Bulk-Type All Solid-State Batteries with 5 V Class LiNi0.5Mn1.5O4 Cathode and Li10GeP2S12 Solid Electrolyte

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ABSTRACT: All solid-state batteries are of key importance in the development of next-generation energy storage devices with high energy density. Herein, we report the fabrication and operation of bulk-type 5 V-class all solid-state batteries consisting of LiNi0.5Mn1.5O4 cathode, Li10GeP2S12 solid-electrolyte, and Li metal anode. The 1st discharge capacity is about 80 mAh g\(^{-1}\) with an average voltage of 4.3 V. The discharge capacity gradually decreases during the subsequent cycles. X-ray diffraction and electrochemical impedance spectroscopy measurements reveal that the capacity fading results from the growth of a resistive interfacial layer on the cathode composite. The development of anode and cathode materials is essential for the development of high-voltage all-solid-state batteries.

1. INTRODUCTION

LiNi0.5Mn1.5O4 (LNMO) has attracted significant research attention as a promising high-energy density cathode material (640 Wh kg\(^{-1}\)) for lithium ion batteries, owing to its high operating voltage for the lithium intercalation/deintercalation (~4.7 V vs Li/Li\(^+\)).1−3 In practical applications, LNMO suffers from significant capacity degradation, especially during high temperature operations (over 60 °C).4−6 On the basis of extensive research, it has been proposed that the capacity degradation is related to Mn dissolution in organic liquid electrolytes.3 The conductivity of Mn ions in solid electrolytes is negligible, which should suppress Mn dissolution. Thus, all solid-state batteries containing solid electrolytes and high voltage cathodes are among the ideal rechargeable battery systems. However, all solid-state batteries containing the LNMO cathode are limited to thin-film battery systems so far, because of the low ionic conductivity of solid electrolytes.7,8

Recently, a new sulfide solid electrolyte, Li10GeP2S12 (LGPS), exhibiting an extremely high lithium ion conductivity of 12 mS cm\(^{-1}\) at room temperature, has been reported.9,10 Bulk-type all solid-state batteries with layered rock-salt type LiMOr (M = Mn, Co, Ni)11−13 or TiS\(_2\)14 cathodes and sulfide electrolytes are reported to deliver reversible charge/discharge performance with high power density.15−18 Despite the promising properties of all solid-state batteries with the LGPS electrolyte,19−21 there have been no reports on the application of the LNMO cathode. Furthermore, there is no information available on the interfacial phenomena between the LNMO cathode and sulfide electrolytes.

In the present study, we report the fabrication and electrochemical properties of bulk-type all solid-state batteries with LNMO as the cathode, LGPS as the electrolyte, Li metal as the anode, and charge–discharge operation up to 5 V.
cathode composite was prepared by blending LNMO, LGPS, and acetylene black (AB) in a weight ratio of 38.5:57.5:4, using a pot mill rotator (Nitto, ANZ-10). LGPS powder (100 mg) was pressed to form the electrolyte, following which the cathode composite (10 mg) was pressed on the LGPS pellet along with Al foil/mesh, which was used as the current collector, under 228 MPa pressure. Finally, Li-In with a weight ratio of 1:60 or Li metal was pressed under 19 MPa pressure onto the pellet.

**Electrochemical Characterization.** The electrochemical properties of the batteries were investigated by charge–discharge measurements using a multichannel potentiostat/galvanostat (Toyo system, TOSCAT-3100). The current density used was 7.3 mA g\(^{-1}\) (0.05 C) at 25 °C. The cyclic voltammogram of the AB/LGPS/Li cell was measured using lithium metal as the counter electrode, between 3.5 and 5.0 V at 25 °C with a scan rate of 1 mV s\(^{-1}\). The interfacial resistances at the electrode/electrolyte interface were measured by EIS measurements (Solartron 1260/1287). The impedance spectra were measured after charging to 4.6 V vs Li, with applied AC voltage and frequency range of 10 mV and 10\(^{-2}\)–10\(^{-1}\) Hz, respectively. To investigate the electrochemical processes at the interfaces on the anode and cathode sides separately, EIS measurements were conducted for symmetric cells composed of Li/LGPS/Li, Li–In/LGPS/In–Li, and LNMO/LGPS/LNMO. Each cell was charged at a current density of 14.6 mA g\(^{-1}\) for 20 min prior to the EIS measurements. The interfacial species formed during electrochemical cycling were characterized by XRD (Rigaku, SmartLab, Cu K\(\alpha\) radiation) and SEM/EDS (JEOL, JSM-7800F) measurements. The samples for SEM/EDS were prepared by ion-milling (Hitachi, SMF2000). XRD and SEM/EDS measurements were conducted under airtight conditions using sample holders that were designed to protect the samples from contact with air.

