

Short communication

Si–Ni alloy–graphite composite synthesized by arc-melting and high-energy mechanical milling for use as an anode in lithium-ion batteries

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Received 20 May 2005; accepted 29 August 2005

Available online 25 October 2005

Abstract

A Si–Ni alloy and graphite composite is synthesized by arc-melting followed by high-energy mechanical milling. The alloy particles consist of an electrochemically active silicon phase with inactive phases such as NiSi₂ and NiSi distributed uniformly on the surface of the graphite. The inactive phases can accommodate the large volume changes of Si during cycling of the composite as an anode material for lithium batteries. The cycle-life of the composite increases with increase in Si content. A large reversible capacity (about 800 mAh g⁻¹) and good cycleability suggest that the composite may prove to be an alternative to conventional graphite-based anode materials for lithium-ion secondary batteries.

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Keywords: Lithium-ion battery; Anode material; Silicon; Graphite; Nickel; Arc-melting

1. Introduction

Lithium-ion batteries have attracted considerable attention due to the increasing demands for portable electronic devices. Graphite has been used extensively as the commercial anode material for the batteries due to its excellent cycling behaviour upon repeated charge and discharge cycles. The theoretical capacity of graphite is, however, limited to 372 mAh g⁻¹ [1,2]. Therefore, many efforts are being made to find an alternative to carbon in order to increase both the volumetric and mass capacity of anode materials for lithium-ion batteries.

Anode materials such as Si or Sn alloys with high specific capacities have been investigated. These materials can form alloy with lithium and have much higher theoretical capacities

than graphite. The use of Si is particularly interesting due to its high theoretical capacity of 4200 mAh g⁻¹ [3,4]. The Si may react reversibly with lithium to form a variety of Si–Li alloys and finally arrive at the Li_{4.4}Si alloy. On the other hand, Si-based anode materials are unable to maintain their structural integrity during the alloying and de-alloying process with lithium due to the large volume changes of Si. These changes cause significant pulverization of the electrodes and decrease the cycling performance to less than few cycles [5,6]. Several approaches have been investigated to overcome this problem. For instance, Li et al. [7] reported that Si powders with small particle size could decrease the volume expansion during cycling, but satisfactory results were not achieved. Another approach is the use of dual-phase composite materials that consist of Si and a phase that is electrochemically inactive with lithium; the Si acts as an active host material. The materials are prepared by mixing Si and inactive materials such as SiC, TiC and TiN [8–11]. The dispersed inactive phase acts as a buffer to suppress or accommodate the large volume changes of the active host materials.

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In other work, composites of Si and graphite prepared by mechanical milling have shown promising results in terms of good cycleability and high reversible capacity. It has been suggested that the improvement in the electrochemical performance of the Si and graphite composite is due to some bonds between Si and graphite and ductile graphite phase suppressing the volume change effectively. Also, the bonds maintain electronic contact between the active materials [12–16].

This study, presents the electrochemical characteristics of Si–Ni alloy and graphite composites. The Si–Ni alloy is prepared by an arc-melting process with three different ratios of Si and Ni. The selection of the inactive phase is based on the characteristics of the material such as electrochemical inertness and electronic conductivity. Si–Ni alloys are inter-metallic compounds composed of NiSi, NiSi₂ and Si phases. The secondary phases of Si and Ni, such as NiSi and NiSi₂, serve as an inactive buffer matrix in the composite and increase the electronic conductivity of the composite materials. Graphite maintains electronic contact and acts as an active host in the composite.

2. Experimental details

The Si–Ni alloys were synthesized using an arc-melting process followed by quenching. Silicon wafer (Siltron Inc.) and nickel sheets of 99.9% purity were used as starting materials to form multi-phase Si–Ni alloy. The Si:Ni molar ratios of the starting materials were 3:1, 5:1 and 6:1. The two components were melted together under argon atmosphere on a cold copper plate in a vacuum arc furnace. The Si–Ni alloy ingots were arc-melted again two or three times to homogenize the compositions. A high-energy mechanical milling (HEMM) process was used to turn the Si–Ni alloy into powder. The Si–Ni alloy ingot was weighed and loaded into a hardened steel vial containing hardened steel balls. The vial was filled with argon to prevent any oxidation of the starting materials. Finally, the Si–Ni alloy and graphite composites were synthesized by means of HEMM for 30 min. The ball to powder weight ratio was maintained as 3.5 to 1.

