Control of the carbon shell thickness in Sn$_{70}$Ge$_{30}@$carbon core–shell nanoparticles using alkyl terminators: Its implication for high-capacity lithium battery anode materials

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1. Introduction

Lithium reactive (group IV) elements (Si, Ge, Sn, Pb) have been investigated as potential high-capacity anode materials for high-capacity Li-ion batteries [1–6]. Regardless of the element, the formation of Li-metal alloys is associated with a large volume change that results in pulverization of the electrode material and a loss of electrical contact between the particles during cycling. Although the degree of volume expansion depends on the element, the resulting rapid capacity fade lowers their practical potential for use as an anode material. In order to improve the capacity and cycle life of the metal anodes, researchers have investigated the encapsulation of a particle in a matrix involving Li$^+$/electron transport. This system is of interest as it possesses mechanical flexibility [6–9]. In terms of material design, the minimization of the particle size is crucial, and each particle should be coated with Li-ion conducting inactive or active phase to prevent particle aggregation during cycling. Accordingly, synthesis is the most important issue in the assurance of the capacity and cycle life of anode materials.

However, previous studies have used aggregated bulk Sn particles for carbon coating [10–14]. For instance, Sn–carbon core–shell powders were prepared using aggregated bulk-sized Sn particles capped with resorcino–formaldehyde microemulsion material [15]. On the other hand, different approaches, such as the firing of the nanoparticles with carbon precursors [11,16], mechanical alloying with active and inactive materials [8,9] or encapsulation of bulk Sn particles in hollow carbon [12] have been reported. These particles showed low first charge capacities with low Coulombic efficiencies.

Recently, a synthetic method that each particle was covered with the carbon layer was reported by Cho and co-workers [17]. In this method, each metal crystallizes with a chloride-passivated surface was reduced by butyllithium, thus forming a stable surface terminated with butyl groups. Upon annealing under vacuum or inert atmosphere, butyl groups tuned into amorphous carbon, leading to uniform coating layers on the particles. Sn$_{90}$Si$_{10}@$carbon core–shell nanoparticles prepared by vacuum annealing of the butyl-capped Sn$_{90}$Si$_{10}$ nanoclusters was reported [17]. The annealed nanoparticles showed a certain amount of abnormal grain growth with a particle size of $>$50 nm, although the average particle size was 20 nm. A similar preparation method used to prepare Sn$_{92}$Co$_8@$carbon core–shell nanoparticles, which led to particle aggregation after thermal annealing [1]. It is believed that this aggregation is due to that partial surface melting between Sn-rich nanoalloys during annealing, necessitating the selection of alloy compositions that are thermally stable and isomorphous. Sn$_{92}$Ge$_{10}$ is such an alloy, and is considered an ideal candidate. In particular, although Ge is more expensive than Si, its much higher average particle size results in a slower rate of aggregation, allowing for a larger particle size without compromising capacity retention.
times greater) lithium diffusivity compared to Si [2] demonstrates its potential as a candidate as an alloy component. For instance, Sn70Ge30@carbon core–shell nanowires exhibited excellent capacity retention above 5C, showing over 1000 mAh/g [18]. In addition, Ge has a lower degree of oxidation compared to Si upon exposure to air, as oxidized metal leads to the formation of inactive Li2O.

In this study, chemical modifications of the surfaces of nanoparticles provide the opportunity to study the effect of the thickness of a carbon shell on the electrochemical properties of the nanoparticles for the first time. This paper presents the synthesis and characterization of spherical-type each Sn70Ge30 nanoparticle that are terminated with different alkyl groups, which are characterized using high-resolution transmission electron microscopy (HRTEM), IR, Raman, and electrochemical cycling.

