Short communication

Nickel sulfides as a cathode for all-solid-state ceramic lithium batteries

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Abstract

The nickel sulfide, Ni_3S_2, was examined as a potential cathode material of the all-solid-state-lithium-batteries using thio-LISICON, $Li_2S–GeS_2–P_2S_5$, as the solid-electrolyte. Ni_3S_2 and $Li_2S–GeS_2–P_2S_5$ system, was synthesized with a new sintering system, which proceed under a flowing argon in the reusable quartz tube. The highest ionic conductivity 2.39×10^{-3} S cm^{-1} was observed for a sample prepared at 700 °C with 10% of excess P_2S_5, and bear comparison with the maximum conductivity reported for the thio-LISICON, $Li_{3.35}Ge_{0.35}P_{0.65}S_4$. An all-solid-state-lithium-battery based on, $Ni_3S_2/Li_{3.35}Ge_{0.35}P_{0.65}S_4/Li–Al$ alloy, showed electrochemical capacities of greater than ~300 mAh g^{-1} after 30 cycles. The cycling performances of the cells were found to be dependent on the Ni_3S_2/thio-LISICON compositions in the cathode mixture, with a cell containing 60 wt.% of Ni_3S_2 exhibiting the most stable reversible capacities. As the depth of the first discharge capacity also influences the cycling properties, Ni_3S_2 consumed during the discharge reaction may play an important role in the nickel reduction mechanism.
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1. Introduction

Lithium ion batteries are now widely used in a wide range of portable devices because of the high operating voltage, large electrochemical capacity, and excellent cycle performance. However, lithium ion batteries contain a flammable organic solvent which increases the possibility of explosion or fire. These safety hazard restrict the wider use of lithium ion batteries in large-scale batteries for electric vehicles or energy storage systems.

Application of solid-electrolyte for the lithium batteries is one of the potential solutions to some of the safety problems, and a variety of solid-electrolyte including crystalline, glass, and polymer system have been investigated previously as nonflammable electrolytes. Among those novel electrolyte materials, crystalline and glassy electrolytes are most attractive

from the point of a fast ion transport properties and a thermal stability. As for lithium ion battery, thio-LISICON system [1] or crystallized glass [2,3] have been examined as promising solid electrolytes, and those all-solid-state-batteries exhibited excellent electrochemical capacity and operating voltage comparable to commercial batteries. Amongst thio-LISICON system, the composition $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ shows the highest lithium ion conductivity, 2.2×10^{-3} S cm^{-1}, and hence the Li–Ge–P–S system is considered to be a suitable material for the solid electrolyte [4–6]. However, difficulty in large-scale synthesis of thio-LISICON and poor choices of electrode materials make it difficult for this solid-state battery to be in practical use.

Generally, thio-LISICON have been synthesized by using a vacuum-encapsulating method [6]. This method has the advantage of controlling the composition of products, whereas quartz tubes must be prepared for every synthesis. Furthermore, the amount of the product is limited by tube size, thus it is impossible to utilise this technique in an industrial environment. In this study, we have developed a novel synthesis system for preparing sulfides by using a reusable quartz tube, and optimized the

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sintering conditions to prepare the thio-LISICON and nickel sulfides.

Selections of a suitable cathode material for the all-solid-state-lithium-battery using thio-LISICON are also important issues. In analogy with liquid-electrolyte lithium battery, $LiCoO_2$ have been investigated as a candidate for the cathode material of solid-state-batteries. At the early stage of the study, $LiCoO_2$ in the solid-state-battery gave poor electrochemical capacity and cycle performance, which is thought to be related to the high resistivity at the electrode–electrolyte interface. Recently, problems at the interface were solved by applying a double layered electrolyte [7], glass ceramic electrolyte [3] or coating the active materials with oxides, such as Li_2O, and over $100\,mAh\,g^{-1}$ of reversible capacities achieved over 50 cycles, although the available current density was still low. On the other hand, the copper–molybdenum sulfide, $Cu_2Mo_6S_8$, shows excellent capacity and cycle performance with the thio-LISICON electrolyte without any special addition [8,9], which may suggest an affinity of sulfides for the thio-LISICON electrolyte. Among the sulfides, we have focused on Ni_3S_2 which has previously given good electrochemical performance with polymer-electrolyte lithium battery [10], and have attempted to use the Ni_3S_2 to the cathode for an all-solid-state-lithium battery.

