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Synthesis and Morphological, Electrochemical Characterization of Sn₉₂Co₈ Nanoalloys for Anode Materials in Li Secondary Batteries

Hyunjung Kim and Jaephil Cho^{*,z}

Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

Uniformly distributed carbon-coated $Sn_{92}Co_8$ nanoalloys with a particle size of 50 and 10 nm were prepared using a butyllithium and naphthalide solution at 500 and 700°C, respectively. The samples annealed at 500°C were covered with an amorphous carbon layer with a thickness of about 40 nm, but its thickness was shrunk to 8 nm when annealed at 700°C. The first charge capacity increased with increasing annealing temperature and exhibited 380 and 662 mAh/g at 600 and 700°C, respectively. This is due to enhanced ordering of the carbon layer structure and full decomposition of the butyl ligands that limited Li-ion intercalation/ deintercalation. The capacity retention of the nanoalloys annealed at 500 and 700°C was 76 and 54% after 30 cycles at a rate of 0.3 C (=210 mA/g), while that of bulk $Sn_{92}Co_8$ alloy was 15%. Much improved capacity retention of the carbon-coated nanoalloys is associated with the thicker carbon layer on the particle surface that acts as a more effective buffer layer for volume expansion during lithium alloying/dealloying than that of the bulk alloy.

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In order to overcome the capacity limits of graphite materials, Sn and Si anode materials have been investigated.¹⁻³ However, these materials showed very rapid capacity fading within a few cycles due to rapid growth of the particles, which resulted in a loss of mechanical integrity between the particles and the current collector. Because the electrical conductivity of Sn is 6–7 times higher than Si,⁴ it has potential applications for requiring high rate cycling. Hence, many studies have focused on improving cycle life by forming alloys, such as Sn_xM_y (M=Fe, Co, Mn, Ag, and Cu), using ballmilling and sputtering methods.⁵⁻¹⁹ Here, M is an inactive material which acts to suppress Sn particle growth, thereby minimizing volume change. For instance, Mao et al. reported that mechanically alloyed Sn-Fe-C composites could deliver the first charge capacity of 650 mAh/g but showed rapid capacity below 200 mAh/g after 20 cycles.¹⁵ Yin et al. demonstrated that Ag₃₆Fe₁₆Sn₄₈ milled with 5 wt % of single-walled nanotubes could maintain 450 mAh/g even after 300 cycles. However, this material had a significant first cycle irreversible capacity corresponding to 47%.16

Some studies on nanoparticles have recently been conducted in order to minimize the mechanical stress in the electrode caused by the volume expansion of the particles.²⁰⁻²⁸ These nanoparticles were prepared by a solvothermal method by using NaBH₄ as a reducing agent, but as-prepared particles were severely aggregated with broad particle distribution. Aggregated nanoparticles have a higher chance for growing into bulk-sized particles during lithium reactions. For instance, Xie et al. reported that nanocrystalline CoSb₂ with a particle size larger than 100 nm prepared by the solvothermal method showed the first charge capacity of 672 mAh/g with a coulometric efficiency of 51% at very low current rate of 20 mA/g.²¹ The charge capacity after 20 cycles was ~550 mAh/g. Accordingly, the most promising nanoparticles for the anode material have narrow particle size distribution with minimized aggregation and prefer to have surface buffer layers during lithium alloying/dealloying, for instance, a carbon layer.

In this study, we prepared and characterized carbon-coated $Sn_{92}Co_8$ bimetallic nanoparticles produced using a butyllithium and naphthalide solution. This synthetic method leads to not only nanoparticle size with 10 nm and good dispersity but also to uniform carbon coating layer on the nanoparticle surface.

Experimental

A method used a modified synthesis technique based on a procedure reported by Yang et al.²⁹ In this method, 7.5 mL of anhydrous

^z E-mail: jpcho@kumoh.ac.kr

SnCl₄ (99.999%) and 0.3 g of CoCl₂ (99.99%) in a dried tetrahydrofuran were thoroughly mixed in a flask under a dry argon atmosphere in a glove box. This mixture was then poured into a solution consisting of 5 g of sodium metal and 10 g of naphthalene dissolved in 30 mL of tetrahydrofuran. This mixed solution was stirred for 24 h and then 60 mL of butyllithium (n-C₄H₉Li) was added. This solution was stirred at room temperature for 4 h with the solvent and naphthalene being removed by using a rotating evaporator at 90°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 liquid with a black color, was annealed at 500 and 700°C for 5 h under a vacuum atmosphere. The obtained Sn₉₂Co₈ nanoparticles were analyzed with inductively coupled plasma-mass spectroscopy (ICP-MS) to ensure the stoichiometry. Based on this analysis, the stoichiometry of the nanoparticles was Sn_{91.5}Co_{8.5}.

