Effect of surface modification and oxygen deficiency on intercalation property of lithium nickel manganese oxide in an all-solid-state battery

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Abstract

LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were synthesized by a sol-gel method, and their intercalation property as a cathode material was investigated using all-solid-state batteries with $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte and In-Li metal anode. The LiNbO_3 coating delivered reversible lithium intercalation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through an electrochemical interface with the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. Oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ with a higher electronic conductivity than $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ improved the intercalation

activity. An all-solid-state battery consisting of 3 wt.-%-LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄₋₈/Li₁₀GeP₂S₁₂/In-Li exhibited a discharge capacity of 80 mAh g⁻¹ at the first cycle with an average discharge voltage of 4.1 V (vs. In-Li), which demonstrates the possibility of 5 V class all-solid-state batteries with a high voltage spinel cathode.

1. Introduction

Lithium ion batteries with high power and energy densities are being intensively investigated for use in new applications such as hybrid electric and electric vehicles. However, safety precautions are strictly required for such large-scale systems due to the flammable organic liquids that are used as the electrolyte. All-solid-state batteries with a nonflammable solid electrolyte have recently attracted growing interest due to their high stability. Another advantage of solid electrolytes is the wide electrochemical window over 5 V (vs. Li/Li⁺) compared to organic liquid electrolytes, which enables the use of high-voltage cathodes for high-energy-density batteries [1].

LiNi_{0.5}Mn_{1.5}O₄ and LiCoMnO₄ with a spinel-type structure are some of the most promising 5 V class cathode materials with energy densities of over 600 Wh kg⁻¹ [2,3]. All-solid-state batteries with Cr-doped LiNi_{0.5}Mn_{1.5}O₄ and LiCoMnO₄ spinel cathodes and oxide-type solid electrolytes, such as Li_{3.2}PO_{3.8}N_{0.2} and Li₃PO₄, have been reported [3,4]. However, these all-solid-state batteries have been limited to thin-film battery systems because of the low ionic conductivity of the oxide electrolytes. Recently, sulfide-type solid electrolytes have been reported to exhibit high ionic conductivity of over 10⁻² S cm⁻¹ [1,5]. After materials discovery, there

have been several studies on all-solid-state batteries comprising 4 V class cathodes and solid sulfide electrolytes for large-scale systems [6,7].

Here, we report on the reversible lithium intercalation from a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode through a solid sulfide electrolyte $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. The surface coating of amorphous LiNbO_3 on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface [8] and the formation of oxygen deficiency in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [9] were investigated to decrease interfacial resistance between the oxide cathode and sulfide electrolyte. The charge–discharge reaction of the LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode was characterized using an all-solid-state battery with a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte and In–Li alloy anode.

2. Experimental

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder (Toda Kogyo; average particle size of 9.5 μm and Brunauer–Emmett–Teller surface area of 0.53 $\text{m}^2 \text{g}^{-1}$) was annealed at 1023, 1073, and 1123 K for 10 h in air to form oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ with high electronic conductivity. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ surfaces were coated with LiNbO_3 using the sol–gel method. Li metal was dissolved in ethanol under dry Ar, and the ethanol solution was mixed with $\text{Nb}_2(\text{OC}_2\text{H}_5)_{10}$. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ samples were immersed into the solution, which was agitated using a magnetic stirrer. The weight ratios of LiNbO_3 to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ were 2, 3, and 4 wt%. The coated samples were dried under vacuum atmosphere and then heated at 623 K for 1 h in air to remove organic species.

The morphologies and crystal structures were characterized by scanning electron microscopy (SEM: JEOL, JSM-6610LV) and X-ray diffraction (XRD: Rigaku,

SmartLab) using Cu $K\alpha_1$ radiation. The electronic conductivity was characterized by direct current (DC) conductivity measurement for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ pellets. Prior to the measurement, Au blocking electrode was coated on both sides of the pellets. A constant voltage of 50 mV was applied to the $\text{Au}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Au}$ pellets. The current was recorded after the current reached a constant value to eliminate the contribution of lithium ion diffusion to the electrical conduction. X-ray photoelectron spectroscopy (XPS) was conducted using a chamber system (ULVAC-PHI, ESCA1700R) with monochromatic Al $K\alpha$ (1486.6 eV) radiation to investigate the oxide state of Mn in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$. Peak fitting was conducted assuming a Gaussian–Lorentzian curve fit with a Shirley background correction. The binding energy scale was calibrated by setting the main C 1s line of adventitious carbon at 284 eV. The amount of LiNbO_3 coating was determined by inductively coupled plasma emission spectrometry (ICP: Shimadzu, ICPS-8100).

