Electrochemical Properties of All-solid-state Lithium Batteries with Amorphous FeS\textsubscript{x}-based Composite Positive Electrodes Prepared via Mechanochemistry

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ABSTRACT
Iron sulfide (FeS\textsubscript{x}) composite positive electrodes were prepared mechanochemically and applied to all-solid-state lithium cells. The prepared composites, consisting of Fe, S, Li\textsubscript{3}PS\textsubscript{4} solid electrolyte (SE), and vapor-growth carbon fiber (VGCF), were in amorphous state after ball milling for 10 h. An all-solid-state cell with an amorphous Fe-S-SE-VGCF composite as the positive electrode exhibits a high reversible capacity of 420 mAh per total weight of the composite electrode at a current density of 0.13 mA cm\textsuperscript{-2} at 25°C. The cell exhibited a capacity retention of 88% after 200 cycles at a current density of 0.64 mA cm\textsuperscript{-2} at 25°C. The all-solid-state cell using the Fe-S-SE-VGCF composite at a current density of 0.13 mA cm\textsuperscript{-2} at 100°C exhibited a higher reversible capacity of 550 mAh g\textsuperscript{-1}. The Fe-S-SE-VGCF composite is thus a promising positive electrode material, with high capacity and good cycle performance for all-solid-state lithium secondary batteries.

Keywords: All-solid-state Battery, Lithium Battery, Iron sulfide

1. Introduction
Lithium-ion batteries (LIBs) are widely used power sources for portable electronic devices. However, there is a need to develop large-scale lithium-ion secondary batteries with high safety and energy density. All-solid-state cells with solid electrolyte have attracted much attention in terms of safety and reliability at large-scale power sources for electric vehicles and plug-in hybrid vehicles. Recently, sulfide solid electrolytes have been used for bulk-type all-solid-state batteries because of their high conductivity (10\textsuperscript{-4} S cm\textsuperscript{-1}). Various high-capacity electrode active materials for all-solid-state lithium batteries with Li\textsubscript{3}S-P\textsubscript{2}S\textsubscript{5} solid electrolytes have been found.\textsuperscript{2,7} However, lithium batteries for practical applications require much larger energy densities. To increase the energy density of all-solid-state batteries, it is important to select suitable electrode-active materials with high capacity for sulfide solid electrolytes.

Sulfur is one of the most promising positive electrode materials, with a theoretical capacity (1672 mAh g\textsuperscript{-1}) that is 5–10 times higher than that of transition metal oxides like LiCoO\textsubscript{2}.\textsuperscript{8,9} However, sulfur is an ionic and electronic insulator. To utilize sulfur as an active material in positive electrodes, a large amount of electrical conducting materials (both ion and electron conductors) must be supplied. This causes a decrease in capacity per total electrode weight because the amount of active materials in the electrodes is limited. Therefore, positive electrodes with high capacity per total electrode weight are needed.

Transition metal sulfides serve as active materials with high conductive properties. Recently, we have reported the use of sulfur-rich titanium sulfides and molybdenum sulfides as electrode-active materials. Amorphous TiS\textsubscript{3} (a-TiS\textsubscript{3}) and MoS\textsubscript{3} (a-MoS\textsubscript{3}) were prepared by mechanical milling (MM) of an equimolar mixture of crystalline TiS\textsubscript{2} or MoS\textsubscript{2} and sulfur, and showed high capacities. Amorphous TiS\textsubscript{3} and MoS\textsubscript{3} showed capacities of 390 and 780 per gram of active material and 150 and 230 mAh per gram of each composite electrode, respectively. They showed good cycle performances in all-solid-state cells with sulfide solid electrolytes.\textsuperscript{10,11} Among metal sulfides, iron sulfides have attracted great attention due to their cost-effectiveness and abundance in nature. FeS\textsubscript{2} is a typical active material for lithium cells and operation of the cells using FeS\textsubscript{2} as a positive electrode with organic liquid electrolytes has been reported.\textsuperscript{12,13} However, the cells suffered from low capacity retention, which decreased to ~50% after 30 cycles in the cell using a conventional liquid electrolyte (1.5 M LiPF\textsubscript{6} in EC-DEC). The electrochemical performances of Li\textsubscript{2}S-FeS\textsubscript{2} and Li\textsubscript{2}S-Fe\textsubscript{3}S\textsubscript{4} active materials were also examined in a cell with a 1 M LiPF\textsubscript{6} in EC-DMC electrolyte.\textsuperscript{14} The cell operation was started from the charge process (lithium extraction) and the first charge capacity was 540 mAh g\textsuperscript{-1} per electrode, while the retention of the cell after 10 cycles was 83%.\textsuperscript{14} The use of FeS\textsubscript{2} and Li\textsubscript{2}FeS\textsubscript{2} as positive electrode materials in all-solid-state cells was also reported.\textsuperscript{15,16} In a cell using FeS\textsubscript{2}, the discharge capacity was ~720 mAh per gram of FeS\textsubscript{2} for the four-electron reaction, and ~400 mAh per gram of FeS\textsubscript{2} for the two-electron reaction at the second cycle.

