



Short communication

# All-solid-state lithium secondary batteries with high capacity using black phosphorus negative electrode

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## ABSTRACT

Black phosphorus was prepared from red phosphorus by using mixer mill and planetary ball-mill apparatuses. The composites with black phosphorus and acetylene black (AB) were also prepared by using the mixer mill apparatus. The mechanical milling of black phosphorus and AB brought about a decrease in size of secondary particles of the composites. The all-solid-state lithium cells with the composite and the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass-ceramic electrolyte exhibited the first discharge capacity of  $1962 \text{ mAh g}^{-1}$  and the coulombic efficiency of 89% at the current density of  $0.064 \text{ mA cm}^{-2}$  ( $24 \text{ mA g}^{-1}$ ). The all-solid-state cells worked at  $3.8 \text{ mA cm}^{-2}$  ( $1.47 \text{ A g}^{-1}$ ) at  $25^\circ\text{C}$  and showed the excellent cycle performance with a high capacity of over  $500 \text{ mAh g}^{-1}$  for 150 cycles. Black phosphorus is one of the most attractive negative electrodes with both high capacity and high-rate performance in all-solid-state lithium rechargeable batteries with sulfide electrolytes.

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## 1. Introduction

Rechargeable lithium-ion batteries have been used as a power source for portable electronic devices such as mobile phones and notebook computers because of their high operating voltage, high energy density and no memory effect. Lithium secondary batteries have drawn attention as storage systems of electric vehicles and hybrid electric vehicles owing to those advantages. As the scale of battery package becomes larger, a concern about safety issues on batteries is growing. Enlarging capacity of lithium batteries is also desired.

All-solid-state lithium secondary batteries using inorganic solid electrolytes have attracted much attention from the point of view of their safety. In particular, bulk-type all-solid-state batteries, which consist of both positive and negative electrode and electrolyte powders, have an advantage of achieving higher energy density. Solid electrolytes with high  $\text{Li}^+$  ion conductivity and electrode active materials with high capacity are key materials for improvement of the electrochemical performance of all-solid-state lithium batteries. In our previous reports,  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass-ceramic electrolytes exhibited a high  $\text{Li}^+$  ion conductivity of more than  $10^{-3} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  and all-solid-state  $\text{In}/\text{LiCoO}_2$  cells using the solid electrolytes retained a high capacity of  $100 \text{ mAh g}^{-1}$  for 700 cycles

[1,2].  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glass-ceramics are promising solid electrolytes for all-solid-state cells.

Graphite is commonly used as a negative electrode for lithium-ion batteries, but the increase in capacity of the batteries is required. A lot of alternatives with higher capacity have been studied recently, and among them transition metal phosphides have several advantages. Metal phosphides show a lower intercalation potential compared to the respective metal oxides and a large specific capacity. Various metal phosphides were applied to the negative electrode of lithium batteries using conventional liquid electrolyte, and the batteries showed high capacity and good cycle performance by controlling cutoff potential [3–5]. We reported that the all-solid-state lithium batteries with the  $\text{NiP}_2$  electrode and the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  solid electrolyte kept a high reversible capacity of over  $600 \text{ mAh g}^{-1}$  in the potential range from 0 to 2.5 V (vs. Li) [6].

It is expected that the performance of lithium secondary batteries is drastically improved by applying phosphorus instead of metal phosphide as negative electrode of the batteries. Phosphorus has a lot of allotropes, and among them black phosphorus is the most stable thermodynamically and has relatively high electronic conductivity. Furthermore, black phosphorus has a layer structure and shows a large theoretical capacity of  $2596 \text{ mAh g}^{-1}$  in the case of the reaction from black phosphorus to  $\text{Li}_3\text{P}$ . In a recent report, black phosphorus was prepared from red phosphorus by using a high energy ball-milling technique [7]. In addition, lithium batteries using a black phosphorus electrode and an organic liquid

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electrolyte (1 M LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate) showed the first reversible capacity of over 1800 mAh g<sup>-1</sup>. However, its capacity decreased drastically in the wide potential range from 0 to 2 V (vs. Li) [7]. In order to improve the capacity retention, the controlling of potential range was useful and the cells showed the excellent cycle performance with the capacity of 600 mAh g<sup>-1</sup> for 100 cycles in the potential range from 0.78 to 2 V (vs. Li) [7].

