



Short communication

Electrochemical performance of NiP₂ negative electrodes in all-solid-state lithium secondary batteries

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ABSTRACT

The cubic NiP₂ crystal was prepared by a mechanical milling technique. All-solid-state cells with the NiP₂ electrode and the Li₂S–P₂S₅ glass-ceramic electrolyte exhibited high reversible capacity of over 600 mAh g⁻¹ for 10 cycles at room temperature. The NiP₂ electrode in solid-state cells underwent the conversion process as reported in the cells using a liquid electrolyte. Lithiated nickel phosphides were also prepared by milling. The composites of Li–Ni–P ternary crystal (Li_{3.4}Ni_{10.6}P₇ or Li₂Ni₁₂P₇) and Li₃P were obtained and they were used as an electrode with lithium source in an all-solid-state cell. The cell with the electrode was initially charged and then discharged and retained cell capacity of about 600 mAh g⁻¹. Nickel phosphides are potential negative electrodes with high capacity in all-solid-state lithium rechargeable batteries with sulfide electrolyte.

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1. Introduction

Development of all-solid-state lithium secondary batteries has been desired because of their high safety and reliability without leakage and inflammability. In particular, bulk-type solid-state cells, which are composed of electrode and electrolyte powders, have an advantage of achieving large energy density. Key materials to realize bulk-type lithium batteries are a solid electrolyte with high Li⁺ ion conductivity and an electrode with high capacity. The Li₂S–P₂S₅ glass-ceramic electrolytes with high Li⁺ ion conductivity of 10⁻³ S cm⁻¹ at room temperature are a promising electrolyte for all-solid-state cells [1,2].

Metal phosphides have recently attracted attention as negative electrodes with high specific capacity [3–5]. A lower intercalation potential compared to the corresponding metal oxides is another advantage of phosphide electrodes. Nickel phosphide NiP₂ has relatively high capacity and good cycle performance in an electrochemical cell using a conventional liquid electrolyte [5]. It was reported for the NiP₂ electrode that Ni nanodomains and Li₃P matrix were simultaneously formed by electrochemical lithium insertion to the electrodes and the electrochemical reaction is called “conversion process” [6]. Electrochemical formation of Li₃P with high lithium ion conductivity [7] in the electrodes is very useful for all-solid-state cells because a favorable solid–solid interface

with a lithium ion path is obtained. On the other hand, lithiated nickel phosphides are compatible with a positive electrode without lithium sources. The Li–Ni–P ternary compounds have never been applied to lithium ion cells.

In the present study, NiP₂ was prepared by a mechanical milling technique. All-solid-state cells using the NiP₂ electrode and the Li₂S–P₂S₅ solid electrolyte were fabricated and the electrochemical performance of the cells was examined. Reaction mechanism of the NiP₂ electrode in all-solid-state cells was investigated by ex-situ XRD measurements. Lithiated nickel phosphides were also prepared by milling and applied to solid-state cells as an electrode with lithium source.

2. Experimental

The NiP₂ crystal was synthesized by a mechanical milling technique. The mixture of nickel (High Purity Chemicals, 99.9%) and red phosphorus (High Purity Chemicals, 99%) powders with the molar ratio of Ni/P = 1/2 was put into a ZrO₂ pot (45 mL) with 10 ZrO₂ balls (10 mm in diameter), and then the mixture was milled for 40 h using a planetary ball mill apparatus (Fritsch Pulverisette 7). The Li–Ni–P compounds were prepared as follows. Firstly, Li–P binary compounds were synthesized from lithium metal and red phosphorus by ball-milling for 20 h. Powder nickel was then added to the obtained sample and ball-milling for 5 h was conducted to form Li–Ni–P ternary compounds with the starting composition of Li_{2.5}Ni_{0.5}P. A stainless-steel pot (45 mL) with 10 stainless-steel balls (10 mm in diameter) was used. In both cases of phosphide

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preparation, the rotation speed was 370 rpm and all the processes were conducted at room temperature in a dry Ar-filled glove box. X-ray diffraction (XRD) measurements ($\text{CuK}\alpha$) were performed in an Ar atmosphere using a XRD diffractometer (Rigaku, UltimaIV). Morphologies of mechanically milled samples were investigated by a scanning electron microscope (SEM, JEOL Model JSM-5300).