To evaluate the electrochemical characteristics, the electrodes were fabricated using a mixture that was made up of 75 wt.% active material and 15 wt.% acetylene black. A solution containing 10 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl-2-pyrrolidinone (NMP) was added to the mixture. The resulting slurry was coated on to a copper mesh. After the electrode was dried at 110 °C for 2 h in vacuum (10^{−3} Torr), it was compressed under a pressure of about 200 kg cm^{−2}. Half (2016 coin-type) cells were used for charging–discharging experiments. The cell assembly was carried out in an Ar-filled glove box with less than 0.1 ppm each of oxygen and moisture. Lithium metal foil was used for both the counter electrodes and reference electrodes, 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) was used as the electrolyte, and Celgard 2400 was used as the separator.

The anodic performance of the Si–Ni alloy and graphite composites was measured over a range from 0.005 to 1.5 V (versus Li/Li⁺). The cycling tests were performed using a Toscat-3000u battery tester (Toyo System Corporation). The struc-

ture and surface morphology of the composite materials were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The composition of each phase in the Si–Ni alloy prepared by arc-melting was analyzed by means of energy dispersion X-ray spectroscopy (EDS).

3. Results and discussion

The X-ray diffraction patterns of the Si–Ni alloy and graphite composites with various ratios of Si and Ni are shown in Fig. 1. All the diffraction lines are indexed to graphite, Si and Si–Ni alloys. Electrochemically inactive NiSi₂ and NiSi phases formed during arc-melting process are clearly seen in the XRD patterns. The data suggest that the Si–Ni alloy has a multi-phase structure that is comprised of electrochemically active and inactive phases. New phases such as SiC were not formed during the high-energy mechanical milling process. Also, the intensity of the Si peak increases in accordance with increase in the Si content and Si is identified as a crystalline phase.

Scanning electron micrographs of the cross-sections of Si–Ni alloys with different ratios of Si and Ni are presented in Fig. 2. These indicate that Si is finely surrounded by an inactive matrix such as NiSi₂ and NiSi phases which act as a buffer to suppress the volume change. The Si–Ni alloy is composed of an electrochemically active Si phase and inactive phases (NiSi₂, NiSi) that were identified using spot-EDS analysis. The black region indicates Si and the grey region indicates a mixture of NiSi₂ and NiSi phases. The amount of inactive phase synthesized during the arc-melting process varies in accordance with the composition of the starting materials. The multi-phase structure of the Si–Ni alloy is suitable to suppress the large volume change of Si during cycling. Hence, it is expected that the electrochemically inactive phases provide structural integrity to the active material and thereby provide stability to the system and capacity retention.

The specific capacity of the Si–Ni alloy and graphite composite material was measured by constant-current charge–discharge testing. The charge and discharge profiles of the above compos-

