



Characteristics of Sn–Ni alloy powders directly prepared by spray pyrolysis

Seo Hee Ju^a, Hee Chan Jang^a, Yun Chan Kang^{a,*}, Dong-Won Kim^b

^a Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

^b Department of Chemical Engineering, Hanyang University, Seungdong-Gu, Seoul 133-791, Republic of Korea

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ABSTRACT

Fine size Sn–Ni alloy powders with spherical shape were directly prepared by spray pyrolysis. The alloy powders prepared at temperatures below 1200 °C had bimodal size distributions of nano- and submicron-sized powders. Nano-sized powders were formed by chemical vapor deposition process from the evaporated Sn component. The powders had main peaks of Sn–Ni alloys irrespective of the preparation temperatures. Ni and Sn components are well dispersed inside the submicron-sized powders. The initial discharge capacity of the Sn–Ni alloy powders prepared at a temperature of 1100 °C was 477 mAh/g. However, the initial discharge capacity of the Sn–Ni alloy powders prepared at temperature of 1000 and 1200 °C were 255 and 411 mAh/g respectively. The Sn–Ni alloy powders prepared at a temperature of 1100 °C had more good cycle performance than those prepared at temperatures of 1000 and 1200 °C.

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1. Introduction

Lithium-ion batteries possess the high energy density among the practical batteries, and the development of its anode material is considered as one of the breakthroughs to meet the demands for power sources with higher performance for portable electronic devices.

Presently, carbon is used as the anode materials for Li-ion batteries, which is now showing a capacity close to its theoretical value of 372 mAh g⁻¹. In order to improve the performance of lithium-ion batteries, the exploiter of new anodic materials that exceed the capacity of carbon materials become the key in the development of Li-ion batteries. Tin was widely studied as alternative anodic materials to carbon for lithium-ion batteries owing to its much higher theoretical capacity (991 mAh g⁻¹) [1] than that of carbon. However, these materials suffer of large volume expansion and contraction during the charge–discharge cycling and this induces mechanical disintegration which in turn results in a very poor cycle ability [1–2]. In order to improve the performance of cyclability, modification of the electrode structure is studied. Extensive attention has been conducted on tin based intermetallic compounds, i.e. Sn_xMy (M: inactive element), such as Sn–Co [3,4], Sn–Sb [5,6], Sn–Ni [7,8], Sn–Cu [9], etc. These materials exhibited longer cyclability than the pure tin. Winter and Besenhard inferred that the inactive element can buffer the large volume change and as a barrier against the aggregation of Sn into large grains during Li-ion inser-

tion and extraction process [10]. However, the capacity retention of the electrode is not satisfactory upon prolonged cycling.

Various methods including ball milling [11], electrodeposition [12], carbothermal reduction [13] and emulsion polymerization [6] are commonly used to prepare the alloy powders. Spray pyrolysis is a useful method for the synthesis of highly pure, fine-sized, and spherical shape materials [14–16]. Spray pyrolysis was also applied to the preparation of pure and mixed metal powders. However, alloy powders for application to the lithium secondary battery as anode material were not prepared by spray pyrolysis. The characteristics of the metal powders prepared by spray pyrolysis were strongly affected by the preparation conditions and the compositions.

In this study, Sn–Ni alloy powders were prepared by spray pyrolysis in reduction atmosphere. The effects of preparation conditions on the morphology, crystal structure and electrochemical properties of Sn–Ni alloy powders prepared by spray pyrolysis were investigated.

2. Experimental

The spray pyrolysis system consists of droplet generator, quartz reactor, and powder collector. A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The reactor temperature was changed from 900 to 1300 °C. The flow rate of the mixture gas (10% H₂ in N₂) used as the carrier gas was 5 l/min. The residence time of droplet/powder inside the hot wall reactor was 2.6 s when the preparation temperature was 1100 °C. The precursor solution was prepared by dissolving a stoichiometric ratio of 3:4 nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] and tin chloride dihydrate [SnCl₂·2H₂O] in distilled water. The overall solution concentration of nickel and tin components were 0.3 M. The crystal structures of the as-prepared Sn–Ni alloy powders were investigated using X-ray diffractometry (XRD, RIGAKU DMAX-33) using Cu Kα radiation. The morphological characteristics of the powders were investigated using scanning electron microscopy

* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

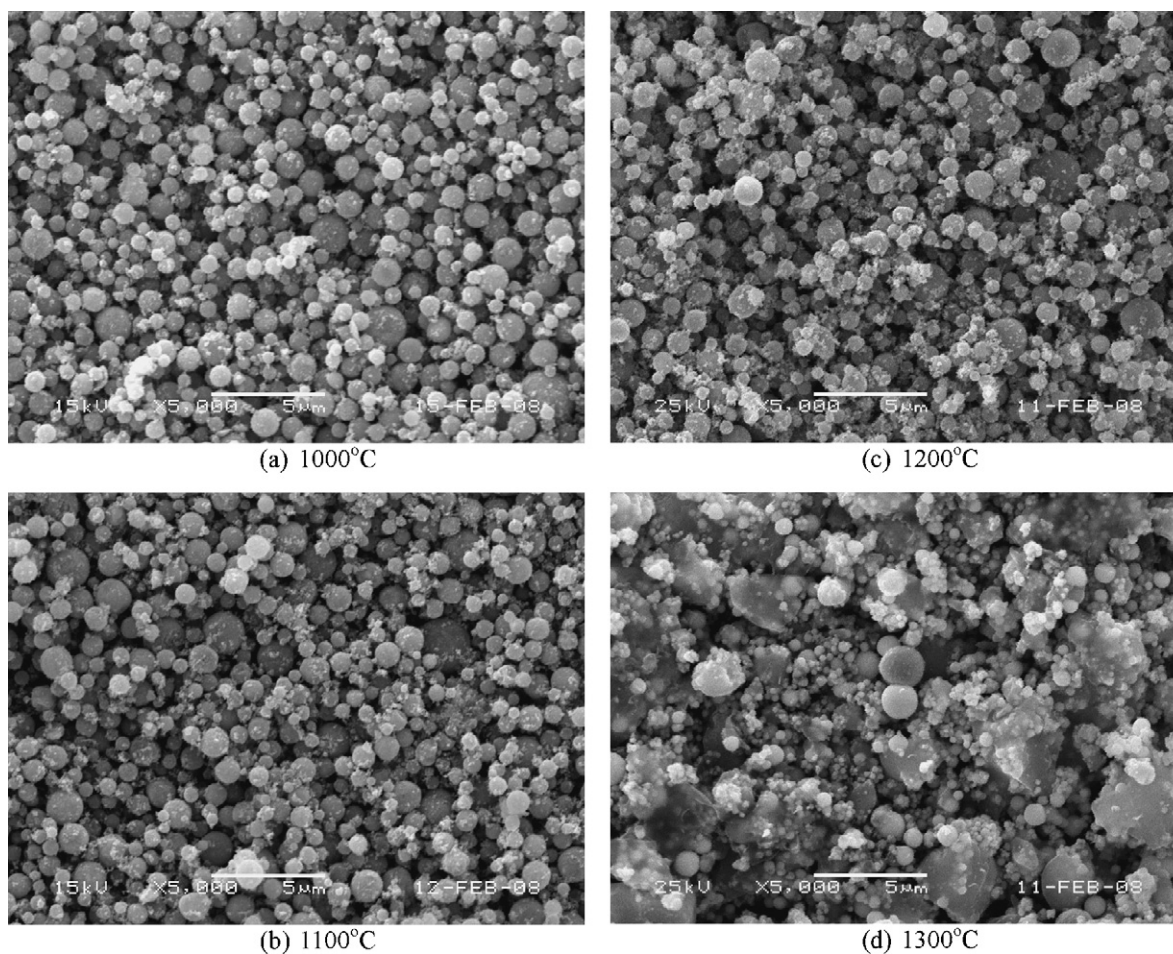


Fig. 1. SEM images of the Sn–Ni alloy powders prepared at different temperatures.

(SEM). The microstructure and compositions of the alloy powders were analyzed using transmission electron microscopy (TEM) and energy dispersive X-ray (EDX). The initial charge/discharge capacities of the prepared Sn–Ni alloy powders were measured. The anode electrode was made of 12 mg of Sn–Ni alloy mixed with 4 mg of conductive binder (3.2 mg of teflonized acetylene black and 0.8 mg of graphite). The lithium metal and polypropylene film were used as the cathode electrode and the separator, respectively. The electrolyte (TECHNO Semichem. Co.) was 1 M LiPF₆ in a 1:1 mixture by volume of EC/DMC. The charge/discharge characteristics of the samples were measured through cycling in the 0.01–1.5 V potential range at a constant current density of 0.1C.

