Articles

Sn_{0.9}Si_{0.1}/Carbon Core-Shell Nanoparticles for High-Density Lithium Storage Materials

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Sn_{0.9}Si_{0.1} core/carbon shell nanoparticles, with the sizes of 16 and 10 nm, were prepared by annealing as-prepared butyl-capped Sn_{0.9}Si_{0.1} particles with an average particle size of 1 μ m. Even though as-prepared samples were severely encapsulated by butyl terminators, annealing led to pulverization of the bulky particles into core—shell nanoparticles with a shell thickness dependent on the annealing temperature. The core Sn_{0.9}Si_{0.1} size was estimated to be constant at 6 nm, and the carbon shell thickness decreased from 10 to 4 nm with increasing annealing temperature from 600 to 700 °C, respectively. In addition, the carbon shell was found to be more ordered at 700 °C than at 600 °C. Sn_{0.9}Si_{0.1} core/carbon shell nanoparticles exhibited excellent lithium storage ability at a high current rate, resulting in a value of 964 mA·h/g at a rate of 0.3 C (1 C = 1200 mA/g), and demonstrated good capacity retention after 50 cycles.

Introduction

Lithium reactive materials, such as Si, Pb, Sn, and Bi, show Li storage capacities that are much higher than those of carbonaceous materials.1 For instance, the formation of Li_{4.4}Sn results in a theoretical capacity of 991 mA·h/g for the Sn metal. Graphite can store 372 mA·h/g corresponding to LiC₆, and tin can store 991 mA·h/g corresponding to Li_{4,4}-Sn. However, those metals exhibited significant volume changes (>300%) that occur during Li alloying and dealloying, which causes cracking and crumbling of the electrode material and the consequent loss of electrical contact between the single particles, resulting in severe capacity loss.² Obtaining good capacity retention with alloy negative electrodes has proven to be difficult, except when the capacity is constrained to values close to graphite. The reason for failure is believed to be the inhomogeneous volume expansion in the coexistence regions of phases within different lithium concentrations with the same particles, resulting in particle pulverization.^{3–8} This is particularly true for coarse-grained, macrostructured metals. However, me-

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- (1) Huggins, R. A. Solid State Ionics 1998, 113, 57.
- (2) Wachtler, M.; Besenhard, J. O.; Winter, M. J. Power Sources 2001, 94, 189.
- (3) Graetz, J.; Ahn, C. C.; Razami, R.; Fultz, B. Electrochem. Solid State Lett. 2003, 6, A194.
- (4) Mao, O, Turner, R. L.; Courtney, I. A.; Fredericksen, B. D.; Buckett, M. I.; Krause, L. J.; Dahn, J. R. *Electrochem. Solid State Lett.* 1999, 2, 3.
- (5) Yang, J.; Wang, B. F.; Kang, K.; Liu, Y.; Xie, J. Y.; Wen, Z. S.; Electrochem. Solid State Lett. 2003, 6, A151.
- (6) Kim, I.-S.; Blomgren, G. E.; Kumta, P. N. Electrochem. Solid State Lett. 2004, 7, A44.

chanical strain can be reduced by tailoring the particle morphology of the Sn_xM_y (M is metals), particularly by employing smaller particle sizes or making composites with the graphite or carbon.^{9–12} However, smaller particle size resulted in severe side reactions with the electrolytes, resulting in huge irreversible capacity.

There have been many studies on core-shell materials for magnetic and photochemical applications,¹⁴⁻²⁰ but only a few studies on lithium reactive metal alloy core/carbon shell materials have been reported in the open literature.^{7,21} Many studies have used graphite or carbon as a major component to buffer the volume increase between Sn(Si) and