3. RESULTS AND DISCUSSION

**Coating Conditions for the LiNbO\(_3\) Layer.** The SEM and EDS images of LiNbO\(_3\)-coated LNMO are displayed in Figure 1. It is clear that the Nb atoms are homogeneously distributed on the LNMO particles, indicating that the LNMO surface is uniformly covered with the LiNbO\(_3\) layer. The analytical weight ratio of LiNbO\(_3\) to LNMO is determined to be 2.4 wt % by ICP measurements, which is slightly smaller than the starting amount (3 wt %). This might be attributed to the loss of coating solution during the sol–gel coating process, because some amount of coating species could be attached to the surface of the glass container. The coating thickness of LiNbO\(_3\) is estimated to be 9.7 nm by using the total surface area of the LNMO particles and the analyzed amount of LiNbO\(_3\) by ICP measurements.

**Electrochemical Properties of the Cells.** The charge–discharge curves and average discharge voltages of the all solid-state batteries composed of LNMO/LGPS/In–Li and LNMO/LGPS/Li are shown in Figure 2. The discharge curves of the LNMO/LGPS/Li and LNMO/LGPS/In–Li battery exhibit two plateau regions at around 4 and 3.4 V, as observed in Figure 2a. These plateaus correspond to lithium intercalation accompanied by the reduction from Ni\(^{4+}\) to Ni\(^{2+}\) and Mn\(^{4+}\) to Mn\(^{3+}\), respectively. These processes are generally observed for LNMO in lithium-ion batteries with organic liquid electrolytes.\(^7\) The charge and discharge capacities are calculated to be 101 and 80 mA h g\(^{-1}\) for the 1st cycle, respectively, and gradually decrease to 71 and 57 mA h g\(^{-1}\) for the 10th cycle. In Figure 2b, the LNMO/LGPS/Li battery exhibits reversible intercalation with charge–discharge capacity and cycle retention values similar to the LNMO/LGPS/In–Li cell. In the case of the LNMO/LGPS/Li cell, the plateau regions in the discharge curves are observed at around 4.6 and 4.0 V, which are higher due to the more negative electrode potential of Li metal compared to that of the In–Li alloy (0.6 V vs Li/Li\(^+\)).\(^23\) The LNMO/LGPS/Li cell does not exhibit internal short-circuits caused by dendrite formation at the initial 10th cycle under the small current density used in this study (7.3 mA g\(^{-1}\)). The average voltages of the discharge curves for the LNMO/LGPS/Li cell remain at about 4.3 V after the 10th cycle, as observed from Figure 2c.

From the average voltage and capacity at 1st discharge, the energy density per unit weight of active material is calculated to be 392 Wh kg\(^{-1}\), which is higher than the corresponding values for LiCoO\(_2\)/LGPS (378 Wh kg\(^{-1}\)),\(^19\) LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\)/LGPS (368 Wh kg\(^{-1}\)),\(^21\) and TiS\(_2\)/LGPS (308 Wh kg\(^{-1}\)).\(^24\) This reveals that LNMO/LGPS is a promising composite cathode candidate for all solid-state batteries with high energy density. In contrast, LNMO/LGPS delivers lower discharge
capacity than the discharge capacity reported for liquid-type cells (140 mAh g⁻¹) and exhibits capacity fading during the first 10 cycles. Generally, the electrochemical reaction in all solid-state batteries initiates at the points of contact at the interface between the electrode particles and solid electrolyte particles. The reaction rate is limited by the contact area at the interface. Furthermore, the contact area may decrease during electrochemical cycling due to volume change of the active materials. To secure the contact points of the particles, chemical cycling due to volume change of the active materials is performed after electrochemical cycling. Prior to the analyses, we can speculate that the electron-insulating layer of Li₂S could stop the reduction of LGPS from Li metal by blocking electron conduction from the reduction of LGPS, leading to a reversible electrochemical reaction field at the Li/LGPS interface. Hence, we can conclude that the semicircle observed at 300 kHz is related to lithium diffusion (RSEI) in the SEI layer, which is formed by the interfacial reaction between LGPS and Li metal. We can calculate that the electron-insulating layer of Li₂S could stop the reduction of LGPS from Li metal by blocking electron conduction from the reduction of LGPS, leading to a reversible electrochemical reaction field at the Li/LGPS interface. However, Li₂S also contributes to interfacial resistance because Li₂S has lower ionic conductivity than LGPS.