2. Experimental

The thio-LISICON used as a solid-state electrolyte was $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ which has been previously reported by Murayama et al. to show the highest lithium ion conductivity, and was prepared by heating appropriate amounts of Li_2S (Kojundo Chemical Lab, 99%), GeS_2 (Kojundo Chemical Lab, 99%), P_2S_5 (Aldrich, 99%). The starting materials were heated at 700 °C for 2 h with the specially designed quartz tube shown in Fig. 1 after mixing and pelletizing in an Ar filled glove box. In the quartz tube, fresh gas is directly provided to the sample, which allows air sensitive materials to be heated under flowing argon gas to 800 °C. A potential problem with synthesis under flowing argon is the difficulty in controlling the elemental composition, if the starting materials are volatile. It is found that a 10% excess of sulfides, P_2S_5 and S, were necessary in order to obtain the required products. The Ni_3S_2 was also prepared by using the same quartz tube from nickel powder (Nacalai Tesque, 99%) and sulfur (Nacalai Tesque, 98%). Starting materials were mixed, pelletized under argon, and then heated at 700 °C for 12 h.
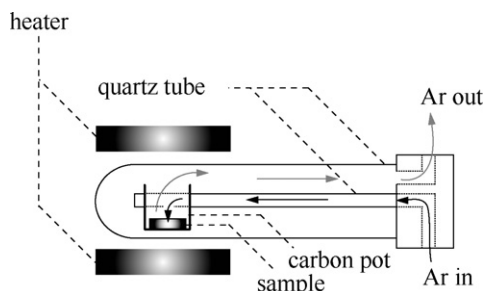
X-ray diffraction data of the samples were collected for characterization using Rigaku RU-200B with Cu K α radiation. The ionic conductivity was measured at room temperature using an ac impedance method in the applied frequency range of 0.1 Hz to 10 MHz using a Solartron 1260 frequency response analyzer connected to a Solartron 1287 electron interface.

All-solid-state cells were constructed according to the methods previously outlined by Kanno et al. [1]. For the charge–discharge test of the all-solid-state cells, the mixture of Ni_3S_2, thio-LISICON, and acetylene black in the ratio of 60:40:5 (wt.%) was prepared as a cathode. Other Ni_3S_2:thio-LISICON compositions were also investigated at 50:50 and 70:30, respectively. The mixing process was used Fritsch P-7 planetary ball milling apparatus. The cathode composite, thio-LISICON, Al foil, and Li sheet were stacked in this order and pressed inside of polyethylene telephthalate (PET) cylinder with an inner diameter of 10 mm, and the cylinder was sealed in a SUS container. A constant-current charge–discharge was performed in the potential range of 0.3–2.3 V at room temperature. The current density used was $0.13\,mA\,cm^{-1}$.