In the present study, black phosphorus was firstly applied to the negative electrode of all-solid-state cells in order to achieve the enhancement of the reversible capacity of the cells. Black phosphorus was prepared from red phosphorus by using two types of ball-mill apparatuses of mixer mill and planetary ball-mill [8]. All-solid-state cells with the black phosphorus electrode and Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> solid electrolyte were fabricated. Moreover, in order to improve electrochemical performance of the cells, the composites with black phosphorus and acetylene black were obtained by using the mixer mill apparatus. The electrochemical performance of the cells using the composite was investigated.

## 2. Experimental

Black phosphorus was prepared by a mechanical milling technique. Red phosphorus powder (Kojundo Chem., 99%) was used as a starting material and put into stainless steel pot with 10 stainless steel balls (10 mm or 12.7 mm in diameter), and mechanical milling process was carried out in an Ar atmosphere for 1 h using a planetary ball-mill (Fritsch Pulverisette 7) and a mixer mill (SPEX, 8000M Mixer/Mill). Composites with black phosphorus and acetylene black (AB) were prepared by the same milling technique for 1 h. The composition of the composite was 80 wt.% black phosphorus and 20 wt.% AB. X-ray diffraction (XRD) measurements (CuKα) were performed using a diffractometer (Rigaku, Ultima IV) to identify crystalline phases. Morphology of the materials was evaluated by a scanning electron microscope (SEM; JEOL, JSM-5300). Electrical conductivity of the composites was examined by using an impedance analyzer (SI 1260, Solartron Analytical).

All-solid-state electrochemical cells were fabricated as follows. The 80Li<sub>2</sub>S:20P<sub>2</sub>S<sub>5</sub> (mol%) solid electrolyte was prepared by the mechanochemical reaction process and then heated at 210 °C for 1 h [9]. The working electrode was prepared by mixing of red phosphorus or black phosphorus, the 80Li<sub>2</sub>S:20P<sub>2</sub>S<sub>5</sub> solid electrolyte and AB with the weight ratio of 40:60:10. The composites obtained by milling of black phosphorus and AB were also mixed with the 80Li<sub>2</sub>S:20P<sub>2</sub>S<sub>5</sub> solid electrolyte to be applied to the working electrode; the weight ratio of the composite and the electrolyte was 50:60. The obtained working electrode (10 mg) and the solid electrolyte were placed in polycarbonate tube (10 mm in diameter) and pressed together under 360 MPa. A Li–In alloy was put on the solid electrolyte layer as a counter and reference electrode and then a pressure of 120 MPa was applied to the three-layered pellet. Finally, two electrodes cells sandwiched by two stainless-steel disks as a current collector were obtained. All the processes described above were carried out in a dry Ar glove box.

The electrochemical tests were conducted at 25 °C in an Ar atmosphere using a charge–discharge measuring device (BTS-2004, Nagano Co.). In order to analyze the structure of the working electrode, the XRD measurements of the working electrode before cycling and after discharge to 0 V (vs. Li) and charge to 2.5 V (vs. Li) were examined. The charge–discharge tests were conducted in a dry Ar atmosphere.

