

# Particle size and performance of SnS<sub>2</sub> anodes for rechargeable lithium batteries

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## Abstract

We have proposed SnS<sub>2</sub> as promising Li-ion battery anode materials in our previous study. Nanoparticles of this material were synthesized by a sonochemical method. In this work, smaller SnS<sub>2</sub> particles were obtained by diluting the starting solution of the synthesis, and particles of 30 nm were observed in the Field Emission SEM (FE-SEM) images. From such SnS<sub>2</sub> particles, higher discharge capacity of 620 mAh/g and suppressed electrode degradation were observed in charge–discharge experiments. This indicates that the enlargement of the surface area was effective in facilitating the Li-ion diffusion through the active material, in simplifying the electrochemical reaction and in restraining the stress within the electrode, caused during charge and discharge.

The discharge capacity in the 30th cycle was improved from 319 to 404 mAh/g by annealing the sample. It is suggested that this may be due to the change in its structure.

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**Keywords:** SnS<sub>2</sub>; Nanoparticles; Sonochemical method; Anode

## 1. Introduction

With the advances of the portable electronic devices, further improvement of the power sources is demanded. Li-ion batteries show the highest energy density within batteries that are in practical use, and the enhancement of its anode materials are counted on as one of the breakthroughs for such demands.

Carbon is the present utilized anode material for the Li-ion batteries, and it shows a theoretical capacity of 372 mAh/g. Sn shows a higher theoretical capacity of 991 mAh/g, and had once been a center of the attention of researchers. However, Sn goes through a large volume change during the reactions that occur in charge and discharge [1]. This phenomenon is considered to cause aggregation of Sn particles, and lead to pulverization and degradation of the electrode [2]. This capacity fade of Sn anode is still a big issue yet to be solved, and though it is a highly attractive anode material, it still has not been applied in the actual batteries.

In 1994, Fuji Photo Film Co. Ltd., Japan filed a patent for Sn oxides of Sn compounds used as anode materials for

Li-ion batteries [3]. Courtney and Dahn [4] have reported the mechanism of such materials. Sn oxides react with Li-ion and forms Sn grains and Li<sub>2</sub>O in the initial charge. During the substantial charge and discharge, the Sn works as the active material and the Li<sub>2</sub>O works as the inert matrix surrounding the active Sn grains, suppressing the failure of the electrode caused from the volume change.

We have suggested SnS<sub>2</sub> as a novel anode material in a similar concept [5], though from this component, Li<sub>2</sub>S is believed to be the matrix instead of Li<sub>2</sub>O. It has shown a better cycle stability compared to that of Sn oxides. Furthermore, better cycle stability was gained from annealing the samples at 400 °C.

In this study, we have examined how the particle size affects the anode performance and the effect of annealing.

## 2. Experimental

The SnS<sub>2</sub> powder was prepared following the literature [6–11]. Three types of solution with different concentration were prepared by dissolving 8.7 + 3.8, 4.35 + 1.9, 2.9 + 1.27 g of SnCl<sub>4</sub>·5H<sub>2</sub>O + thioacetamide into 70 ml of water, where 30 min of supersonic radiation was applied

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to synthesize  $\text{SnS}_2$  particles. Field Emission SEM (FE-SEM) was equipped to observe the morphology of the sample. The working electrodes were prepared with  $\text{SnS}_2$  as the electroactive material, acetylene black (AB) as the conducting material, and poly(vinylidene fluoride)-hexafluoropropylene (PVdF-HFP) as the binder, mixed by the weight ratio of 8:1:1. Electrochemical measurements were performed in conventional glass cells with two pieces of lithium foils as counter and reference electrodes, and 1 M  $\text{LiClO}_4$ /ethylene carbonate (EC) + propylene carbonate (PC) (1:1 vol.%) as the organic electrolyte. The electrochemical performances of the cells were evaluated within the potential range of 0–3 V versus  $\text{Li/Li}^+$ . Both charge and discharge were carried out galvanostatically at current density of 50 mA/g of  $\text{SnS}_2$ . XRD was equipped to evaluate the structural difference between  $\text{SnS}_2$  as-prepared and as-annealed.

The concentration of the solution with 8.7 + 3.8 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  + thioacetamide dissolved is defined as the standard of this study, and is named “1/1”. The solution with half its concentration is “1/2”, and with third is “1/3”.

### 3. Results and discussion

Fig. 1 shows the images of FE-SEM equipped to observe the morphology of the samples. From the images, it can be confirmed that there is a sure relationship between the concentration of the starting solution and the gained particle size. The particle size of  $\text{SnS}_2$  from solution “1/1” varied from 400 to 1000 nm, from solution “1/2” it was 90–240 nm, and from solution “1/3” it was approximately 30 nm. From a more diluted solution, smaller particles were gained. In this study,  $\text{SnS}_2$  are formed from the  $\text{Sn}^{4+}$  ions and  $\text{S}^{2-}$  ions colliding within the high-energy microspace of cavitation formed from the sonochemical radiation [12]. With lower concentration of the solution, smaller  $\text{SnS}_2$  particles were gained. Furthermore, as there will be less  $\text{SnS}_2$  in the whole system, its aggregation would be more suppressed in solution “1/2” than in solution “1/1”, and more in solution “1/3” than in solution “1/2”. The obtained images fit well with this consideration.