In this study, we focus on the preparation of sulfur-rich FeS\textsubscript{2} composite electrodes and their application to all-solid-state cells. Bulk-type all-solid-state cells are often assembled with a solid electrolyte layer, and both positive and negative composite electrode layers are composed of three powder materials: active material, a solid electrolyte as an ion conduction path, and a carbon additive as an electron conduction path. Sulfur-rich FeS\textsubscript{2} composite positive electrodes were prepared from Fe (or FeS\textsubscript{2}), S, Li\textsubscript{3}PS\textsubscript{4} solid electrolyte (SE) and vapor grown carbon fiber (VGCF) by high-energy ball milling process. We have already found that the SE functioned not only as an ionic conductor, but also as an active material when a nanocomposite with carbon is prepared by ball milling.
milling. Both FeS₂ and Li₃PS₄ are expected to play a role as active materials, thus enabling higher capacity per total weight of the composite electrode.

All-solid-state cells with the prepared FeS₂ composite electrodes were fabricated and their charge-discharge performance was evaluated. In order to analyze the structures of the composite electrodes, X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray (SEM-EDX), and transmission electron microscopy (TEM) analyses were performed.

2. Experimental

2.1 Fabrication of Fe-S-SE-VGCF and FeS₂-S-SE-VGCF composites

The Fe-S-SE-VGCF composite electrode materials were prepared by ball milling in a planetary ball mill apparatus (Fritsch Pulverisette 7) under an Ar atmosphere. The composite material consisted of Fe (Aldrich, 99.9%), S (Aldrich, 99.98%), 75Li₂S·25P₂S₅ (mol%) glass SE and VGCF (Denki Kagaku Kogyo) in a weight ratio of 18:32:40:10 (Fe:S molar ratio = 3:1). For mechanical milling, a zirconia vessel (45 ml) with 30 g zirconia balls (4 mm diameter) was used, with a fixed rotation speed of 510 rpm. The milling time was 10 h.

The FeS₂-S-SE-VGCF composite electrode material using a different iron source was also prepared under the same conditions. The composite material consisted of FeS₂ (Aldrich, 99.9%), S (Aldrich, 99.99%), 75Li₂S·25P₂S₅ (mol%) glass SE and VGCF (Denki Kagaku Kogyo) in a weight ratio of 42:8:40:10 (Fe:S molar ratio = 3:1). The milling time was 30 h.

The 75Li₂S·25P₂S₅ glass SE exhibits high room temperature conductivity (ca. 10⁻⁴ S cm⁻¹) and moderate chemical stability, and was prepared by a mechanochemical reaction process.

2.2 Characterization of the composite electrodes

XRD measurements of the prepared materials were performed using CuKα radiation (Ultima IV; Rigaku) to identify the crystalline phases. The morphologies of the materials were evaluated by SEM-EDX (JSM-6610A; JEOL) and TEM (JEM-2100F; JEOL).