2. Experimental

The spherical type nanoparticles were prepared via a solution synthesis route modified using Yang et al. [20] and Baldwin et al. [19] methods. The reaction of SnCl4 and GeCl4 was performed under a Schlenk line in an Ar atmosphere. This reaction produces nanometer-sized Sn70Ge30–Cl crystallites with a chloride-passivated surface (Fig. 1). The reaction was allowed to reflux for 12 h. Further reaction with alkyl lithium (RLi) provided a stable surface terminated with alkyl (Sn/Ge-R) (Fig. 1). Initially, 5.4 g of Na and 19.38 g of naphthalene were added separately to a round-type three-neck flask containing 100 ml of glyme. This was refluxed for 24 h under an argon atmosphere in order to obtain a sodium naphthalene solution. 3.42 ml of SnCl4 (99.9%, anhydrous) and 1.25 ml of GeCl4 (99.999%, anhydrous) were mixed into 100 ml of glyme for 30 min, and the previously prepared sodium naphthalene solution was added to this solution, stirring followed for 1 h at room temperature. Here, 30 ml of n-butyllithium (ethyl lithium, methyl-lithium) were added and stirred overnight to terminate the surface from Sn/Ge–chloride to Sn/Ge–butyllithium (ethyl lithium, methyl-lithium). After termination with the alkyl groups, the solvent and naphthalene was removed in a vacuum at 100 °C for 48 h. The resulting viscous yellow gels were rinsed with water and hexane several times. The gels were then fired at 600 °C for 5 h under a vacuum.

HRTEM samples were prepared by the evaporation of the dispersed nanoparticles in acetone or hexane on carbon-coated copper

![Fig. 1. Schematic diagram of the Sn70Ge30–Cl reaction with LiC4H9.](image1)

![Fig. 2. TEM images of Sn70Ge30@carbon core–shell nanoparticles prepared by annealing nanoparticles that terminated with alkyl groups (–butyl (C4H9) (a–c), –ethyl (C2H5) (d–f), –methyl (CH3) (g and h). Image (h) shows a schematic diagram of the formation of Sn70Ge30@carbon core–shell nanoparticles with different carbon shell thicknesses.](image2)
3. Results and discussion

Fig. 2 shows TEM images of the Sn70Ge30@carbon core–shell nanoparticles prepared by annealing the nanoparticles terminated with alkyl groups (–butyl (C4H9), –ethyl (C2H5), –methyl (CH3)). Overall, the as-annealed nanoparticles have spherical-type morphologies with a uniform particle size distribution depending on the alkyl terminator. The particle sizes of the nanoparticles prepared from the butyl and ethyl terminators are estimated to be ~30 and ~25 nm, respectively, according to images (a) and (d) in the figure, and the carbon shell thicknesses are ~16 and ~8 nm, respectively. HREM image c confirms the formation of the amorphous carbon. It is also possible that core–shell nanoparticles may be embedded in another carbon matrix, which is observed by the lighter background colors in the nanoalloy particles. On the other hand, the nanoparticles terminated with methyl groups show the largest particle sizes of ~40 nm (Fig. 2g), and the HREM image shown in Fig. 2(h) shows no carbon layer. This may be due to the disappearance of the carbon layer during annealing or it may be too thin to detect by TEM. In consequence, the different chain lengths of the alkyl terminators determine the final shell thickness of the nanoparticles, as depicted the schematic diagram in Fig. 2(i). The annealed nanoparticles clearly show the formation of tetragonal Sn with lattice fringes of (2 0 0) and (2 1 1), corresponding to 2.9 and 2.01 Å (Figs. 2 c, f, and h). In addition, due to the large substitution of Ge atoms into Sn sites, lattice fringe of (2 2 0) plane, corresponding to d-spacing value of 2.0 Å of Ge. In addition, oxide contamination of the samples must be monitored, as MO produces an inactive Li2O phase.

In the FT-IR spectra of the butyl-capped Sn70Ge30 nanoparticles before annealing, as shown in Fig. 3, six characteristic peaks can be observed: 2960, 2920, 2840, 1460, 1340, and 780 cm⁻¹. These peaks are assigned to terminal –CH3, asymmetric stretching, –CH2 symmetric stretching, –CH3 bending, C–H bending, and terminal –CH2 rocking, respectively, which is in good agreement with previous studies [19,20]. After vacuum annealing at 600 °C, the bands associated with alkyl groups completely disappeared due to decomposition into C and H2, as evidence by the FT-IR spectra. It is important to note that the weak peak in the spectra of the sample prepared from methyl terminators at ~730 cm⁻¹ is associated with the partial formation of the oxides.

