Electrochemical Properties of C-coated Cu₆Sn₅ Nanoparticles Dispersed on Carbon Matrix Prepared by Spray Drying Process

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Spherical hollow Cu₆Sn₅/C composite powders are prepared by a post-treatment of the precursor powders obtained by a scalable spray drying process. Metal citrates are formed by chelation of the Sn and Cu components with citric acid, and they have good drying properties under high water vapor pressure. Citric acid used as a chelating agent is a key material in synthesizing the composite powders. Decomposition and reduction of the precursor powders under reducing atmosphere produces phase-pure Cu₆Sn₅/C composite powders with unique morphology. Cu₆Sn₅ alloy particles coated with an amorphous carbon layer are uniformly dispersed on the inner and outer surface of spherically shaped carbon powders. The mean sizes of Cu₆Sn₅ alloy and carbon matrix particles are 0.4 and 7 μ m, respectively. The discharge capacities of the composite powders reduced at 600°C and 800°C are 380 and 275 mAh g⁻¹, respectively, after 20 cycles at a constant current density of 300 mA g⁻¹. The corresponding capacity retentions are 93% and 89%, respectively.

Keywords: anode material; tin alloy; spray drying; composite powders; electrochemical properties

1. INTRODUCTION

Tin-based alloys including Cu-Sn system have been widely studied to improve the cycling properties of Sn metal anode with high specific gravimetric capacity (about 990 mAh g^{-1}) and volumetric capacity (about 7200 mAh cm⁻³) for lithium ion secondary batteries [1-4]. Micrometer–sized powders of these alloys exhibit well-known problems when used as electrode material, particularly a large specific volume change during charging and discharging, which leads to rapid pulverization of the electrode, as well as a significant decrease in the electrical conductivity between chemically active material particles. Therefore, powders of nanometer-sized alloys and alloy/C composite powders were studied in order to improve the electrochemical properties of the anode

material. Nano-alloys dispersed on carbon sheets and carbon-coated alloy particles were recently investigated [5-12]. The carbon sheet and shell act as a barrier to obstruct the aggregation between nanometer-sized alloy particles, thereby reducing their volume change during lithium insertion/extraction. However, the development of an easy and efficient production process for large quantities of alloy/C composite powders is a major challenge.

Spray drying is the most widely used industrial process for the production of a dry powder from a liquid or slurry by rapid drying with a hot gas. It has been commonly used in the industry to produce hollow or spherical particles. It has already been employed to prepare nanoporous spherical materials for applications in lithium ion batteries [13-16]. However, owing to the low melting point of Sn, the preparation of Sn nanometer-sized particles by spray drying still remains a challenge [17,18]. Furthermore, the spray drying process has not been studied with respect to the production of alloy/C composite powders for application in lithium secondary batteries.

In this study, precursor powders with a hollow and thin-walled structure were prepared by commercial spray drying process from an aqueous solution of Sn and Cu components. Citric acid used as chelating agent was a key material in synthesizing the composite powders. Reduction of the prepared powders under reducing atmosphere produced the Cu_6Sn_5/C composite material in form of thin hollow spheres.

2. EXPERIMENTAL



Figure 1. Schematic diagram of the spray drying process for preparation of precursor powders.

A schematic diagram of the spray drying process is shown in Fig. 1. Usually, a liquid containing a high concentration of the product material is pumped to an atomizing device where it is transformed into a spray of small droplets. These droplets meet a stream of hot air. Their moisture evaporates very rapidly while they are still being suspended in the drying air. The dry powder is separated from the humid air in a cyclone system by centrifugal forces. The centrifugal separation is caused by the great increase in air speed when the mixture of particles and air enters the cyclone system. The particles are forced towards the cyclone walls while the lighter, moist air is directed away through exhaust pipes. Conditions such as inlet temperature, feeding rate, and atomization pressure are controlled during the spray drying process. In the present study, the temperatures of the inlet and outlet of the spray dryer were 350° C and 150° C, respectively. A two-fluid nozzle was used as atomizer and the atomization pressure was 1 bar. The spray solution was prepared by dissolving a stoichiometric ratio of copper nitrate hydrate [Cu(NO₃)₂·3H₂O, Junsei] and tin sulfate hydrate [Sn(SO₄)₂·2H₂O, Junsei] in distilled water. Citric acid was used as a chelating agent. The overall concentration of copper and tin components of the solution was 0.5 M.