To elucidate the mechanism of capacity fading, EIS analyses were performed after electrochemical cycling. Prior to the analyses, the reaction elements in the LNMO/LGPS/LNMO, Li–In/LGPS/Li–In, and Li/LGPS/Li symmetric cells are identified in Figure 3a–c. The fitting models and the refined parameters are shown in Figure S2 and Table S1 (see section S2 in the Supporting Information). The LNMO/LGPS/LNMO symmetric cell shows a semicircle, the diameter of which corresponds to the reaction resistance at the cathode/electrolyte interface (Rc). The values of capacitance and the frequency corresponding to the apex of the semicircle (fmax) are 10⁻⁵ F and 30 Hz, respectively. On the other hand, the Li–In/LGPS/Li–In and Li/LGPS/Li symmetric cells exhibit semicircles with capacitance and fmax values of 10⁻⁴ F and 10⁻⁵ Hz, respectively, which correspond to the reaction resistance at the anode/electrolyte interface (Ra). Note that the difference in the fmax values between the cathode and anode side elements is very small (within one order), which makes it difficult to distinguish between the semicircles for the two interfaces in the EIS curves for LNMO/LGPS/Ln–Li and LNMO/LGPS/Li cells. Another semicircle is observed at around 300 kHz for the Li/LGPS/Li cell. The capacitance value corresponding to this semicircle is 10⁻⁸ F, which is comparable to the value reported for the solid electrolyte interphase (SEI) layers in all solid-state lithium batteries with sulfide solid electrolyte. XRD measurements after electrochemical cycling confirm the formation of Li₂S at the Li/LGPS interface (see section S3 in the Supporting Information). Furthermore, a first-principles study has predicted the decomposition of LGPS in the low voltage region. Hence, we can conclude that the semicircle observed at 300 kHz is related to lithium diffusion (RSEI) in the SEI layer, which is formed by the interfacial reaction between LGPS and Li metal. We can calculate that the electron-insulating layer of Li₂S could stop the reduction of LGPS from Li metal by blocking electron conduction from the reduction of LGPS, leading to a reversible electrochemical reaction field at the Li/LGPS interface. However, Li₂S also contributes to interfacial resistance because Li₂S has lower ionic conductivity than LGPS. The EIS spectra of the LNMO/LGPS/Ln–Li and LNMO/LGPS/Li batteries after the 1st and 10th cycle are shown in Figure 3d,e. After the 1st cycle, the LNMO/LGPS/Ln–Li and LNMO/LGPS/Li batteries exhibit a clear semicircle at around 30 Hz. However, we cannot distinguish between the reaction resistances at the cathode and anode sides, as the preliminary
analyses with the symmetric cells indicated. Thus, we use equivalent circuit models with a cathode/anode composite reaction resistance parameter $R_E$ ($E$: electrodes). In addition, the parameter for the SEI layer is also included in the equivalent circuit model for the LNMO/LGPS/Li cell. Table 1 summarizes the values of the refined parameters. The composite capacitance values of the anode/electrolyte and cathode/electrolyte interfaces ($C_a$) are on the order of $~10^{-5}$ F, which is similar to the $C_a$ value for the LNMO/LGPS/LNMO cell rather than the $C_a$ value. This result indicates that the reaction resistance is larger at the cathode ($R_C$) than at the anode ($R_A$). This is consistent with the results for the symmetric cells. During the initial 10th cycle, the $R_E$ values increased from 783 to 3210 $\Omega$ and from 832 to 2240 $\Omega$ for the LNMO/LGPS/In–Li and LNMO/LGPS/Li batteries, respectively. For the SEI, the $C_{SEI}$ values are on the order of $10^{-8}$ F, which is consistent with that observed for the Li/LGPS/Li symmetric cell. The $R_{SEI}$ value increases to 1683 $\Omega$ after the 10th cycle. Considering that (i) the value of $R_C$ is much larger than that of $R_A$ and $R_{SEI}$ and (ii) the LNMO/LGPS/In–Li and LNMO/LGPS/Li batteries show similar cycle retention, the cathode/electrolyte interface might be the dominant factor determining deterioration in the cell performance during cycling.

