Electrochemical Performances of the Sn-Cu Alloy Negative Electrode Materials through Simple Chemical Reduction Method

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ABSTRACT

Sn-Cu alloy powders were prepared *via* a simple chemical reduction method for the negative electrode materials in lithium-ion batteries. The addition of Cu can suppress the growth of Sn particles during synthetic process. Furthermore, the Cu also acts as a matrix phase against the volume change during cycling. With increasing amount of the Cu, a stable Cu₆Sn₅ phase formed in the Sn-Cu alloy and its cycle performance greatly enhanced depending on the Cu content. To promote the generation of the Cu₆Sn₅ phase, the synthesis temperature is raised to 60-100°C from the ambient temperature. The Sn-Cu alloy powders prepared at elevated temperatures showed remarkable cycle performances. The Sn-Cu alloy powder obtained at 60°C exhibited a significantly high volumetric capacity of over 2,000 mAh/cc at the 50th cycle.

Keywords : Sn-Cu alloy, Chemical Reduction, Cycle Performance, Lithium-ion Batteries

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1. Introduction

With the development of electric vehicles and energy storage systems, the demand for larger-capacity batteries has increased. Hence, the interest in new high-capacity electrode materials has increased. Sn is the one of the promising candidates of negative electrode materials based on its alloying reaction with Li because Sn offers a large specific capacity (960 mAh/g for Li₁₇Sn₄) and volumetric capacity (6,970 mAh/cc) compared with carbonaceous materials such as graphite (372 mAh/g and 818 mAh/cc), which is the most frequently used negative electrode material in commercial lithium-ion batteries. However, it is widely known that the high-capacity materials that can alloy with lithium ions during cycling have poor

cyclability because the Sn-based electrodes undergo severe volume change upon Li⁺ ion insertion/extraction from the active materials [1-5].

To overcome these problems, many researchers have tried to suppress the loss of electrically conductive path due to volume change, which causes performance degradation [6-10]. Among the proposed approaches, the alloying of Sn with Cu, which has an excellent electrical conductivity and can easily form an alloy phase with Sn, has led to a great improvement in the cycle performance [11-15]. The addition of Cu can not only increase the electronic conductivity, but also acts as a matrix phase against the volume change during cycling. Negative electrode materials containing a Sn-Cu alloy have been prepared by various synthetic methods. However, we attempted to find a fast and simple synthetic method.

We synthesized a bimetallic alloy comprising Sn and Cu by a simple chemical reduction method. The homogeneous alloy material was obtained by mixing Sn and Cu ions in an aqueous solution and simultaneously reducing them using NaBH₄, a reducing agent.

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Therefore, the Sn-Cu bimetallic alloys can be prepared according to the amount of Cu and bath temperature. The crystal structure, powder morphology, and electrochemical characteristics of the prepared samples were investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and electrochemical analyses.

2. Experimental

To prepare the Sn powders and Sn-Cu bimetallic alloy powders, Sn and Cu aqueous solutions were prepared. SnSO_4 (Junsei, >95%) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Daejung, >99.5%) were dissolved in distilled water with various mole ratios of Sn and Cu [Sn:Cu = 100:0 (SC100), 90:10 (SC90), 75:25 (SC75), and 50:50 (SC50)]. The total concentration of the two metal ions was fixed as 0.1 M. The same volume of 1.0 M NaBH_4 (Aldrich, 98%) solution as a reducing agent was added into the prepared solution containing Sn^{2+} and Cu^{2+} ions with stirring for 20 min. The precipitates were filtered and dried overnight at 70°C. XRD analysis was conducted at 5°/min using a Bruker D8 advance equipment with $\text{Cu-K}\alpha$ radiation (1.54056 Å), and FE-SEM images were obtained using a NOVA NANO 200 field emission scanning electron microscope.

For the electrochemical tests, the Sn-Cu powders (as an active material), Super P (as conductive carbon), and PAA (polyacrylic acid, as a binder) (8:1:1 ratio, w/w) were mixed with distilled water, and the slurry was coated on a Cu foil and dried at 120°C for 8 h under vacuum. The loading amount, electrode thickness, and electrode density were controlled within $2.5 \pm 0.2 \text{ mg/cm}^2$, $13 \pm 2 \text{ }\mu\text{m}$, and $2.0 \pm 0.3 \text{ g/cc}$, respectively. Then, 2032-type coin half-cells were assembled with the prepared composite electrodes, a polypropylene separator (Celgard 2400), an electrolyte, and a counter electrode of lithium foil. The used electrolyte was 1.0 M LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 volume ratio) with 2.0 wt% vinylene carbonate (VC). After cell assembly, galvanostatic cycling was performed with a current of 100 mA/g in the voltage range of 0.0–1.2 V (vs. Li/Li^+) at 25°C using a Wonatech WBCS3000 system. The electrode thickness was measured using a micrometer (Mitutoyo Co.) after cell disassembly was carried out in the glove box.