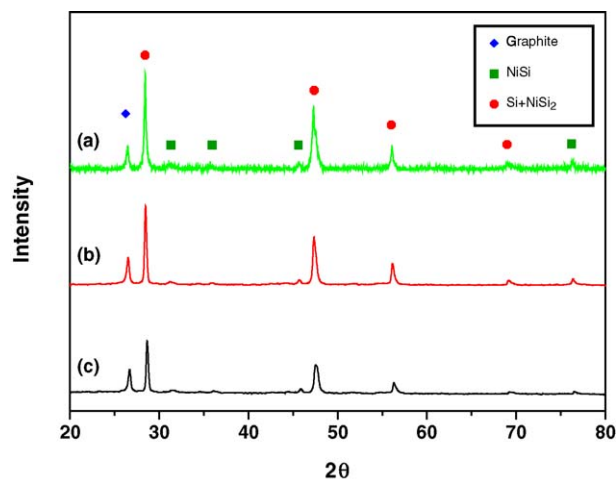
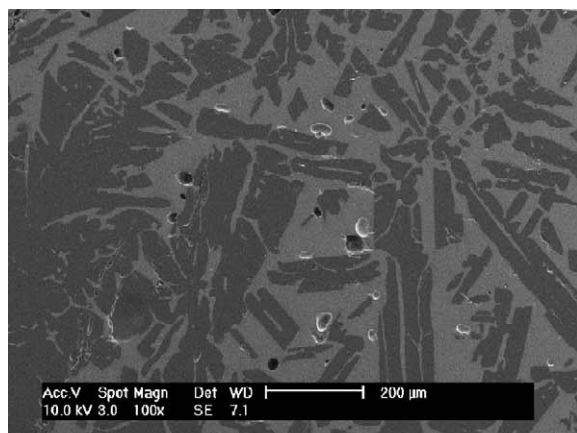
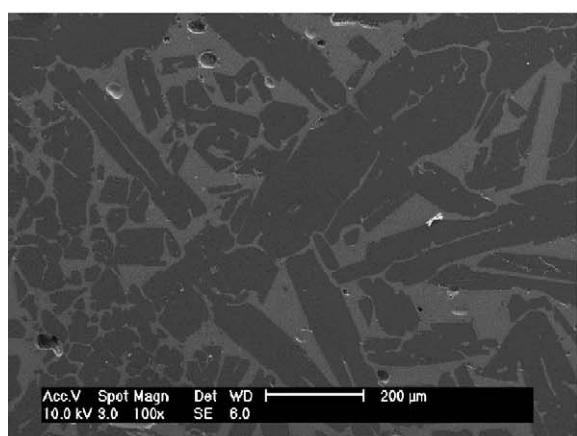


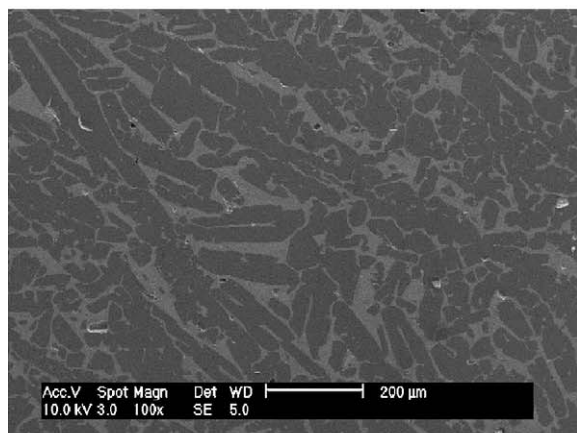
Fig. 1. X-ray diffraction patterns of Si–Ni alloy and graphite composites with various ratios of Si and Ni: (a) 6:1, (b) 5:1 and (c) 3:1 (molar ratio).



(a)



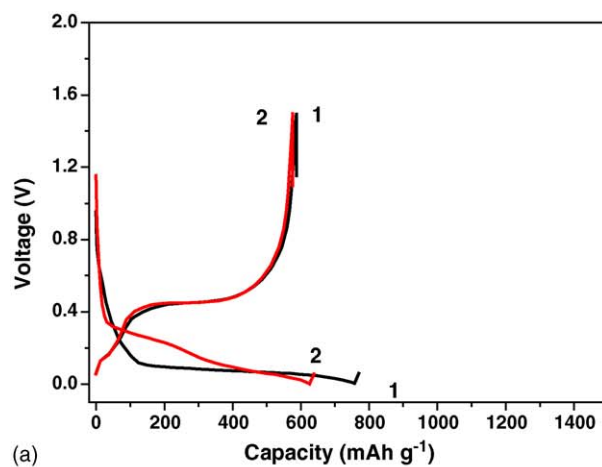
(b)