Two-electrode all-solid-state batteries were used to investigate the electrochemical properties of the composite electrode [10]. The cathode composite comprised $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, and acetylene black with a weight ratio of 40:60:4 and it was prepared using a pot mill rotator (Nitto, ANZ-10). Two layers of the cathode composite (10 mg) and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte (100 mg) were pressed together in a polycarbonate tube, and then, In–Li alloy as the anode was pressed on the pellet. Charge–discharge measurements were performed using a multichannel potentio/galvanostat (Toyo system, TOSCAT-3100). The current density was 0.05 C (7.3 mA g^{-1}) and the cut off voltages were set at 4.4 and 2.9 V (vs. In–Li) for charge and discharge, respectively. Electrochemical impedance

spectroscopy was performed to investigate the interfacial resistance between the cathode and the solid electrolyte using an impedance analyzer with an electrochemical interface (Solartron, 1260/1287). The frequency range and the applied potential were 10^6 – 10^{-2} Hz and 10 mV, respectively.

3. Results and discussion

Figure 1 shows XRD patterns of uncoated and LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄ powders. All the reflections can be indexed on the basis of the cubic spinel structure. Lattice parameters calculated using XRD patterns are 8.170(1), 8.171(1), 8.171(2), and 8.172(2) Å for uncoated, 2 wt.%, 3 wt.%, and 4 wt.% LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄, respectively. There were no changes in the lattice parameters; this revealed that the LiNbO₃ coating caused no crystal structure change in the LiNi_{0.5}Mn_{1.5}O₄ lattice. The analytical weight ratios were smaller than the calculated values, which were calculated from the amount of starting materials (Table 1). This might be due to loss of coating solution during the sol–gel coating process because some amount of coating solution was stuck on the surface of the glass container. The coating thicknesses calculated using the analyzed amount of LiNbO₃ and the total surface area of the LiNi_{0.5}Mn_{1.5}O₄ particles were 6.5, 9.7, and 14.3 nm for the 2, 3, and 4 wt% LiNbO₃, respectively.

Figure 2 shows the first charge and discharge curves for all-solid-state batteries with uncoated and LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄. No electrochemical activity was observed for the uncoated LiNi_{0.5}Mn_{1.5}O₄. The behavior was similar to that reported previously for batteries with oxide cathodes and solid electrolytes,

wherein an interfacial layer with high resistance forms at the cathode–solid electrolyte interface [3]. In contrast, the LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄ showed charge–discharge activity. A plateau region was observed at approximately 4.0 V (ca. 4.6 V vs. Li/Li⁺), which corresponds to the Ni⁴⁺/Ni³⁺ and Ni³⁺/Ni²⁺ redox reactions due to lithium deintercalation from and intercalation into LiNi_{0.5}Mn_{1.5}O₄.

This result indicates that the LiNbO₃-coating layer sufficiently reduced the interfacial resistance between the LiNi_{0.5}Mn_{1.5}O₄ and the Li₁₀GeP₂S₁₂. The discharge capacities were 38, 53, and 26 mAh g⁻¹ for the 6.5, 9.7, and 14.3-nm-LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄, respectively. The increase in capacity for the 9.7 nm coating compared to the 6.5 nm coating indicates that the higher coverage of the LiNbO₃ layer effectively reduced the interfacial resistance. In contrast, for the 14.3-nm-LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄, the thick LiNbO₃ layer acted as a resistive layer due to the low lithium conductivity of 6×10^{-7} – 8×10^{-7} S cm⁻¹ [11].

The discharge capacity of the 9.7nm-LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄ was much smaller than that of the LiNi_{0.5}Mn_{1.5}O₄ using a liquid-type cell operated under the same voltage window (146 mAh g⁻¹) [2]. One possible reason is the low electronic conductivity of LiNi_{0.5}Mn_{1.5}O₄ (10^{-6} S cm⁻¹ at room temperature) [9], which could increase the resistance of the charge transfer reaction. **There are two main ways to improve the reaction rates of intercalation electrodes with low electronic conductivity: (i) decrease the particle size to shorten the diffusion distance for the electrons and to increase the contact area at the electrode/electrolyte interface, which can enhance reaction rates of lithium (de)intercalation [12,13]. (ii) coat conductive carbon on the electrode particles to improve surface electronic**

