Fabrication and electrochemical properties of a LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ composite electrode for use in all-solid-state batteries

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Abstract

Composite positive electrodes composed of a LiNbO_3 -coated LiCoO_2 active material and a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte were fabricated using a mill pot rotator, applying varying rotation rates, mixing durations and mill ball sizes. Mild grinding with a low rotation rate prevented significant aggregation of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ particles during the mixing process, leading to a well-dispersed composite with a large contact area between the LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. An all-solid-state battery using the optimized composite cathode with the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte and an In-

Li anode delivered a first discharge capacity of 124 mAh g⁻¹, which is equal to the theoretical value for LiCoO₂.

1. Introduction

All-solid-state lithium batteries show significant promise in large-scale applications such as plug-in hybrid electric vehicles and purely electric vehicles due to their inherent safety and high volumetric energy density [1-3]. However, the power density of these batteries, which is generally much lower than that of conventional lithium-ion batteries, must be addressed to allow their widespread use. The main rate determining step in all-solid-state batteries is the diffusion of lithium in the solid electrolyte since the lithium ion conductivity in such materials is low compared to that in liquid organic electrolytes, and this limits both the capacity and current density of the associated charge/discharge reactions [4,5,6]. Recently, it has been reported that a new sulfide solid electrolyte, Li₁₀GeP₂S₁₂ (LGPS), exhibits an extremely high lithium ionic conductivity of 12 mS cm⁻¹ at room temperature, a value that exceeds even those of the organic electrolytes [10-14]. All-solid-state batteries with LGPS electrolytes therefore allow for possible improvements in power density [15]. Another rate determining step in these devices is the lithium diffusion at the point of contact interface between the electrode and electrolyte particles since a small contact area will reduce the reaction rates at the interface. For this reason, the positive electrodes in these devices are composed of an active material together with a solid electrolyte so as to increase the contact area. Hence, the fabrication process of such composite electrodes should be investigated with the aim of obtaining a highly dispersed composite electrode exhibiting minimal aggregation [6-9, 15-17]. However, there

have been few reports investigating all-solid-state batteries incorporating LGPS electrolytes, so little is known about the key factors associated with the fabrication process that may be able to improve the battery performance.

Here we report the effects of the LiCoO_2 and LGPS mixing conditions on the charge/discharge properties of a LiCoO_2 /LGPS composite cathode/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte/In-Li anode cell. The composite electrodes in this study were fabricated using a mill pot rotator, applying various rotation rates. The morphologies of the composite cathodes were investigated by scanning electron microscopy (SEM), and electrochemical charge/discharge and ac impedance measurements were performed to determine the interfacial resistance between the composite electrode and the electrolyte. The key factors involved with developing an all-solid-state battery showing a high discharge capacity are discussed based on the mixing conditions and resulting electrochemical performances of the LiCoO_2 /LGPS composite cathodes.

2. Experimental Section

The LiCoO_2 surface was coated with a thin LiNbO_3 layer using a fluidized bed granulator (Powrex, MP-01) to suppress formation of a highly resistive layer between the LiCoO_2 and LGPS [7]. LiCoO_2 powder (500 g, average particle size (d_{50}): 16.7 μm , surface area: 0.23 $\text{m}^2 \text{g}^{-1}$) was used as the starting material. An ethanol alkoxide solution consisting of anhydrous ethanol (39.68 g), Li metal (0.23 g) and niobium pentaethoxide (10.96 g) was sprayed onto the LiCoO_2 at a rate of 2 g min^{-1} . The weight ratio of the coating layer to the LiCoO_2 was controlled by the duration of the spraying process. Each sample was annealed at 350 $^\circ\text{C}$ for 1 h in air to remove any organic contaminants. X-ray diffraction (XRD)

patterns of pristine, coated and annealed samples were acquired with an X-ray powder diffractometer (Rigaku, Smart lab) using Cu $K\alpha_1$ radiation. The morphology of each sample was observed by SEM (VE-8600, Keyence).

Composite positive electrodes of LiNbO_3 -coated LiCoO_2 and LGPS were prepared to improve the lithium ion conduction between the LiCoO_2 and the LGPS solid electrolyte. The LGPS powder was synthesized using a previously reported procedure [10] and was subsequently manually ground for 10 min in an agate mortar to decrease the particle size. A mill pot rotator (ANZ-10S, Nitto) was used to fabricate the composites because this device allowed ready control over the mixing conditions by changing the rotating speed, the size of the agate mill balls and the grinding time. Mixtures of LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ in a weight ratio of 70:30 were ground under the following conditions: rotation rates of 140, 250 or 350 rpm, a ball size of 3 mm (ϕ) and grinding times of 10, 20, 25 or 30 min. The morphologies of the resulting composites were assessed by SEM (JSM-6610LV, JEOL).

