

High capacity carbon-coated Si₇₀Sn₃₀ nanoalloys for lithium battery anode material

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Received (in Cambridge, UK) 29th October 2007, Accepted 6th December 2007

First published as an Advance Article on the web 2nd January 2008

DOI: 10.1039/b716694j

Carbon-coated Si₇₀Sn₃₀ nanoalloys with a particle size < 10 nm were prepared from butyl-capped analogues via firing at 900 °C under a vacuum showed a reversible capacity of 2032 mAh g⁻¹ and excellent capacity retention.

Si can alloy with lithium up to Li_{4.1}Si, corresponding to 4212 mAh g⁻¹, but the large volume change due to the formation of various Li_xSi_y phases (Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄ and Li₂₁Si₅) over 300% generates enormous mechanical stress within the ionic character material, which becomes pulverized during the first few cycles and loses electrical integrity.^{1,2} In order to provide a conduction path after pulverization, the creation of composites with synthetic graphite or carbon precursors followed by firing at higher temperatures to convert to the carbon precursors to amorphous or partially crystalline carbon has been reported.^{3–13} However, these results used nano-Si powders that were severely aggregated and that have higher chances for earlier particle pulverization compared to well-dispersed n-Si particles. Thus, the aggregated n-Si showed rapid capacity fading if the weight portion of the carbon was not increased to at least 60%. Wang *et al.* reported that composite electrodes based on n-Si and carbon aerogel showed a first reversible capacity of 1450 mAh g⁻¹ with no capacity decay in as much as 50 cycles.⁷ Li *et al.* reported that mechanical ball milling with nano-Si and carbon black in air led to a reversible capacity of 1700 mAh g⁻¹ at 0 and 0.8 V.³ A composite with n-Si and graphite was prepared *via* pyrolysis of SiH₄ and showed a reversible capacity of 1000 mAh g⁻¹ (20 wt%Si : 80 wt% graphite).¹¹ Ng *et al.* reported that citric acid with aggregated nano-Si in ethanol fired at 400 °C showed a charge capacity of 1857 mAh g⁻¹; however, due to the aggregated Si nanoparticles, the capacity is lowered to 1500 mAh g⁻¹ after 20 cycles.¹⁰

Therefore, it is very important to obtain a dispersion between Si particles and to coat each Si particle with carbon. Many studies have focused on Si particles, but Si has a much lower electrical conductivity than Sn.¹⁴ Hence, additional conducting agent, such as carbon black, is required. Recently, a method in which carbon was chemically coated onto n-Si or Sn₈₇Co₁₃, Sn₉₀Si₁₀ nanoparticles in the course of synthesis was reported.^{15–17} However, as a result of a tin-rich phase, the

firing temperatures could not exceed 700 °C, implying that the carbonization degree ($I_{D \text{ band}}/I_{G \text{ band}}$) based upon Raman scattering analysis is larger than 2.1, which is larger than that of ordered graphite (0.09). Such a low carbonization degree led to decrease in Li-ion diffusivity into the active materials.

In this paper, well-dispersed Si₇₀Sn₃₀ nanoalloys coated with carbon prepared by vacuum annealing butyl-capped analogues at 900 °C are reported.[‡] They showed a reversible capacity of 2032 mAh g⁻¹ and capacity retention of 97% after 60 cycles.

Fig. 1 shows TEM images of the Si₇₀Sn₃₀ nanoalloys annealed at 900 and 1000 °C for 5 h using butyl-capped analogues. The particle size annealed at 900 °C is 10 nm with a carbon layer thickness of 2 nm. In contrast to the carbon-coated Sn₉₀Si₁₀ and Si nanoalloys, which showed a loosely packed carbon coating layer,^{15,17} Si₇₀Sn₃₀ nanoalloys have a completely covered carbon layer on the nanoalloys without showing any lattice fringes of the nanoalloy. A selected area electron diffraction pattern of the sample showed the presence of point and ring patterns, indicating the presence of single- and poly-crystals. Also observed were ring patterns corresponding to the (220), (400) and (420) planes of Si. The carbon contents of the samples annealed at 900 and 1000 °C were estimated at 11 and 10.7 wt%, respectively. On the other hand, the sample annealed at 1000 °C showed more uniform spherical particles with a particle size of 50 nm. A carbon layer thickness of 2 nm was observed to be similar to that annealed at 900 °C. As the carbon contents of the sample remain constant at 1000 °C, compared with those at 900 °C, while particles were grown to 50 nm, the carbon layer was believed to be loosely packed on the nanoparticles, as shown in Fig. 1(c). The sample shows the lattice fringe of the (220) plane (Fig. 1(d)), which corresponds to 1.92 Å of the face-centered cubic structure of Si with a space group of $Fd\bar{3}m$.