3. Results and Discussion

The bimetallic alloy was prepared by chemical reduction of Sn^{2+} and Cu^{2+} ions in an aqueous solution by NaBH_4 . The Sn-Cu bimetallic alloys were easily synthesized through the simple chemical reduction method, and the prepared powders were characterized by FE-SEM and XRD. The addition of Cu can not only promote the electrical conductivity, but also suppresses the growth of Sn particles during synthesis. The SC90 powder was sub-micron and SC75 and SC50 powders were nanosized, while the Sn particles grew to a few micrometers (Fig. 1).

Fig. 1. FE-SEM images of the synthesized Sn-Cu alloy powders: (a) SC100, (b) SC90, (c) SC75, and (d) SC50.

Fig. 2. X-ray diffraction patterns of the synthesized Sn-Cu alloy powders: (a) SC100, (b) SC90, (c) SC75, and (d) SC50.

Fig. 3. The galvanostatic charge/discharge voltage profiles at first cycle obtained from Li/Sn-Cu alloy half-cells.

Fig. 4. The dealloying (discharge) capacity delivered by Li/Sn-Cu alloy half-cells.

Moreover, as the amount of Cu increased, a Cu_6Sn_5 intermetallic phase was formed as well as Sn, as observed from the XRD profiles (Fig. 2). It is difficult to measure the exact relative amounts of Cu, Sn and Cu_6Sn_5 . However, the ratio of inactive Cu to active Sn in the synthesized alloys was expected to be maintained at the concentration ratio of the synthetic bath because the excessively large amount of reducing agent was used.

The first voltage profiles of the Sn-Cu electrodes are shown in Fig. 3. The SC100 sample (Sn only) exhibited a large overpotential and a rather small charge (lithiation) capacity at the first cycle due to its large particle size and small surface area. The reversible (delithiation) capacity in the first cycle decreased as the Cu content increased because of the increase in

Fig. 5. FE-SEM images of the Sn-Cu alloy electrodes after 10 cycles: (a) SC100, (b) SC90, (c) SC75, and (d) SC50.

the inactive Cu ratio. Therefore, the initial capacity tends to decrease proportionally according to the Cu content.

The cycle performance of the Sn-Cu alloy electrodes are shown in Fig. 4. The addition of Cu decreased the initial specific capacity and enhanced the cycle performance of the cell. SC100 has a reversible capacity (de-alloying) of about 645 mAh/g, while SC50 has a capacity of about 427 mAh/g at the first cycle. However, with further cycling, SC100 and SC90 showed larger capacities due to the higher contents of Sn and drastic capacity fading due to the larger volume change during cycling. In contrast, SC75 and SC50, which had higher Cu contents, exhibited significantly improved performances. SC50 showed a good cycle performance over 50 cycles without any sharp capacity drop. This is because of the reduction in the degree of volume change due to the decrease in Sn content, and the smaller particle size of Sn-Cu alloy because of the suppression of growth of Sn particles during synthesis. It is also believed that the Cu matrix of the Cu_6Sn_5 intermetallic works more effectively against electrode pulverization caused by the volume change [16-20].

The FE-SEM photographs of the Sn-Cu alloy electrode after 10 cycles were shown in Fig. 5 and the increase of electrode thickness measured in the glove box after first cycle and 10 cycles was displayed in

Fig. 6. As the content of Cu increased, the crack of electrode decreased and the increase in the electrode thickness after cycling was decreased. The Cu addition alleviates the pulverization problem of the electrode by decreasing the degree of volume change, facilitating the formation of smaller particles, and imparting a good adhesion property.

To promote the production of Cu-Sn alloy, the reduction temperature of the reactor was raised to 60°C and 100°C, while the chemical composition was fixed at a Sn:Cu mole ratio of 1:1 (SC50). Fig. 7 shows the FE-SEM images of the samples prepared at room temperature and elevated reaction temperatures. The size and shape of the Sn-Cu alloy were similar to those of SC50 prepared at room temperature (RT). The XRD profile showed that the formation of Cu_6Sn_5 phase greatly increased and the Cu was also expected to be generated, while the formation of Sn phase decreased (Fig. 8). A broad diffraction peak of Cu_6Sn_5 was observed, which is due to

Fig. 6. Thickness increase of the Sn-Cu alloy electrodes after 1 cycle and 10 cycles.

the formation of nano-sized crystallites. It is expected that crystallite of about 200 nm size is formed by calculated from the width of main peak using the Scherrer equation.