Two-electrode all-solid-state batteries were used to investigate the electrochemical properties of the composite electrodes [8]. These batteries were fabricated using LGPS and In-Li metal as the solid electrolyte and the negative electrode, respectively. In making these batteries, a 100 mg sample of the LGPS electrolyte was pressed into a pellet with a 10 mm diameter and aluminum foil and aluminum mesh were employed as current collectors for the positive electrode. Composite electrode powder (10 mg) was pressed onto the LGPS electrolyte pellet at a pressure of 555 MPa. The negative electrode was composed of Li foil (5 mm ϕ , 0.1 mm) and In foil (10 mm ϕ , 0.1 mm) on a Cu mesh current collector. Finally, the three layers (positive electrode/electrolyte/negative

electrode) were pressed together under a pressure of 19 MPa to fabricate the all-solid-state batteries. All the above processes were performed in a dry Ar-filled glovebox (DBO-1.5-T1000, Miwa).

Charge/discharge measurements were performed at 25 °C using a multi-channel potentiogalvanostat (TOSCAT-3100, Toyo system). The upper and lower cutoff voltages were 3.6 and 1.9 V, which could correspond to 4.2 V and 2.5 V vs. Li/Li⁺, respectively, with an applied current rate of 7 mA g⁻¹ (0.05 C). Specific capacities were calculated based on the active mass of LiCoO₂. The interfacial condition between the In/Li and the LGPS electrolyte gradually changed with the cycle number, as we will show later. The differences in the performance among composite cathodes were evaluated at the first cycle to minimize effects of the anode condition on the charge/discharge capacity. Electrochemical impedance spectroscopy (EIS) measurements were performed for batteries after the 10th and 20th discharging using an impedance analyzer with an electrochemical interface (1260/1287, Solartron). The applied voltage during these trials was 10 mV and the frequency range was 0.1 to 10⁵ Hz.

3. Results and discussion

Figure 1 shows SEM images and XRD patterns of LiCoO₂ powders before and after spray coating with LiNbO₃. Whereas the pristine LiCoO₂ powder had very flat surfaces and sharp particle edges (Fig. 1(a)), the spray-coated LiCoO₂ powder exhibited rounded edges (Fig. 1(b)). The XRD patterns showed no changes in the peak positions and intensities after the coating process (Fig 1(c, d)), confirming that no chemical reaction occurred between the LiCoO₂ and the LiNbO₃ during the coating and annealing processes. Table 1 summarizes the

weight ratios of the LiNbO_3 layer to the LiCoO_2 and the average thicknesses of the LiNbO_3 layers. The LiNbO_3 weight ratios in the products were determined by ICP analyses, and the average coating thicknesses were calculated using the weight ratio in the product and the surface area ($0.23 \text{ m}^2 \text{ g}^{-1}$) together with the weight of the LiCoO_2 powder (500 g) employed during spray coating. As the spray coating duration increased, the LiNbO_3 weight ratios were gradually reduced below the starting values. In this study, we obtained LiNbO_3 -coated LiCoO_2 with weight ratios ranging from 0.12 to 1.76 wt%.

A 1.76 wt% LiNbO_3 -coated LiCoO_2 sample was used to investigate the effects of mixing conditions when combining this material with the LGPS electrolyte to fabricate the composite positive electrodes. Figure 2 shows a schematic of the mixing process using a mill pot rotator, along with SEM images of the LiCoO_2 /LGPS composites ground for 30 min at different rotation rates. Small LGPS particles are seen to have been dispersed on each LiCoO_2 particle in the composite ground at 140 rpm (Fig 2(b)). In contrast, some LGPS aggregates are observed on the composites as the rotation rate is increased (Fig. 2(c, d)). Thus mild mixing with a low rotation rate of 140 rpm generated well-dispersed composite electrodes. Figure 3a shows the first charge-discharge curves obtained from 1.76 wt% LiNbO_3 -coated LiCoO_2 /LGPS composite positive electrodes fabricated at different rotation rates. A plateau was observed in the vicinity of 3.4 V (vs. In-Li anode) in these curves, corresponding to reversible lithium (de)intercalation into the LiCoO_2 . The composite ground at 140 rpm exhibited a first discharge capacity of 105 mAh g^{-1} , while the first discharge capacities decreased to 99 and 71 mAh g^{-1} for the composites ground at 250 and 350 rpm, respectively. The well-dispersed composite electrodes could have had a greater