3. Result and discussion

Fig. 2 shows the X-ray diffraction patterns obtained for $Li_{3.25}Ge_{0.25}-P_{0.75}S_4$ and Ni_3S_2 synthesized using the argon flow system. Peaks for nickel sulfide were indexed by Ni_3S_2. Patterns for the thio-LISICON obtained were similar to that of $Li_{3.35}Ge_{0.35}P_{0.65}S_4$ reported previously [5]. Li ion conductivity measurement for the thio-LISICON using a Li/thio-LISICON/Li symmetric cell gave a conductivity of $2.39 \times 10^{-3}\,S\,cm^{-1}$, which makes it suitable for use as solid-electrolyte in a all-solid-state cell. Total products in the range 1–3 g of products were obtained using the Ar-flow-sintering system, and the yield could be further improved with a larger carbon pot in the quartz tube.
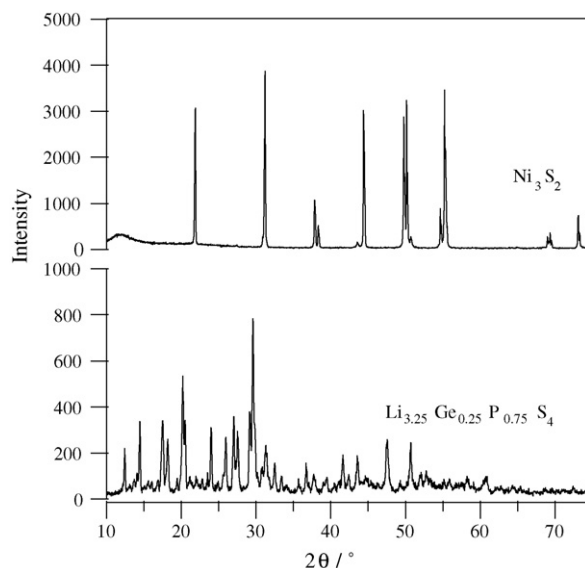

Fig. 1. Schematic illustration of a sintering tube. A sample in a carbon pot is exposed to flesh Ar gas.

Fig. 2. X-ray diffraction patterns for Ni_3S_2 (upper) and thio-LISICON (lower), $Li_{3.25}Ge_{0.25}-P_{0.75}S_4$, prepared by using the Ar-flow sintering tube.
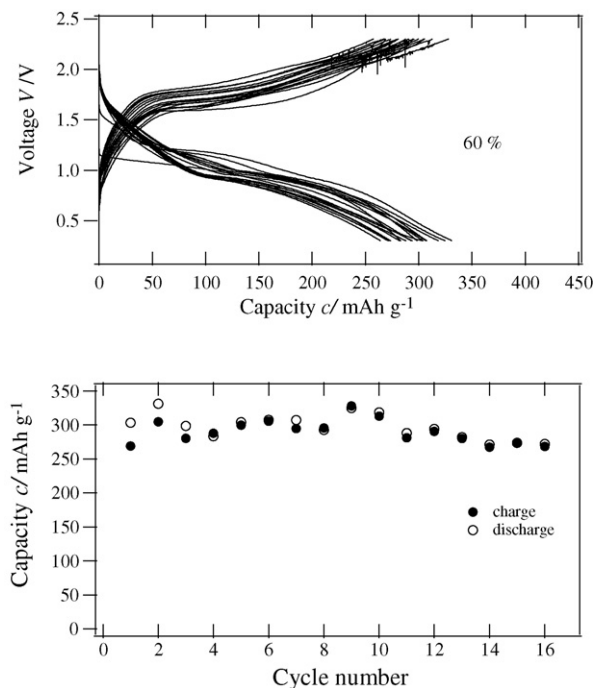
Fig. 3. Charge–discharge curves for Ni_3S_2/thio-LISICON/Li–Al all solid-cell; the cathode consists of 60 wt.% of Ni_3S_2 and 40 wt.% of thio-LISICON.

Charge–discharge curves for a Ni_3S_2/thio-LISICON/Li–Al solid-state-cell is shown in Fig. 3. In all the charge–discharge graphs, the capacity indicates a electric quantity per unit weight of the Ni_3S_2. The measurement was started with discharge, and terminated at 0.3 V. The first discharge curve showed two plateau at ~1.2 and 1.0 V, and ~200 mAh g^{-1} of total capacity was obtained. The capacity of plateau at 1.2 V decreased

with cycle numbers from ~150 to 100 mAh g^{-1}, and then disappeared after 10th cycle. Subsequent charges also proceeded, indicating two plateau at ~1.5 and 2.0 V; the voltage 1.5 V of first plateau gradually increased to 1.8 V with increasing cycle number. The discharge is thought to correspond to the reaction below:

$$Ni_3S_2 + 4Li \rightarrow 3Ni + 2Li_2S \quad (1)$$

This material has a theoretical capacity of approximately 446 mAh g^{-1}. For these measurements, ca. 350 mAh g^{-1} of electrochemical capacity were obtained, and it is in agreement with reaction (1). It is remarkable that over 300 mAh g^{-1} of reversible electrochemical capacity can be obtained from this all solid-state cell, although its working potential is still relatively low.