In order to observe the ordering of the carbon layer (carbonization degree) on the Si₇₀Sn₃₀ nanoalloys, Raman scattering of the annealed Si₇₀Sn₃₀ nanoalloys was performed (Fig. 2(a)). The two peaks at ~1360 and ~1580 cm⁻¹ are assigned to the (disordered band) D band and (graphene band) G band, respectively.¹⁷ The dimensional ratios of the D and G band of the samples annealed at 900 and 1000 °C were estimated; the intensity ratios of D and G were found to be 1.47 and 1.43, indicating that the carbonization degrees in both samples are similar. However, these values are much smaller than the carbon-coated Si and Sn_{0.9}Si_{0.1} nanoparticles with a ratio larger than 2.^{15–17} Accordingly, the lower carbonization degree limited the Li ion intercalation with the

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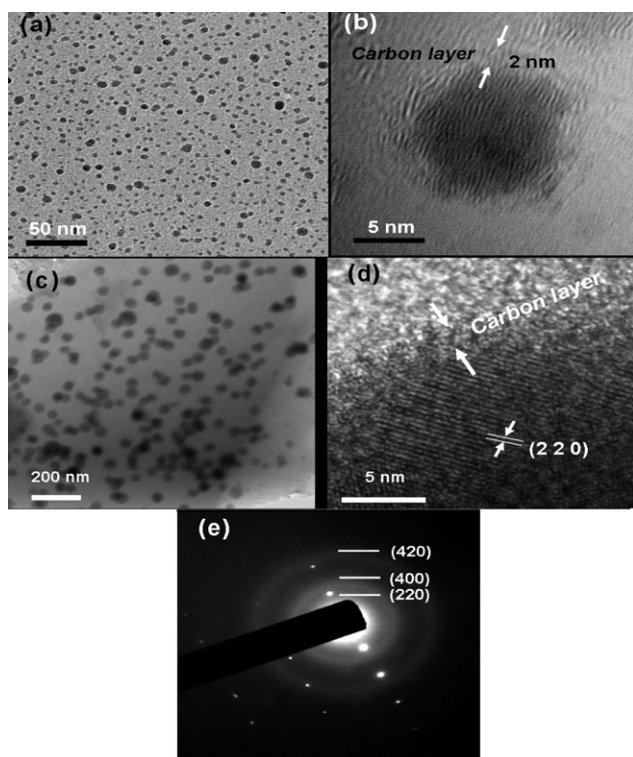


Fig. 1 TEM images of $\text{Si}_{70}\text{Sn}_{30}$ nanoalloys annealed at 900 °C (a, b) and 1000 °C (c, d); (e) is the selected area electron diffraction pattern of (a).

particles; for instance, the discharge capacity of the amorphous carbon-coated Si nanoparticles prepared at 600 °C was limited to 1500 mAh g^{-1} .¹⁷ However, $\text{Si}_{70}\text{Sn}_{30}$ is expected to provide more lithium reactions due to the much higher ordering of the carbon coating layer.