- (7) Lee, K. T.; Jung, Y. S.; Oh, S. M. J. Am. Chem. Soc. 2003, 125, 5652.
- (8) Dong, Q. F.; Wu, C. Z.; Jin, M. G.; Huang, Z. C.; Zheng, M. S.; You, J. K.; Lin, Z. G. Solid State Ionics 2004, 167, 49.
- (9) Yang, J.; Takeda, Y.; Li, Q.; Imanishi, N.; Yamamoto, O. J. Power Sources 2000, 90, 64.
- (10) Yin, J.; Wada, M.; Yoshida, S.; Ishihara, K.; Tanse, S.; Sakai, T. J. Electrochem. Soc. 2003, 150, A1129.
- (11) Yin, J.; Wada, M.; Tanase, S.; Sakai, T. J. Electrochem. Soc. 2004, 151, A583.
- (12) Li, H.; Wang, Q.; Shi, L.; Chen, L.; Haung, X. Chem. Mater. 2002, 14, 103–107.
- (13) Yang, J.; Wachtler, M.; Winter, M.; Besenhard, J. O. *Electrochem. Solid State Lett.* **1999**, *2*, 161.
- (14) Teng, X.; Yang, H. J. Am. Chem. Soc. 2003, 125, 14559.
- (15) Kim, H.; Achermann, M.; Balet, L. P.; Hollingsworth, J. A.; Klimov, V. I. J. Am. Chem. Soc. 2005, 12, 544.
- (16) Lee, W.-R.; Kim, M. G.; Choi, J.-r.; Park, J.-I.; Ko, S. J.; Oh, S. J.; Cheon, J. J. Am. Chem. Soc. 2005, 127, 16090.
- (17) Shi, W.; Zeng, H.; Sahoo, Y.; Ohulchansky, T. Y.; Ding, Y.; Wang, Z. L.; Swihart, M.; Prasad, P. N. Nano Lett. 2006, 6, 875.
- (18) Wang, Q.; Iancu, N.; Seo, D.-K. Chem. Mater. 2005, 17, 4762.
- (19) Grebinski, J. W.; Richter, K. L.; Zhang, J.; Kosel, T. H.; Kuno, M. J.
- Phys. Chem. B 2004, 108, 9745.
- (20) Shutter, E.; Sutter, P.; Zhu, Y. Nano Lett. 2005, 5, 2029.
- (21) Jung, Y. S.; Lee, K. T.; Ryu, J. H.; Im, D.; Oh, S. M. J. Electrochem. Soc. 2005, 152, A1452.

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 $Li_x Sn(Si)$.^{22–25} However, all these studies used conventional mechanical milling for making the carbon/Si or Sn composite, and the mechanically milled metals did not show good dispersity in the carbon matrix. In addition, Sn and tin alloys have not yet reached the reversible capacity of 950 mA•h/g nor good capacity retention at higher C rates.

Recently, new synthetic methods for preparing Sn-based metal alloys and carbon composites were reported. For instance, Wang et al. reported tin graphite loaded with graphite prepared by NaBH₄ reduction of (phen)SnCl₄ in water.²⁶ The composite consisting of 19.8 wt % Sn and 80.2 wt % graphite showed reversible capacity of \sim 400 mA·h/g. Lee et al. reported that tin-encapsulated spherical hollow carbon could be prepared by annealing of sol with tributylphenyltin and the mixture of resorcinol and formaldehyde at 700 °C.⁷ This study showed reversible capacity of \sim 400 mA•h/g with rapid capacity fading, which was attributed to relatively large Sn particle size of >200 nm.⁷ Kim et al. reported that Sn/C composite synthesized by infiltrating tetraethyltin into mechanically milled polystyrene resin powder, followed by heat treatment of these at 600 °C. Sn particle embedded carbon with a weight ratio of 1:1 has reversible stable capacity of \sim 480 mA·h/g out to 30 cycles. This enhancement is due to uniformly dispersed tin particles in the carbon matrix. Capacities of these materials were limited to <500 mA•h/g.²³

In this study, we report the preparation and lithium storage characterization of the $Sn_{0.9}Si_{0.1}$ core/carbon shell nanoparticles with a particle size of 6 nm. We found that as-prepared bulk-sized particles, capped with butyl groups, were fragmentized into nanosized core—shell particles with a different carbon shell thickness, depending on the annealing temperature. Further, these materials demonstrated the reversible capacity of 964 mA•h/g.

Experimental Section

Baldwin et al. prepared octanol-capped Si nanocrystals with a particle size of ~6 nm. However, their method is not appropriate for anode materials because octanol led to the formation of SiO_x on the Si particles after heat treatment at 700 °C.²⁷ Similarly, they also reported that tetrahedrally shaped Si nanocrystals with a particle size of ~100 nm could be prepared using SiCl₄ and sodium naphthalenide in tetrahydrofuran. In this case, the Si particle size is too large for anode material application.²⁸ In this study, we used 0.5 mmol of tetraoctylammonium bromide and 0.1 mmol of PtCl₂ as catalysts to enhance the yield and to control the particle size. Sodium naphthalide solution was prepared from 1.8 g of sodium and 4 g of naphthalene stirred into 80 mL of 1.2-dimethoxyethane. Then 3.2 mL of SnCl₄ (99.999%, Aldrich), 0.8 mL of SiCl₄

- (25) Dimov, N.; Kugino, S.; Yoshio, M. J. Power Sources 2004, 136, 108.
 (26) Wang, Y.; Lee, J. M.; Deivaraj, T. C. J. Electrochem. Soc. 2004, 115,
- (20) Wang, 1., Ecc, J. M., Delvanaj, 1. C. J. Electrochem. Soc. 2004, 115, A1804.
- (27) Baldwin, R. K.; Pettigrew, K. A.; Ratai, E.; Augustine, M. P.; Kauzlarich, S. M. Chem. Commun. 2002, 1822.
- (28) Baldwin, R. K.; Pettigrew, K. A.; Garno, J. C.; Power, P. P.; Liu, G.; Kauzlarich, S. M. J. Am. Chem. Soc. 2002, 124, 1150.



