

SnP_{0.94} active material synthesized in high-boiling solvents for all-solid-state lithium batteries

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Tin phosphide (SnP_{0.94}) particles were synthesized by thermal decomposition of tin acetate in a mixed solution of trioctylphosphine and a high-boiling solvent. Teardrop-shaped SnP_{0.94} particles with the size of about 500 nm were obtained by using trioctylphosphine oxide as a coordinating solvent. In the case using oleylamine as a solvent, the shape of SnP_{0.94} particles was not uniform. Formation mechanism of teardrop-shaped SnP_{0.94} was discussed. SnP_{0.94} particles prepared by using the trioctylphosphine oxide as a coordinating solvent were applied as an active material to all-solid-state lithium cells. The cell Li-In/80Li₂S·19P₂S₅·1P₂O₅/SnP_{0.94} exhibited the initial discharge capacity of 1000 mAh g⁻¹ at a current density of 1.3 mA cm⁻².

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1. Introduction

Lithium-ion batteries have been used as power sources for mobile electronic devices. An organic liquid electrolyte is widely used in lithium-ion batteries. Recently, all-solid-state batteries using an inorganic solid electrolyte instead of a conventional liquid electrolyte attract much attention because they have safety advantages. We have developed a series of Li₂S-P₂S₅ solid electrolytes.^{1,2)} The 80Li₂S·19P₂S₅·1P₂O₅ (mol %) glass-ceramic exhibited a higher electrochemical stability and retained a higher ionic conductivity 7.4×10^{-4} S cm⁻¹ at room temperature than the 80Li₂S·20P₂S₅ glass-ceramic.³⁾

Metal phosphides have recently attracted attention as negative electrodes with high specific capacity. Metal phosphide electrodes show a lower potential compared to the corresponding metal oxides and sulfides. Nickel phosphide NiP₂ was reported to have relatively high capacity and good cycle performance in an electrochemical cell using a liquid electrolyte.⁴⁾ We have also reported that all-solid-state cells Li-In/80Li₂S·20P₂S₅/NiP₂ exhibited high reversible capacity of over 600 mAh g⁻¹ for 10 cycles at room temperature.⁵⁾ The NiP₂ electrode in solid-state cells undergoes the conversion process as reported in the cells using a liquid electrolyte.

On the other hand, Y. Kim et al. reported that tin phosphide SnP_{0.94} has good cycleability and high reversible capacity in liquid electrolyte cells.⁶⁾ The SnP_{0.94} electrode in the cells using a liquid electrolyte undergoes the lithium intercalation/deintercalation mechanism. Lithium intercalation materials are preferable as an active material for all-solid-state batteries because a small volume change is expected during charge-discharge processes. In that paper, SnP_{0.94} was synthesized by thermal decomposition of tin acetate in high-boiling solvents of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO). TOP was used as both a phosphorus source⁷⁾ and coordinating solvent,⁸⁾ while TOPO was

used as a coordinating solvent.⁹⁾ In general, coordinating solvents affect the size and shape of obtained particles.¹⁰⁾ Oleylamine (OAm) is also widely used as a coordinating solvent. However, the synthesis of SnP_{0.94} by changing coordinating solvents has not been investigated. In addition, SnP_{0.94} particles have not been applied as an active material to all-solid-state cells.

We reported that the size of an active material affected the charge-discharge capacities in all-solid-state cells.¹¹⁾ All-solid-state cell Li-In/80Li₂S·20P₂S₅/α-Fe₂O₃ using submicron α-Fe₂O₃ particles exhibited higher capacity than the cell using micron-size α-Fe₂O₃ particles. The preparation of active materials with a favorable size and morphology for all-solid-state cells is important for improving cell performance.

Here, we report the synthesis of SnP_{0.94} particles by changing the kind of the coordinating solvent, the amount of the coordinating solvent, and the reaction time. In addition, the reaction mechanism to form SnP_{0.94} will be discussed. The obtained SnP_{0.94} particles were then applied as an active material to all-solid-state cells with sulfide electrolytes.

