Amorphous Carbon-Coated Tin Anode Material for Lithium Secondary Battery

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Considerable effort has been devoted to the use of Sn-based metals as alternative anodes (negative electrodes) to carbonaceous compounds in lithium-ion batteries.[1−4] In principle, the alloying/dealloying reaction offers a much higher specific capacity than that of carbon intercalation. For example, 4.4 Li atoms can react with Sn to deliver a specific capacity of 992 mAh/g. However, it was found that these alloy systems showed poor capacity retention during their cycle life. The reason for this is believed to be pulverization of the particles due to differences in volume (>300%) caused by the compositional changes occurring during cycling. As the particles fragment, they become electrically isolated, which reduces the cell capacity. Several strategies have been proposed to improve the cycling performance of lithium alloy systems. Besenhard and Huggins used tin-based intermetallics, M_xSn_y, where M is an electrochemically inactive transition metal (M = Fe, Ni, Mn, and Co).[5−8] The role of M mainly provides a matrix that will absorb the massive volume changes that occur with the electrode upon the lithiation/delithaition processes. Therefore, it is proposed that the mechanical integrity between the particles and also with the current collector can be maintained. However, capacity fading is inevitable, and for example, these compounds (Sn_2Fe) exhibit high specific capacities of 800 mAh/g and 650 mAh/g during the first charge and discharge, respectively, but the capacity decreases to almost 0 after 50 cycles, indicating that Sn aggregation is unavoidable.[9] Hence, the only way to improve the cycling stability was to increase the ratio of "inactive" atoms in the alloys despite the large decrease in capacity. For example, a $Sn_2Fe-SnFe_3C-C$ composite anode (24:72:4 wt %) shows only 200 mAh/g, but prevents the reaction between lithium and tin, and limits the capacity of these materials.[10] In contrast, the thin-film tin anode has been demonstrated to show good cycling stability, while retaining a relatively good cycling stability.[11] However, the expensive processing cost and a lack of electrode flexibility compared with graphite has hindered its use in Li secondary batteries. Therefore, sustaining the dimensional stability of the alloys during cycling is the most critical factor in solving these problems. This study reports that amorphous carbon-coated tin particles are an alternative material to ensure the dimensional integrity during Sn alloy/dealloy.

A 100 mL ethylene glycol solution containing 5 mL of $SnCl_4$ and 10 g of tri-sodium citrate was prepared in a conical flask. Next, 5 g of $NaBH_4$ was added to the solution with vigorous stirring. Here, citrate serves only as a capping agent.[12] The solution turned black immediately after adding $NaBH_4$, indicating that particle formation had occurred according to the following reaction:

$$(CH_2)_2(OH)_2 + SnCl_4 + NaBH_4 \rightarrow NaCl(s) + Sn(s) + 2H_2O + C_2H_6(g) + BCl_3(g)$$

When water was used as a solvent for dissolving the $SnCl_4$, the precipitated tin nanoparticles instantly aggregated into larger particles (>1 μm), regardless of the concentration of the capping agent. During the reduction of Sn^{4+} to Sn^0, BCl_3 gas was generated due to its low boiling point (12.5 °C). The resulting mixed solution containing the precipitated Sn nanoparticles was centrifuged at 3000 rpm for 5 min and rinsed in distilled and deoxygenated water 3 times to remove the NaCl, which was followed by centrifugation, and vacuum-drying at 100 °C. This experiment was similar to the Ni reduction method reported by Glavee et al. in terms of using $NaBH_4$ as the reducing agent.[13]

To encapsulate the Sn nanoparticles with the amorphous carbon, glucose (1 g) was dissolved in distilled and deoxygenated water (40 mL) until a clear solution was observed. The Sn particles (1.5 g) were then dispersed in the solution. It was reported that the carbon spheres could be prepared from glucose under hydrothermal conditions between 160 °C and 180 °C. This is higher than the normal glycosidation temperature, which leads to aromation and carbonization.[14−16] The mixture was then placed in a 100 mL Teflon-sealed autoclave purged with the Ar and maintained at 180 °C for

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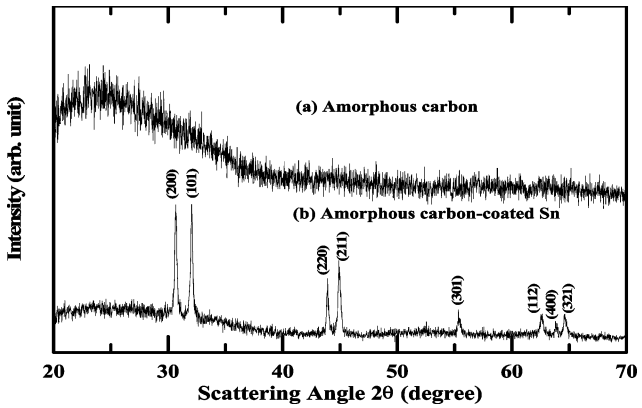

Figure 1. XRD diffraction patterns of the amorphous carbon and amorphous carbon-coated tin particles.