For bulk $Sn_{92}Co_8$, 1.65 g of tetrammonium bromide was dissolved in 15 mL of CCl₄ while 0.95 g of SnCl₂·2H₂O and 0.297 g of CoCl₂·6H₂O were dissolved in 30 mL of distilled water. While stirring, 6 g of NaBH₄ that was previously dissolved in 15 mL of distilled water was slowly poured into the mixed solution. After stirring for 4 h, the solution was centrifuged, washed with distilled water to remove residual NaCl, rinsed with acetone, and vacuumdried at 90°C for 12 h to obtain $Sn_{92}Co_8$ nanoparticles.

High-resolution transmission electron microscopy (HRTEM) samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper grids. The fieldemission electron microscope was a JEOL 2000F operating at 200 kV. FTIR spectra for the nanoparticles were obtained at room temperature by dropping the hexane colloid on KBr single-crystal plates and allowing the solvent to evaporate. Powder X-ray diffraction measurements were carried out using a Rigaku DMax/2000PC with a Cu-target tube. The carbon concentrations were measured using a CHNS analyzer (Flash EA 1112, Thermo Electron Corp.). ICP-MS (ICPS-1000IV, Shimadzu) was used to determine the Sn and Co contents. Raman spectroscopy (Renishaw 3000) was used to characterize Ge nanocrystals confined in an amorphous carbon matrix and 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.

The cathodes for the battery test cells were made of $Sn_{92}Co_8$ material, 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 glove box, contained a cathode, a Li metal anode, a microporous polyethylene

^{*} Electrochemical Society Active Member.



Figure 1. XRD diffraction patterns of $Sn_{92}Co_8$ nanoalloys annealed at 500 and 700°C for 5 h.

separator, and an electrolyte solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %) (Cheil Industries).

Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of $Sn_{92}Co_8$ nanoparticles annealed at 500 and 700°C. The samples annealed at 500°C were of an amorphous phase but then converted into a crystalline phase at 700°C, of which particle size was estimated to be 10 nm. In the phase diagram,³⁰ at the composition of 92 atom % Sn and 8 atom %, the mixture phase of β -tin phase and $CoSn_2$ phase is formed. However, the XRD patterns of the sample annealed clearly show tetragonal β -tin phase without showing $CoSn_2$ phase. This indicates that Co atoms completely incorporated into the Sn lattices, and increase the melting point. From the phase diagram, the melting point of the alloy composition consisting of 8 atom % Co and 92 atom % Sn exceeds 900°C.³⁰ In nanoscale materials, supersaturated alloys can be formed without phase segregation, and, for example, 10 atom % Ni can be supersaturated into tetragonal tin.³¹ Similarly, in a macroporous Sn–Co alloy, over 40 atom % Co was reported to be supersaturated in Sn lattices.³²

Figure 2a shows FTIR spectra of Sn₉₂Co₈ nanoparticles in the



Figure 2. (a) FTIR spectra and (b) Raman scattering of $Sn_{92}Co_8$ nanoalloys annealed at 500 and 700 °C.

as-prepared state, as well as for those annealed at 500 and 700°C. The peaks between 3000 and 2850 cm⁻¹ are assigned to C-H stretches of butyl groups, and the two peaks at 1480 and 1380 cm⁻¹ are assigned to symmetric and asymmetric bends of the butyl groups, respectively.²⁹ A minor peak at 750 cm⁻¹ is due to oxygen contamination of Sn₉₂Co8 nanoparticles and is assigned to Sn-O stretch.³³ The detection limit of the FTIR is below the 100 ppm level, and impurities with 100 ppm level can be easily detected. ICP-MS analysis of the sample annealed at 700°C confirmed no oxide contamination. In accordance, the samples are believed to have negligible amount of oxide contaminant. When the Sn nanoparticles were prepared using Mg₂Sn and SnCl₂,³³ the Sn nanoparticles were severely contaminated with SnO₂, and the particle size from the XRD patterns was estimated to be more than 50 nm. The intensity of butyl groups rapidly decreased after annealing at 500°C and completely disappeared after annealing at 700°C. We believe that C_4H_9 groups turned into amorphous carbon at 500°C. Figure 2b exhibits Raman scattering of the identical samples for measuring FTIR spectra, and two distinct scattering peaks at 1330 cm⁻¹ (D band) and 1570 cm⁻¹ (G band). A relative intensity ratio of these peaks (D band/G band) is an indication of the ordering degree of carbon structure,^{34,35} and the carbon ordering enhances as its ratio decreases. Its ratio of the samples annealed at 500 and 700°C is 2.75 and 1.97, respectively, and fully ordered carbon shows 0.09. In this regard, the sample annealed at 500°C shows a much more disordered carbon structure than that at 700°C, which indicates formation of the amorphous carbon. Amorphous carbon has limited Li-ion intercalation/deintercalations compared with fully ordered carbon (i.e., graphite).³

