All-solid-state lithium batteries with Li_3PS_4 glass as active material

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Abstract

For increasing energy densities of all-solid-state cells, utilizing solid electrolytes in the electrode layer as an active material is useful. Favorable electron conduction paths to the Li_3PS_4 glass electrolyte were formed by mechanical milling with AB as the conductive additives. The all-solid-state cells with Li_3PS_4 glass only or mixture prepared by grinding the Li_3PS_4 glass and AB as a positive electrode did not work. On the other hand, the cell with Li_3PS_4 -AB composite electrodes prepared by milling was successfully charged and then discharged. Initial charge capacity of the cell with the Li_3PS_4 -AB composite electrode was 220 mAh g^{-1} at 0.064 mA cm^{-2} . Open circuit voltage of the cell was 2.6 V vs. Li, which was higher than that with Li_2S active material. In the cell with the Li_2S - Li_3PS_4 -AB composite electrode, the Li_3PS_4 glass functioned as not only Li^+ ion conductive paths to Li_2S but also active material itself, suggesting that the use of the solid electrolytes as active materials in electrode layers is useful for increasing reversible capacity per gram of a positive electrode.

Keywords:

All-solid-state battery; Lithium secondary battery; Solid electrolyte; Composite electrode

1. Introduction

Recently, new vehicles such as electric vehicles and plug-in hybrid electric vehicles have been attracting attention. Therefore, there are strong needs to develop large-scale lithium-ion secondary batteries with high safety and high energy densities.

All-solid-state lithium secondary batteries with inorganic solid electrolytes (SEs) attract much attention in terms of safety and reliability.

Bulk-type solid-state cells composed of electrode and electrolyte powders have an advantage of achieving large energy density. Key materials to realize bulk-type lithium batteries are SEs with high Li^+ ion conductivity and active materials with high capacities which are suitable for all-solid-state lithium batteries. Sulfide-based SEs have been studied because of their remarkably high lithium-ion conductivities at room temperature [1-3]. We have developed $\text{Li}_2\text{S-P}_2\text{S}_5$ glass ceramics as SEs with lithium-ion conductivities of over $10^{-3} \text{ S cm}^{-1}$ [3, 4] and various high-capacity electrode active materials for all-solid-state lithium batteries with $\text{Li}_2\text{S-P}_2\text{S}_5$ SEs [5-10]. In particular, we have focused on sulfur and Li_2S as positive electrode active materials to increase energy densities of the all-solid-state cells [11-14]. Sulfur and Li_2S active materials have high theoretical capacities (*ca.* 1642 mAh g^{-1} and 1167 mAh g^{-1} , respectively), which are much higher than that of conventional positive electrode materials such as LiCoO_2 [15].

Bulk-type solid-state cells are typically assembled using solid electrolyte and composite electrode powders. The composite electrodes are composed of three kinds of powder materials: an active material, a solid electrolyte as a Li^+ ion conduction path to the active material, and a conductive additive as an electron conduction paths. To secure favorable solid-solid contacts with conducting paths to the active material is very important. To form a good interface among the active material, SE, and a conducting additive such as acetylene black (AB) or Cu, composite electrodes with S or Li_2S active material were prepared by mechanical-milling [11-14]. The all-solid-state cells using S or Li_2S composite electrode exhibited good cyclabilities with large reversible capacities per weight of each active material [13, 14].

However, capacities per gram of total positive electrodes for all-solid-state batteries are small because the amount of active materials in the electrodes is limited. An increase of the active material content in the electrode layer is needed, but it tends to lower utilization of the active material, resulting in the decreasing capacity of solid-state cells. The Li_2S - P_2S_5 SEs used for all-solid-state batteries include a Li_2S component and thus the electrolyte itself has a potential utilization as an active material by adding conducting additives. Increase of capacity for all-solid-state cells are expected by electrochemically extracting Li^+ ions from not only Li_2S active material but also the

$\text{Li}_2\text{S-P}_2\text{S}_5$ SE in the composite electrode.

