Fabrication and All Solid-State Battery Performance of TiS$_2$/Li$_{10}$GeP$_2$S$_{12}$ Composite Electrodes$^*$

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TiS$_2$/Li$_{10}$GeP$_2$S$_{12}$ composite electrodes were fabricated using a mill pot rotator, and their electrochemical properties were investigated in all solid-state batteries of TiS$_2$ cathode/Li$_{10}$GeP$_2$S$_{12}$ solid-electrolyte/In-Li anode. The batteries compressed under a pressure of 19 MPa demonstrated poor cycle stability and rate capability because of the deterioration of physical contact between the TiS$_2$ and the Li$_{10}$GeP$_2$S$_{12}$. The battery performance was considerably improved by applying a pressure of 228 MPa throughout the electrochemical cycling while maintaining the contact area. The battery delivered the reversible a capacity of over 160 mAh g$^{-1}$ under 1 C operation with high capacity retention.

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1. Introduction

The use of solid in place of liquid electrolytes in lithium-ion batteries has greatly improved reliability owing to the greater range of safe operating temperatures of all-solid-state batteries$^{1–3}$. However, low ionic conductivity of solid electrolytes compared to liquid electrolytes is a major technical issue for their practical use. During these 15 years, lithium ion conductors having high conductivity have been developed as a solid electrolyte$^{4–8}$. Among them, a lithium germanium phosphosulfide Li$_{10}$GeP$_2$S$_{12}$ exhibits an extremely high lithium ion conductivity of 12 mS cm$^{-1}$ at room temperature, which exceeds even that of organic liquid electrolytes$^7$. Recently, some reports have demonstrated successful operation of all-solid-state batteries with the Li$_{10}$GeP$_2$S$_{12}$–type electrolytes and oxide cathode materials such as LiCoO$_2$,$^{7,9}$ LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$,$^{10}$ LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$.$^{11}$ However, the oxide cathode-solid electrolyte interfaces exhibit a high-ly-resistant interfacial layer for lithium diffusion due to formation of lithium-depleted space-charge layer$^{12}$ and/or mutual diffusion of cation species$^{13}$, thus giving a very low capacity for solid-state batteries. Although surface coating on cathode materials by lithium ion conductive oxides is an efficient way to decrease the interfacial resistance$^{13,14}$, it could take a cost to fabricate a uniform coating$^{15}$. When there is no observable resistance between the sulfide cathode and sulfide electrolyte, it is not necessary to modify the cathode$^{16–19}$. However, to date, there have been few reports of solid-state batteries comprising a sulfide cathode and Li$_{10}$GeP$_2$S$_{12}$ electrolytes$^{19}$, and the cell cycling characteristics remain unclear.

In this study, we focused on TiS$_2$ with a layered structure as the cathode. TiS$_2$ has a hexagonal close-packed structure where each Ti is surrounded by six S in an octahedral structure. TiS$_6$ octahedra shared the edges to form a layered structure$^{20}$. Li can intercalate into possible spaces between the TiS$_6$ layers$^{20}$. The electrochemical reaction is as follows: TiS$_2$ + Li$^+$ + e$^-$ $\leftrightarrow$ LiTiS$_2$; moreover, the theoretical capacity is 239 mAh g$^{-1}$. This capacity is much higher than that of conventional LiCoO$_2$ used as a cathode for all solid-state batteries (130 mAh g$^{-1}$). Jung et al. has reported a TiS$_2$ cathode and Li$_{10}$GeP$_2$S$_{12}$ electrolyte solid-state battery having a capacity 200 mAh g$^{-1}$.$^{19}$ When Li intercalates into all possible spaces in TiS$_2$, the volume of TiS$_2$ layer expands by approximately about 12%$^{21}$. The TiS$_2$ composite cathode comprises the TiS$_2$ active material and Li$_{10}$GeP$_2$S$_{12}$ electrolyte, and contact between the bulk grains is very important. The large volume change of Li$_x$TiS$_2$ during charge-discharge cycles could lead to the decrease in the physical contact between the TiS$_2$ and the Li$_{10}$GeP$_2$S$_{12}$ electrolyte. However, the physical contact and the related cycle stability of the the TiS$_2$/Li$_{10}$GeP$_2$S$_{12}$ composite electrodes have not been clarified. In this study, we fabricated all solid-state batteries with the TiS$_2$/Li$_{10}$GeP$_2$S$_{12}$ composite cathode and characterized their electrochemical properties. Furthermore, effects of applied pressure during charge-discharge cycles were investigated to improve the cycle stability and the rate capability.