Figure 3 is a TEM image of the Sn₉₂Co₈ nanoparticles annealed at 500 and 700°C, respectively. Sn₉₂Co₈ nanoparticles annealed at 500°C (Fig. 3a and b) show a rather uniform distribution of the nanoparticles with a particle size of 50 nm (Fig. 3b is a magnified image of Fig. 3a). Since residual butyl groups were observed in FTIR spectra, both amorphous carbon and butyl groups were expected to coat the Sn₉₂Co₈ nanoparticles. Upon heating at 700°C for 5 h, the particle size drastically decreased to 10 nm (Fig. 3c and d) due to complete decomposition of butyl groups, but the amorphous carbon layer is observed on the particle surface with a thickness of 4 nm (Fig. 3d). This result suggests that 10 nm sized particles were covered by a 40 nm thick layer consisting of the amorphous carbon and butyl groups at 500°C. Upon further annealing at 700°C, the total carbon thickness is reduced to 8 nm (see Fig. 4). This phenomenon is due to the enhanced ordering of carbon structure, and fully decomposed butyl ligands. In the magnified TEM image of Fig. 4c (Fig. 3d), (200) lattice fringe of tetragonal Sn is clearly observed. The estimated amount of carbon content in the samples at 500 and 700°C was 10 wt %, but H content was significantly decreased to 0.01 wt % from 6 wt % with increasing temperature to 700°C from 500°C, respectively.

Figure 5 exhibits the voltage profiles and cycle life performances of the Sn₉₂Co₈ after annealing at 500 and 700°C at a rate of 0.3 C (=210 mA/g), showing the first charge capacities of 380 and 662 mAh/g with irreversible capacity ratios of 60 and 26%, respectively. The bulk sample shows the first charge capacity of 625 mAh/g with an irreversible capacity ratio of 30%. The very large irreversible capacity of the sample annealed at 500°C is associated with side reactions of the electrolytes with the amorphous carbon layer and residual C4H9. The capacity retention of the sample annealed at 500 and 700°C after 30 cycles were 76% and 54%, respectively. Superior capacity retention of the sample annealed at 500°C shows direct evidence that a thicker amorphous carbon layer is more effective to buffer the volume expansion of the nanoparticles. However, this result is superior to that bulk analogy which shows fast capacity fade after 30 cycles, retaining only 17% of the first charge capacity. When the current rate decreased to 0.1 C



Figure 3. TEM images of $Sn_{92}Co_8$ nanoalloys annealed at (a and b) $500^{\circ}C$ and (c and d) $700^{\circ}C$. b and d are expanded images of a and c, respectively.

(=70 mA/g), the capacity retention of the sample annealed at 700° C was significantly improved by 32%, compared with 0.3 C rate cycling.

Figure 6 compares the differential capacity as a function of potential for $Sn_{92}Co_8$ samples during the first cycle. Sharp peaks between ~0.6 and ~0.8 V in the sample annealed at 700°C during charge are quite similar to those in the bulk sample and represent Li–Sn alloying reactions. However, such sharp peaks between ~0.35 and ~0.7 V that represent the dealloying reaction (Li_xSn \rightarrow Sn) disappeared in the sample annealed at 700°C during discharge, as opposed to the to bulk sample reaction. It means that Sn atoms did not aggregate into larger clusters as they did in the bulk sample. The $Sn_{92}Co_8$ electrode annealed at 500°C did not show peaks between 0.6 and 0.8 V due to the presence of the amorphous phase, as evidenced by the XRD result. This indicates that tin atoms are incorporated into the amorphous phase during cycling.