The relationship between the electrochemical properties and Ni_3S_2 composition in the cathode was investigated in order to optimize the mixing ratio of the cathode mixture. The mixing ratio is a very important factor for the all-solid-state-batteries because the Li ion and electronic conductivity are governed by the amount of the thio-LISICON. Figs. 4–6 show charge–discharge behaviors which are dependent on the Ni_3S_2 composition in the cathodes. The capacities of early discharges were found to increase with Ni_3S_2 composition such as 200 (second), 300 (first), and 450 (first) mAh g^{-1} for 50, 60, and 70 wt.% of Ni_3S_2, respectively. On the other hand, the cycle performance of 70 wt.% was significantly worse with the discharge capacity found to decrease to ~150 mAh g^{-1}. As no difference in the cycle performance was observed between 50 and 60 wt.% of Ni_3S_2, the cathode consisting of 60 wt.% of Ni_3S_2 was considered to be the best composition.

The X-ray diffraction measurements for cathode mixtures during charge–discharge were performed in order to clarify the
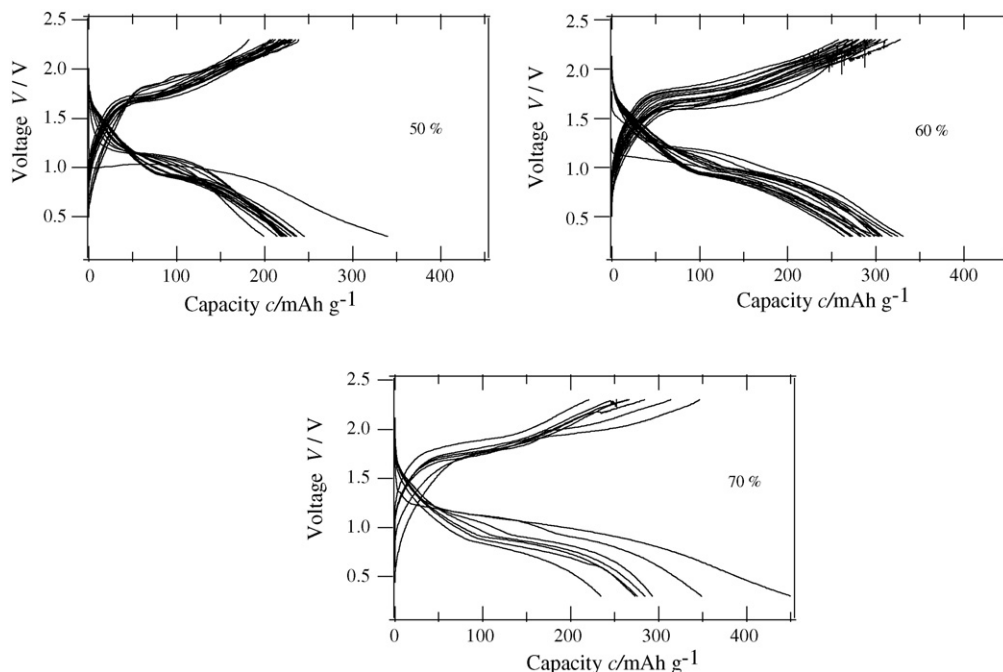