The crystal structure of the alloy powders was investigated by X-ray diffractometry (XRD, RIGAKU DMAX-33) at the Korea Basic Science Institute (Daegu). The morphological characteristics of the samples were investigated using scanning electron microscope (SEM, JEOL JSM-6060) and high-resolution transmission electron microscope (TEM, JEOL JEOL-2100F). The thermal properties of the prepared powders were studied using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range of 25–1000°C in air. The capacities and cycling properties of the Cu₆Sn₅/C composite powders were measured by 2032-type coin cells. The electrode was made by mixing 40 mg of Cu₆Sn₅/C composite with 5 mg carbon black and 5 mg sodium carboxymethyl cellulose (CMC) in distilled water. Lithium metal and a polypropylene film were used as counter electrode and separator, respectively. 1 M LiPF₆ dissolved in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) with a volume ratio of 1:1 was used as electrolyte (TECHNO Semichem. Co.). The entire cell was assembled in a glove box under argon atmosphere. The charge/discharge characteristics of the samples were measured by cycling in the 0.1–1.5 V potential range at a constant current density of 300 mA g⁻¹.

3. RESULTS AND DISCUSSION

The precursor powders for the Cu-Sn-C composite powders were prepared by spray drying process from solutions of Cu and Sn components with and without citric acid. Complete drying could not be achieved for spray solution without citric acid even at a high inlet temperature of 350°C. Therefore, the precursor powders formed from the spray solution without citric acid were not collected by the cyclone system. Metal citrates formed by chelation of Sn and Cu components with citric acid had good drying properties even at short residence times of the droplets within the spray dryer, and showed a high stability in the presence of water vapor. Therefore, the metal citrate powders were easily separated by the cyclone. The corresponding morphologies of the precursor powders are shown in Fig. 2. During spray drying of aqueous salt solutions, the salt compositions precipitate around the surface of the droplets by evaporation of water. Chelating agents are compounds capable of forming

strong chemical bonds with metal ions, forming chelates. Citric acid is widely used as a chelating agent for liquid solutions.



Figure 2. SEM images of the Cu-Sn/C precursor powders prepared by spray drying process.



Figure 3. XRD patterns of the Cu-Sn/C composite powders reduced at various temperatures.

The dried precursor formed from the metal chelates of citric acid had poor gas penetration properties during spray drying. Therefore, the resulting precursor powders had a large size of several tens of micrometers and a hollow morphology with a thin-walled structure.

The precursor powders prepared by the spray drying process were post-treated at various temperatures under reducing atmosphere. Fig. 3 shows the XRD patterns of the final Cu-Sn/C composite powders. The sample reduced at 400°C showed a main crystal structure of Cu₃Sn with additional impurity peaks originating from Sn and SnO₂. The oxides SnO₂ and CuO were obtained by

the decomposition of the metal citrates and their subsequent reduction formed the metal and alloy components of the composites. Likewise, reduction of the composite powders at 500°C yielded to the

main Cu₃Sn-type crystal structure. However, (-,113) and (-,314) peaks associated with the Cu₆Sn₅

phase were additionally observed. The (-,314) peak of the Cu₆Sn₅ phase overlapped with the (101) peak associated with the Cu₃Sn phase and its intensity increased upon increasing reduction temperature, corresponding to the intensity growth of the (132) peak of the Cu₆Sn₅ phase. In contrast, the intensity of the (101) peak of the Cu₃Sn phase decreased with increasing reduction temperature. This was because Cu₃Sn crystals transferred to the Sn-rich Cu₆Sn₅ upon increasing reduction temperature. Finally, the composite powders reduced at 600°C had a crystal structure of pure Cu₆Sn₅ phase without impurity peaks.



Figure 4. SEM images of the Cu-Sn/C composite powders reduced at (a) 400 $^{\circ}$ C, (b) 500 $^{\circ}$ C, (c) 600 $^{\circ}$ C, (d) 700 $^{\circ}$ C, and (e) 800 $^{\circ}$ C.