Therefore, we have investigated the use of the solid electrolyte as an active material in composite electrode layers. The addition of copper metal and carbon as conductive additives enabled the $\text{Li}_2\text{S-P}_2\text{S}_5$ SEs to function as the active material [16, 17]. An all-solid-state cell using the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol%) SE-AB composite electrodes exhibited a charge capacity of 240 mAh per gram of the SE [17]. The $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ SE is composed of Li_2S crystal and Li_3PS_4 glass, and thus Li^+ ions could be extracted from not only Li_2S but also Li_3PS_4 . The function of the Li_3PS_4 glass itself as the active material has not been clearly understood. We have investigated electrochemical characteristics and chemical stability of the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte. Cell performances of all-solid-state C/LiCoO₂ cells using $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolytes were investigated. The cell using the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol %, Li_3PS_4) glass showed a superior cycle performance to the cell using the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass-ceramic with the highest Li^+ ion conductivity in the $\text{Li}_2\text{S-P}_2\text{S}_5$ system [18]. The amount of H_2S generated from $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses exposed to air was also examined because the chemical stability of $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolytes in the atmosphere is concerned. The glass at the composition of Li_3PS_4 generated the smallest amount of H_2S in the $\text{Li}_2\text{S-P}_2\text{S}_5$ binary system [19]. The Li_3PS_4 glass is therefore a promising solid electrolyte for

all-solid-state lithium batteries in terms of cell performance and chemical stability. Fundamental understanding of the electrochemical characteristic of the Li_3PS_4 glass is important, but it has not been investigated.

In this study, to utilize the Li_3PS_4 glass as the active material, composite electrodes were prepared by mechanical milling of the mixture of the Li_3PS_4 glass and AB. The prepared Li_3PS_4 -AB composites were analyzed by XRD and SEM. Electrochemical properties of all-solid-state cells with Li_3PS_4 -AB composite electrodes were investigated.

2. Experimental

To prepare the Li_3PS_4 glass powders, mixture of reagent-grade Li_2S (Idemitsu Kosan Co., > 99.9%) and P_2S_5 (Aldrich, 99%) powders were placed into ZrO_2 pot (45ml) with 500 ZrO_2 balls (diameter: 4 mm) and then mechanically milled with a planetary ball mill (Fritsch Pulverisette 7) for 10 h at 510 rpm. The 80 Li_2S ·20 P_2S_5 (mol%) glass-ceramic SE[24] used as solid electrolyte layers for all-solid-state cells was prepared by mechanical milling (MM) under the same condition mentioned above, and then heated at 210 °C for 1h. Li_3PS_4 -AB composite electrodes were prepared by grinding the Li_3PS_4 glass and AB (Denki kagaku kogyo) with the weight ratio of 70:30

in a dry Ar-filled glove box. Three types of electrodes were prepared: Li_3PS_4 only, ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture, and Li_3PS_4 -AB composite. The ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture electrode was obtained by hand grinding of a mixture of Li_3PS_4 and AB. The Li_3PS_4 -AB composite electrode was obtained by ball milling of the mixture of the Li_3PS_4 and AB at 370 rpm for 1h in a ZrO_2 pot (45 ml) with 160 ZrO_2 balls (diameter: 4 mm). The Li_2S - Li_3PS_4 -AB composite electrodes were prepared by grinding Li_2S , Li_3PS_4 glass and AB with the weight ratio of 25:50:25 and then milled in the same condition of the Li_3PS_4 -AB composite electrode. The morphology of the electrodes was investigated by a scanning electron microscope (SEM; JEOL, JSM-6610A) coupled with an energy dispersive X-ray spectroscopy (EDX).

All-solid-state cells of In / Li_3PS_4 -AB composite electrodes were fabricated as follows. The Li_3PS_4 -AB composite electrodes were directly used as a working electrode, and the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic was used as a solid electrolyte layer. The obtained working electrode (5-6 mg) and the solid electrolyte layer (80 mg) were set in a polycarbonate tube (diameter: 10 mm) and pressed together under 360 MPa. An indium foil with a thickness of 100 μm was then placed on the surface of the SE side of the bilayer pellet as a counter-reference electrode. The three-layered pellet was then sandwiched between two stainless-steel disks as a current collector. Finally,

electrochemical solid-state cells were obtained by pressing under 120 MPa. Electrochemical tests of the cells were conducted at a constant current density of 0.064 mA cm⁻² at 25 °C in an Ar atmosphere using a charge-discharge measuring device (BTS-2004, Nagano Co.).