contact area between the LiCoO_2 and LGPS, which would serve to increase the utilization efficiency of the LiCoO_2 active material in the composite electrode. Effects of the grinding time on the charge/discharge capacity were investigated at a fixed rotation rate of 140 rpm (Fig. 3(b)). The first discharge capacity increased from 65 to 108 mAh g^{-1} when the grinding time was increased from 10 to 20 min, and thus a short time grinding under the mild conditions led to insufficient mixing. No significant change in the capacity was observed when increasing the grinding time from 20 to 30 min. Longer mixing times over 20 min with low grinding energy gave better mixing of the LiCoO_2 and LGPS with no LGPS aggregation.

To allow fabrication of the $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}$ composites under optimal mixing conditions, the LGPS was ground to reduce the particle size before mixing with the $\text{LiNbO}_3/\text{LiCoO}_2$. Figure 4 presents SEM images of LGPS powders ground for different time spans and the first charge/discharge curves of the $\text{LiCoO}_2/\text{LGPS}$ composite electrode fabricated using each LGPS powder. The LGPS powder ground for 5 min (LGPS5) consisted of primary particles with particle sizes over 5 μm as well as micro-sized aggregates of these nanosized primary particles. The $\text{LiCoO}_2/\text{LGPS5}$ composite electrode showed a low discharge capacity of 87 mAh g^{-1} compared to the theoretical capacity of 125 mAh g^{-1} when the LiCoO_2 cathode is charged to 4.2 V vs. Li/Li^+ [18]. This result indicated insufficient dispersion of the LGPS, generating a reduced contact area with the LiCoO_2 due to the large sizes of the primary particles and the aggregates. The LGPS powder ground for 10 min (LGPS10) consisted of small particles less than 2 μm in size, and no severe aggregation was observed. The discharge capacity of the $\text{LiCoO}_2/\text{LGPS10}$ increased to 124 mAh g^{-1} , corresponding to the theoretical capacity. Thus the use of small LGPS particles with no aggregation led to a highly-dispersed composite

electrode with a large contact area between the LiCoO_2 with LGPS. The particle size gradually decreased with increasing grinding time from 10 min through 30 to 120 min, although aggregates of the small LGPS particles increased at longer grinding times. The discharge capacities of the $\text{LiCoO}_2/\text{LGPS}_{30}$ and $\text{LiCoO}_2/\text{LGPS}_{120}$ devices were 104 and 102 mAh g^{-1} , respectively. Thus prolonged grinding of the LGPS could not improve the utilization efficiency of the LiCoO_2 active material. This result indicated that the aggregation of LGPS had a greater impact than the particle size with regard to the fabrication of $\text{LiCoO}_2/\text{LGPS}$ composites with high electrochemical reactivity.

Figure 5(a-d) shows the charge/discharge curves obtained from $\text{LiCoO}_2/\text{LGPS}_{10}$ composite electrodes using LiCoO_2 coated with LiNbO_3 , applying varying weight ratios between the LiNbO_3 and LiCoO_2 of 0.12, 0.48, 1.16 and 1.76 wt%. The rotation rate and grinding time for mixing were fixed at 140 rpm and 30 min, respectively. The uncoated LiCoO_2 electrode exhibited no reversible capacity (see Supporting Information), while charge/discharge reactions were observed with the composite electrode incorporating the 0.12 wt%- LiNbO_3 coated LiCoO_2 . It has been proposed that a high resistance layer is formed by ionic diffusion from a sulfide electrolyte to LiCoO_2 due to a large difference in electrochemical potentials of Li between the sulfide and the oxide. [6,7,19]. The LiNbO_3 coating, however, suppresses the interfacial layer formation, leading to reduced reaction resistance. Similar to previous reports regarding other sulfide electrolytes, an interfacial layer with a high resistance was formed between the LiCoO_2 and the LGPS electrolyte, but this resistance was decreased by the application of the LiNbO_3 layer. The discharge capacity of the 0.12 wt%- $\text{LiNbO}_3/\text{LiCoO}_2$ specimen increased from 35 to 74 mAh g^{-1} from the first to 20th cycle with decreasing overvoltages.