Fig. 3 shows the voltage profiles during the first discharge and charge between 1.2 and 0 V, respectively, at a rate of 0.2 C ($= 1000 \text{ mA g}^{-1}$) in coin-type half cells containing $\text{Si}_{70}\text{Sn}_{30}$ nanoalloys annealed at 900 and 1000 °C. The sample annealed at 900 °C showed first discharge and charge capacities of 2532 and 2032 mAh g^{-1} , respectively, showing a coulombic

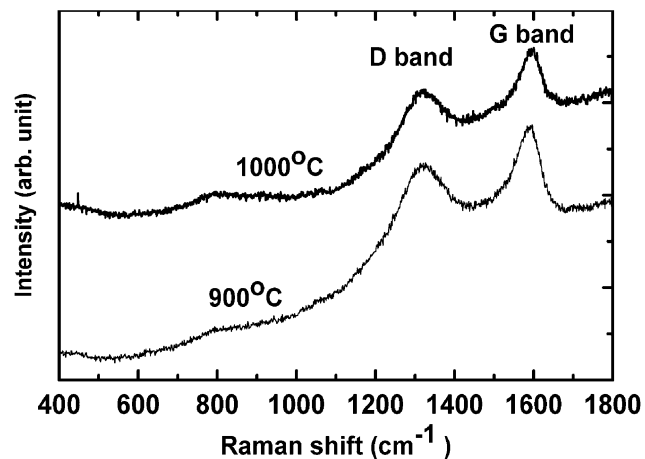


Fig. 2 Raman scattering of $\text{Si}_{70}\text{Sn}_{30}$ nanoalloys annealed at 900 and 1000 °C.

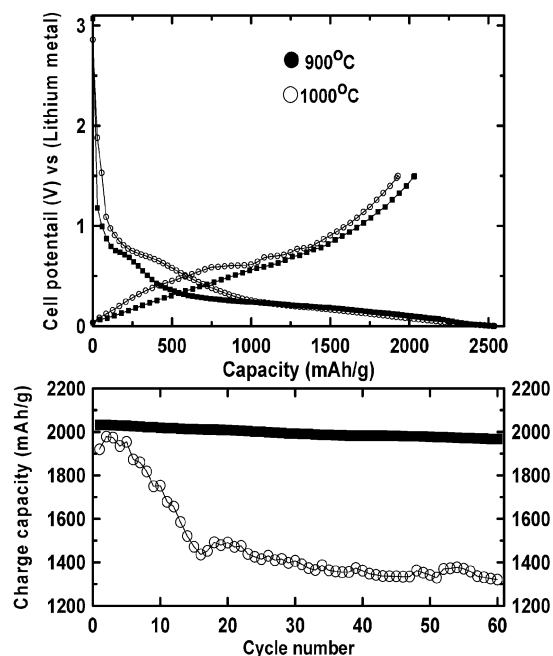


Fig. 3 (a) Voltage profiles of the $\text{Si}_{70}\text{Sn}_{30}$ nanoalloys annealed at 900 and 1000 °C in coin-type half cells between 1.2 and 0 V at a rate of 0.2 C ($= 1000 \text{ mA g}^{-1}$) and (b) charge capacity vs. cycle number of (a).

efficiency of 80%, while that annealed at 1000 °C showed 2537 and 1927 mAh g^{-1} , respectively, showing a coulombic efficiency of 76%. The enhanced coulombic efficiency of the sample annealed at 900 °C may be related to the densely packed carbon that reduced the side reactions with the electrolyte. Capacity retention after 60 cycles for the samples annealed at 900 and 1000 °C was 97 and 66%, respectively. The enhanced capacity retention of the sample annealed at 900 °C compared to that annealed at 1000 °C is related to the nucleation energy barrier for the formation of the new phase, which should be smaller as a larger fraction of Si and Sn atoms are in higher energy states on the highly curved surfaces. Hence, the large volume change due to nucleation of the new phase can be more readily accommodated.^{18,19}

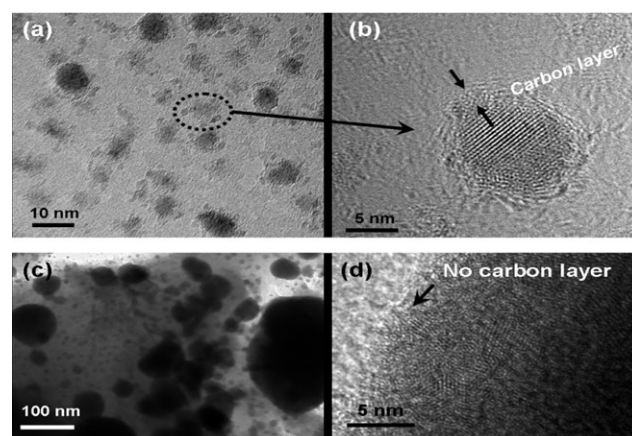


Fig. 4 TEM images of the $\text{Si}_{70}\text{Sn}_{30}$ nanoalloys annealed at (a, b) 900 °C and (c, d) 1000 °C after 60 cycles.