All-solid-state electrochemical cells Li–In/ NiP_2 or Li–Ni–P were assembled as follows. The $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol.%) glass-ceramic with high ambient temperature conductivity of about $10^{-3} \text{ S cm}^{-1}$ was used as a solid electrolyte. The glass-ceramic material was prepared by mechanical milling and subsequent crystallization at around 230°C [1]. A composite material was obtained by mixing of the nickel phosphide compound prepared (38 wt.%), the glass-ceramic electrolyte (57 wt.%), and acetylene-black (5 wt.%) powders. The composite powder as a working electrode and the solid electrolyte powder were put in a polycarbonate tube, and then was 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 $64 \mu\text{A cm}^{-2}$ at 25°C in an Ar atmosphere using a charge–discharge measuring device (Nagano Co., BTS-2004). In order to analyze charge–discharge mechanism of the NiP_2 electrode in all-solid-state cells, XRD measurements of the working electrode after charge–discharge tests were carried out.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-mixed powder and NiP_2 powder prepared by mechanical milling for 40 h. XRD peaks attributable to Ni were only observed for the mixture before milling because amorphous P was used in this study. The NiP_2 cubic phase was synthesized by milling for 40 h. It was revealed by SEM observation that the obtained particles were aggregated and the size of secondary particles was below $5 \mu\text{m}$. Electrical conductivity of the pelletized NiP_2 was 0.7 S cm^{-1} .

Fig. 2 shows the charge–discharge curves of the all-solid-state cell Li–In/ $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/ NiP_2 at the current density of $64 \mu\text{A cm}^{-2}$. The y-axis on the left hand side denotes the cell voltage vs. Li–In electrode, while the y-axis on the right hand side means the voltage vs. Li electrode, which was calculated from the difference in voltages between Li–In and Li. The cell was discharged and then charged in the voltage range from 0 to 2.5 V (vs. Li) and an average voltage of 0.9 V (vs. Li) was almost the same as that in the

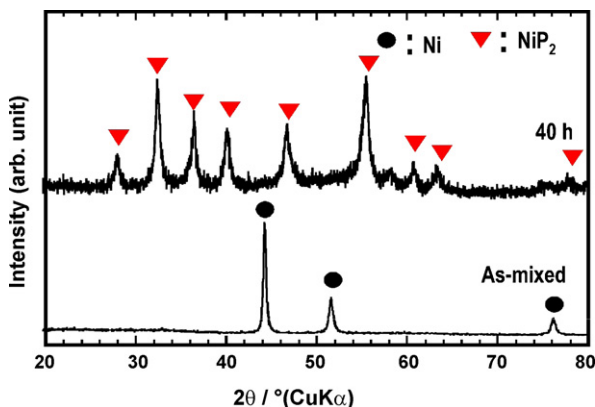


Fig. 1. XRD patterns of as-mixed powder and NiP_2 powder prepared by mechanical milling for 40 h.

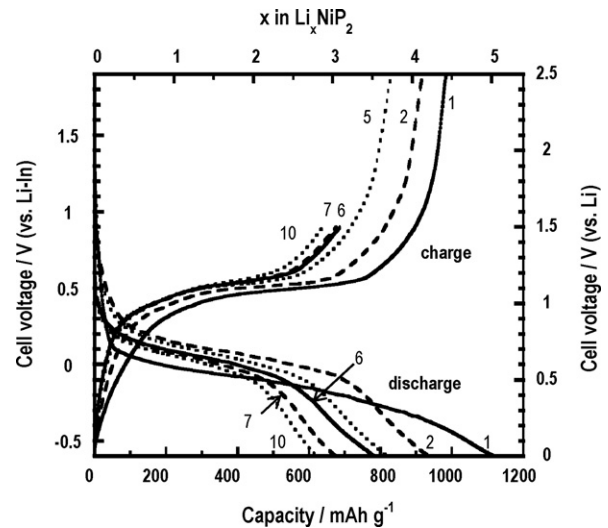


Fig. 2. Charge–discharge curves of the all-solid-state cell Li–In/ $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/ NiP_2 at the current density of $64 \mu\text{A cm}^{-2}$.

cell using a liquid electrolyte (1 M LiPF_6 in EC–DMC) reported so far [5]. The initial discharge and charge capacities were respectively about 1100 and 1000 mAh g^{-1} , which correspond to the insertion of 5.0 molar Li^+ and the extraction of 4.5 molar Li^+ per formula unit (Li_xNiP_2), respectively. The charge–discharge capacity was gradually decreased during cycling. The cutoff voltage was then changed from 2.5 to 1.5 V after the 5th cycle. The cell retained 600 mAh g^{-1} for consecutive five cycles and the cycling performance of the cell was improved.