3 h. At this temperature, the tin nanoparticles were coated with amorphous carbon. The reddish brown products were isolated by centrifugation and washed with water/acetone three times, respectively, and the supernatants were discarded. Finally, the powder was vacuum-dried overnight at 100 °C. Inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the Sn in the coated carbon showed that Sn wt % was 80, and the remaining 20 wt % was estimated to be carbon. An element analyzer also showed that the carbon and hydrogen content was 19.7 and 0.03 wt %, respectively. This result indicates that most hydroxyl groups in glucose were removed during the hydrothermal reaction. The electrolyte for the coin-type half cells (2016 type) was 1 M $LiPF_6$ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol %) (Cheil Industries). The coin-type half cells were cycled at the rate of 0.1 C (1 C = 800 mA/g) for the first cycle and cycled at a rate of 0.5 C rate for the subsequent 49 cycles between 0 and 1.5 V. The electrode was composed of 60 wt % of the active material, 20 wt % of the poly(vinyliedene fluoride) binder, and 20 wt % Super P carbon black. In addition, an electrode composition consisting of 85 wt % of the active material, 10 wt % of the poly(vinyliedene fluoride) binder, and 5 wt % Super P carbon black was used to compare the electrochemical properties of the cell with the above. Super P carbon black additive did not contribute to the total capacity because it acts as only a conducting agent. Normally, 7 coin-cells were tested to check the capacity variation at the same cycling condition, and its value was less than ±4 mAh/g.

Figure 1 shows XRD patterns of the as-prepared amorphous carbon and the amorphous carbon-coated tin particles. Carbon shows a broad peak at ~23°, indicating the formation of an amorphous phase. The XRD pattern of Sn nanoparticles showed no impurity phases, and the nanoparticles were indexed as β-Sn (JCPDS #04-0673). The amorphous carbon-coated Sn nanoparticles also shows only Sn peaks, indicating there was no SnO_2 formed during the hydrothermal process. Figure 2 shows TEM images of the as-prepared Sn nanoparticles and amorphous carbon-coated tin particles. The tin nanoparticles size was ~200 nm (Figure 2a), and there was a distinct contrast difference in the image (Figure 2b), which confirmed the existence of two phases, amorphous carbon and tin particles. Further EDXS (energy-dispersive X-ray

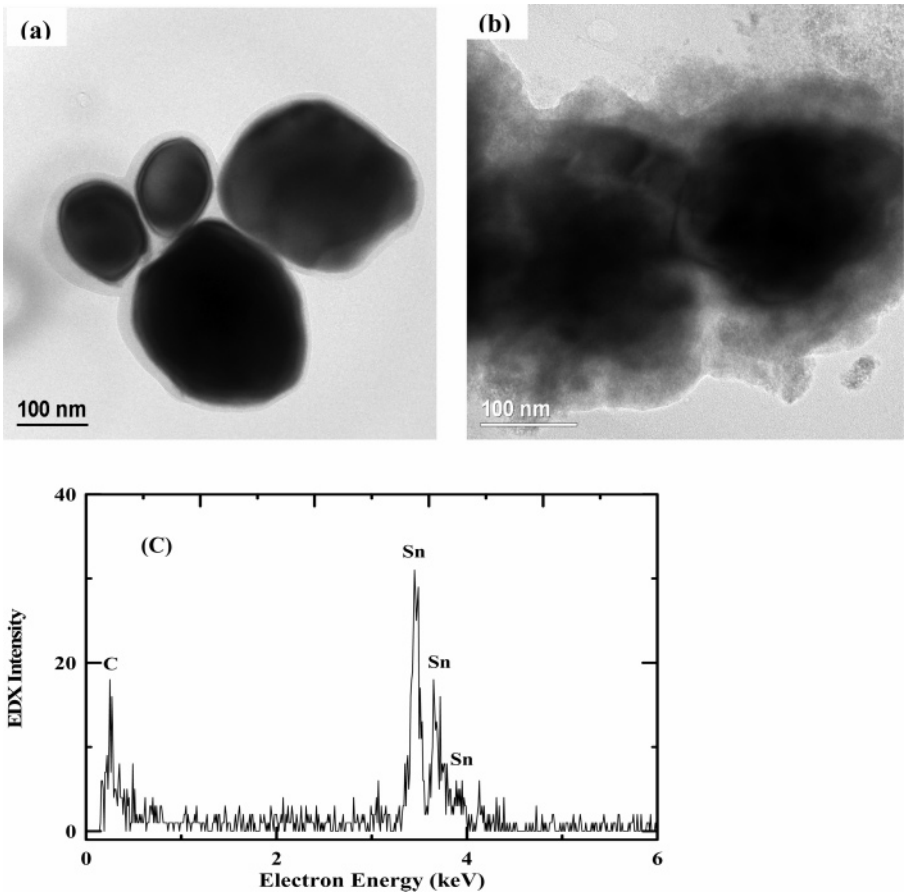

Figure 2. TEM images of (a) tin particles and (b) amorphous carbon-coated tin particles, and (c) EDAX spectra of the identical sample in Figure 2b.