Fig. 2 shows the cycle performance of these samples. They are a result of a galvanostatic experiment performed to evaluate the difference caused from particle size. The discharge capacity of the 1st and the 30th cycle of sample 1/1 were 401 and 127 mAh/g, of sample 1/2 were 514 and 247 mAh/g, of sample 1/3 were 620 and 319 mAh/g. Table 1 lists the discharge capacity of the 30th cycle and the capacity loss of the samples after 30 cycles from the 1st cycle, calculated from the data shown in Fig. 2. Higher discharge capacity and smaller degradation were seen from smaller  $\text{SnS}_2$  grains, indicating that better performance could be gained from smaller particles. Smaller particles have larger surface area per gram, which would make the diffusion of the Li-ion into the active element easier and decrease the overvoltage of the Sn–Li alloying reaction,

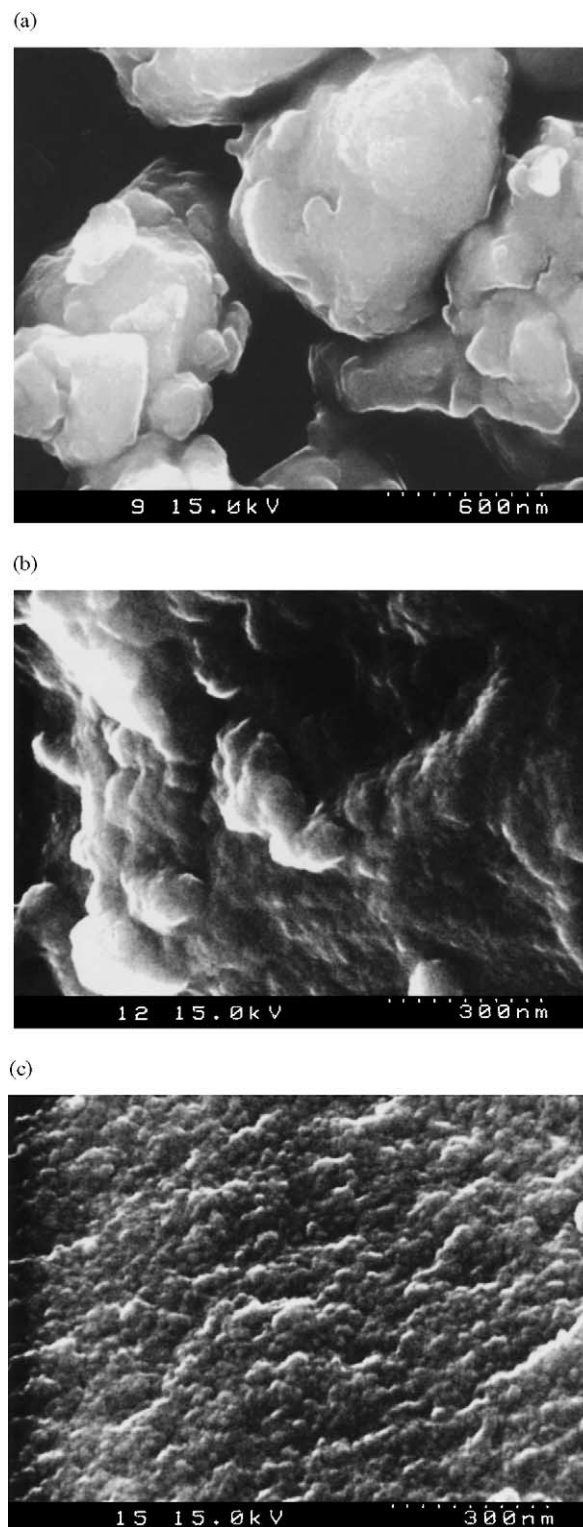


Fig. 1. FE-SEM images of  $\text{SnS}_2$  synthesized from (a) solution 1/1, (b) solution 1/2, (c) solution 1/3.

leading to a higher discharge capacity. Further more, after the initial charge, smaller  $\text{SnS}_2$  grains could result in smaller Sn grains. This could contribute to the lightening of stress caused by its volume change during the substantial charge and discharge, and suppress the degradation of the electrode.