To investigate reaction mechanism of NiP_2 electrode in all-solid-state cells, ex-situ XRD measurements were performed. Fig. 3 shows the XRD patterns of the NiP_2 electrode before and after

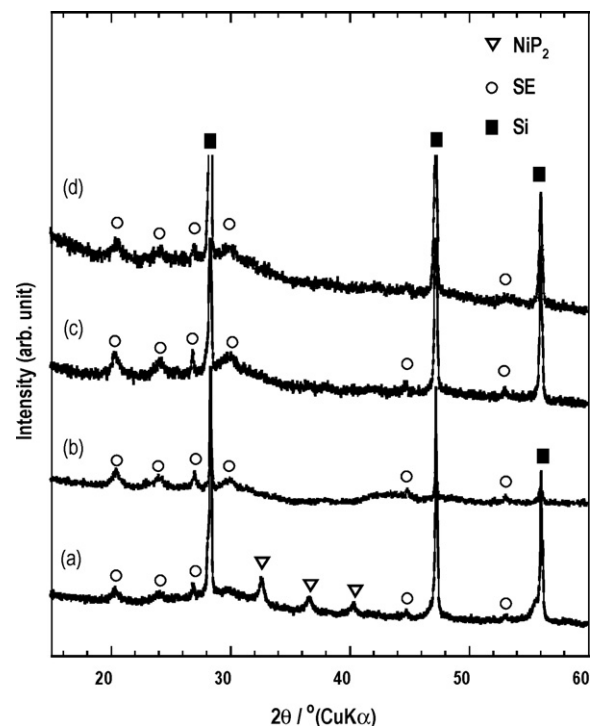


Fig. 3. XRD patterns of the NiP_2 electrode before and after charge–discharge cycles: (a) before cycle, (b) after the 1st discharge, (c) after the 1st charge, and (d) after the 5th charge.

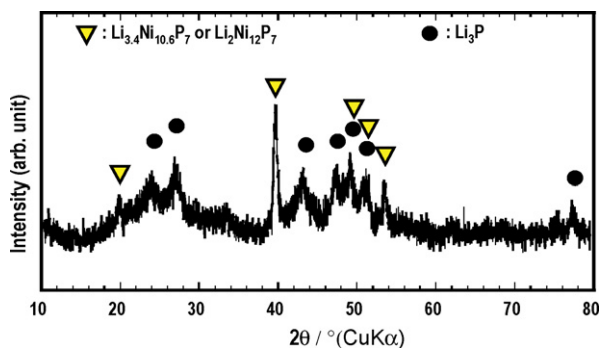
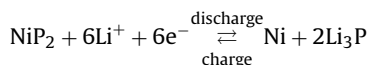


Fig. 4. XRD pattern of the milled sample at the starting composition of $\text{Li}_{2.5}\text{Ni}_{0.5}\text{P}$.

charge–discharge cycles: (a) before cycle, (b) after the 1st discharge, (c) after the 1st charge, and (d) after the 5th charge. XRD peaks attributable to NiP_2 as well as the solid electrolyte (SE, the mixture of thio-LISICON analog [1] and Li_2S) were observed before cycle (a). After the initial discharge to 0 V (vs Li) (b) the peaks due to NiP_2 completely disappeared and the peaks due to SE remained. The XRD peaks of SE were only observed after the initial charge, suggesting that cubic NiP_2 was not recrystallized at the charge process. The XRD pattern after the 5th charge was similar to that after the 1st charge.

Gillot et al. [5] reported that the reaction mechanism of cubic NiP_2 in liquid electrolyte cells is based on “conversion process” which is described below:



In their report, the NiP_2 peaks disappeared after the 1st discharge process and no obvious peaks were observed for further cycles in in-situ XRD measurements for the NiP_2 electrode. The behavior of XRD patterns due to NiP_2 during cycles in all-solid-state cells was similar to that in liquid electrolyte cells. We thus presume that the NiP_2 electrode in solid-state cells undergoes the conversion process described above. There is no trace for the reason of capacity fading during initial cycles from the viewpoint of XRD measurements. A possible explanation of capacity decay is the presence of NiP_2 particles becoming electrically disconnected.