2. Experimental Procedure

Composite cathodes were fabricated by mechanical mixing of TiS$_2$ and Li$_{10}$GeP$_2$S$_{12}$ powders. As smaller-sized of particles could have a larger surface area, a high-energy ball mill (Fritsch pulverisette 7) was performed for commercial TiS$_2$ powder (Kojundo Chemical Laboratory Co. Ltd, Japan) at 320 rpm for 16 h prior to the mixing. The crystal structure and morphology of the milled TiS$_2$ were verified using X-ray diffraction (XRD: Smartlab CuK$_\alpha$, Rigaku) and scanning electron microscope (SEM: JSM-6610LV, JEOL). Brunaure-Emmett-Teller (BET: BELSORP-mini, Microtrac-BEL) were conducted to verify the specific surface area of TiS$_2$ samples. The synthesis of Li$_{10}$GeP$_2$S$_{12}$ was as previously reported$^7$, followed by hand-grinding the product 10 min using an agate mortar to decrease the particle size. The weight ratio between TiS$_2$ and Li$_{10}$GeP$_2$S$_{12}$ was 30:70, which were mixed using a vortex miller (TTM-1, SIBATA) at 2500 rpm for 10 min.

The Li$_{10}$GeP$_2$S$_{12}$ electrolyte (100 mg) was prepared as a pellet with a 10 mm diameter. An aluminum foil and mesh
were used as current collectors for the cathode. The cathode powder (10 mg) was pressed onto the Li10GeP2S12 electrolyte pellet under 555 MPa. The negative electrode was consisted of Li foil (ϕ5 mm, t0.1 mm) and In foil (ϕ10 mm, t0.1 mm) on a copper mesh current collector. Finally, the three-layers of the cathode/electrolyte/anode were pressed together at 19 MPa to fabricate the all solid-state batteries. A pressure of 230 MPa was applied on the battery during the charge-discharge operation. All the processes for the solid-state batteries were performed in a dry Ar-filled glovebox (DBO-1.5-T1000, Miwa). After fabricating the battery, two further tests were performed: (1) encasing the cell in a stainless steel container and (2) maintaining the cells under 228 MPa using the pressure instrument during the charge-discharge operation (TOSCAT-3100, Toyo system). The range of cut-off voltage was from 2.5–1.0 V and the applied current densities were 0.088 mA g\(^{-1}\) (0.1 C) to 1.76 mA g\(^{-1}\) (2 C).

3. Results and Discussion

Figure 1 shows the XRD patterns and SEM images of TiS\(_2\) before and after grinding with ball milling. Before ball milling, the TiS\(_2\) powder showed a layer structure (P-3m1), with the lattice parameters \(a = 3.4079(3)\) Å and \(c = 5.6989(6)\) Å. Whereas no changes in the peak position were observed after ball milling, the diffraction peaks became broader and their intensity decreased. This indicates that the average size of the TiS\(_2\) particles decreased after ball milling. SEM images from before and after ball milling showed that the average size of TiS\(_2\) particles reduced from 1–2 \(\mu\)m to 200–500 nm. Using BET measurements, it was observed that the surface area of TiS\(_2\) increased from 3.2 m\(^2\) g\(^{-1}\) to approximately 45.6 m\(^2\) g\(^{-1}\) after ball milling.

Figure 2 shows charge/discharge curves of TiS\(_2\)/Li\(_{10}\)GeP\(_2\)S\(_{12}\)/In-Li batteries under different current densities of 0.1, 0.2, 1 C and 2 C. The batteries were fabricated using a compressive forming pressure of 19 MPa and were sealed into a unpressed cell. At current density of 0.1 C, the first discharge and charge capacity were 206 and 185 mA h\(^{-1}\), respectively. It has been reported that the lithium intercalation into TiS\(_2\) proceeds at around 2.1 V vs. Li/Li\(^+\). Because the potential of the In-Li alloy is about 0.6 V higher than that of Li/Li\(^+\), the observed charge-discharge curves confirm the lithium (de)intercalation from/into the TiS\(_2\) lattice. Approximately 0.8 mol Li takes part in intercalation into the TiS\(_2\) lattice, which are estimated from the observed capacities. The irreversible capacity of the first charge-discharge operation is about 21 mA h\(^{-1}\). A first principle calculation has shown...
that Li_{10}GeP_{2}S_{12} is unstable below 2 V vs. Li / Li^+ and electrochemically decomposes to form a thin interfacial layer. Thus, the irreversible capacity could be associated with the interfacial layer formation. The charge-discharge efficiency was approximately 100% at the subsequent cycles. However, after the 5th cycle, the reversible capacity gradually decreased to 140 mAh g\(^{-1}\) by the 18th cycle. When the current density was 0.2 C, the performance of the initial five cycles was similar to that at a current rate of 0.1 C. The capacity decreased sharply to around 120 mAh g\(^{-1}\) by the 20th cycle, representing around a 60% decrease. When the current densities were 1 C and 2 C, the charge-discharge capacities decreased obviously. Particularly at 2 C, the discharge-charge capacities decreased from 113 and 101 mAh g\(^{-1}\) to 79 and 78 mAh g\(^{-1}\), respectively, from the first to fifth cycle. These results indicate that the capacity and cycle stability decrease as the current density increases.