The electrochemical performances were evaluated under the same conditions as mentioned above, and the voltage profiles and the cycle characteristics are shown in Fig. 9 and Fig. 10 with the theoretical capacity of graphite, which was used as a standard negative electrode material. The decrease of specific capacity was observed with the increase of the synthesis temperature, but the voltage curves were very similar. Although the initial capacity of the sample

Fig. 8. X-ray diffraction patterns of SC50 alloy powders synthesized (a) at room temperature (RT), (b) 60°C, and (c) 100°C.

Fig. 7. FE-SEM images of SC50 alloy powders synthesized at (a) room temperature (RT), (b) 60°C, and (c) 100°C.

Fig. 9. The galvanostatic charge/discharge voltage profiles at first cycle obtained from Li/SC50 alloy half-cells according to the synthesis temperature.

Fig. 10. Cycle performance of the Li/SC50 half cell according to the synthesis temperature: (a) specific capacity and (b) volumetric capacity (based on the mass and volume of active materials).

synthesized at an elevated temperature reduced, the cycle performance improved remarkably. The alloy materials prepared at 60°C and 100°C exhibited

reversible capacities of 307 and 205 mAh/g at the first cycle, respectively. However, their cycle performances were excellent without observable capacity degradation from the second cycle and their capacities were maintained over 90% up to 50 cycles. As the content of Cu₆Sn₅ increased, the bimetallic alloy electrode can be preserved more stably against the volume change of Sn by the strong interfacial adhesion between Cu and Sn. The specific capacity does not reach the theoretical value of graphite (372 mAh/g); however, the Sn-Cu alloy occupied a smaller space because Sn and Cu are much denser than graphite. The cycle performance is shown in Fig. 10(b) on the basis of the volumetric capacity. The Sn-Cu alloy showed a much higher volumetric capacity on the basis of active materials than that of graphite (818 mAh/cc). The average density of the synthesized alloy materials was calculated and used according to its content ratio of Cu (8.935 g/cc, JCPDS 04-0836), Sn (7.287 g/cc, JCPDS 04-0673), and Cu₆Sn₅ (8.282 g/cc, JCPDS 45-1488), relatively. The density of the SC50 alloy (Sn:Cu=1:1 mol ratio) was calculated to be between 7.79 g/cc (when considered as a mixture of Sn and Cu) and 8.16 g/cc (when considered as a mixture of Cu₆Sn₅ and Sn). The density of the smaller value (7.79 g/cc) was applied to the calculation of the volumetric capacity of SC50 regardless of synthesis temperature. The Sn-Cu alloy prepared at 60°C (SC50@60) exhibited a volumetric capacity of 2,031 mAh/cc (on the basis of active materials) even after 50 cycles, which is 2.5 times that of the theoretical capacity of graphite. When the volumetric capacity is calculated based on the actual electrode, the volumetric capacity of SC50@60 electrode is 613 mAh/cc at initial cycle and 511 mAh/cc at 50th cycle which is higher than that of the practical graphite electrode (450 mAh/cc) [21]. As the charge and discharge progresses, the volume of the SC50 electrode also increases continuously. Based on the electrode thickness measured by disassembling the half-cell after cycling, the electrode thickness of SC50@60 increased by 40% after 10 cycles and increased by 89% after 50 cycles. The volumetric capacity of SC50@60 is recalculated taking into account thickness variations to 276 mAh/cc at 50th cycle. The practical use of Sn-Cu alloy materials will require further improvement.

Based on these results, it was confirmed that Sn-Cu alloy negative electrode materials could be easily

synthesized with various compositions by the simple reduction method. The Sn-Cu alloy negative electrode materials for lithium-ion batteries having excellent cycle characteristics can be obtained by increasing the content of Cu and conducting the reaction at 60°C.

4. Conclusions

Sn-Cu bimetallic alloys were easily synthesized through a simple chemical reduction method, and the prepared powders were characterized by FE-SEM and XRD. The addition of Cu resulted in the formation of smaller particles and a Cu_6Sn_5 phase.

The cycle performances of Sn-Cu bimetallic alloys improved as the content of Cu increased. Thus, Cu plays an important role in the structural stability of Sn-Cu alloy by the formation of a stable Cu_6Sn_5 phase and the suppression of Sn aggregation during synthesis. With increasing amount of Cu, the initial reversible capacity decreased; however, the cycle performance was greatly enhanced. The SC50 powder synthesized at an elevated reaction temperature of 60°C showed an excellent cycle performance and a higher volumetric capacity than that of graphite on the basis of active materials.

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