Figure 7 shows XRD patterns of the electrodes prepared after 30 cycles. Interestingly, the samples annealed at 500°C turned into crystalline phases after cycling, although the samples before cycling consisted of amorphous phases. This indicates that subsequent cyclings led to gradual crystallization of the sample. In addition, the



Figure 4. (Color online) Schematic diagrams of the $Sn_{92}Co_8$ nanoalloys annealed at 500 and 700 °C for 5 h.

particle sizes for cycled particles obtained at 500 and 700 °C were estimated to be about 60 and 40 nm, respectively. Because a carbon layer thickness of the samples after cycling was not changed, the particle size of cycled electrodes obtained at 500 and 700 °C was



Figure 5. (a) Voltage profiles during the first cycle and (b) charge capacity vs cycle number in coin-type half-cells containing $Sn_{92}Co_8$ nanoalloys. Cells were cycled between 1.5 and 0 V at the rate of 0.3 C (=210 mA/g). For the cell containing $Sn_{92}Co_8$ nanoparticles were annealed at 700°C and cycled at a rate of 0.1 C.

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Figure 6. Differential capacities as a function of cell potential in coin-type half-cells containing Sn₉₂Co8 nanoalloys.

increased by a factor of 2.5 and 4, respectively, compared with that before cycling. Figure 8 exhibits the TEM images of the cycled $\mathrm{Sn}_{92}\mathrm{Co}_8$ electrode annealed at 500 and 700°C. In particular, the sample annealed at 700°C (Fig. 8c) shows different particle sizes with some particles as large as 50 nm, which is an increase of a factor of 4 compared with their size before cycling. The enlarged TEM image (Fig. 8d) shows the aggregation of tin grains with different lattice fringes. The larger Sn₉₂Co₈ clusters assemble smaller clusters in order to minimize the surface energy among the particles. These large particles may not maintain their integrity due to the large volume change during cycling, resulting in poor capacity retention.

Conclusion

Sn₉₂Co₈ nanoparticles with particle sizes less than 10 nm were prepared by terminating with butyl groups and subsequent annealing at 500 and 700°C. This method also led to the formation of the uniform carbon coating layer on the nanoparticles. Even though these materials showed good electrochemical properties at a low current rate, cycle life should be improved at high current rates. We believe that this is due to decreased carbon layer thickness and modification of the carbon thickness and layer could be improve the cycle life.



Figure 7. Ex situ XRD patterns of the Sn₉₂Co₈ nanoalloys after 30 cycles (annealing at 500 and 700°C).



Figure 8. TEM images of Sn₉₂Co₈ electrodes after 30 cycles [annealing at (a and b) 500°C and (c and d) 700°C]. d is an expanded image of c.