Compared to this, weight ratios of 0.48, 1.16 and 1.76 wt% LiNbO_3 to LiCoO_2 showed much higher discharge capacities of 124, 97 and 95 mAh g^{-1} at the first cycle. Furthermore, the overvoltages of the 0.48, 1.16 and 1.76 wt% $\text{LiNbO}_3/\text{LiCoO}_2$ were much smaller than that of the 0.12 wt% $\text{LiNbO}_3/\text{LiCoO}_2$. These results confirmed that the interfacial resistance could be changed by varying the thickness of the coating layer. Figure 5e summarizes the variations in the first discharge capacities of $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}$ composite electrodes with varying amounts of the LiNbO_3 coating layer.

Finally, we investigated the origin of the capacity fading of the $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}$ composite electrodes. Figure 6(a, b) shows Nyquist plots of the electrochemical impedances of an all-solid-state battery composed of $\text{LiNbO}_3(0.48 \text{ wt}\%)-\text{LiCoO}_2/\text{LGPS}/\text{In-Li}$ after the 10th and 20th discharges. Two semicircles were observed at approximately 500 and 1 Hz. The electrochemical impedance spectra of $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}/\text{LiNbO}_3/\text{LiCoO}_2$ and $\text{In-Li}/\text{LGPS}/\text{In-Li}$ symmetric cells exhibited a semicircle with a characteristic frequency of 500 and 1.5 Hz, respectively, shown in Figs. 6(c, d). Hence, the diameters of the semicircles observed in the vicinity of 500 and 1 Hz for each cell are attributed to the interfacial resistances between the $\text{LiNbO}_3/\text{LiCoO}_2$ cathode (R_c) and the LGPS electrolyte and between the In-Li anode and the LGPS electrolyte (R_a), respectively. These characteristic frequency values are similar to those of the interfaces of LiCoO_2 and In-Li with other sulfide electrolytes [2,17]. The R_a value increased from 690 Ω at the 10th discharge to 2420 Ω at the 20th discharge. In contrast, no significant increase in the R_c value was observed from the 10th discharge (280 Ω) to the 20th discharge (290 Ω). This result indicates that the capacity fading of the $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}/\text{In-Li}$ cell is caused by an increase in

the resistance of the In-Li/LGPS interface. A first principles calculation suggests that the LGPS is unstable at **low electrochemical potential of Li** and is decomposed to another phase [20]. An interfacial layer with a high resistance could thus be formed at the In-Li/LGPS interface due to the LGPS decomposition induced by the contact with the In-Li anode (at about 0.6 V vs. Li/Li⁺) [21]. The In-Li/LGPS interface should thus also be modified to improve the cycling stability of LiNbO₃/LiCoO₂/LGPS/In-Li batteries.

4. Conclusion

A composite cathode consisting of a LiNbO₃-coated LiCoO₂ active material and a LGPS super lithium ionic conductor was fabricated under various conditions to clarify the key parameters associated with the improvement of the reaction efficiency of LiNbO₃/LiCoO₂/LGPS/In-Li cells. The effects of the fabrication process on the charge/discharge capacities of the batteries may be summarized as follows.

- (i) The LGPS particles readily aggregate during the mixing process. Highly dispersed composites were successfully obtained by mild grinding applying a mill pot rotation rate of 140 rpm for 30 min with 3 mm ϕ agate balls.
- (ii) The weight ratio of the LiNbO₃ layer to the LiCoO₂ affects the resistance at the LiCoO₂/LGPS interface. The weight ratio should be over 0.5 wt% to decrease the interfacial resistance.
- (iii) The first discharge capacity of the composite electrode fabricated with the optimized conditions was 124 mAh g⁻¹ when operating at a current density of 7 mA g⁻¹.

- (iv) The capacity fading observed for the cell using the $\text{LiNbO}_3/\text{LiCoO}_2/\text{LGPS}$ composite cathode was primarily caused by the increase in the resistance to lithium diffusion at the In-Li anode/the LGPS electrolyte interface.

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

Fraction of LiNbO_3 in starting material (wt%)	0.11	0.59	1.34	2.49
Fraction of LiNbO_3 in product (wt%)	0.12	0.48	1.16	1.76
Average thickness of LiNbO_3 on LiCoO_2 particles (nm)	1.0	4.8	11.4	17.4

Figure captions

Figure 1. SEM images and XRD patterns of (a, c) uncoated LiCoO_2 and (b, d) LiNbO_3 -coated LiCoO_2 . The weight ratio of LiNbO_3 to LiCoO_2 was 0.12 wt% in the product.

