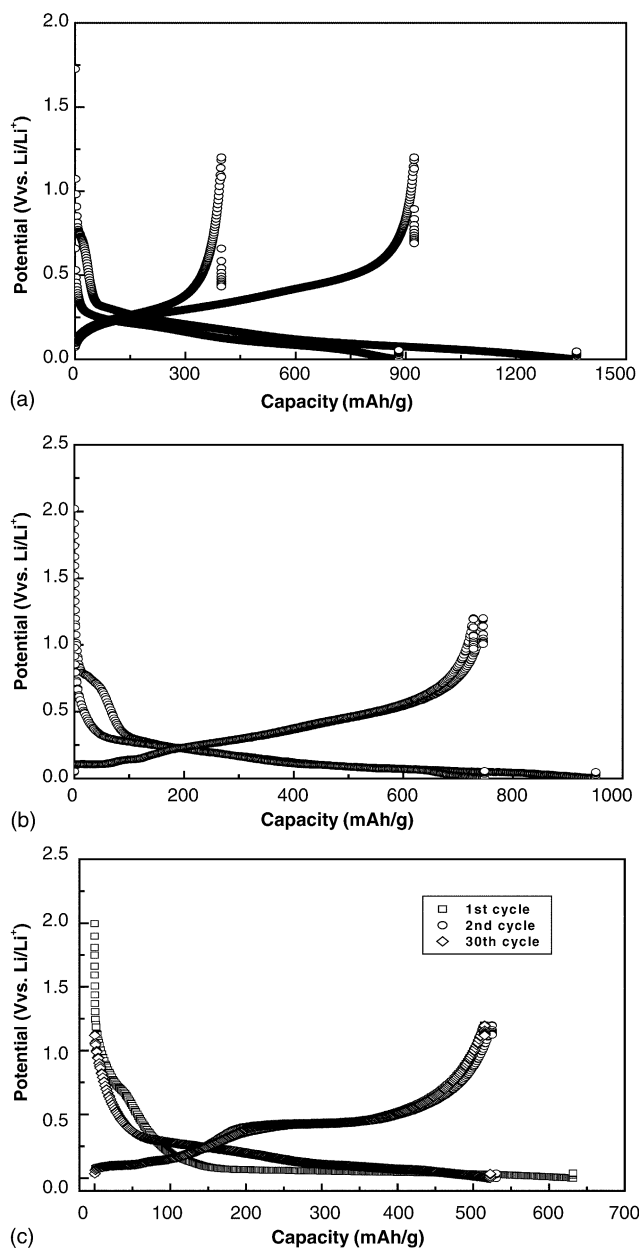


Fig. 2. Charge–discharge curves for first two cycles of electrodes described in Fig. 1. Note that, for the carbon-coated composite electrode (sample c) the 30th cycle profiles are additionally compared.

performance of the $\text{Ni}_{20}\text{Si}_{80}$ alloy is improved significantly by making a composite with graphite, and that further improvement is achieved by carbon coating treatment on the composite. The carbon-coated composite electrode displays excellent capacity retention and also stable charge–discharge behaviour as illustrated in Fig. 2(c). These results suggest that graphite imparts a buffering action on the volume changes of $\text{Ni}_{20}\text{Si}_{80}$ alloy as well as electrical conductivity improvement during cycling. These effects are strongly enhanced by carbon coating treatment.

The XRD pattern obtained for the electrode after 30 cycles is shown in Fig. 4 and is identical to that in Fig. 1(c). This

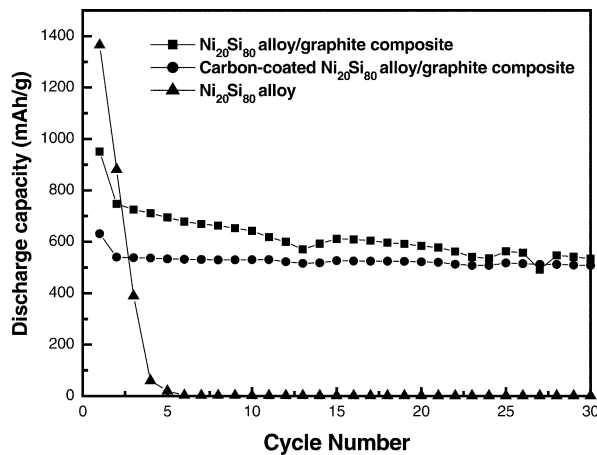


Fig. 3. Cycling behaviour of electrodes described in Figs. 1 and 2.