Figure 1. TEM images of (a) Sn₈₀Si₂₀ and (b) Sn₇₀Si₃₀ nanoparticles.

(99.999%, Aldrich), and 100 mL of 1.2-dimethoxyethane were thoroughly mixed, followed by decanting into the sodium naphthalide solution. This mixed solution was stirred for 2 h, and then 20 mL of butyllithium was added. Finally, 0.5 mmol of tetraoctylammonium bromide and 0.1 mmol of PtCl₂, previously dissolved in 1.2-dimethoxyethane, were added dropwise to the solution. A yellow solution was obtained, and the solvent and naphthalene were removed by using both a rotating evaporator and a vacuum at 120 °C, using excess *n*-hexane. Finally, the resulting orange solution was washed with water six times and heat-treated at 600 and 700 °C for 5 h in a tube furnace under vacuum. In the case of $Sn_{1-x}Si_x$, in which x > 0.1, we could not get uniformly distributed core/shell nanoparticles with a particle size <20 nm, resulting in severe particle aggregation. As can be seen in Figure 1, as-prepared $Sn_{80}Si_{20}$ and $Sn_{70}Si_{30}$ nanoparticles show severe particle aggregation and nonuniform particle size distribution. We believe that excess Si may enhance the abnormal particle growth of the $Sn_{1-x}Si_x$.

The cathodes for the battery test cells were made of the annealed samples, super P carbon black, and polyvinylidene fluoride (PVDF) binder (Solef) in a weight ratio of 8.5:0.5:1. The slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone (NMP) (Aldrich) solution of PVDF, carbon black, and the anode material. The cointype half cells (2016R size), prepared in a helium-filled glovebox, contained a cathode, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %) (Cheil Industries).

HRTEM samples were prepared by the evaporation of the dispersed naoparticles in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2000F operating at 200 kV. The carbon concentrations were measured using a CHNS analyzer (Flash EA 1112, Thermo Electron Corp.). Raman spectroscopy (Renishaw 3000) was used to obtain the graphitization degree of an amorphous carbon phase in the sample (ratio of D- and G-band of the carbon), using 633 nm laser excitation.

Results and Discussion

Figure 2 shows Raman scattering of the samples annealed at 600 and 700 °C. The intensity ratio of the D band to the G band (I_{Dband}/I_{Gband}), indicative of the graphitization degree, decreased with increasing annealing temperature. Its values of 2.78 and 2.15 at 600 and 700 °C, respectively, indicate that the annealed sample at 700 °C has a more ordered carbon structure. For comparison, fully graphitized carbon has a I_{Dband}/I_{Gband} of 0.09. This result indicates that the amorphous nature of the coating layer may offer a limited number of lithium intercalation into the Sn_{0.9}Si_{0.1} particles. Cross-linking of carbon layers in disordered carbons hampers the shift to AA stacking, which is necessary for accommodation for a

⁽²²⁾ Yang, J.; Wang, B. F.; Wang, K.; Liu, Y.; Xie, J. Y.; Wen, Z. S. *Electrochem. Solid State Lett.* **2003**, *6*, A154.

⁽²³⁾ Kim, I.-S.; Blomgren, G. E.; Kumta, P. N. *Electrochem. Solid State Lett.* **2004**, *7*, A44.
(24) Wang, G. X.; Yao, J.; Liu, H. K. *Electrochem. Solid State Lett.* **2004**,

^{7,} A250.



Figure 2. Raman scattering of $Sn_{0.9}Si_{0.1}$ core/carbon shell nanoparticles obtained from annealing as-prepared $Sn_{0.9}Si_{0.1}$ particles, capped with butyl groups, at 600 and 700 °C for 5 h.



Figure 3. TEM images of (a) as-prepared $Sn_{0.9}Si_{0.1}$ particles capped with butyl groups, annealed sample (b) at 600 °C and (c) at 700 °C.

higher lithium amount into graphitic sites. Correspondingly, rather low capacity of $<200 \text{ mA}\cdot\text{h/g}$ is observed in disordered carbons such as soft carbons and cokes.²⁹ Accordingly, the sample annealed at 600 °C is expected to show low lithium storage ability.