Ordering of the carbon is determined by Raman scattering of the annealed nanoparticles in Fig. 4. Two peaks at ~1360 and 1580 cm⁻¹ are assigned to the disorder band (D band) and the graphene band (G band), respectively. The relative peak dimension ratio of the D and G bands depends on the perfection of the graphite layer, and the ordered graphite showed that the intensity ratio of the D to G band (I_D/I_G) is 0.09 [1]. However, the butyl-, ethyl- and methyl-capped Sn70Ge30 showed 2.34, 2.38, and 2.40, respectively, confirming the formation of disordered carbon. In particular, a peak at ~200 cm⁻¹, which is indicative of Ge–Ge vibration, is noted. The presence of this peak indicates that the Sn70Ge30 nanoparticles were not fully covered with the amorphous carbon. The C and H contents of the samples were measured after annealing, and the samples that terminate with butyl groups showed the highest value of 35 wt%. Additionally, the carbon contents of the samples terminated with ethyl and methyl are 16 and 8 wt%, respectively. The hydrogen contents of the samples are similar to each other irrespective of the alkyl chain length, showing 1 wt% after annealing.

Fig. 5(a) shows the first discharge and charge curves of Sn70Ge30@carbon core–shell nanoparticles prepared by annealing the nanoparticles terminating with alkyl groups and uncapped...
Sn_{70}Ge_{30} (bare) between 1.2 and 0 V at a rate of 0.2 C (=300 mA/g). The first discharge and charge capacities of the bare Sn_{70}Ge_{30} exhibit 2103 and 742 mAh/g, respectively, showing irreversible capacity ratio of 65%, indicating that nanoparticles accelerate electrolyte decomposition at the nanoparticle and electrolyte interface, which leads to increased consumption of the lithium from the enhanced formation of the SEI layer [5]. However, the first discharge capacity decreases as the alkyl chain length increases in the order of methyl, ethyl and butyl, showing 1910, 1370, and 1106 mAh/g, respectively. Similarly, the first charge capacities of the samples increases with increasing the alkyl chain length, showing 900, 1020, and 1040 mAh/g, respectively. Coulombic efficiency of the nanoparticles prepared using butyl and ethyl groups show 100% after 4 cycles out to 40 cycles while that using methyl groups shows only 90% out to 40 cycles. Increased charge capacity with increasing the carbon chain length is related to that thicker carbon layer is more efficient to reducing the side reactions with the electrolytes and to buffer the volume change during the lithium alloy and dealloy. Furthermore, this result indicates that the irreversible capacity comes mainly from SnGe component, and the irreversible contribution from carbon shell is insignificant.

The particle pulverization associated with these materials, which originates from a large volume change (>200%) during lithium alloying and de-alloying, can result in electrically disconnected smaller particles, causing the electrode capacity to fade. In order to reduce this considerable volume change, a carbon phase can prevent the aggregation of the particle growth and acts as electrically connecting media between anode particles and current collector when the particle is pulverized. In this regard, butyl-capped nanoparticles with smallest particle size and the largest carbon shell thickness is the most effective candidate to sustain the initial capacity retention during cycling among the others.

Fig. 5. (a) First discharge and charge curves and (b) charge capacity and Coulombic efficiencies vs. cycle number of uncapped Sn_{70}Ge_{30} and Sn_{70}Ge_{30}@carbon core–shell nanoparticles prepared by annealing the nanoparticles terminated with alkyl groups between 1.2 and 0 V at a rate of 0.2 C (=300 mA/g).