conductivity [14]. However, any change in particle size and/or surface coating would also change the contact area and the conditions between the electrode and the solid electrolyte, which affects the electrode properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. To investigate the effect of the electronic conductivity on the intercalation properties with a fixed condition of the composite electrode, we controlled the electronic conductivity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by the introduction of oxygen deficiencies using high-temperature annealing in air [9]. No significant changes in shape and size were observed for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ particles after annealing (See Figure S1 in supplemental information), which leads to a similar mixing condition of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ with $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ to that of the unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Figure 3 shows XRD patterns, cell parameters, electronic conductivities, and Ni 2p and Mn 2p XPS spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed in air at 1023, 1073, and 1123 K. XRD patterns shifted to lower angles after high-temperature annealing. Cell parameters increased from 8.170(1) Å for the unannealed sample to 8.181(15) and 8.184(12) Å for the 1023 K and 1073 K annealed samples, respectively. The increase in the lattice parameter corresponds to the formation of oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ [15], which includes larger Mn^{3+} ions that were changed from Mn^{4+} ions in the structure for charge balance. The 1123 K annealed sample had a much larger cell parameter of 8.205(2) Å. The 222 diffraction peak observed at 38° had a shoulder at a low-angle region [16]. The formation of the secondary $\text{Li}_y\text{Ni}_{1-y}\text{O}$ phase resulted in broad diffraction peaks and an apparently large lattice parameter [15]. To confirm the increase in the Mn^{3+} content in annealed samples, valence states of Ni and Mn ions at the particle surface were analyzed by XPS measurements. The Ni

2p peak was observed at 854.8 eV for unannealed and annealed samples, which corresponded to the oxidation state of 2+ [17]. The Mn 2p peaks contained the two components Mn^{3+} and Mn^{4+} observed at 641.9 and 643.2 eV, respectively [17]. The charge-discharge curves shown in Figure 2 exhibited no redox reaction of $\text{Mn}^{4+}/\text{Mn}^{3+}$, which clarified the tetravalent oxidation state of Mn in the pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [18]. Considering that the escape depth of a photoelectron is very small (~ 1 nm), trivalent Mn could exist only at the electrode surface for unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. It has been reported that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface reacts with moisture and carbon dioxide in air, which leads to the reduction from Mn^{4+} to Mn^{3+} [19], which is consistent with the existence of Mn^{3+} in the unannealed sample. The intensity ratio of Mn^{3+} to Mn^{4+} peaks gradually increased with the increase in the annealing temperature, which indicates the further reduction from Mn^{4+} to Mn^{3+} by the formation of oxygen vacancies at high-temperature annealing. Electronic conductivities of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at 1023 and 1073 K were 7.6×10^{-4} and $8.9 \times 10^{-4} \text{ S cm}^{-1}$, respectively, which are higher than that of unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($5.6 \times 10^{-6} \text{ S cm}^{-1}$). The increase in the Mn^{3+} content in the spinel lattice stimulates electron hopping between Mn^{3+} and Mn^{4+} , which causes a high electronic conductivity in oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ [20,21]. A slight decrease in the conductivity was observed for the 1123 K annealed sample ($4.8 \times 10^{-4} \text{ S cm}^{-1}$), which could be related to the formation of the secondary phase detected by the XRD.

Figure 4 shows the first discharge curves for an all-solid-state battery with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. All samples were coated by 3 wt. % LiNbO_3 after high-temperature annealing. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at 1023 and

1073 K showed a higher capacity at a 4 V plateau region. Furthermore, in the annealed sample, plateaus were observed at a high-voltage region compared with the unannealed sample. These results indicate that the high electronic conductivity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ improved lithium intercalation into $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte. In addition to the 4 V plateau region, another plateau was observed at approximately 3.4 V for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, which could be attributed to lithium intercalation accompanied by the reduction from Mn^{4+} to Mn^{3+} that has been generally observed for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ in lithium ion batteries with organic liquid electrolytes [18]. The discharge capacity of the 3.4 V plateau increased with the annealing temperature. This is in agreement with the higher $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at a higher temperature, which was indicated by XRD and XPS results. Total discharge capacities of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at 1023 and 1073 K were 69 and 80 mAh g^{-1} , respectively, which were higher than that of the unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (53 mAh g^{-1}). In contrast to the 1023 and 1073 K annealed samples, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at 1123 K showed a small capacity of 38 mAh g^{-1} . The small capacity could be caused by the poor electrochemical activity of the secondary phases such as $\text{Li}_{1-y}\text{Ni}_y\text{O}$, Li_2MnO_3 , and Mn_2O_3 [16].