The intensity ratio of the (,113) and (132) peaks for the composite powders reduced at temperatures between 600°C and 800°C were consistent with a pure Cu₆Sn₅ phase (JCPDS card 45-1488). A high mixing degree of the Cu and Sn components in the precursor powders formed by spray drying enabled the formation of the pure Cu₆Sn₅ phase at low reducing temperatures. In this study, the carbon material of the composite powders decreased the reduction temperature of the Cu and Sn materials.

Fig. 4 shows the morphologies of the Cu-Sn/C composite powders reduced at temperatures between 400°C and 800°C. In comparison with the shell, the nanosized particles imbedded inside the shell appear as brighter spots in the SEM images, thus demonstrating the formation of a metallic Cu-Sn alloy. Segregation of the Cu and Sn components occurred during the decomposition and reduction processes of the metal salts while forming the nanosized metallic alloy particles. Therefore, the Cu-Sn nanoparticles are uniformly dispersed on the inner and outer surface of the spherically shaped carbon powders. Carbon spheres were formed by the decomposition of metal citrate under reducing atmosphere. The mean size of the Cu-Sn alloy nanoparticles increased with increasing the post-treatment temperature up to 600°C because of the low melting temperatures of 700°C and 800°C. This result indicates that the alloy nanoparticles do not aggregate even at higher temperature than their melting temperature, because of the carbon matrix on which they are dispersed. The mean sizes of the Cu-Sn nanoparticles reduced at 400°C and 600°C were 169 and 414 nm, respectively.



Figure 5. Schematic diagram of the formation mechanism of Cu₆Sn₅ alloy nanoparticles dispersed on a carbon matrix.

Fig. 5 shows the schematic diagram of the formation mechanism of Cu_6Sn_5 alloy nanoparticles dispersed on a carbon matrix. As described above, the precursor powders with a spherical and hollow morphology were prepared by spray drying from spray solutions with citric acid. The decomposition of metal chelates occurred under a reducing atmosphere and formed SnO₂-CuO/C composite powders.

The subsequent reduction of SnO_2 –CuO resulted in the formation of Cu_6Sn_5/C alloy composite powders for reduction temperatures between 600°C and 800°C. The particle growth of the Cu-Sn alloys occurred during the reduction process in order to minimize the total surface energy. Some of the alloy powders entered to the inner part of the spherical carbon powders and the others moved out to the outside of the carbon powders.



Figure 6. TEM images of the Cu₆Sn₅/C composite powders post-treated at 600°C.

Fig. 6 shows the TEM images of the Cu_6Sn_5/C composite powders post-treated at 600°C. The alloy powders are well dispersed on the spherical carbon matrix. The mean sizes of the Cu_6Sn_5 alloy and the carbon powder are 0.4 μ m and 7 μ m, respectively.





Figure 7. TG/DSC curves of the precursor powders and Cu₆Sn₅/C composite powders post-treated at 600°C.

Fig. 6 (b) shows a high-resolution TEM image of the Cu_6Sn_5 alloy particles dispersed on a carbon matrix. The alloy particles are fully covered by amorphous carbon with a uniform thickness of 4 nm. The carbon shell acts as a barrier to obstruct the aggregation between alloy particles.



Figure 8. The initial charge/discharge curves of Cu-Sn/C composite powders reduced at different temperatures at a constant current density of 300 mA g⁻¹ in the voltage range of 0.01–1.5 V.

Fig. 7 shows the TG/DSC curves of the precursor powders and Cu_6Sn_5/C composite powders post-treated at 600°C. In the case of the precursor powders, various major weight loss steps are

apparent between room temperature and 1000°C. The first prominent weight loss region at temperatures from 40°C to 100°C resulted from loss of adsorbed water. Upon heating the precursor powders up to 1000°C, a high weight loss of 70 % was observed.



Figure 9. Cycle performances of the Cu-Sn/C composite powders reduced at: (a) 400 °C, (b) 600 °C, and (c) 800 °C at a constant current density of 300 mA g⁻¹.

This indicates that a decomposition of the metal chelates formed from the Sn and Cu components and citric acid did not occur during the spray drying process. The DSC curves of the precursor powders exhibited several endothermic and exothermic peaks at temperature below 450°C by decomposition of the metal chelates and carbon components. The DSC curve of Cu₆Sn₅/C composite powders post-treated at 600°C showed two exothermic peaks at temperatures of 400°C and 550°C due to decomposition of the carbon and oxidation of the alloy parts. The corresponding weight loss and gain are observed in the TGA curve.