**Side Reaction at 5 V in the LNMO/LGPS/AB Cell.** In Figure 2, both the batteries exhibit an irreversible capacity of ca. 20 mAh g$^{-1}$ at the 1st cycle. Irreversible capacity is often observed for all solid-state batteries with sulfide solid electrolytes during the initial cycle and corresponds to the formation of an interfacial layer accompanied by the decomposition of the solid electrolyte species. However, in the present case, irreversible capacities were observed at every cycle for the LNMO/LGPS/In–Li and LNMO/LGPS/Li batteries. Thus, we can speculate that the excessive interfacial reactions cause an increase in the interfacial resistance. To confirm this, we investigated the charging process in the constant current/constant voltage (CC/CV) mode. Figure 4 presents the charge/discharge curves of the LNMO/LGPS/Li cell under CC/CV charging. At the 1st cycle, the charge and discharge capacities are 119 and 89 mAh g$^{-1}$, which are slightly higher than those obtained under the CC charging mode. Additional lithium deintercalation from the LNMO lattice during CV charging leads to a higher discharge capacity. In contrast, the irreversible capacity also increases to 30 mAh g$^{-1}$ compared to the value observed in the CC mode (20 mAh g$^{-1}$). This result indicates that some side reactions irreversibly occur at the cathode/electrolyte interface when the cell voltage is maintained at 5 V. During the subsequent cycles, the charge–discharge capacities severely decrease and are accompanied by an increase in the over potential. This agrees with our assumption that the side reactions that occur in the high voltage region lead to capacity fading.

For further understanding the capacity fading mechanism at the cathode/electrolyte interface, ex situ XRD analysis was conducted to clarify the phase change at the interface. The diffraction peaks before cycling are attributed to LNMO and LGPS as shown in Figure 5a. After the 1st charging cycle, two diffraction peaks are observed at diffraction angles higher than those for pristine LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (Figure 5b) and correspond to the lithium deintercalated Li$_{1-x}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ and Li$_{1-x}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ ($x \sim 0$) phases. This result is consistent with the fact that lithium deintercalation from LNMO proceeds by two-phase reactions. At 1st discharge, lithiated LNMO is observed as the main phase (Figure 5c), in addition to a weak fraction peak corresponding to the Li$_{0.5}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ phase. Reversible lithium intercalation does not occur in parts of the delithiated LNMO phase during discharging. After the 10th cycle, irreversible phase change is observed more clearly (Figure 5d). It should be noted that no significant change in the peak positions is observed for the lithiated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ phase in the cycled cell. Lithium intercalation proceeds reversibly in the active LNMO domains with no structural degradation. In the case of liquid-type batteries with organic electrolyte, the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ lattice gradually shrinks due to the dissolution of Mn ions into the electrolyte during charge–discharge cycling. These results suggest that the capacity fading could be associated with the interfacial resistance of lithium conduction between LNMO and LGPS throughout the LiNbO$_3$ coating layer and/or electron conduction between LNMO and the conductive AB additive.

**Interfacial Reaction of AB with LGPS at 5 V.** To clarify the interfacial reactions of LiNbO$_3$ and AB with LGPS, CV measurements were conducted for the LiNbO$_3$/Au/LGPS and AB/LGPS composite electrodes. Au nanoparticles were used as

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Figure 4. Charge–discharge curves of a LNMO/LGPS/Li cell charged and discharged under CC–CV and CV modes, respectively. The cell was charged to 5 V by applying a constant current and was maintained at 5 V for a total of 20 h. The constant current used for charge and discharge was 7.3 mA g$^{-1}$.