Open circuit voltage (OCV) of all-solid-state cells with Li₃PS₄-AB composite electrode on the first charge process was obtained by galvanostatic intermittent titration technique (GITT). The GITT measurement was performed using a Solartron 1470 ES cell test. A constant current of 0.064 mA cm⁻² was applied to the cells for each charging of 10 mAh g⁻¹ with intervals of rest for 10 h.

3. Results and discussion

Fig. 1 shows XRD patterns of the (a) mixture and (b) composite composed of the Li₃PS₄ glass and AB prepared by hand grinding and mechanical milling, respectively. No new peaks were observed in the pristine composite electrode, suggesting that new crystal was not formed by ball milling.

Fig. 2 shows SEM images of the (a) (Li₃PS₄ + AB) mixture or (b) Li₃PS₄-AB composite. EDX mappings of sulfur, phosphorus and carbon for the mixture and the composite are also shown, respectively. The (Li₃PS₄ + AB) mixture was composed of

the Li_3PS_4 glass particles with the size of several tens of micrometers and agglomerated AB particles. On the other hand, the Li_3PS_4 -AB composite was composed of the particles with a few micrometers; Li_3PS_4 particles were pulverized by milling treatment. EDX mapping revealed that the area of carbon (from AB) overlapped those of sulfur and phosphorus (from Li_3PS_4 glass) throughout the composite, suggesting that AB was highly dispersed in the Li_3PS_4 particles, and thus electron conduction paths to Li_3PS_4 glass were formed.

Fig. 3 shows charge-discharge curves of all-solid-state cells with the Li_3PS_4 only, the (Li_3PS_4 + AB) mixture prepared by hand grinding and the Li_3PS_4 -AB composite prepared by ball milling as working electrodes. In the voltage profiles of the all-solid-state cells, the left vertical axis denotes the potential versus Li-In electrode, whereas that on the right represents the potential versus Li electrode, which was calculated based on the potential difference between Li-In and Li (0.62 V). The obtained capacity was normalized by the weight of Li_3PS_4 glass. The cells were initially charged and then discharged and a cyclability test was performed.

The all-solid-state cells using Li_3PS_4 or the (Li_3PS_4 + AB) mixture as a working electrodes did not work as secondary batteries because the Li_3PS_4 glass itself was electrochemically inactive. On the other hand, the all-solid-state cell with the

Li₃PS₄-AB composite electrode was successfully charged and then discharged, suggesting that the Li₃PS₄ glass functioned as an active material. The cell with the Li₃PS₄-AB composite electrode exhibited first charge capacity of 220 mAh g⁻¹ and a first coulombic efficiency of 68 % at 0.064 mA cm⁻². The cell with the Li₃PS₄-AB composite electrode was discharged although Li⁺ ions were extracted from the composite. This suggests that the Li_{3-x}PS₄ component formed after charging probably keeps ionic conductivity and the ionic conduction paths are therefore retained throughout the electrode reaction. Partial density of states (PDOS) for Li₃PS₄ crystal was calculated with density functional theory [20]. The PDOS of the Li₃PS₄ glass is assumed to be similar to that of the Li₃PS₄ crystal. From the PDOS, a HOMO of the Li₃PS₄ crystal was contributed by S 3p orbital, suggesting that the electrochemical oxidation of Li₃PS₄ glass is caused by an extraction of electron from the S 3p orbital. However, an electrochemical reaction mechanism of the Li₃PS₄ glass has not been understood at the present stage. The reaction mechanism of the all-solid-state cells with the Li₃PS₄ glass as an active material needs to be clarified by analyzing local structure and electronic states of the Li₃PS₄ active material in the near future.

Fig.4 shows cycle performance of the all-solid-state cell with the Li₃PS₄-AB composite electrode. The cell retained a capacity of 100 mAh g⁻¹ for 30 cycles after the

first cycle. Rapid degradation of the capacity was not observed, suggesting that charge-discharge reaction of the Li_3PS_4 active material was reversible.

