Synthesis and Morphological, Electrochemical Characterization of Sn$_{92}$Co$_8$ Nanalloys for Anode Materials in Li Secondary Batteries

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In order to overcome the capacity limits of graphite materials, Sn and Si anode materials have been investigated. 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, it has potential applications for requiring high rate cycling. Hence, many studies have focused on improving cycle life by forming alloys, such as Sn$_x$M$_{1-x}$ (M = Fe, Co, Mn, Ag, and Cu), using ball milling and sputtering techniques. 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. Yin et al. demonstrated that Ag$_{54}$Fe$_{10}$M$_{45}$ 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%. 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. These nanoparticles were prepared by a solvothermal method by using NaBH$_4$ 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 Co$_x$S$_{1-x}$/C was annealed at 100 nm while the other particles were between 2 and 40 nm. Diverse HRTEM studies showed the first charge capacity of 672 mAh/g with a coulombic efficiency of 51% at very low current rate of 20 mAh/g. 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 naphthaldehyde solution. This synthetic method leads to only nanoparticles 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. In this method, 7.5 mL of anhydrous SnCl$_4$ (99.999%) and 0.3 g of CoCl$_2$ (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 ($n$-C$_4$H$_9$Li) 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 Sn$_{92}$Co$_8$ nanoparticles were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS) to ensure the stoichiometry. Based on this analysis, the stoichiometry of the nanoparticles was Sn$_{92}$Co$_8$. For bulk Sn$_{92}$Co$_8$, 1.65 g of tetrammonium bromide was dissolved in 15 mL of CCl$_4$ while 0.95 g of SnCl$_2$·2H$_2$O and 0.297 g of CoCl$_2$·6H$_2$O were dissolved in 30 mL of distilled water. While stirring, 6 g of NaBH$_4$ 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 vacuum-dried 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 field-emission electron microscopy 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 DMax2500PC 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 coin-type half-cells (2016R size), prepared in a helium-filled glove box, contained a cathode, a Li metal anode, a microporous polyethylene carbon coating layer on the nanoparticle surface.
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,\(^{20}\) 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,\(^{20}\) the melting point of the alloy composition consisting of 8 atom % Co and 92 atom % Sn exceeds 900°C.\(^{20}\) 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 Sn_{92}Co_{8} nanoparticles in the 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 Sn_{92}Co_{8} 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 Mg_{2}Sn and SnCl_{2}, the Sn nanoparticles were severely contaminated with SnO_{2}, 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_{4}H_{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).\(^{36}\)

Figure 3 is a TEM image of the Sn_{92}Co_{8} nanoparticles annealed at 500 and 700°C, respectively. Sn_{92}Co_{8} 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 Sn_{92}Co_{8} 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 Sn_{92}Co_{8} 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 C_{4}H_{9}. 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...
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$_x$Sn → 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 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...
increased by a factor of 2.5 and 4, respectively, compared with that before cycling. Figure 8 exhibits the TEM images of the cycled Sn$_92$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 Sn$_92$Co$_8$ 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

Sn$_92$Co$_8$ nanoparticles with particle sizes less than 10 nm were prepared by terminating bulk systems 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.

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