Figure 5. XRD patterns of the LNMO/LGPS/AB cathode pellet (a) before cycling, (b) after 1st charging, (c) after 1st discharging, and (d) after 10th discharging. The same charge–discharge conditions as that used for the battery in Figure 4 were used in this case.
the current collector, because no electrochemical reactions involving LGPS and Au occur between 3 and 5 V. \(^9\) Figure 6 shows the CV curves of LiNbO_3/Au/LGPS and AB/LGPS at the 1st and 2nd scans. LiNbO_3/Au/LGPS shows no oxidation and reduction currents between 3.5 and 5 V. LiNbO_3 is electrochemically stable in LGPS in the high voltage region. In contrast, AB/LGPS exhibits an oxidation current in the 1st cycle and shows no significant decrease in the current during the following cycles. This reveals that no stable interfacial layer is formed at the AB/LGPS interface.

Figure 7 shows the XRD pattern of the AB/LGPS interface after electrochemical cycling. In Figure 7a, a few new peaks are observed at 32.1, 32.7, and 34.4° along with the LGPS peaks. In addition, diffraction peaks corresponding to unknown phases are detected in the XRD pattern of AB/LGPS after the CV tests, which suggests that the AB/LGPS interface is unstable.

Figure 8 shows the cross-sectional SEM image and EDS line profiles of the AB/LGPS composites from bulk LGPS to the AB/LGPS interface. Before electrochemical cycling, the ratio of P to Ge in the EDS profiles shows no significant changes from the LGPS bulk to the AB/LGPS interface (Figure 8c), which confirms that no interfacial reactions occur. In contrast, the low Ge content of the electrolyte is low at 200 to 300 nm from the AB/LGPS interface after cycling (Figure 8d). The decomposition of LGPS initiates electrochemically in the interfacial region.

Figure 9 shows a schematic illustration of the interfacial reactions occurring in the LNMO/LGPS/Li battery, as determined from the XRD, EIS, and SEM/EDS analyses. Reversible lithium intercalation occurs between the LNMO cathode and the LGPS electrolyte. The LiNbO_3 coating layer acts as a buffer to facilitate lithium diffusion at high voltages above 4.5 V, similar to the case of 4 V-class cathode/LGPS interfaces.\(^7\) In contrast, electrochemical decomposition of LGPS continuously occurs at the LGPS/AB interface above 4.5 V during the charging process, which causes irreversible capacity loss. Furthermore, the decomposition layer could isolate the delithiated Li\(_{x}\)Ni_0.5Mn_1.5O_4 (x \(\sim\) 0) phase from the lithium ion and/or electron conduction pathways in the cathode composite, resulting in severe capacity fading upon cycling. No significant decomposition is detected at the LGPS/Au interface, which suggests the extent of decomposition reaction is related to the nature of the conductive materials. On the LGPS/Li side, LGPS decomposes to form a SEI layer containing Li_2S during the initial cycles. Further decomposition of LGPS is suppressed by the SEI layer owing to its low electronic conductivity during the subsequent cycles. SEI formation results in reversible electrochemical reactions at the Li anode, although the interfacial resistance increases with SEI formation.
4. CONCLUSION

A bulk type 5 V-class all solid-state battery employing LNMO cathode, LGPS electrolyte, and Li anode has been successfully operated. The average voltage of the discharge curves of the LNMO/LGPS/Li cell remains at about 4.3 V. The ability to operate the bulk type solid-state battery at 5 V paves the way for the development of next-generation batteries with high energy density. In the LNMO/LGPS/Li battery, the electrochemical reactions at the LNMO/LiNiO2/LGPS and Li/LGPS interfaces proceed reversibly. In contrast, the decomposition products formed at the LGPS/AB interface could restrict the performance of high-voltage all solid-state batteries. The study of suitable conductive additive and sulfide solid electrolyte materials is crucial for addressing the poor cycle performance of high-voltage all solid-state batteries.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04940.

Electrochemical properties of 7.9 μm LNMO particles, procedures of EIS analyses, and XRD patterns of the anode/LGPS interfaces after 10 cycles (PDF)

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Notes

The authors declare no competing financial interest.

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