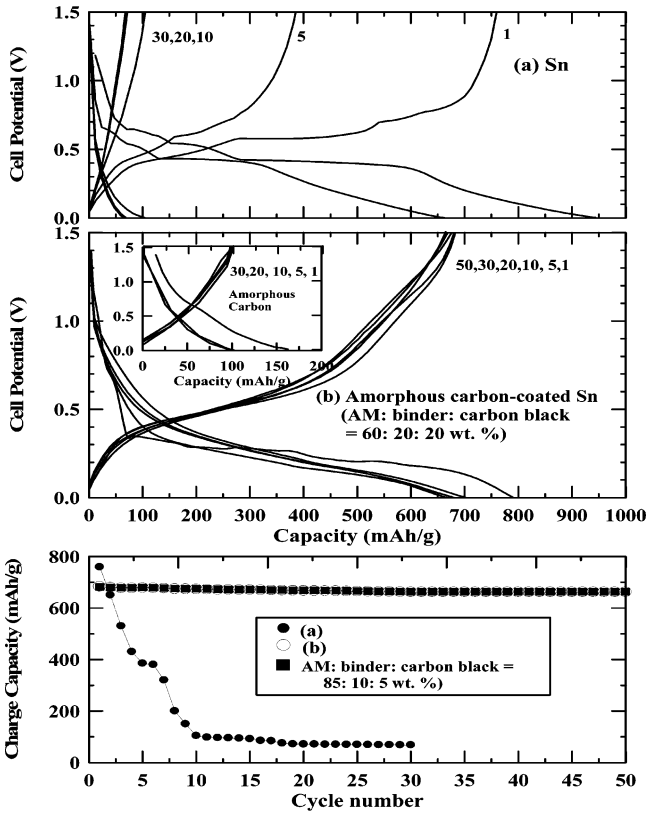

Figure 3. Plots of (a) the voltage profiles of the tin particles, and (b) amorphous carbon-coated tin particles in a coin-type half cell (Li metal as a counter electrode) between 0 V and 1.5 V. The bottom figure compares the charge capacities from the cells in (a), (b) and the electrode composition consisting of 85 wt % of the active material (amorphous carbon-coated Sn), 10 wt % of the poly(vinyliedene fluoride) binder, and 5 wt % Super P carbon black vs cycle number. The cells made using the tin particles and amorphous carbon-coated tin particles were cycled at a rate of 0.1 C (1 C = 800 mA/g) for the first cycle and at a rate of 0.5 C rate for the subsequent cycles. The inset shows the voltage profiles of the amorphous carbon.

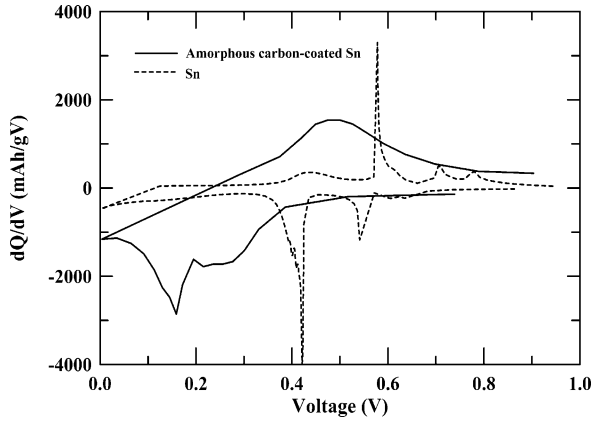

Figure 4. Differential charging and discharging voltage profiles of the Sn and amorphous carbon-coated Sn anodes for the first discharge and charge of the cell.

spectroscopy) of the amorphous coated tin particles (Figure 2c) confirmed the presence of tin and C, but no oxygen peak was observed.

Figure 3 shows the voltage profiles of the Sn nanoparticles and the amorphous carbon-coated tin particles. Figure 4 shows differential charging and discharging voltage profiles of the Sn and amorphous carbon-coated Sn anodes for the first discharge and charge of the cell. The differential capacity of the composite is smooth, showing suppression of the sharp peaks, indicative of phase changes during the reaction with Li opposite that of the tin metal. Further, it should be noted that phase transition voltages of the coated Sn are quite different from those in pure Sn metal. This may be because the amorphous carbon coating layer may influence the overall change in phase-change rate. Similar behavior was reported in the cathodes, and simple metal coating suppressed the phase transitions or changed in phase transition voltages.[17,18] However, a more detailed study is underway to investigate our result.