Fig. 4. Charge–discharge curves for Ni_3S_2/thio-LISICON/Li–Al all solid-cell; the cathode consists of 50 wt.% of Ni_3S_2 and 50 wt.% of thio-LISICON.
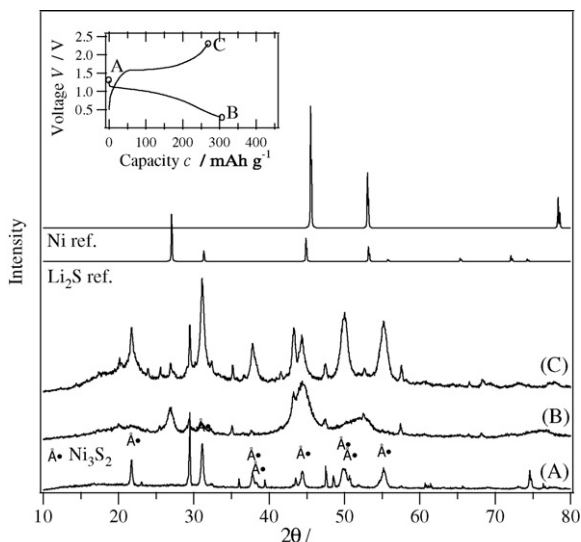
Fig. 5. Charge–discharge curves for Ni_3S_2/thio-LISICON/Li–Al all solid-cell; the cathode consists of 70 wt.% of Ni_3S_2 and 30 wt.% of thio-LISICON.

reaction mechanisms. The cathode mixtures after first discharge and charge, as indicated in Fig. 7 (top) with B and C, respectively, were measured in the sealed case filled with Ar gas. X-ray diffraction patterns for the cathode mixtures include 60 wt.% of Ni_3S_2 before and after charge–discharge measurements are shown in Fig. 7(bottom). The pattern before discharge (A) was indexed as Ni_3S_2 and thio-LISICON. The intensity of the peaks for the thio-LISICON were found to decrease after the ball-milling. After the first discharge, X-ray diffraction pattern (B) showed narrow peaks corresponding to Ni and Li_2S, and also indicated small amount of Ni_3S_2, which suggests that the reac-
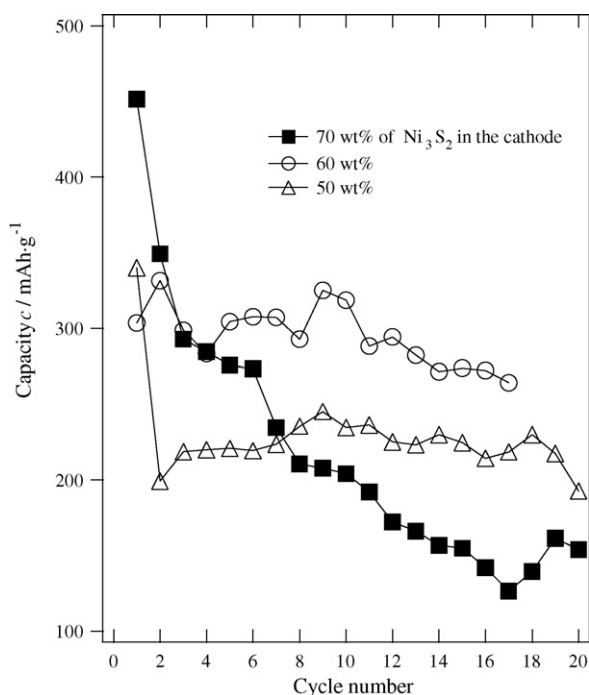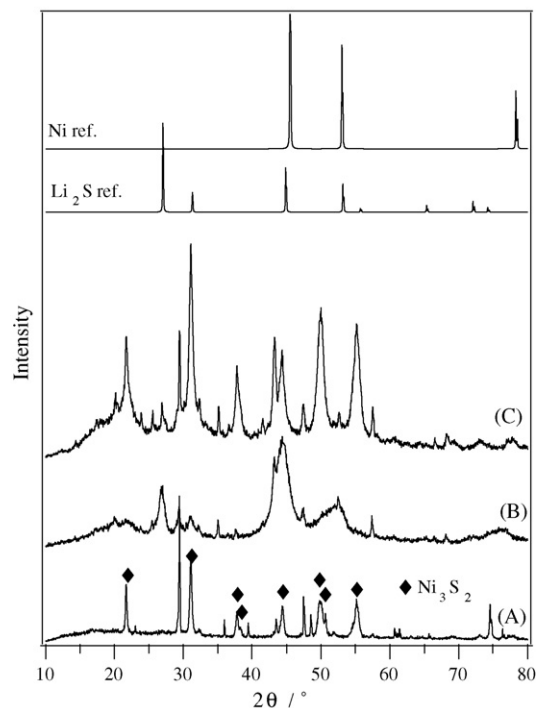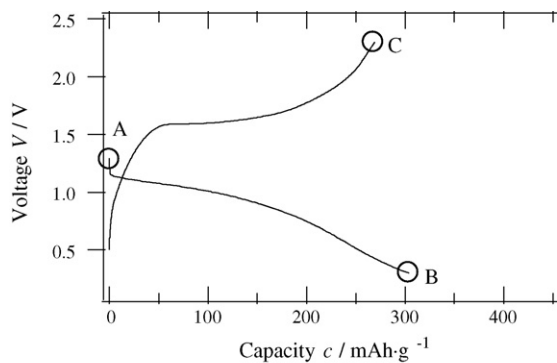