2. Experimental

2.1 Synthesis of SnP_{0.94} particles

Tin acetate (0.36 g, 1.5×10^{-3} mol) was mixed with TOP (10 ml, 2.2×10^{-2} mol) and a high-boiling solvent in a 200 ml four-necked flask. Y. Kim et al. reported the synthesis of SnP_{0.94} by using TOPO as a high-boiling and coordinating solvent.⁶⁾ In this paper, TOPO (2.5 g, 6.5×10^{-3} mol) or OAm (6 ml, 1.8×10^{-2} mol or 1.5 ml, 4.5×10^{-3} mol) as a coordinating solvent was added to the flask. The mixture in the flask was heated to 360°C in the liquid and refluxed for 1 hour. Afterward, the mixture was cooled to room temperature, and subsequently hexane and ethanol were added to the mixture. The SnP_{0.94} particles were isolated by centrifuging the mixture, and then removing the supernatant.

2.2 Materials characterization

X-ray diffraction (XRD) measurements (Cu Kα) were per-

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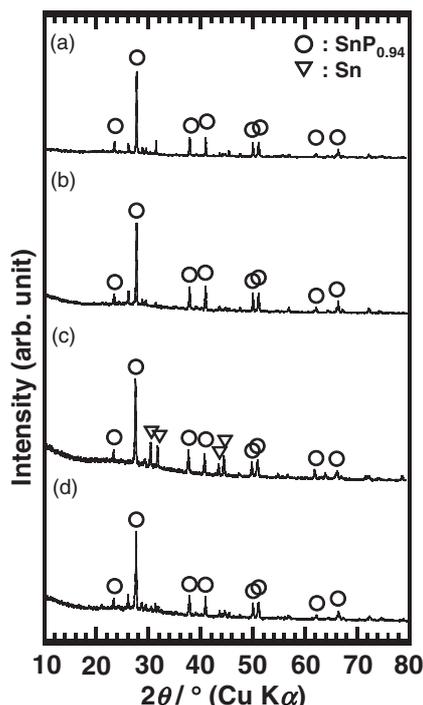


Fig. 1. XRD patterns of the samples prepared (a) without addition of TOPO or OAm, (b) with TOPO (6.5×10^{-3} mol), (c) with OAm (1.8×10^{-2} mol), and (d) with OAm (4.5×10^{-3} mol).

formed in an Ar atmosphere using a XRD diffractometer (Ultima IV; Rigaku). The morphology of the obtained particles was investigated using a transmission electron microscope (TEM; JEM2010; JEOL).

2.3 Electrochemical test of all-solid-state batteries

Laboratory-scale solid-state cells were fabricated as follows. The $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$ (mol %) glass-ceramic solid electrolyte was prepared using mechanical milling and subsequent heat treatment.³⁾ A composite material was obtained by mixing of the obtained $\text{SnP}_{0.94}$ active material (5.7 mg), the glass-ceramic electrolyte (8.5 mg), and vapor grown carbon fiber as a conductive additive (0.8 mg). The composite powder as a working electrode and the solid electrolyte powder were put in a polycarbonate tube, and then pressed under 360 MPa to obtain a bilayer pellet. The Li–In alloy foil as a counter electrode was pressed under 120 MPa on the obtained bilayer pellet. After releasing the pressure, the three-layer pellet was sandwiched by two stainless-steel disks as current collectors to form two electrodes cells. The cells were charged and discharged under a constant current density of 1.3 mA cm^{-2} at 25°C in an Ar atmosphere using a charge–discharge measuring device (BTS-2004; Nagano Co.).