## 3. Results and discussion

Fig. 1 shows XRD patterns of red phosphorus powder (a) and black phosphorus powder prepared by mechanical milling pro-

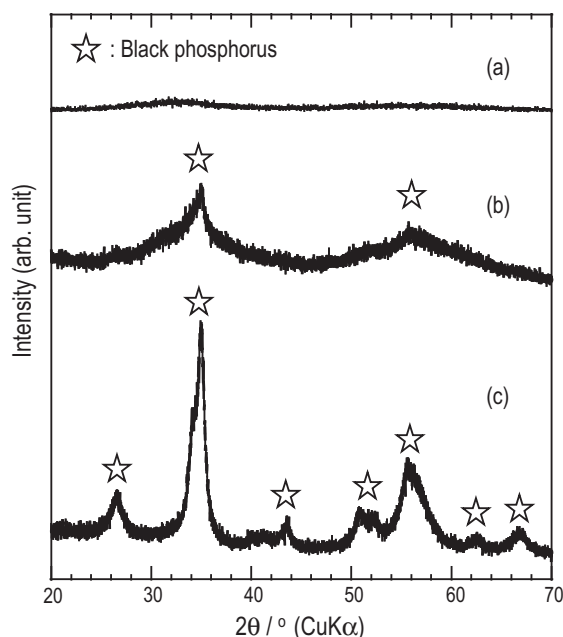


Fig. 1. XRD patterns of red phosphorus (a) and black phosphorus prepared by mechanical milling with a planetary ball-mill (b) and a mixer mill (c).

cess for 1 h with the planetary ball-mill apparatus (b) and the mixer mill apparatus (c). Red phosphorus used as a starting material was amorphous. Black phosphorus was prepared by milling for 1 h. The peaks of black phosphorus prepared by milling with the mixer mill apparatus were sharper than those of black phosphorus with the planetary ball-mill apparatus. This suggests that black phosphorus with higher crystallinity was prepared by using the mixer mill apparatus. The difference in crystallinity of black phosphorus as shown in Fig. 1(b) and (c) would be based on the difference of impact for mechanochemical reaction in two types of ball mill apparatuses. Oumellal et al. reported that the reaction between magnesium hydride and lithium metal were conducted by using the two ball mill apparatuses, and a higher yield of reaction was achieved by using the mixer mill apparatus [10]. Because the mixer mill apparatus gave more efficient impact interaction for reaction from red phosphorus to black phosphorus than the planetary ball-mill apparatus, black phosphorus was effectively prepared in the former case. The black phosphorus prepared by the mixer mill apparatus was used for electrochemical measurements. Electronic conductivity of the obtained black phosphorus was  $8.1 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature.

Fig. 2 shows SEM images of (a) black phosphorus powder and (b) the composites with black phosphorus and AB prepared by milling with the mixer mill apparatus. The prepared black phosphorus (a) was agglomerated to form secondary particles and their size was about 30 μm. On the other hand, the composites (b) showed less agglomeration and included smaller secondary particles with the size of 1–5 μm. The mechanical milling of black phosphorus and AB brought about a decrease in size of secondary particles of black phosphorus.

Fig. 3 shows the first charge–discharge profiles of all-solid-state cells of Li–In/80Li<sub>2</sub>S:20P<sub>2</sub>S<sub>5</sub> glass-ceramic/phosphorus under the current density of 0.064 mA cm<sup>-2</sup> (24 mA g<sup>-1</sup>) at 25 °C. Red phosphorus (a), black phosphorus (b) and the composites with black phosphorus and AB (c) were used as an active material. A Li–In alloy was used as a counter electrode because a Li–In alloy shows a stable voltage plateau at 0.62 V vs. Li in all-solid-state cells with sulfide solid electrolyte [11]. In this figure, the axis of ordinate on the left side represents the cell potential vs. Li–In electrode

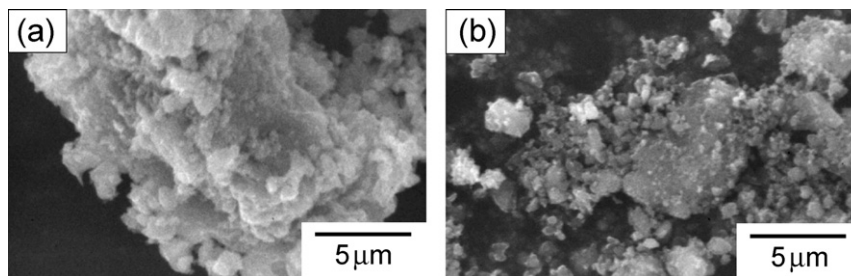


Fig. 2. SEM images of black phosphorus powders (a) and the composites with black phosphorus and AB (b).