The Li–Ni–P active materials with lithium source were prepared by mechanical milling. Fig. 4 shows the XRD pattern of the milled sample at the starting composition of $\text{Li}_{2.5}\text{Ni}_{0.5}\text{P}$; the molar ratio of Ni/P = 1/2 of the composition corresponds to that of NiP_2 and the molar ratio of Li/Ni = 5 is based on the initial insertion of lithium to NiP_2 as indicated in Fig. 2. Broad XRD peaks of the sample are attributable to Li–Ni–P ternary crystal ($\text{Li}_{3.4}\text{Ni}_{10.6}\text{P}_7$ or $\text{Li}_2\text{Ni}_{12}\text{P}_7$) and Li_3P . The molar ratio of Li/Ni in the obtained Li–Ni–P crystal is less than the starting composition because Li_3P coexisted with the Li–Ni–P crystal. Although the milling conditions such as rotation speed of 370 rpm and milling time of 5 h were respectively changed to 510 rpm and 20 h, the XRD pattern was almost the same as that shown in Fig. 4.

Fig. 5 shows the charge–discharge curves of the all-solid-state cell Li–In/80 Li_2S ·20 P_2S_5 glass-ceramic/the Li–Ni–P compound prepared at the current density of $64 \mu\text{A cm}^{-2}$. The cell was initially charged and then discharged and thus the Li–Ni–P compound is used as a lithium source in the solid-state cell. The initial charge capacity was about 500mAh g^{-1} , which corresponds to the extraction of 3.0 molar Li^+ per Ni. The initial discharge capacity was about 700mAh g^{-1} ; an excess amount of Li^+ ions was inserted to the Li–Ni–P electrode from the Li–In counter electrode in the first discharge process. Although the reversible capacity was gradually

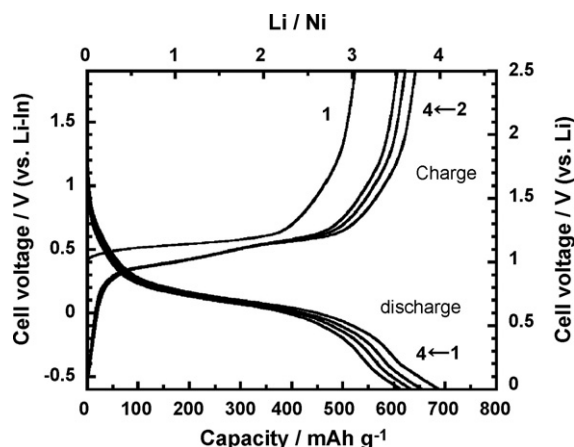


Fig. 5. Charge–discharge curves of the all-solid-state cell Li–In/80 Li_2S ·20 P_2S_5 glass-ceramic/Li–Ni–P at the current density of $64 \mu\text{A cm}^{-2}$.

decreased during cycling, the cell retained 600mAh g^{-1} for four cycles. The charge–discharge profile is almost the same as that of the NiP_2 electrode, suggesting that reaction mechanism of the Li–Ni–P electrode is similar to that of the NiP_2 electrode. We confirmed that the cell using Li_3P as an active material was not charged at $64 \mu\text{A cm}^{-2}$; the addition of Ni is needed for Li_3P to be used as an active material. The Li–Ni–P compound at the targeted composition ($\text{Li}_{2.5}\text{Ni}_{0.5}\text{P}$) was not synthesized and the obtained material was a mixture of Li_3P and $\text{Li}_{3.4}\text{Ni}_{10.6}\text{P}_7$ or $\text{Li}_2\text{Ni}_{12}\text{P}_7$ in the present study. The preparation of homogeneous Li–Ni–P compounds with the targeted composition is a possible solution to enhance the cell performance of capacity and cyclability.

4. Conclusions

The cubic NiP_2 crystal was prepared by mechanical milling. All-solid-state cells with the NiP_2 electrode and the Li_2S – P_2S_5 glass-ceramic electrolyte exhibited high reversible capacity of over 600mAh g^{-1} for 10 cycles at room temperature. The NiP_2 electrode in solid-state cells underwent the conversion process as reported in the cells using a liquid electrolyte. Mechanochemically prepared Li–Ni–P ternary active materials were also used as an electrode with lithium source. The cell with the electrode was initially charged and then discharged and retained cell capacity of about 600mAh g^{-1} for four cycles. Nickel phosphides are potential negative electrodes with high capacity in all-solid-state lithium rechargeable batteries with sulfide electrolyte.

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