Fig. 7. The charge–discharge curve of first cycle of the Ni_3S_2/thio-LISICON/Li–Al cell with 60 wt.% of Ni_3S_2 in the cathode (top), and X-ray diffraction patterns for the cathode composites at the each indicated positions (bottom): before measurement (A), after discharge (B), and after charge (C).

tion during the discharge proceeds following the chemical Eq. (1), and the Ni_3S_2 remains as a result of the incomplete discharge. Peaks for Ni_3S_2 appeared again in the X-ray diffraction pattern after the first charge (C), and the peaks corresponding to Ni and Li_2S were found to get weaker. The X-ray diffraction pattern for the cathode after charge is similar to that before the electrochemical measurements, indicating a favorable reversibility of the charge–discharge reaction.

In all the charge–discharge measurements, the cells showing the highest initial discharge capacities tended to result in poorer cycling properties. The reason for this effect is not clear at this stage of investigation, however, residual Ni_3S_2 after discharge may play an important role in the decomposition of Li_2S and the recombination of Ni_3S_2. Differences in cycle performances depending on Ni_3S_2 composition can be derived from the same reason.

Fig. 6. Ni_3S_2 composition dependences of cycling properties of Ni_3S_2/thio-LISICON/Li–Al all solid-cell.

4. Conclusion

The electrochemical properties of Ni_3S_2 as a cathode of the all-solid-state-lithium-battery using thio-LISICON, $Li_2S–GeS_2–P_2S_5$, were investigated. The sulfides, Ni_3S_2 and $Li_{3.25}Ge_{0.25}P_{0.75}S_4$, which were synthesized in a reusable quartz tube under flowing argon atmosphere with 10% of excess sulfur sources, were examined by means of X-ray diffraction, AC impedance, and galvanostatic charge–discharge measurements. The thio-LISICON sintered at 700 °C showed the similar X-ray diffraction pattern to $Li_{3.35}Ge_{0.35}P_{0.65}S_4$ previously reported by Kanno et al. [5], and gave an ionic conductivity of 2.39×10^{-3} S cm^{-1}. Over 300 mAh g^{-1} of reversible capacity was obtained from the Ni_3S_2/thio-LISICON/Li–Al all-solid-state cell, whereas the cycling properties thought to be dependent on the Ni_3S_2 composition in the cathode mixture. The cell with Ni_3S_2/thio-LISICON (40/60 in weight ratio) gave the best electrochemical performance, which is thought to be related to the influence of the residual Ni_3S_2 present after the first discharge. The Ni_3S_2/thio-LISICON/Li–Al all-solid-state-lithium-battery has superior electrochemical capacity when compared to other all-solid-batteries. However, its operating voltage and cycling performance are still poor when their practical uses are taken into account. As the discharge and charge reactions proceed at the solid–solid interface, the mixing states of the cathode composite can be related to the electrochemical properties. Further optimization of the mixing condition of the cathode will be necessary for higher capacity and more stable cycling performance of the Ni_3S_2-all-solid-state-cell.

Acknowledgement

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