Figure 5 shows the electrochemical impedance spectra of the all-solid-state batteries with LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ after the first charging to 4.1 V. A semicircle with a low frequency of approximately 10 Hz was observed for all batteries. Considering that the $\text{Li-In}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ interfaces were fabricated by the same condition, changes in cell resistances should be related to the reactions at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ interfaces. The resistances calculated from the

semicircles were 1873 and 870 Ω for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ synthesized at 1023 and 1073 K, respectively, which were smaller than those of unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (3377 Ω). This result indicates that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ with high electronic conductivity decreases the charge transfer resistance at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ interface.

Figure 6 shows the capacity retention of all-solid-state batteries using unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. The discharge capacities decreased with voltage fading during the initial 5 cycles, independently of the annealing condition. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at 1073 K showed the capacity retention at the twentieth cycle of 43.9 % of the first discharge capacity. Oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ has been reported to be unsuitable for practical use in liquid-type lithium batteries because two Mn^{3+} ions undergo disproportionation to Mn^{2+} and Mn^{4+} ions, followed by dissolution of Mn^{2+} into the liquid electrolyte [22,23]. As the conductivity of manganese ions in a solid electrolyte should be negligibly small, the electrode fading caused by the disproportionation is expected to be suppressed at solid/solid interfaces. No significant impact of the oxygen deficiency on the cycle retention was observed, which agrees with this expectation. Furthermore, the all solid-state batteries with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ showed the small voltage fading upon the cycles, compared to batteries with conventional organic electrolytes [22,23]. Thus, we presume that the fading is associated with side reactions between the electrode and solid electrolyte interfaces such as decomposition of the coating layer and/or the solid electrolyte at high voltages. Further understanding of the interfacial reactions could be crucial to

develop high-voltage all solid-state batteries with oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$.

4. Conclusion

Intercalation activity of spinel-type $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes through the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte has been investigated using a bulk-type all-solid-state battery. The surface coating of LiNbO_3 on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is an effective method to form an electrochemically active interface with the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte. The oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ phases deliver higher charge and discharge capacities than stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. An all-solid-state battery consisting of LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{In-Li}$ achieves a discharge capacity of 80 mAh g^{-1} with an average voltage of 4.1 V at the first cycle. Surface modification by the LiNbO_3 coating and the introduction of oxygen deficiency is a key to improve the lithium intercalation properties of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode through the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte.

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Tables

Table 1. Fractions of LiNbO_3 in starting materials and products and average layer thicknesses.

Fraction of LiNbO_3 in starting material	2 wt%	3 wt%	4 wt%
Fraction of LiNbO_3 in product	1.6 wt%	2.4 wt%	3.5 wt%
Average thickness of LiNbO_3 on particles	6.5 nm	9.7 nm	14.3 nm

Figure captions

Figure 1. XRD patterns of uncoated and 2, 3, and 4 wt% LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Figure 2. The first charge and discharge curves of all-solid-state batteries with uncoated and LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Figure 3. XRD patterns, cell parameters, electric conductivities, and XPS spectra of (a) unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at (b) 1023, (c) 1073, and (d) 1123 K in air.

Figure 4. The first discharge curves of all-solid-state batteries using unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. All samples were coated with 3 wt% LiNbO_3 layer after annealing. The In–Li alloy was used as an anode, and the current density was 0.05 C.

Figure 5. Nyquist plots of the all-solid-state batteries with 3 wt% LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ after the first charging to 4.1 V.

Figure 6. Variation of discharge capacities with cycle number for all-solid-state batteries using unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. All samples were coated with 3 wt% LiNbO_3 layer

after annealing. The In–Li alloy was used as an anode, and the current density was 0.05 C. Inset depicts the discharge curves of 1073 K-annealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$.

Figure 1. XRD patterns of uncoated and 2, 3, and 4 wt% LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Figure 2. The first charge and discharge curves of all-solid-state batteries with uncoated and LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Figure 3. XRD patterns, cell parameters, electric conductivities, and XPS spectra of (a) unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at (b) 1023, (c) 1073, and (d) 1123 K in air.

Figure 4. The first discharge curves of all-solid-state batteries using unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. All samples were coated with 3 wt% LiNbO_3 layer after annealing. The In-Li alloy was used as an anode, and the current density was 0.05 C.

Figure 5. Nyquist plots of the all-solid-state batteries with 3 wt% LiNbO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ after the first charging to 4.1 V.

Figure 6. Variation of discharge capacities with cycle number for all-solid-state batteries using unannealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ annealed at various temperatures. All samples were coated with 3 wt% LiNbO_3 layer after annealing. The In-Li alloy was used as an anode, and the current density was 0.05 C. Inset depicts the discharge curves of 1073 K-annealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$.