The electrochemical properties of two composite electrodes, made of Fe-S-SE-VGCF and FeS₂-S-SE-VGCF, were investigated in all-solid-state cells. All-solid-state cells were fabricated as follows. The obtained composite electrode (5 mg, working electrode) and the solid electrolyte (80 mg) were placed in a polycarbonate tube (ca. 3 µm). The obtained composite electrode (5 mg, working electrode) and the solid electrolyte (80 mg) were placed in a polycarbonate tube (ca. 3 µm) and pressed together under 360 MPa. Li-In alloy was used as a counter electrode because it exhibits a stable voltage plateau at 0.62 V vs. Li⁺/Li in an all-solid-state cell using a sulfide SE. A Li-In alloy was placed on the SE layer and a pressure of 120 MPa was then applied to the three-layered pellet. Finally, two electrode cells sandwiched with two stainless-steel disks as a current collector were obtained. All processes described above were conducted in a dry Ar glove box. The electrochemical tests were conducted at several constant current densities from 0.13 to 1.3 mA cm⁻² at 25°C or 100°C in a dry Ar atmosphere using a charge-discharge measuring device (BTS-2004; Nagao Co.).

3. Results and Discussion

Figure 1(a) shows XRD profiles of the Fe-S-SE-VGCF and FeS₂-S-SE-VGCF composites prepared by milling the mixture of Fe or FeS₂, S, Li₃PS₄ (SE) and VGCF. In the Fe-S-SE-VGCF mixture before milling, diffraction peaks attributable to crystalline Fe and S are detected. The Fe-S-SE-VGCF composite after milling for 10 h shows no diffraction peak, indicating that Fe and S in the Fe-S-SE-VGCF composite became amorphous. On the other hand, the FeS₂-S-SE-VGCF mixture before milling shows diffraction peaks attributable to FeS₂ and S. After milling for 30 h, the diffraction peaks attributable to FeS₂ are still observed, suggesting that it is difficult to form FeS₃ from FeS₂ and S under the present ball mill condition. Figure 1(b) shows a high-resolution TEM image of the Fe-S-SE-VGCF composite prepared by milling for 10 h. The inset shows an electron diffraction pattern of the sample.

Figure 2 shows a SEM image and EDX mappings of the Fe-S-SE-VGCF and FeS₂-S-SE-VGCF composite samples before and after milling. The inset shows an electron diffraction pattern of the sample.

Figure 3(a) shows the charge-discharge curves of the cell using the Fe-S-SE-VGCF and FeS₂-S-SE-VGCF composites at 25°C under 0.13 mA cm⁻². The right-side ordinate axis represents the cell potential vs. Li⁺/Li, as calculated based on the potential difference between the Li-In and Li electrodes (0.62 V). The charge-discharge curves at the 5th cycle are shown as a typical profile of the cell because charge-discharge capacities gradually increase.
during pre-cycling. The cell using amorphous Fe-S-SE-VGCF composite exhibited a high reversible capacity of 420 mAh per total weight of composite electrode from the 2nd to 10th cycles. The capacity is higher than that of TiS$_3$ (400 mAh g$^{-1}$ per composite electrode). The discharge capacity of the cell using the FeS$_2$-SE-VGCF composite was $\sim$100 mAh per total weight of composite electrode.

The cell using the FeS$_2$-SE-VGCF composite showed a smaller capacity compared to the cell using the Fe-S-SE-VGCF composite. This is due to the fraction of insulating sulfurs which remain in the FeS$_2$-SE-VGCF composite without reacting to FeS$_2$. On the other hand, amorphous Fe$_{S_x}$, formed when Fe and S are used as the starting materials, resulted in a high capacity in the Fe-S-SE-VGCF composite.

The rate performance of the cells with the Fe-S-SE-VGCF composite is shown in Fig. 3(b). The discharge capacities of 340, 230 and 150 mAh g$^{-1}$ were obtained at the current densities of 0.13, 0.64 and 1.3 mA cm$^{-2}$, respectively, while the corresponding charge capacities of 325, 235 and 150 mAh g$^{-1}$ were achieved at 0.13 mA cm$^{-2}$. It is noted that the lithiation and delithiation capacities were almost reversible.

Figure 3(c) shows the cycling performance of an all-solid-state cell with the Fe-S-SE-VGCF composite at a current density of 0.64 mA cm$^{-2}$, at 25°C, for 200 cycles. The cell with the Fe-S-SE-VGCF composite maintained a capacity retention of 88% after the 200th cycle. The capacity retention was based on the 2nd capacity of 260 mAh g$^{-1}$. The all-solid-state cell with the Fe-S-SE-VGCF composite electrode showed a high capacity retention and Coulombic efficiency during 200 cycles.