3. Results and discussion

The characteristics of the alloy powders prepared by spray pyrolysis are affected by the preparation conditions such as preparation temperature and residence time of powders inside the hot wall reactor. Enough residence time of the powders inside the hot wall reactor is necessary to prepare the alloy powders in the spray pyrolysis. In this study, the optimum preparation temperature was investigated at the constant flow rate of carrier gas as 5 l/min. Fig. 1 shows the SEM images of the Sn–Ni alloy powders obtained by the spray pyrolysis at different temperatures. The alloy powders prepared at temperatures below 1200 °C had similar morphologies irrespective of the preparation temperatures. The alloy powders prepared at temperatures below 1200 °C had bimodal size distributions of nano- and submicron-sized powders. One submicron-sized alloy powder was formed from one droplet by drying, decomposition and melting processes. However, the nano-sized alloy powders were formed by a chemical vapor deposition (CVD) process. Evaporation of some components composing the alloy powders occurred

inside the high temperature reactor. Nano-sized alloy powders were formed from the evaporated vapors by the CVD process. The number of nano-sized alloy powders increased with an increase of the preparation temperature. Fig. 2 shows the TEM image of the alloy powders prepared at a temperature of 1100 °C. The alloy powders had spherical shape, dense structure and non-aggregated morphology. The mean size of powders formed by CVD process had several tens nanometer. On the other hand, the alloy powders prepared at a temperature of 1300 °C had aggregated structure between the powders. In the spray pyrolysis, collisions between the powders did not occur in the gas phase inside the hot wall reactor. Therefore, aggregation between the powders at a preparation temperature of 1300 °C occurred in the powder collection system.

Fig. 3 shows the XRD patterns of the as-prepared Sn–Ni alloy powders obtained at different temperatures. The powders had main peaks of Sn–Ni alloys irrespective of the preparation temperatures. The peaks of Sn₂Ni₃, and Sn–Ni alloys are coexisted. However, the peaks of SnO₂ as impurity was observed from the XRD patterns of the powders prepared at temperatures below 1200 °C. On the other hand, the peaks of SnO₂ disappeared from the XRD pattern of the powders prepared at a temperature of 1300 °C.

To confirm the chemical composition of the Sn–Ni alloy powders, TEM-EDX analysis and dot mapping were performed. Fig. 4 shows the TEM-EDX spectrum of the submicron-sized Sn–Ni alloy powders as shown in Fig. 2. In the TEM-EDX spectrum, the composition ratio of nickel and tin components were analyzed. The average ratio of Ni and Sn components of the powders was about 1:1. The ratio of Ni and Sn components in the spray solution was 3:4. Therefore, the submicron-sized alloy powder was Sn deficient compared

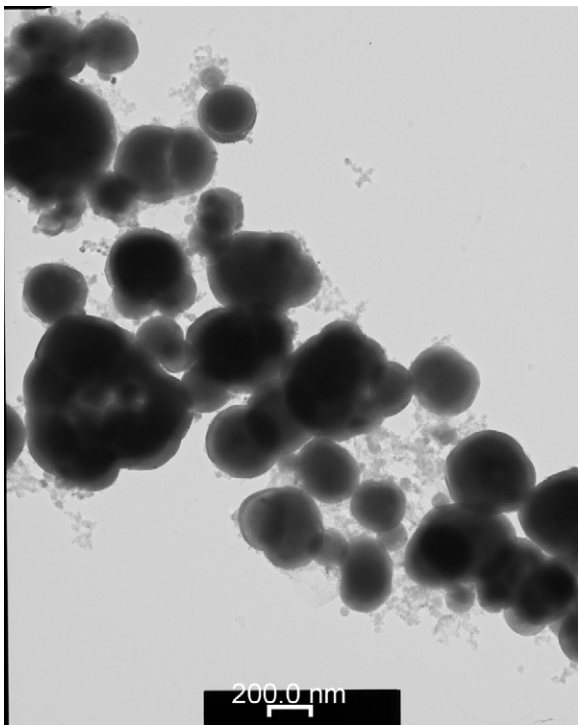


Fig. 2. TEM image of the Sn–Ni alloy powders.

to that of the spray solution. Some of the Sn component evaporated inside the hot wall reactor because of high volatility of tin chloride at high temperatures. Fig. 5 shows the results of dot mapping of the alloy powders prepared at a temperature of 1100 °C.