Fig. 5 shows open circuit voltage (OCV) of the cells with the Li_3PS_4 -AB or Li_2S - Li_3PS_4 -AB composite electrodes at the charge process. The Li_2S - Li_3PS_4 -AB composite electrode with Li_2S as an active material was prepared by ball-milling under the same conditions as the Li_3PS_4 -AB composite electrode. The cell with Li_3PS_4 glass as the active material showed a potential of about 2.6 V vs. Li, which was higher than that with Li_2S active material. A redox potential of LiFeP_2S_6 crystal exhibited a high potential of ca. 3.0 V vs. Li [21]. Donor levels of the LiFeP_2S_6 crystal were considered to comprise of Fe 3d and S 3p, suggesting that electrons were extracted from S 3p as well as Fe 3d at the high potential [19]. A presence of P-S bond would raise the redox potential of Fe and S and thus the redox potential of S in the Li_3PS_4 glass is probably increased for the same reason.

Fig. 6 shows charge-discharge curves of the cell with the Li_2S - Li_3PS_4 -AB composite. The cell with Li_2S - Li_3PS_4 -AB composite showed two plateaus at about 2.5 V and 2.8 V vs. Li on the charge process. The results of OCV (Fig. 5) for the cells suggested that the Li_2S and Li_3PS_4 , respectively functioned as active materials on the potential of 2.5 V and 2.8 V vs. Li in the cell with the Li_2S - Li_3PS_4 -AB composite

electrode. A high capacity of ca. 300 mAh g⁻¹ per gram of the Li₂S-Li₃PS₄ was obtained in the cell. The Li₃PS₄ glass worked as not only Li⁺ ion conductive paths to the Li₂S active material but also an active material, suggesting that the use of the solid electrolytes as active materials in electrode layers is useful for increasing reversible capacity per gram of total positive electrode. Furthermore, development of sulfide glass active materials with higher capacity is expected by optimizing the milling condition of the composite electrode and selecting glass formers with lighter elements than phosphorus.

4. Conclusions

For increasing energy densities of the all-solid-state cells, the use of the Li₃PS₄ glass SE as an active material was investigated. To utilize the Li₃PS₄ glass SE as the active material, favorable electron paths to the Li₃PS₄ glass SE were formed by milling with AB as conductive additives. The all-solid-state cells with the Li₃PS₄-AB composite electrode were successfully charged and then discharged, suggesting that Li₃PS₄ glass worked as an active material by milling with AB. The cell with the composite electrode exhibited a first charge capacity of 220 mAh g⁻¹ and a first coulombic efficiency of 68 % at 0.064 mA cm⁻². The cell retained a capacity of 100 mAh g⁻¹ for 30 cycles after

the first cycle and rapid degradation of the capacity was not observed, suggesting that the charge-discharge reaction of the Li_3PS_4 active material was reversible. The cell with Li_3PS_4 glass as the active material showed a potential of about 2.6 V vs. Li, which was higher than that with Li_2S active material. In the cell with the Li_2S - Li_3PS_4 -AB composite electrode, the Li_3PS_4 glass worked as not only Li^+ ion conduction paths to the Li_2S active material but also active material. We conclude that the use of the solid electrolytes as an active material in electrode layers is useful for increasing reversible capacity per gram of a positive electrode.

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Figure captions

Figure 1. XRD patterns of (a) ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture and (b) $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrodes prepared by hand grinding and mechanical milling, respectively.

Figure 2. SEM images of (a) ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture and (b) $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrodes. EDX mappings of sulfur, phosphorus and carbon are also shown for the ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture (a) and $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrode (b).

Figure 3. Charge–discharge curves of all-solid-state cells of In / $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic / Li_3PS_4 only, ($\text{Li}_3\text{PS}_4 + \text{AB}$) mixture, or $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrodes at 0.064 mA cm^{-2} at 25°C .

Figure 4. Cycle performance of the all-solid-state cell with the $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrode at 0.064 mA cm^{-2} at 25°C .

Figure 5. Open circuit voltage (OCV) of the all-solid-state cells with the $\text{Li}_3\text{PS}_4\text{-AB}$ composite electrode and the $\text{Li}_2\text{S-Li}_3\text{PS}_4\text{-AB}$ composite electrode. Closed and Open squares indicate OCV of the cells with the $\text{Li}_3\text{PS}_4\text{-AB}$ and $\text{Li}_2\text{S-Li}_3\text{PS}_4\text{-AB}$ composite electrodes, respectively.

Figure 6. Charge-discharge curves of the all-solid-state cell with the $\text{Li}_2\text{S-Li}_3\text{PS}_4\text{-AB}$ composite electrode.

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