Fig. 4 shows TEM images of the nanoalloys annealed at 900 and 1000 °C after 60 cycles. One interesting point that was not previously observed was the existence of the carbon layer; the sample annealed at 900 °C shows the existence of the carbon layer, and the particle size was similar to that before cycling. On the other hand, the sample annealed at 1000 °C shows particle aggregation and the disappearance of the carbon layer. This result demonstrates that the particle size and carbon layer played an important role in cycle life performance of the material. Furthermore, the particle size must be controlled below 10 nm in order to prevent particle growth during the lithium alloy and de-alloy processes.

Highly reversible and high-capacity Si₇₀Sn₃₀ nanoparticles were prepared from a butyl-capped analogue by vacuum annealing at 900 °C. The reversible capacity was 2050 mAh g⁻¹ and the capacity retention after 60 cycles was 97%.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-331-C00162).

Notes and references

‡Preparation of carbon-coated Si₇₀Sn₃₀ nanoparticles: all the experimental procedures were carried out in purified Ar atmosphere except for the washing process. Sodium naphthalide solution was prepared from 5.4 g (0.23 mol) of sodium (Aldrich, 99.9%) and 19.38 g (0.15 mole) of naphthalene (99%, Aldrich), stirred in 100 ml 1,2-dimethoxyethane for 24 h. 3.1 ml of anhydrous SiCl₄ (Aldrich, 99.999%) and 1.6 ml of SnCl₂ (Aldrich, 99.99%) in a dried 50 ml of 1,2-dimethoxyethane (Aldrich, 99%) were thoroughly mixed in a flask under a dry argon atmosphere in a glove-box. This mixed solution was stirred for 24 h and then 60 ml of butyllithium (n-C₄H₉Li) (Aldrich, 99%) was added. This solution was stirred at room temperature for 4 h and naphthalene being removed by using a rotating evaporator at 110 °C. The product was washed with distilled water seven times and finally vacuum-dried at 120 °C for 48 h. The obtained product, which was a viscous black liquid, was annealed at 900 or 1000 °C for 5 h under a vacuum atmosphere. The obtained nanoparticles were analyzed with ICP-MS to ensure the stoichiometry.

Characterization: HRTEM samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2010F operating at 200 kV. The carbon concentrations were measured using a CHNS analyzer (Flash EA 1112, Thermo Electron Corp.). Inductively coupled plasma-mass spectroscopy (ICP, ICPS-1000IV, Shimadzu) was used to determine the Si and Sn contents. Raman spectroscopy (JASCO, NRS-3000) was used to obtain the graphitiza-

tion degree of an amorphous carbon phase in the sample (ratio of D- and G-band of the carbon), using 633 nm laser excitation. It was necessary to use low laser power density with a ×20 microscope objective with an exposure time of 30 s, in order to avoid laser heating effects. The laser spot diameter reaching the sample was about 2 μm. The laser power at the sample used in this study was 1 mW. The spectra were recorded at 2 cm⁻¹ resolution between 3000 and 50 cm⁻¹. To test the cycle-life performance of each cathode material, a slurry was prepared by mixing the active materials, super P carbon black and a poly(vinylidene fluoride) (PVDF) binder with weight ratio of 80 : 10 : 10 in *N*-methyl-2-pyrrolidone (NMP). A coin-type half cell (2016-size) contained a test electrode, a lithium-metal counter-and-reference electrode, a 15 μm-thick microporous polyethylene separator, and an electrolyte solution of 1.1 M LiPF₆ in EC-DMC (1 : 1 vol%) (Cheil Industries, Korea). The water content and HF level in the electrolyte solution determined by gas chromatography (GC) is 10 and 20 ppm, respectively.

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