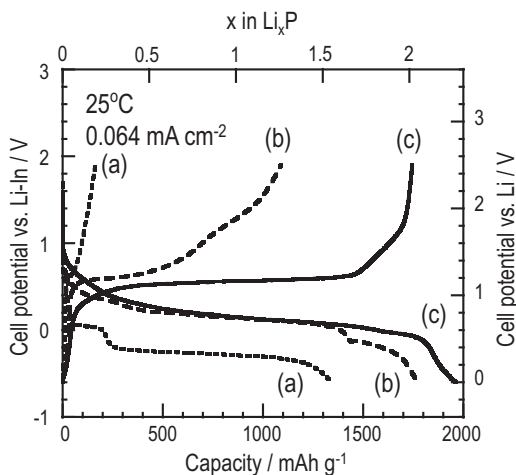


Fig. 3. The first charge–discharge curves of all-solid-state cells of Li–In/80Li<sub>2</sub>S·20P<sub>2</sub>S<sub>5</sub> glass-ceramic/phosphorus. Red phosphorus (a), black phosphorus (b) and the composites with black phosphorus and AB (c) were used as an active material.

(counter electrode), and that on the right side represents the potential vs. Li electrode which was calculated on the basis of potential difference between Li–In and Li electrode (0.62 V). The all-solid-state lithium cell using red phosphorus (a) as an active material showed the first discharge capacity of 1345 mAh g<sup>-1</sup>. However, the charge–discharge coulombic efficiency was only 12% and the large irreversible capacity was observed. On the other hand, the cell using black phosphorus (b) as an active material exhibited the discharge capacity of 1777 mAh g<sup>-1</sup> and the coulombic efficiency of 61%. In addition, in order to enhance the electrochemical performance of the cells, black phosphorus and AB were milled and the obtained composites were applied to the electrode of all-solid-state cells. The all-solid-state cell using the composites (c) exhibited superior electrochemical performance than the cell using the mixture of black phosphorus and AB, and the discharge capacity of 1962 mAh g<sup>-1</sup> and the coulombic efficiency of 89% were obtained in the former cell. One long plateau at about 0.7 V (vs. Li) during discharge process and the discharge capacity were in agreement with those reported in the cells with liquid electrolytes under a current density of 100 mA g<sup>-1</sup> [7]. In order to understand the difference in the specific capacity of the cells between (b) and (c), we measured the total conductivity of the pellets of these working electrodes sandwiched with two stainless steel plates (current collectors) by the AC impedance method. Both the working electrodes were composed of black phosphorus, AB and the sulfide electrolyte components. The electronic conductivity at room temperature of the electrode (b) was  $4.0 \times 10^{-2} \text{ S cm}^{-1}$  and that of the electrode (c) was  $4.3 \times 10^{-2} \text{ S cm}^{-1}$ ; it is hard to clarify the cause of the difference in the specific capacity in terms of the conductivity of the working electrodes. It is thus considered that a smaller particle size

of the black phosphorus/AB composite in the electrode (c) as shown in Fig. 2 contributes to the enhancement of the capacity and the coulombic efficiency of the cells.