Figure 2. (a) Schematic of the LiCoO_2 and LGPS mixing process using a mill pot rotator. SEM images of 1.76 wt% LiNbO_3 -coated LiCoO_2 /LGPS mixtures ground with rotation rates of (b) 140, (c) 250 and (d) 350 rpm. The grinding time was 30 min in all cases. The large, dark grey particles and small, light grey particles in (b-d) correspond to LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, respectively.

Figure 3. The first charge/discharge curves of 1.76wt% LiNbO_3 -coated LiCoO_2 /LGPS composite electrodes fabricated (a) by grinding for 30 min at rotating rates of 140 rpm, 250 rpm, and 350 rpm and (b) by grinding for 10, 20, and 30 min at the rotating rate of 140 rpm. The constant current density used was 7 mA g^{-1} .

Figure 4. SEM images of LGPS powders pre-ground in a mortar for different times of (a) 5 min, (b) 10 min, (c) 30 min, and (d) 120 min. (e) The first charge/discharge curves of 0.48wt% LiNbO_3 -coated LiCoO_2 /LGPS composite

electrodes using each LGPS powder. The composites were fabricated at a rotating rate of 140 rpm for 30 min. The constant current density used was 7 mA g⁻¹.

Figure 5. (a-d) Charge/discharge curves of LiNbO₃-coated LiCoO₂/LGPS composite electrodes fabricated at a rotating rate of 140 rpm for 30 min. Weight ratios of LiNbO₃ to LiCoO₂ were (a) 0.12wt%, (b) 0.48wt%, (c) 1.16wt%, and (d) 1.76wt%. The constant current density used was 7 mA g⁻¹. (e) Variation of the first discharge capacity with calculated thickness of LiNbO₃ coating.

Figure 6. Electrochemical impedance spectra of LiNbO₃(0.48wt%)/LiCoO₂/LGPS /In-Li cell after (a) tenth and (b) twentieth discharging and of (c) LiNbO₃-LiCoO₂/LGPS/LiNbO₃-LiCoO₂ and (d) In-Li/LGPS/In-Li symmetric cells.

Figure 1. SEM images and XRD patterns for uncoated LiCoO_2 (a,c) and LiNbO_3 coated LiCoO_2 (b,d). The weight ratio of LiNbO_3 to LiCoO_2 was 0.12wt% in the starting solution.

Figure 2. (a) Schematic of mixing process of LiCoO_2 and LGPS using a mill pot rotator and SEM images of 1.76wt% LiNbO_3 -coated $\text{LiCoO}_2/\text{LGPS}$ mixtures ground under different rotating rates of (b) 140 rpm, (c) 250 rpm, and (d) 350 rpm. The ground time was 30 min. Large particles with dark gray color and small particles with white gray color in Fig. (b-d) correspond to LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, respectively.

Figure 3. The first charge/discharge curves of 1.76wt% LiNbO₃-coated LiCoO₂/LGPS composite electrodes fabricated (a) by grinding for 30 min at rotating rates of 140 rpm, 250 rpm, and 350 rpm and (b) by grinding for 10, 20, and 30 min at the rotating rate of 140 rpm. The constant current density used was 7 mA g⁻¹.

Figure 4. SEM images of LGPS powders pre-ground in a mortar for different times of (a) 5 min, (b) 10 min, (c) 30 min, and (d) 120 min. (e) The first charge/discharge curves of 0.48wt% LiNbO₃-coated LiCoO₂/LGPS composite electrodes using each LGPS powder. The composites were fabricated at a rotating rate of 140 rpm for 30 min. The constant current density used was 7 mA g⁻¹.

Figure 5. (a-d) Charge/discharge curves of LiNbO₃-coated LiCoO₂/LGPS composite electrodes fabricated at a rotating rate of 140 rpm for 30 min. Weight ratios of LiNbO₃ to LiCoO₂ were (a) 0.12wt%, (b) 0.48wt%, (c) 1.16wt%, and (d) 1.76wt%. The constant current density used was 7 mA g⁻¹. (e) Variation of the first discharge capacity with calculated thickness of LiNbO₃ coating.

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Supporting Information for Reviewers

Fig. S1 Charge/discharge curves of uncoated LiCoO₂/LGPS composite electrodes fabricated at a rotation rate of 140 rpm for 30 min. The LiCoO₂ powder was annealed at 350 °C in air before grinding with the LGPS. A constant current density of 7 mA g⁻¹ was applied.

Fig. S2. XRD patterns of the LGPS after ground for 30 min under different rotation rates of 140, 250 and 350 rpm.