Fig. 8 shows the initial charge/discharge curves of Cu-Sn/C composite powders reduced at different temperatures at a constant current density of 300 mA g^{-1} in the voltage range of 0.01–1.5 V. The composite powders post-treated at 400°C showed a different behavior upon lithium insertion as compared to the powders post-treated at 600°C and 800°C, due to their different crystal structure. The initial discharge capacities of the composite powders reduced at 400°C, 600°C, and 800°C were 387, 277, and 188 mAh g^{-1} , with corresponding Coulombic efficiencies of 46%, 56%, and 52%, respectively. The composite powders reduced at 400°C included inhomogeneous mixtures of Cu₃Sn, Sn, and SnO₂. Therefore, the extra lithium insertion capacity observed might be caused by lithium reacting with SnO₂ to form Li₂O, which is irreversible.

Fig. 9 shows the cycle performances and Coulombic efficiencies of Cu-Sn/C composite powders at a constant current density of 300 mA g⁻¹. The discharge capacities of the composite powders reduced at 400°C decreased monotonically from 387 to 315 mAh g⁻¹ during 20 cycles, the capacity retention being 82%. The discharge capacities of the composite powders reduced at 600°C increased from 277 to 409 mAh g⁻¹ during the first five cycles, while reduction at 800°C led to a gradual increase from 188 to 309 mAh g⁻¹ during the first ten cycles. This indicates that the inner part of large Cu₆Sn₅ particles gradually reacted with Li during cycling. After 20 cycles, the discharge capacities of the composite powders reduced at 600°C and 800°C were 380 and 275 mAh g⁻¹ and the corresponding capacity retentions 93% and 89%, respectively.



Figure 10. The cyclic voltammetry profiles of the Cu-Sn/C composite powders reduced at 600°C for the first five cycles.

The Coulombic efficiencies of the Cu-Sn/C composite powders increased during the first several cycles and then saturated slightly above 96%, irrespective of the reduction temperatures.

Fig. 10 shows the cyclic voltammetry profiles of the Cu-Sn/C composite powders reduced at 600°C for the first five cycles. During the first cycle, the composite powders exhibited a different anodic and cathodic performance compared to the following cycles. It can be seen that the cyclic voltammetry curve declines smoothly with a peak appearing at about 0.27 V, which corresponds to the early stage of Li reacting with Sn [19]. In particular, the current increases when the potential is reduced from 0.3 to 0.01 V, which results from the intercalation of Li into amorphous carbon [20]. This indicates that there is only a small amount of the Sn phase and a lot of amorphous carbon in the matrix reacting with Li during the first cycle. However, the peak observed at 0.27 V, which is attributed to Li insertion into the crystalline Sn phase, becomes more pronounced from the second cycle. This result suggests that an increasing amount of the Sn phase reacts with Li, in addition to the carbon, after activation in the first cycle. The subsequent anodic sweeps result in smoothly increasing curves with two distinct peaks at 0.53 and 0.83 V, respectively; no difference is observed for the first and the following cycles. These two peaks are attributed to the extraction of Li from Sn, while the broad background is related to Li extraction from amorphous carbon [20]. This result proves that the use of a carbon matrix or a carbon shell improved the electrochemical properties of nanosized Cu-Sn alloy materials.

4. CONCLUSIONS

Spherically hollow precursor powders of Sn and Cu components are prepared by spray drying from aqueous solution with citric acid as a chelating agent. The high mixing degree of Cu, Sn, and carbon components in the precursor powders formed by spray drying enables the formation of phase-pure Cu₆Sn₅ powders at a low reduction temperature of 600°C. Submicron-sized Cu-Sn alloy particles are uniformly dispersed on the inner and outer surfaces of spherically shaped carbon powders during the reduction process. The discharge capacities of the composite powders reduced at 600°C increase during the first five cycles. During cycling, the inner part of large Cu₆Sn₅ particles gradually reacts with Li. The discharge capacities of the composite powders are 277, 409, and 380 mAh g⁻¹ during the first, fifth, and twentieth cycle, respectively. The new-concept spray drying process could be widely applied to the large production of the alloy-C composite powders with various compositions as anode materials for lithium ion batteries.

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