The discharge–charge reaction mechanism of black phosphorus electrode was investigated by ex situ XRD measurements. XRD patterns of black phosphorus electrodes before cycling (a), after discharge to 0 V (vs. Li) (b) and after charge to 2.5 V (vs. Li) (c) are shown in Fig. 4. Silicon was used as an internal standard in XRD measurements. Before cycling, the peaks due to black phosphorus and thio-LISICON analog in the electrolyte were observed. The peaks of black phosphorus disappeared and the peaks attributable to Li<sub>3</sub>P newly appeared after the cell was discharged to 0 V. After charge from 0 V to 2.5 V, no obvious peaks derived from black phosphorus electrode were observed. Because the cells using the composite exhibited the high coulombic efficiency for the first cycle, the reversible electrochemical reaction between black phosphorus and Li<sub>3</sub>P would occur and the reaction products in charge process are probably amorphized black phosphorus. A similar reaction mechanism of the black phosphorus active material (P → Li<sub>3</sub>P) has already been reported in an electrochemical cell with an organic liquid electrolyte [7]. Although the formation of Li<sub>3</sub>P was confirmed by XRD measurement, the obtained capacity is equivalent to two-thirds of the theoretical capacity of black phosphorus; this suggests

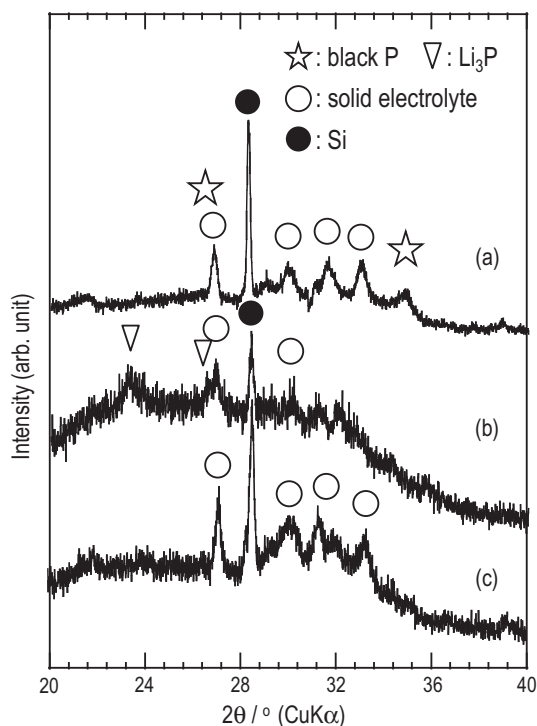
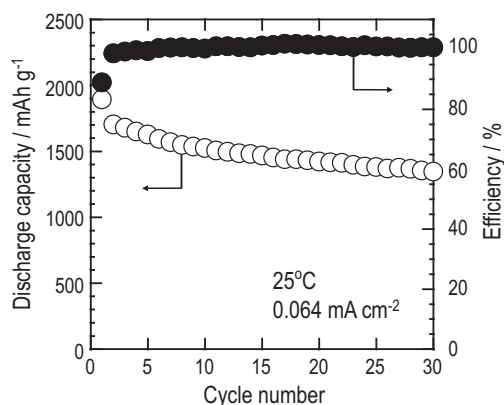


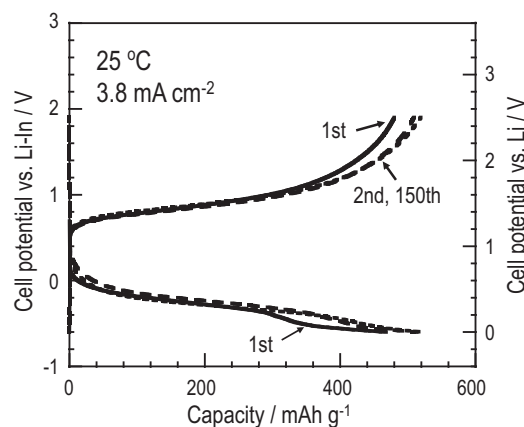
Fig. 4. XRD patterns for the working electrode using black phosphorus before cycling (a), after discharge to 0 V (vs. Li) (b) and after charge to 2.5 V (vs. Li) (c).