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References

- 1. M. Winter and J. O. Besenhard, Electrochim. Acta, 45, 31 (1999)
- 2. J. Graetz, C. C. Ahn, R. Yazami, and B. Fultz, Electrochem. Solid-State Lett., 6, A194 (2003).
- M. N. Obrovac and L. Christensen, Electrochem. Solid-State Lett., 7, A93 (2004). 3. 4. L. H. Van Vlack, Elements of Materials Science and Engineering, Addison-Wesley Publishing Co., Inc., Reading, MA (1989).
- J. R. Dahn, R. E. Mar, and A. Abouzeid, J. Electrochem. Soc., 153, A361 (2006).
- H. Yu, P. C. Gibbons, K. F. Kelton, and W. E. Buhro, J. Am. Chem. Soc., 123, 9198 6. (2001).
- 7. C. S. Yang, Q. Liu, and S. M. Kauzlarich, Chem. Mater., 12, 983 (2000) 8
- W. Choi, J. Y. Lee, and H. S. Lim, Electrochem. Commun., 6, 816 (2004) J.-H. Kim, G.-J. Jeong, Y.-W. Kim, H.-J. Sohn, C. W. Park, and C. K. Lee, J. Electrochem. Soc., 150, A1544 (2003). 9.
- I. A. Courtney and J. R. Dahn, J. Electrochem. Soc., 144, 2045 (1997). 11. D. Larcher, L. Y. Beaulieu, O. Mao, A. E. George, and J. R. Dahn, J. Electrochem.
- Soc., 147, 1703 (2000). 12. H. Zhao, C. Yin, H. Guo, and W. Qui, Electrochem. Solid-State Lett., 9, A281
- (2006).J. Yang, M. Wachtler, S. Martin, and J. O. Besenhard, Electrochem. Solid-State 13. Lett., 2, 161 (1999).
- 14. H. Li, Q. Wang, L. Shi, L. Chen, and X. Huang, Chem. Mater., 14, 103 (2002).
- O. Mao, R. A. Dunlap, and J. R. Dahn, J. Electrochem. Soc., 146, 405 (1999).
 J. T. Yin, M. Wada, K. Ishihara, S. Tanse, O. Kajita, and T. Sakai, J. Electrochem.
- Soc., 150, A1341 (2005). 17. G. M. Ehrlich, C. Durand, X. Chen, T. A. Hugener, F. Spiess, and S. L. Suib, J.
- Electrochem. Soc., 147, 886 (2000). J. R. Dahn, R. L. Turner, O. Mao, R. A. Dunlap, A. E. George, M. M. Buckett, D. J. McClure, and L. Krause, *Thin Solid Films*, 408, 111 (2002).
- 19. H. Li, X. Huang, L. Chen, Z. Wu, and Y. Liang, *Electrochem. Solid-State Lett.*, 2, 547 (1999).
- 20 Y. Wang, J. Y. Lee, and T. C. Deivaraj, J. Electrochem. Soc., 151, A1804 (2004).
- 21. J. Xie, X. B. Zhao, G. S. Cao, Y. D. Zhong, M. J. Zhao, and J. P. Tu, Electrochim. Acta, 50, 1903 (2005).
- X. P. Gao, J. L. Bao, G. L. Pan, H. Y. Zhu, P. X. Huang, F. Wu, and D. Y. Song, J. 22. Phys. Chem. B, 108, 5547 (2004).
- 23. A. R. Armstrong, G. Armstrong, J. Canales, R. Garcia, and P. G. Bruce, Adv. Mater. (Weinheim, Ger.), **17**, 862 (2005). Y. Wang and J. Y. Lee, J. Phys. Chem. B, **108**, 17832 (2004).
- 24
- 25. D. C. Schnitzler, M. S. Meruvia, I. A. Hummelgen, and A. J. G. Zarbin, Chem. Mater., 15, 4658 (2003).
- D. Aurbach, A. Nimberger, B. Markovsky, E. Levi, E. Sominski, and A. Gedanken, 26. Chem. Mater., 14, 4155 (2002).
- 27. M. Noh, Y. Kwon, H. Lee, J. Cho, Y. Kim, and M. G. Kim, Chem. Mater., 17, 1926 (2005)
- 28. M. Noh, Y. Kim, M. G. Kim, H. Lee, H. Kim, Y. Kwon, Y. Lee, and J. Cho, Chem.

Journal of The Electrochemical Society, 154 (5) A462-A466 (2007)

- 13, 286 (2001).
- B. R. Taylor and S. M. Kauzlarich, *Chem. Mater.*, **11**, 2493 (1999).
 A. C. Ferrari and J. Robertson, *Phys. Rev. B*, **61**, 14095 (2000).
- 35. D. H. Lee, B. Park, D. B. Poker, L. Riester, Z. C. Feng, and J. E. E. Baglin, J. Appl. Phys., 80, 1480 (1996).
- Mater., 17, 3320 (2005).
 29. C.-S. Yang, A. Bley, S. M. Kauzlarich, H. W. H. Lee, and G. R. Delado, J. Am. Chem. Soc., 121, 5191 (1999).
 30. P. Villars and L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, 2nd ed., Vol. 4, ASM International, Metals Park, OH (1991).
 31. T. Watanabe, Nanoplating: Microstructure Control Theory of Plated Film and Data Place of Plated Film Microstructure Elsavier Publishers. Amsterdam The Nethers. Base of Plated Film Microstructure, Elsevier Publishers, Amsterdam, The Netherlands (2004).
- 32. Q. Lu, Z. Liu, L. Li, S. Xie, J. Kong, and D. Zhao, Adv. Mater. (Weinheim, Ger.),
- 36. M. Winter, K.-C. Moeller, and J. O. Besenhard, in Science and Technology of Lithium Batteries, G.-A. Nazri and G. Pistoia, Editors, Chapter. 5, Kluwer Academic Publishers, Norwell, MA (2004).