3. Results and discussion

Figure 1a and Fig. 2a respectively show XRD pattern and TEM image of the sample synthesized without addition of TOPO or OAm. Teardrop-shaped $\text{SnP}_{0.94}$ particles are obtained. However, the shape of the obtained particles is not uniform. Figure 1b and Fig. 2b show XRD pattern and TEM image of the sample synthesized by using TOPO as a coordinating solvent. Teardrop-shaped particles with the size of 500 nm are obtained. It is suggested that TOPO plays an important role in the preparation of the teardrop-shaped $\text{SnP}_{0.94}$ particles with uniform size and shape. On the other hand, the sample prepared by using OAm

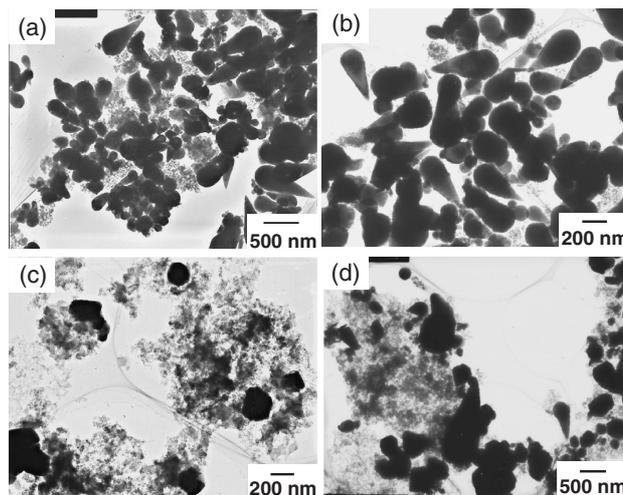


Fig. 2. TEM images of the samples prepared (a) without addition of TOPO or OAm, (b) with TOPO (6.5×10^{-3} mol), (c) with OAm (1.8×10^{-2} mol), and (d) with OAm (4.5×10^{-3} mol).

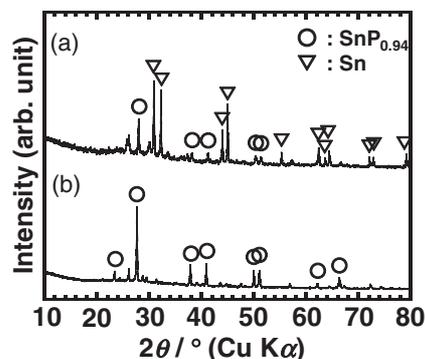


Fig. 3. XRD patterns of the samples prepared by refluxing for (a) 3 min and (b) 1 h in the case using TOPO.

(1.8×10^{-2} mol) is a mixture of $\text{SnP}_{0.94}$ and Sn (Fig. 1c), and the shape of the obtained particles is not uniform (Fig. 2c). In the case using OAm (1.8×10^{-2} mol), Sn disappeared by increasing the refluxing time from 1 to 4 hours, but the shape of the obtained particles was not still uniform. Figure 1d shows the XRD pattern of the sample synthesized by decreasing the amount of OAm (4.5×10^{-3} mol). The sample is identified as $\text{SnP}_{0.94}$, but the shape of the obtained particles is not still uniform (Fig. 2d). The crystal phase and morphology of the obtained particles were changed by using two different coordinating solvents.

By decreasing the refluxing time from 1 hour, the crystal phase of the obtained particles was investigated and the results were shown in Fig. 3 and Fig. 4. In the case using TOPO as a coordinating solvent, the product obtained by refluxing for 3 minutes is the mixture of Sn and $\text{SnP}_{0.94}$ (Fig. 3a), while $\text{SnP}_{0.94}$ is prepared by refluxing for 1 hour (Fig. 3b). However, in the case using OAm (4.5×10^{-3} mol) as a coordinating solvent, Sn is prepared by refluxing for 20 minutes (Fig. 4a), while a mixture of Sn and $\text{SnP}_{0.94}$ is obtained by refluxing for 40 minutes (Fig. 4b). This result suggests that Sn particles is formed first by thermal decomposition of tin acetate in a mixture of TOP and a coordinating solvent, and then $\text{SnP}_{0.94}$ particles are prepared by diffusion of phosphorus derived from TOP into Sn. It is expected that OAm has a stronger capping ability than TOPO, and thus OAm interferes with the diffusion of phosphorus into Sn.