**Fig. 5.** Cycle performance of the all-solid-state cells using the composites with black phosphorus and AB at 25 °C. The cutoff voltage is between 0 V and 2.5 V (vs. Li).

that a part of black phosphorus in the working electrode did not contribute to the electrochemical reaction. To enhance the utilization of black phosphorus, further research about preparation conditions such as weight ratio and milling condition of composites is important.

Cycle performance and high-rate performance of all-solid-state cells using the composites with black phosphorus and AB were examined. Fig. 5 shows the cycle performance of the all-solid-state cell at the current density of 0.064 mA cm<sup>-2</sup>. The cutoff potential was between 0 V and 2.5 V (vs. Li). The all-solid-state cells retained the reversible capacity of 1350 mAh g<sup>-1</sup> for 30 cycles with a little capacity-fading with increasing the cycle number. Although the coulombic efficiency of the cell was 89% at the first cycle, the cell subsequently exhibited the coulombic efficiency of about 100% for 30 cycles. Drastic capacity-fading was observed in the cell with a black phosphorus electrode and an organic liquid electrolyte in the potential range from 0 to 2 V (vs. Li) [7]. On the other hand, all-solid-state cell exhibited good cycle performance in the wide potential range from 0 to 2.5 V (vs. Li). Fig. 6 shows the performance of the cell at 25 °C in the potential range from 0 to 2.5 V (vs. Li) at the current density of 3.8 mA cm<sup>-2</sup> (1.47 A g<sup>-1</sup>), which is much higher than the current density (0.1 A g<sup>-1</sup>) reported in the cell using a liquid electrolyte [7]. The discharge–charge profiles at the 2nd cycle and the 150th cycle were almost the same, although the profile at the 1st cycle was slightly different and two plateaus were observed for the discharge process. The cell exhibited an excellent cycle performance with the capacity of over 500 mAh g<sup>-1</sup> for 150 cycles at 3.8 mA cm<sup>-2</sup> (1.47 A g<sup>-1</sup>). The cell with a liquid electrolyte demonstrated the reversible capacity of 600 mAh g<sup>-1</sup> at the current density of 0.1 A g<sup>-1</sup> [7]. The all-solid-state cells exhibited the similar capacity of over 500 mAh g<sup>-1</sup> even at the current density of 1.47 A g<sup>-1</sup> which is about 15 times larger than that for the cell with a liquid electrolyte. It is noteworthy that the rate performance of the all-solid-state cells was superior to that of the cell with a liquid electrolyte. High capacity and high rate performance were achieved in the all-solid-state cells using black phosphorus-AB composite and



**Fig. 6.** High rate performance of the all-solid-state cells using the composites with black phosphorus and AB at 3.8 mA cm<sup>-2</sup> at 25 °C.

Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> glass-ceramic solid electrolyte. Black phosphorus is one of the most attractive negative electrodes for all-solid-state cells with high capacity.

#### 4. Conclusions

Black phosphorus was prepared by using mixer mill and planetary ball-mill apparatuses. The composites with black phosphorus and AB were prepared by the same mechanical milling technique. The mechanical milling of black phosphorus and AB brought about a decrease in size of secondary particles of the composite material. The all-solid-state lithium cells with the composites and Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> glass-ceramic electrolyte exhibited the first discharge capacity of 1962 mAh g<sup>-1</sup> and the coulombic efficiency of 89%. The all-solid-state cells worked at the current density of 3.8 mA cm<sup>-2</sup> (1.47 A g<sup>-1</sup>) at 25 °C and showed the excellent cycle performance with a high capacity of over 500 mAh g<sup>-1</sup> for 150 cycles. Black phosphorus is one of the most attractive negative electrodes with both high capacity and high-rate performance in all-solid-state lithium rechargeable batteries with sulfide electrolytes.

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