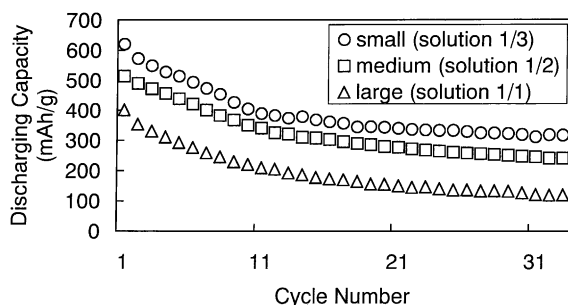


Fig. 2. Size dependence of the cycle performance of  $\text{SnS}_2$ .

Table 1

Comparison of discharge capacity and capacity loss after 30 cycles of the samples synthesized from starting solution with different concentration

Solution	Discharge capacity after 30 cycles (mAh/g)	Capacity loss <sup>a</sup> after 30 cycles (%)
1/1	127	69.6
1/2	247	52.3
1/3	319	48.6

<sup>a</sup> Capacity loss = (1st capacity – 30th capacity)/(initial capacity).

We have reported in our previous paper [5] that there has been an enhancement in the cycle ability of  $\text{SnS}_2$  when annealed at  $400^\circ\text{C}$ . Therefore, we annealed the finest sample (from solution “1/3”) at  $400^\circ\text{C}$  and compared its cycling performance with the as-prepared sample. Fig. 3 shows the results from the galvanostatic experiment. The annealing of the sample of solution 1/3 enhanced the discharge capacity from 620 to 736 mAh/g in the 1st cycle, and from 319 to 404 mAh/g in the 30th cycle. Table 2 lists the discharge capacity of the 30th cycle and the capacity loss of the samples after 30 cycles from the 1st cycle, calculated from Fig. 3. Likewise our previous report, improvement was confirmed from the annealing.

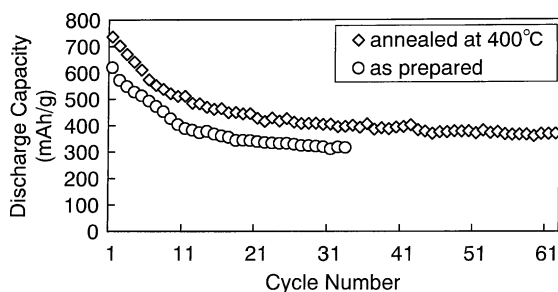


Fig. 3. Annealing condition dependence of the cycle performance of  $\text{SnS}_2$ .

Table 2

Comparison of discharge capacity and capacity loss after 30 cycles of the sample of solution 1/3 as-prepared and as-annealed at  $400^\circ\text{C}$

Annealing condition	Discharge capacity after 30 cycles (mAh/g)	Capacity loss <sup>a</sup> after 30 cycles (%)
As-prepared	319	48.6
Annealed at $400^\circ\text{C}$	404	45.2

<sup>a</sup> Capacity loss = (1st capacity – 30th capacity)/(initial capacity).

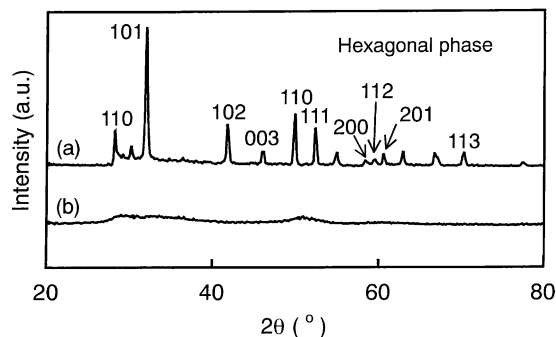


Fig. 4. Difference in the XRD pattern between (a) annealed  $\text{SnS}_2$  and (b) as-prepared  $\text{SnS}_2$ .

To see what differs between the  $\text{SnS}_2$  samples as-prepared and as-annealed at  $400^\circ\text{C}$ , XRD was applied to these two samples. Fig. 4 shows the resulting patterns. The figure indicates that the amorphous or nanocrystalline structure of the as-prepared sample changes to a crystalline hexagonal structure of  $\text{SnS}_2$ . Although further investigation is needed to discuss the reason of the improved cycle performance, this change in the structure may be the key to the enhancement of the  $\text{SnS}_2$  anode property.

#### 4. Conclusion

Particles of  $\text{SnS}_2$  as small as 30 nm were gained by diluting the starting solution of the synthesis.

Such small  $\text{SnS}_2$  particles showed higher capacity and enhanced cycle ability compared to those of bigger size. The 30 nm sized  $\text{SnS}_2$  showed the initial discharge capacity of 620 mAh/g in the constant current charge discharge test. This may be due to the enlarged surface area, which would be effective in facilitating the Li-ion diffusion through the active material and in restraining the stress within the electrode, caused during charge and discharge.

By annealing the sample, further improvement of the anode performance exhibiting 736 mAh/g of initial discharge capacity was confirmed. It is suggested that this may be due to the change in its structure, but further investigation would be indispensable.

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