Figure 3a shows a TEM image of as-prepared particles capped with butyl groups. The average particle size was ~ 1 μ m. Considering the chain length of C₃H₉, this particle size is very large, suggesting that it may consist of nanosized Sn_{0.9}Si_{0.1}. This hypothesis is well-supported by the TEM images of the annealed samples. Figures 3b and 3c are the TEM images of the butyl-capped Sn_{0.9}Si_{0.1} nanoparticles, annealed at 600 and 700 °C, respectively, for 5 h under vacuum. Annealing at 600 °C resulted in ~16 nm particles that were relatively well-dispersed, and annealing at 700 °C resulted in ~10 nm particles. Particles size was an averaged value, and we assumed that the shell thickness was uniform regardless of the core particle size. Figure 4 displays the HRTEM images of the samples annealed at 600 and 700 °C to estimate the carbon shell thickness and Sn_{0.9}Si_{0.1} nanoparticle size. (To clarify the formation of the carbon shell in the sample annealed at 700 °C, shrunken image of the TEM image was added in Figure 4b, and it shows the difference



Figure 4. Magnified high-resolution TEM images of Figures 2b and 2c.

morphology to that of the carbon-coated copper grid (see the parts indicated by arrows)). The sample annealed at 600 $^{\circ}$ C had \sim 5 nm coating thickness, whereas that at 700 $^{\circ}$ C had ~ 2 nm coating thickness. Due to relatively low annealing temperatures, Sn_{0.9}Si_{0.1} nanocrystal size is assumed to remain constant and therefore can be estimated to ~ 6 nm. Decreased shell thickness is due to the formation of more densely packed carbon shells as the graphitization degree increased. Both results indicate that the pure Sn_{0.9}Si_{0.1} nanoparticle size remained constant without particle growth. In addition, both samples show the lattice fringes (200) and (101) which correspond to d spacing values of 2.98 and 2.84 Å, respectively. These values are a little larger than tetragonal tin in JCPDS (#04-0673). In nanoscale materials, supersaturated alloys can be formed without phase segregation and, for example, 10 atom % Ni can be supersaturated into tetragonal tin.³⁰ Similarly, in a macroporous Sn-Co alloy, over 40 atom % Co was reported to be supersaturated in Sn lattices.³¹ The carbon content in both samples remained constant at 11 wt %, but the hydrogen content decreased from 2 from 0.01 wt % as the annealing temperature increased from 600 to 700 °C.

Figure 5 exhibits a schematic diagram for the formation of $Sn_{0.9}Si_{0.1}$ core/shell nanoparticles based upon the above results, dependent on the annealing temperature, and demonstrates that the as-prepared bulk sample with an average particle size of 1 μ m contains many $Sn_{0.9}Si_{0.1}$ nanoparticles terminated with butyl groups. However, upon annealing, the bulk particles fragmentize into many nanosized $Sn_{0.9}Si_{0.1}$ nanocrystals covered with carbon shells.

Figure 6 shows voltage profiles of the $Sn_{0.9}Si_{0.1}$ core/shell nanoparticles at a rate of 0.3 C (1 C = 1200 mA/g). The

⁽³⁰⁾ Watanabe, T. Nanoplating: Microstructure control theory of plated film and data base of plated film microstructure; Elsevier Publishers: Amsterdam, The Netherlands, 2004.

⁽²⁹⁾ Nazri, G. -A.; Pistoia, G. *Lithium Batteries Science and Technology*; Kluwer: Boston, 2004.

⁽³¹⁾ Luo, Q.; Liu, Z.; Li, L.; Xie, S.; Kong, J.; Zhou, D. Adv. Mater. 2001, 4, 286.



Figure 5. Schematic view of the formation of $Sn_{0.9}Si_{0.1}$ core/carbon shell nanoparticles with different thicknesses of the carbon shell.



Figure 6. Plots of (a) voltage profiles of the samples, annealed at 600 and 700 $^{\circ}$ C between 0 and 1.5 V at a rate of 0.3 C, in a coin-type half cell and (b) charge capacity retention vs cycle life of the same samples in (a).