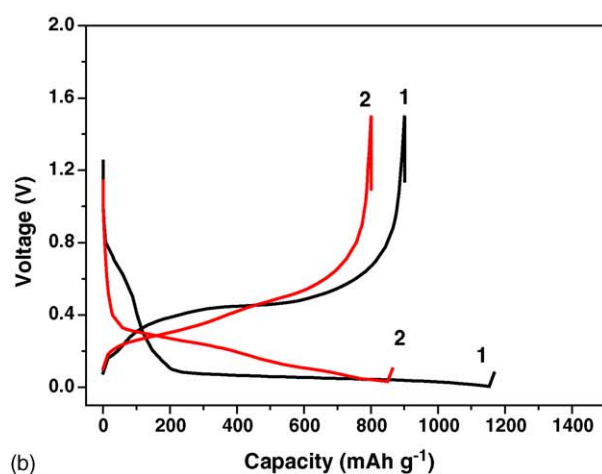
(c)

Fig. 2. Scanning electron micrographs of Si–Ni alloys for the various ratios of Si and Ni: (a) 3:1, (b) 5:1 and (c) 6:1 (molar ratio).

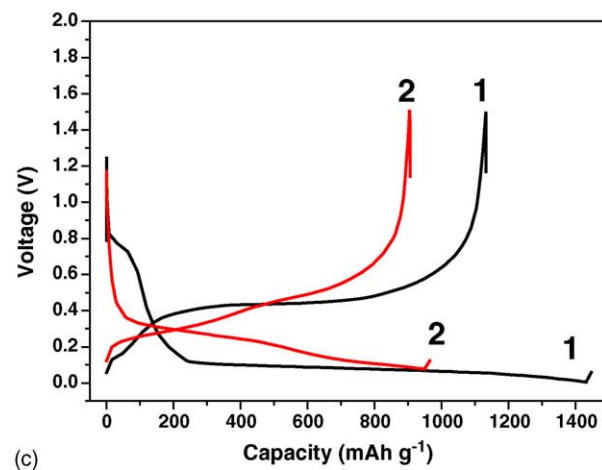
ite material for different ratios of Si and Ni are shown in Fig. 3. The electrode with Si:Ni=3:1 delivers a discharge capacities of about 780 mAh g^{-1} in the first cycle, but with a irreversible capacity of about 180 mAh g^{-1} . On the other hand, electrodes with Si:Ni=5:1 and 6:1 give discharge capacities of about 1150 and 1430 mAh g^{-1} in the first cycle, but with the irreversible capacities of about 250 and 300 mAh g^{-1} , respectively. Part of



(a)



(b)



(c)

Fig. 3. Charge–discharge profiles of Si–Ni alloy and graphite composites with various ratios of Si and Ni: (a) 3:1, (b) 5:1 and (c) 6:1 (molar ratio).

these irreversible capacities is used to form passive solid electrolyte interfaces (SEIs) on the surfaces of the electrodes. The irreversible capacity decreases in the second cycle. In the first cycle, there are discharge plateaus in the range of 0.7–0.8 V, which correspond to the formation of SEI layers. For all composites, no distinctive plateaus are evolved from the second cycle. This indicates the characteristic of amorphous Si.

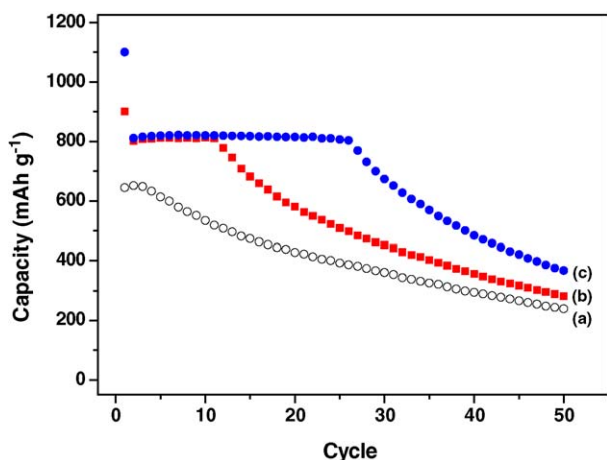


Fig. 4. Cycling performance of Si–Ni alloy and graphite composites with various ratios of Si and Ni: (a) 3:1, (b) 5:1 and (c) 6:1.