Fig. 6 shows the dQ/dV vs. the potential relationship for Sn_{70}Ge_{30}@carbon core–shell nanoparticles prepared from butyl, ethyl, and methyl terminators during first discharge and charge. Among the curves, only the nanoparticles terminating with methyl groups have peaks, and very smooth differential curves appear in the samples prepared from the butyl and ethyl groups. This may be because the amorphous carbon-coating layer may influence the overall change in phase-change rate. A similar phenomenon is also observed in carbon-coated V_{2}O_{5} [21], and quite smooth peak shapes of the nanoalloys indicate that the thick carbon layer partially may act as a barrier for smooth Li-ion transport into the Sn_{70}Ge_{30} nanoparticles. With the nanoparticles prepared from methyl groups, the peaks are much broader compared to reference bulk Sn. This effect is related to that the alloy clusters which form after the first cycle are very small. The 40-nm-sized Sn_{70}Ge_{30} alloys consist of the much smaller grains than those of the bulk particles, and therefore, such small grains did not grown into larger grains, compared to bulk Sn metal which shows relatively sharp peaks. In particular, the downshift of the oxidation peak (O3), compared to that of Sn, may be related to that the Ge is incorporated in the Li_{x}Sn phase (Li_{x}Sn_{1-y}Ge_{y}); a similar result has been reported with SiZn phase [22]. Since both Sn and Ge are lithium reactive species, Sn_{70}Ge_{30} follows the basic lithium reaction according to xLi + Sn_{70}Ge_{30} → Li_{x}Sn_{1-y}Ge_{y}.

In contrast to the graphite with a very stable SEI layer (solid electrolyte interface) upon extended cycling due to the low volume change (<15%), lithium alloys show a large volume change (>200%), which induces particle pulverization. Hence, whenever a fresh surface of active material is exposed to an electrolyte, new filming takes place and the lithium is consumed. In the end, the particles electrically isolated from the Cu current collector decrease the capacity. Uncapped sample shows only 54%
capacity retention after 20 cycles (Fig. 5). On the other hand, the nanoparticles prepared using butyl groups appear to be dimensionally stable compared with those terminated with the ethyl and methyl groups. The capacity retention of the samples prepared from the butyl groups show the highest capacity retention ratio of 96%; this decreases as the alkyl chain length decreases. The samples prepared from ethyl and methyl groups have capacity retention ratios of 82 and 60%, respectively, after 40 cycles (Fig. 5b).

Fig. 7 shows TEM images of Sn_{70}Ge_{30} @carbon core–shell nanoparticles after 40 cycles; in the ethyl groups the spherical-shaped nanoparticles disappear while aggregated nanoparticles covered with carbon (Fig. 7a and b) are formulated. In the samples prepared from core–shell nanoparticles prepared using butyl groups, the initial particle morphology is maintained without showing aggregation (Fig. 7d). However, it cannot be ruled out the possibilities that carbon shell was separated from the particles or crack formation on the carbon shell due to the repeated volume changes of the core particles. The samples prepared from core–shell nanoparticles prepared using butyl groups, the initial particle morphology is maintained without showing aggregation (d). This result indicates that a carbon shell thickness of 16 nm is necessary to maintain dimensional stability during a lithium alloy/dealloy process.

4. Conclusions

Among spherical-type Sn_{70}Ge_{30}@carbon shell nanoparticles prepared from butyl, ethyl, and methyl terminators, nanoparticles prepared from butyl terminators demonstrated the best capacity retention with the minimum level of irreversible capacity. The first charge capacity was 1040 mAh/g and the capacity retention after 40 cycles was 96%, as the core nanoparticles with a carbon shell thickness of 16 nm provided dimensional stability under mechanical strains during the lithium alloy/dealloy process. Moreover, it should be noted that a control of the particle size was also important, and smaller particles decreased an absolute volume change of the active material during cycling, resulting in improved the capacity retention. On the other hand, the carbon thickness decreased to 8 nm and the capacity retention decreased to 84%. Thus, for the capacity retention of core–shell nanoparticles, control of the carbon shell thickness is very important to guarantee a longer life cycle.

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References