During the lithium (de)intercalation, the host lattice is expanded and contracted repeatedly. When the volume changes are large, the contact between the solid electrolyte and conductive additive is disrupted, reducing the electrochemically-active region. The lithiated LiTiS\(_2\) phase has a considerably larger lattice volume (64.1 Å\(^3\)) than TiS\(_2\) (57.1 Å\(^3\)), therefore, the severe capacity fading could be associated to decrease in the electrochemically active regions in the composite electrodes. In contrast, an all solid-state battery with a LiCoO\(_2\)/Li\(_{10}\)GeP\(_2\)S\(_{12}\) composite electrode, which is fabricated using the same cell conditions, has exhibited excellent electrochemical performance, when Li intercalates to give Li\(_{0.55}\)CoO\(_2\). In this case, the volume change is about 2% of the LiCoO\(_2\) host lattice. This result supports that the sharp volume changes have a more obvious effect on the cycle stability of all solid state batteries.

To clarify the influence of the lattice volume change on the cycle stability, a higher pressure of 228 MPa was applied to fabricate the TiS\(_2\)/Li\(_{10}\)GeP\(_2\)S\(_{12}\)/In-Li batteries. Figure 3(a) shows the charge-discharge curve of the TiS\(_2\)/Li\(_{10}\)GeP\(_2\)S\(_{12}\)/In-Li battery, which was compressed at 230 MPa and sealed into an unpressed cell container. At a current density of 1 C, the reversible capacities at the first and second cycles were 106 and 127 mAh g\(^{-1}\), respectively, which are similar values to the battery compressed at 19 MPa (Fig. 2(c)). In contrast, at the tenth cycle, the battery compressed at 230 MPa exhibited the discharge-charge capacities of 120 and 117 mAh g\(^{-1}\), respectively. Increasing the pressure during fabrication improved the cycle stability. Figure 3(b) shows the charge-discharge curves of a battery compressed at 230 MPa and maintained at the applied pressure during charge-discharge operation. The first discharge-charge capacities were 200 and 145 mAh g\(^{-1}\), respectively. The discharge-charge capacities were improved to 175 and 168 mAh g\(^{-1}\), respectively, at the second cycle and were in the initial ten cycles. This result demonstrates that the cycle stability is considerably improved by increasing the applied pressure. Figure 4 shows the rate capability of a TiS\(_2\)/Li\(_{10}\)GeP\(_2\)S\(_{12}\)/In-Li cell under an applied pressure of 228 MPa throughout the charge-discharge operation at 1 C. The current densities used were 0.1, 0.5, 1.0, 2.0, and 5 C, and each rate test was performed for three cycles. At 0.1 C, the capacity was 1.7 times higher than that at 1 C. The capacity at 5 C was half of that at 1 C, which is much better than that of a cell under no pressure. After rate testing, the cell was operated again at 0.1 C, and no significant change in the capacity was observed compared to that of the initial cycle at 0.1 C. This result indicates that the cell did not degrade even when operated at high current densities. The applied pressure maintains good contact between the active material and solid electrolyte, resulting in high charge-discharge capacities with high cycle retention.

Generally, sulfide electrolytes are chemically unstable to moisture in ambient air. Note that the electrochemical tests with applying the pressure of 230 MPa were performed in the Ar-filled glove box. Thus, the inert condition could suppress the degradation of the Li\(_{10}\)GeP\(_2\)S\(_{12}\) electrolyte and lead to the
high cycle stability of the battery. To separate the effects of pressure and moisture, the following experiments were performed: (a) a cell was operated with a 230 MPa pressing for 40 cycles in the glove box; (b) a cell was operated with a 230 MPa pressing for 20 cycles and then was operated with no applying pressure for 20 cycles, with all tests performed in the glove box; (c) a cell was operated with a 230 MPa pressing for 20 cycles in glove box and then was operated with no applying pressure for 20 cycles in air. Figure 5 shows the capacity retention per cycle number for the TiS2/Li10GeP2S12/In-Li cells operated under the above conditions. The initial capacities are normalized to 1. The cell tested under condition (a) showed the high capacity retention of the discharge capacity from the second to fortieth cycle. Under conditions (b) and (c), the capacities drastically decreased after the applying pressure was stop at the twentieth cycle. No significant contamination of moisture into the cell was observed under the experimental conditions in this study. These results reveal that the physical contact between the TiS2 electrode and Li10GeP2S12 electrolyte determines the rate capability and cycle stability of all-solid-state batteries with the TiS2 cathode.

4. Conclusion

All-solid-state batteries were fabricated using a TiS2 cathode, a Li10GeP2S12 electrolyte, and an In/Li anode, and their electrochemical properties were investigated based on the applied pressure during charge-discharge cycles. The batteries exhibited poor rate capability and severe cycle retention with no applying pressure during the cycles, because the physical contact between the TiS2 and the Li10GeP2S12 deteriorated by the large volume change of the Li,TiS2. The rate capability and severe cycle retention were greatly improved in the batteries operated with an applying pressure of 230 MPa. Eliminating the volume change of the composite electrodes is important for achieving stable battery operation and performance.

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REFERENCES