The reversible capacities of the Si–Ni alloy and graphite composites with various ratios of Si and Ni as a function of the cycle number are presented in Fig. 4. The cycleability of Si–Ni alloy and the graphite composites increases with increase of Si content. The Si–Ni alloy (Si:Ni = 6:1) and graphite composite show

a reversible capacity of about 800 mAh g^{-1} up to the 28th cycle, which is reasonably a high value. Among the three compositions, the 6:1 ratio of Si–Ni alloy and graphite composite material is superior in terms of capacity and cycle-life.

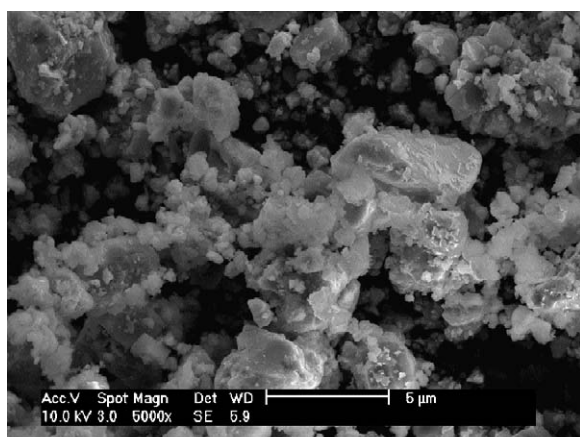
Scanning electron micrographs of Si–Ni alloy powder and a Si–Ni alloy-graphite composite after high-energy mechanical milling for 30 min are given in Fig. 5. The Si–Ni alloy is found to have a particle size of 1–3 μm . It is evident from Fig. 5(b) that the size of the graphite particles is reduced from its original size ($\sim 17 \mu\text{m}$) due to the action of HEMM. The fine Si–Ni particles are uniformly distributed on the graphite surface and the composite has a porous structure that can accommodate volume changes during cycling.

4. Conclusions

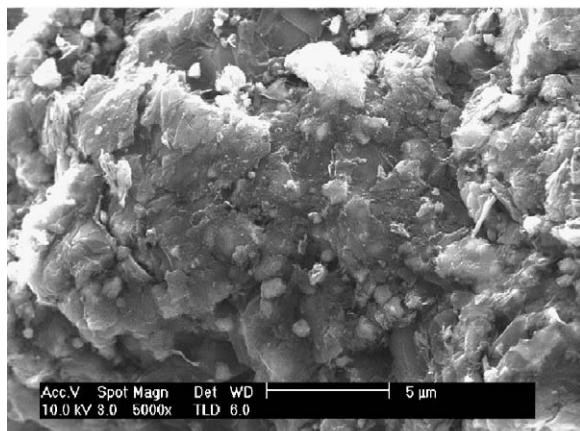
A Si–Ni alloy and graphite composite as an anode material was synthesized by arc-melting followed by high-energy mechanical milling. The Si–Ni alloy particles are comprised of an electrochemically active Si phase and inactive phases such as NiSi_2 and Ni_3Si_2 that are distributed uniformly on the surface of graphite. The inactive phases can accommodate the large volume changes of Si during cycling. It is found that the cycle-life of the composite increases with the increase in Si content the large reversible capacity (about 800 mAh g^{-1}) and good cycleability suggest that the composite could be an alternative to conventional graphite-based anode materials for lithium-ion secondary batteries.

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(a)



(b)

Fig. 5. Scanning electron micrographs of: (a) Si–Ni (6:1) alloy powder prepared by HEMM and (b) Si–Ni (6:1) alloy and graphite composite.