sample annealed at 600 °C had a charge capacity of 772 $mA \cdot h/g$ with a coulometric efficiency of 48%. On the other hand, the samples annealed at 700 °C exhibited a charge capacity of 964 mA·h/g with a coulometric efficiency ratio of 78%. Since the reversible capacity of the amorphous carbon has $\sim 100 \text{ mA} \cdot \text{h/g}$,³² the capacity contribution from the carbon shell is negligible. The increased capacity with increasing annealing temperature is believed to be due to the enhanced graphitization degree of the carbon shell structure. Figure 6b shows the capacity retention of the samples as a function of cycle number. The samples, annealed at 600 and 700 °C, showed capacity retentions of 85% and 80%, respectively, after 50 cycles. Stabilizing the cyclability indicates that Sn_{0.9}Si_{0.1}/carbon core-shell nanoparticles effectively alleviate the volume change during lithium alloying/dealloying. In the case of pure tin, its first



Figure 7. TEM images of the cycled $Sn_{0.9}Si_{0.1}$ core/carbon shell nanoparticles prepared at 700 °C. The inset TEM image is a magnified image of the cycled $Sn_{0.9}Si_{0.1}$ core/carbon shell nanocrystal.

discharge and charge capacity was 950 and 760 mA•h/g, respectively; further cycling led to a rapid capacity decay to 67 mA•h/g after 30 cycles.³²

To confirm the data reliability, five cells were tested at the same time and a similar result was obtained. It should be noted that the nature of the lithium-insertion reaction in Li-metal alloy phases depends on the particle size, particle size uniformity, potential window, etc. For instance, bulk metallic Sn anode continued to crack and crumble as a result of the large volume change on cycling. The cracking and crumbling during cycling keep generating new active surfaces that were previously passivated by the stable surface films. Hence, the repeated reaction between the electrolyte and Li– Sn induces capacity fading. However, in our case, capacity stabilization of the Sn₉₀Si₁₀ nanoparticles after 30 cycles is believed to be related to the formation of stable passivation layer between the anode and electrolyte.

The lower charge capacity but higher capacity retention of the sample annealed at 600 °C than that at 700 °C is related to the low graphitization degree and thicker shell size that is more effective in buffering the volume expansion during lithium alloying/dealloying. Interestingly, the capacity value (lithium storage value) is significantly improved under a relatively high rate of cycling, compared with previously reported Si or Sn composite samples.^{6–9} Bulk-sized Sn particles encapsulated in the hollow carbons exhibited rapid capacity fading within several cycles, showing charge capacity below 200 mA•h/g.⁷ This indicates that hollow carbons were destroyed by the severe volume expansion of bulk tin particles during lithium alloying/dealloying.

Figure 7 exhibits the TEM image of the core-shell nanoparticles prepared at 700 °C after 30 cycles. The particle size is quite similar to that before cycling in Figure 2c, and the magnified TEM image in the inset shows a lattice fringe (200) of tetragonal Sn. In nanomaterials, the energy barriers for alloy formations are smaller than the bulk materials because a large fraction of the Sn and Si atoms are in high energy states on the high curvatured surfaces.³³ In this regard, the large volume change due to nucleation of the new phase

⁽³²⁾ Noh, M.; Kown, Y.; Lee, H.; Cho, J.; Kim, Y.; Kim. M. G. Chem. Mater. 2005, 17, 1926.

($\text{Li}_x \text{Sn}_{0.9} \text{Si}_{0.1}$) can be readily accommodated. Further, results indicate that original Sn phase was maintained during cycling and led to good capacity retention of the sample. The plateaus in the potential curves of the samples clearly show evidence of one-phase formation ($\text{Li}_x \text{Sn}_{0.9} \text{Si}_{0.1}$), as shown in Figure 5. On the other hand, amorphous Si-rich Si_{0.65} \text{Sn}_{0.35} alloy exhibited no two-phase regions during a charge and discharge profile and therefore two local environments ($\text{Li}_x \text{Sn}$ and Li_x -Si) appeared as random throughout the particles.³⁴ This result indicates that core—shell morphology was maintained during cycling and led to good capacity retention of the sample.

Conclusion

Nanoparticles have a beneficial effect on the cyclability through better accommodation of the structural changes than

bulk materials during lithium alloying/dealloying, although they with aggregation were larger particles during lithium reactions and then pulverized again. However, carbon shell acts as a buffer layer to prevent the aggregation between nanoparticles. $Sn_{0.9}Si_{0.1}$ core/carbon shell nanoparticles, obtained from butyl-capped particles after annealing at 600 °C and 700 °C, showed excellent initial capacity and capacity retention up to 50 cycles. We believed that this core—shell nanostructure has greatly improved the development of new anode materials for high-density lithium rechargeable batteries.

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⁽³⁴⁾ Beaulieu, L. Y.; Hewitt, K. C.; Turner, R. L.; Bonakdarpour, A.; Abdo, A. A.; Chirstensen, L.; Eberman, K. W.; Krause, L. J.; Dahn, J. R. J. Electrochem. Soc. 2003, 150, A149.