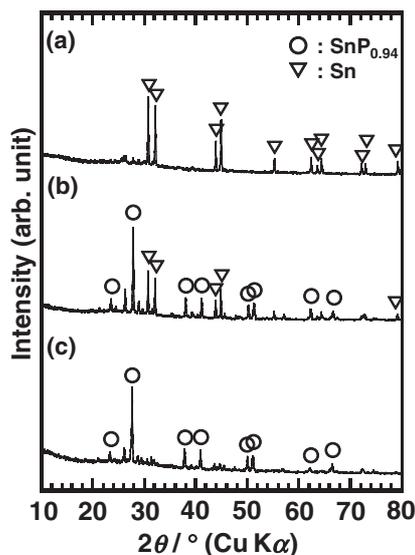


Fig. 4. XRD patterns of the samples prepared by refluxing for (a) 20 min, (b) 40 min, and (c) 1 h in the case using of OAm.

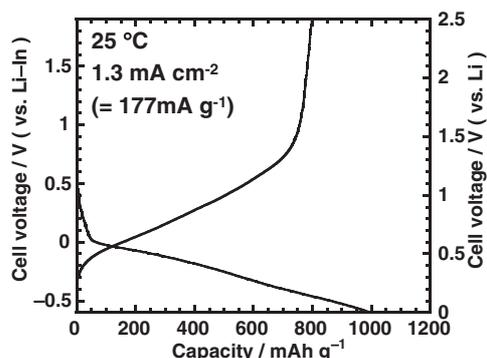


Fig. 5. Initial charge-discharge curve of the all-solid-state cell Li-In/80Li₂S·19P₂S₅·1P₂O₅/SnP_{0.94}.

Therefore, SnP_{0.94} particles prepared by using OAm are not uniform.

The SnP_{0.94} particles prepared by using the TOPO as a coordinating solvent were applied to the all-solid-state cell. SnP_{0.94} active materials have not been investigated in all-solid-state batteries. **Figure 5** shows initial charge-discharge curve for the all-solid-state cell Li-In/80Li₂S·19P₂S₅·1P₂O₅/SnP_{0.94}. The cell shows the capacity of about 1000 mAh g⁻¹ at the current density of 1.3 mA cm⁻² (177 mA g⁻¹) at the 1st cycle. It was reported that the cell using a liquid electrolyte exhibited the initial discharge capacity of 850 mAh g⁻¹ at the current density of 120 mA g⁻¹.⁶⁾ The all-solid-state cell using submicron SnP_{0.94}

particles exhibits higher capacity than the cell with a liquid electrolyte even at a higher current density. We reported that the all-solid-state cell using submicron α -Fe₂O₃ particles with uniform size as an active material exhibited higher capacity than the cell using micron-size α -Fe₂O₃ particles.¹¹⁾ These results show that submicron particles with uniform size are favorable for an active material of all-solid-state cells.

4. Conclusions

Tin phosphide SnP_{0.94} particles were synthesized by using high-boiling solvents. In the case using TOPO as a coordinating solvent, teardrop-shaped SnP_{0.94} particles with the size of 500 nm were obtained. On the other hand, in the case of OAm, the shape and size of the obtained SnP_{0.94} particles was not uniform. In addition, SnP_{0.94} was prepared by using TOPO with refluxing for 3 minutes, while only Sn was still present after refluxing for 20 minutes by using OAm. It was expected that OAm has a stronger capping ability than TOPO, and thus OAm interferes with the diffusion of phosphorus derived from TOP into Sn. The teardrop-shaped SnP_{0.94} particles prepared by using the TOPO as a coordinating solvent were applied to the all-solid-state cell. The cell Li-In/80Li₂S·19P₂S₅·1P₂O₅/SnP_{0.94} exhibited the capacity of about 1000 mAh g⁻¹ at the current density of 1.3 mA cm⁻² at the 1st cycle. The all-solid-state cell exhibited higher capacity than the cell using a liquid electrolyte.

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