The reversible capacity of the cell studied here is compared to that of the all-solid-state cell with the FeS$_2$ or Li$_2$FeS$_2$ electrode. The cell with FeS$_2$ showed the reversible capacity of 400 mAh per gram of FeS$_2$, which corresponds to 125 mAh per gram of total composite positive electrode. The cell operation was done at 0.144 mA in the potential range of 1.5–2.5 vs. Li. The other cell with the Li$_2$FeS$_2$ electrode exhibited the capacity of 150 mAh per gram of the composite positive electrode (300 mAh per gram of Li$_2$FeS$_2$) at the current density of 0.064 mA cm$^{-2}$ in the potential range of 1.6–3.6 vs. Li. It is noteworthy that the cell with the Fe-S-SE-VGCF electrode as shown in Fig. 3(a) achieved a larger reversible capacity of 420 mAh per gram of the composite electrode than that with the iron sulfide electrodes mentioned above.

Figure 4 shows the XRD patterns of the Fe-S-SE-VGCF composite before charge-discharge and after the 200th charge at a current density of 0.64 mA cm$^{-2}$, at 25°C. The composite retained the amorphous states after the 200th charge.
Figure 4. XRD patterns of the Fe-S-SE-VGCF composite electrodes before charge-discharge and after the 200th charge.

Figure 5. The 5th charge-discharge curves of all-solid-state cells with Li-In/Li3PS4/Fe-S-SE-VGCF composite electrode at 100°C and 0.13 mA cm⁻².

Figure 5 shows the charge-discharge curves of the all-solid-state cell with the Fe-S-SE-VGCF composite as the active material at a current density of 0.13 mA cm⁻², at 100°C. The cell exhibited a reversible capacity of 550 mAh g⁻¹ per composite electrode. The cell operating at 100°C showed higher capacity than the one operating at 25°C. The capacity of 550 mAh g⁻¹ per composite electrode corresponds to 1100 mAh g⁻¹. The cell resistance decreased upon increasing the current density of 0.13 mA cm⁻² vs. Li. Since the resistance turned apparent. Since the cell resistance decreased upon increasing the operation temperature, the cell exhibited a higher capacity. Based on the charge-discharge profiles of the all-solid-state cell using FeS₂ active material, the plateau attributable to FeS₂ under the two-electron reaction was observed at around 2.2 V vs. Li at the discharge process. The Li₃PS₄ component functioned as an active material in the potential range of 1.5–2.0 V vs. Li. The all-solid-state cell using S active materials also showed a plateau attributable to S redox at around 2.0 V vs. Li. Since the potential operating ranges of FeS₂, S and Li₃PS₄ overlapped in the range of 2.2–1.5 V vs. Li, cooperative electrochemical-reactions of these species are expected to occur at the two plateaus in Fig. 5. Detailed structural analyses for the composite electrodes during charge-discharge will be performed in the near future to understand the reaction mechanism.

4. Conclusions

To increase the energy densities of all-solid-state cells, FeS₂ and Li₃PS₄ were employed as active materials. The cell using the amorphous Fe-S-SE-VGCF composite exhibited a high capacity of 420 mAh g⁻¹ per composite weight at a current density of 0.13 mA cm⁻² at 25°C. The cell at a current density of 0.64 mA cm⁻² at 25°C showed a capacity retention of 88% after 200 cycles. In contrast, the cell using the FeS₂-S-SE-VGCF composite as active material showed a smaller capacity (100 mAh g⁻¹) than that with Fe-S-SE-VGCF composite (420 mAh g⁻¹). The Fe-S-SE-VGCF composite maintained an amorphous state after charge-discharge measurements. At 100°C, both FeS₂ and Li₃PS₄ components were used as an active material, and the cell with amorphous Fe-S-SE-VGCF exhibited a high capacity of 550 mAh g⁻¹ per composite weight in the Fe-S-SE-VGCF composite. Therefore, the Fe-S-SE-VGCF composite is a promising positive electrode, with high capacity and good cycle performance, for all-solid-state lithium secondary batteries.

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References