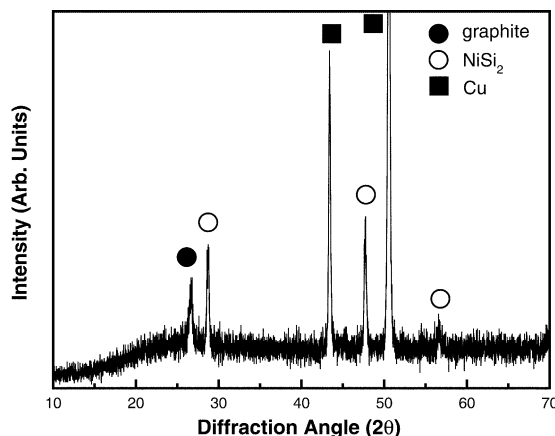


Fig. 4. X-ray diffraction pattern for carbon-coated $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite electrode after 30 cycles.

indicates that the NiSi_2 phase is stable during cycling and the reversible capacity of the carbon-coated composite electrode is due mainly to the silicon phase in the $\text{Ni}_{20}\text{Si}_{80}$ alloy. The electrochemical performance of the carbon-coated composite electrode could be further improved through optimization of the relative amounts of the components, i.e., alloys, graphite and coated carbon, in the composite. At this point, it is important to note that transition metal–silicon alloys as a core active material in the composite can be produced simply by using relatively inexpensive equipment such as ball-milling and a rapid solidification process. The following process for the synthesis of carbon-coated composites is also simple. This means that the carbon-coated composites investigated here are very promising for practical application as Li-ion battery anodes.

4. Conclusions

A carbon coating treatment has been applied to a $\text{Ni}_{20}\text{Si}_{80}$ alloy–graphite composite that is synthesized by mechani-

cal ball-milling, followed by a simple method of pyrolysing the coal tar pitch with the composite. The carbon coating treatment substantially improves the cycling performance and reduces the initial irreversible capacity loss. This is attributed to buffering and conductive actions of the graphite that are greatly enhanced by the carbon coating treatment. The carbon-coated composite appears to be promising as an anode material.

Acknowledgement

This research was supported by the University IT Research Center Project.

References

- [1] H. Li, X. Huang, Li. Chen, Z. Wu, Y. Liang, *Electrochem. Solid State Lett.* 2 (1999) 547.
- [2] I.S. Kim, P.N. Kumta, G.E. Blomgren, *Electrochem. Solid State Lett.* 3 (2000) 493.
- [3] S.M. Hwang, H.Y. Lee, S.W. Jang, S.M. Lee, S.J. Lee, H.K. Baik, J.Y. Lee, *Electrochem. Solid State Lett.* 4 (2001) 97.
- [4] M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, *J. Electrochem. Soc.* 149 (2002) 1598.
- [5] N. Dimov, S. Kugino, M. Yoshio, *Electrochim. Acta* 48 (2003) 1579.
- [6] J. Yang, B.F. Wang, K. Wang, Y. Liu, J.Y. Xie, Z.S. Wen, *Electrochem. Solid State Lett.* 6 (2003) A154.
- [7] H. Dong, X.P. Ai, H.X. Yang, *Electrochem. Commun.* 5 (2003) 952.
- [8] X.W. Zhang, P.K. Patil, C. Wang, A.J. Appleby, F.E. Little, D.L. Cocke, *J. Power Sources* 125 (2004) 206.
- [9] W.J. Weydanz, M. Wohlfahrt-Mehrens, R.A. Huggins, *J. Power Sources* 81–82 (1999) 237.
- [10] G.X. Wang, L. Sun, D.H. Bradhurst, S. Zhong, S.X. Dou, H.K. Liu, *J. Power Sources* 88 (2000) 278.
- [11] H.Y. Lee, S.M. Lee, *J. Power Sources* 112 (2002) 649.
- [12] H.Y. Lee, S.M. Lee, *Electrochem. Commun.* 6 (2004) 465.
- [13] H.Y. Lee, J.K. Baek, S.W. Jang, S.M. Lee, S.T. Hong, K.Y. Lee, M.H. Kim, *J. Power Sources* 101 (2001) 206.
- [14] I. Kuribayashi, M. Yokoyama, M. Yamashita, *J. Power Sources* 54 (1995) 1.
- [15] W. Qiu, G. Zhang, S. Lu, Q. Liu, *Solid State Ionics* 121 (1999) 73.
- [16] M. Yoshio, H. Wang, K. Fukuda, Y. Hara, Y. Adachi, *J. Electrochem. Soc.* 147 (2000) 1245.