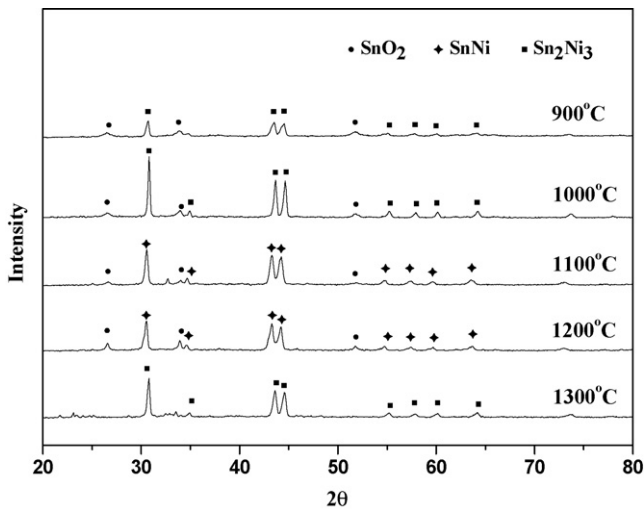


Fig. 3. XRD patterns of the Sn–Ni alloy powders prepared at different temperatures.

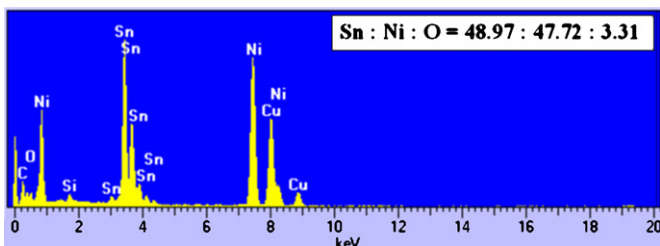
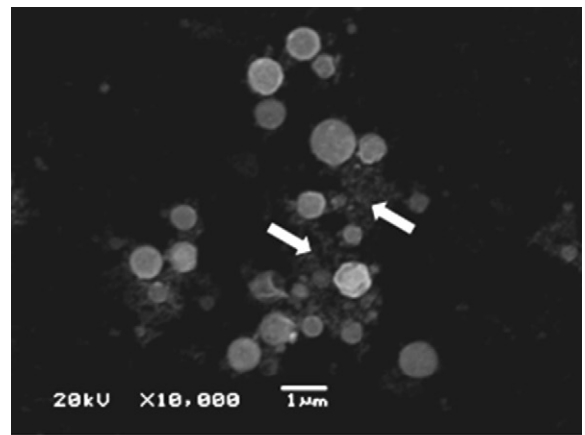
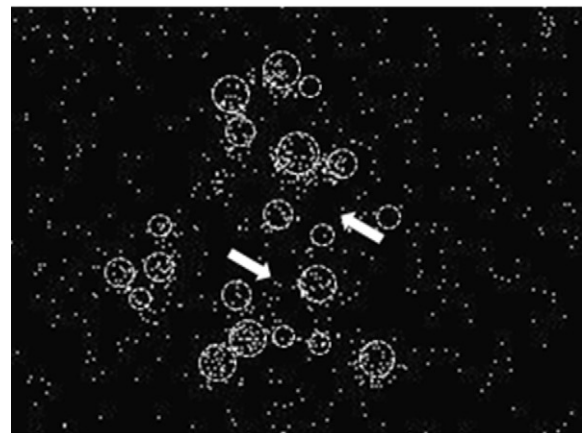


Fig. 4. EDX spectrum of the Sn–Ni alloy powders.

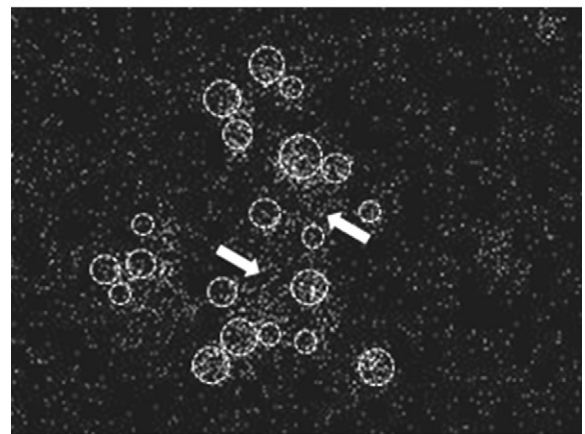


(a) powder



Ni Ka1

(b) Ni component



Sn La1

(c) Sn component

Fig. 5. Dot mapping of the Sn–Ni alloy powders.

Ni and Sn components are well dispersed inside the submicron-sized powders. However, Sn component was only detected from the nano-sized powders as shown by arrows in Fig. 5(c). Therefore, nano-sized Sn powders were formed by CVD process from the evaporated Sn component.