Even though first discharge and charge capacity of the tin electrode was 950 mAh/g and 760 mAh/g, respectively, further cycling led a to rapid capacity decay to 67 mAh/g after 30 cycles. Note that an initial ratio of the irreversible capacity was 20%. This result is consistent with the Sn−SnSb composite with particle size <300 nm, exhibiting rapid capacity fading although the electrochemical performance is better than that with the >1 μm particles.[19] This indicates that a particle size reduction cannot prevent micrometer-scale tin aggregation. In contrast, the first charge and discharge capacities of the amorphous carbon-coated tin particle electrode shows were 789 mAh/g and 681 mAh/g, respectively. The ratio of the irreversible capacity was 14%, which decreased by 6%, compared with the Sn particle only. Considering the Sn particle only, the charge and discharge capacities were estimated to be 631 mAh/g and 587 mAh/g, respectively. (The ratio of the irreversible capacity is 7%.) Low discharge capacity (150 mAh/g) of the amorphous carbon suggests that the degree of carbonization is very low, and the specific resistance measurement can be an indicative of the degree of the carbonization (Measured specific resistance of the amorphous carbon using a 4-probe measurement was 9×10^{-3} Ωcm which is much higher than the value (5×10^{-3} Ωcm) of the natural graphite with a high crystallinity.) The irreversible capacity (68 mAh/g) from amorphous carbon contributes to the increase in the irreversible capacity. However, capacity retention after 50 cycles was 664 mAh/g, which is equivalent to 98% capacity retention. Additional work was carried out using a decreased amount of conducting agent super P carbon black (5 wt %) in the electrode composition from 20 wt %. That is, compositions of the binder and active material used were 10 and 85 wt %, respectively. However, the initial capacity and capacity retention were similar to that with 20 wt % super P conducting agent (see Figure 3). Overall, the electrochemical performance of the sample is superior to the other alloy systems. For example, Lee et al. reported that tin-encapsulated spherical hollow carbon particles exhibited an initial charge capacity of ∼400 mAh/g, which rapidly decreased to 250 mAh/g even after 10 cycles.[1]

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In addition, the specific reversible capacities for the amorphous tin-based oxide ($Sn_{1.0}B_{0.56}P_{0.4}Al_{0.42}O_{3.6}$) were 650 mAh/g at the beginning and 585 mAh/g after 50 cycles.[19] Capacity retention after 50 cycles is a typical value, and Li et al.[20] reported a similar capacity retention ratio. They reported that nanosized SnSb alloy pinned with hard nongraphic carbon spheres exhibited a capacity of 480 mAh/g, and a small decrease in capacity after 35 cycles.[21] However, it should be noted that the coating method in the current study is different from the above in that amorphous carbon was coated on the ~200-nm-sized tin particles. Despite the decreased carbon content in the electrode, the capacity retention was similar to that containing 20 wt % carbon black. This indicates that high capacity retention was associated with the structural and dimensional stability of the amorphous carbon-coated Sn. However, a partial contribution from a good electrical contact between the tin particles cannot be ruled out. Figure 5 shows a TEM image of the amorphous carbon-coated tin after cycling, and cracks in carbon layer and pulverization of tin particles were not observed, indicating that the amorphous matrix acts as a "buffer-zone" that accommodates a volume change in the tin−lithium alloys.

In conclusion, an almost uniform amorphous carbon coating on the tin nanoparticles was prepared from aqueous glucose solutions using a hydrothermal method at 180 °C, which facilitated enhanced dimensional stability during Li alloying/dealloying. This material showed excellent initial capacity and capacity retention, 681 mAh/g and 98% retention after 50 cycles, respectively. This amorphous carbon-coated tin electrode has great potential as a material for improving the energy density of a lithium secondary battery.

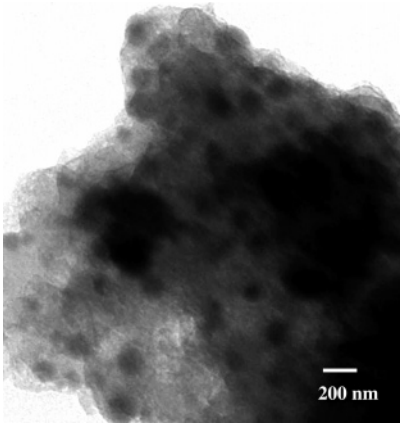

Figure 5. TEM image of the amorphous carbon-coated tin particles after cycling.

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