Fig. 6 shows the initial charge/discharge curves of the Sn–Ni alloy powders prepared at different temperatures. The initial charge and discharge capacities of the Sn–Ni alloy powders were affected by the preparation temperatures. The initial discharge capacity of the Sn–Ni alloy powders prepared at a temperature of 1100 °C was 477 mAh g⁻¹. However, the initial discharge capacity of the Sn–Ni

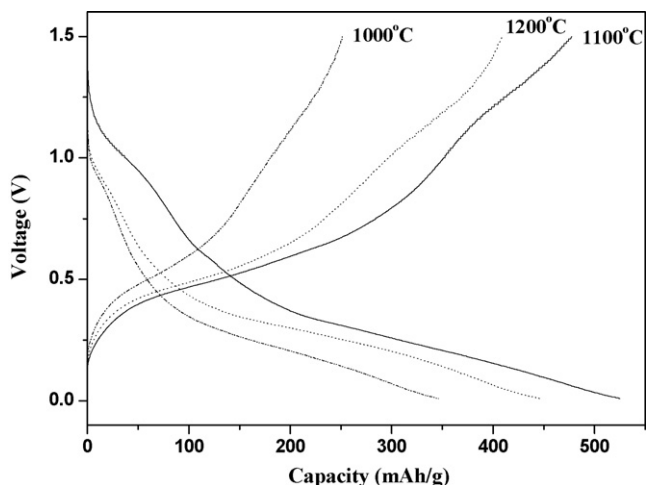


Fig. 6. Initial charge/discharge curves of the Sn–Ni alloy powders prepared at different temperatures.

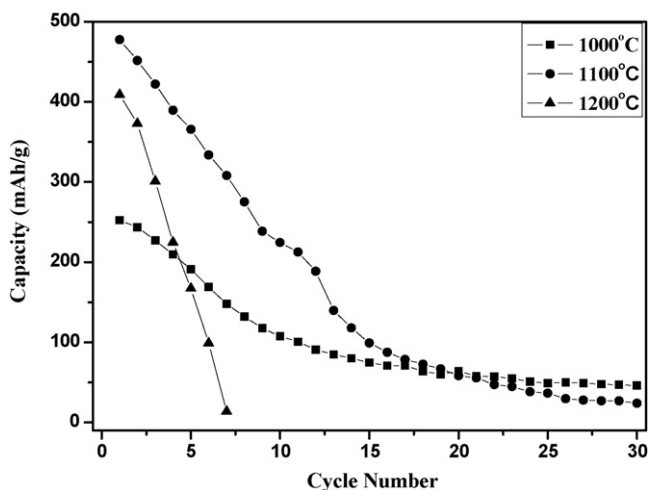


Fig. 7. Cycling performances of the Sn–Ni alloy powders at a constant current density of 0.1C.

alloy powders prepared at temperatures of 1000 and 1200 °C were 255 and 411 mAh g⁻¹, respectively. On the other hand, the coin cell obtained from the alloy powders prepared at a temperature of 1300 °C was not performed. The cycle properties of the Sn–Ni alloy powders prepared by spray pyrolysis at different tempera-

tures were shown in Fig. 7. The Sn–Ni alloy powders prepared at a temperature of 1100 °C had more good cycle performance than those prepared at temperatures of 1000 and 1200 °C. However, the Sn–Ni alloy powders prepared by spray pyrolysis had poor cycle performances compared to those prepared other processes reported in previous paper [7]. In this study, phase pure Sn–Ni alloy powders were not directly prepared by spray pyrolysis because of high volatility of source material of tin component. Therefore, in the spray pyrolysis, the cycle performances of the Sn–Ni alloy powders could be improved by optimizing the compositions. The compositions of the Sn–Ni alloy powders could be controlled by using the source materials with low volatilities and by optimizing the preparation conditions. This study was a preliminary investigation of the possibility to prepare the alloy powders for anode applications.

4. Conclusions

Sn–Ni alloy powders as anode material for lithium secondary battery were first prepared by spray pyrolysis. The powders directly prepared by spray pyrolysis without post-treatment at high temperatures had main peaks of Sn–Ni alloys with small impurity peaks of SnO₂. The morphologies, crystal structures, compositions and electrochemical properties of Sn–Ni alloy powders prepared by spray pyrolysis at various temperatures were investigated. The optimum preparation temperature of Sn–Ni alloy powders in the spray pyrolysis was 1100 °C when the flow rate of the carrier gas was 5 l/min.

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