Preparation of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$/Li$_3$PS$_4$ cathode composite particles using a new liquid-phase process and application to all-solid-state lithium batteries

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The sulfide based electrolyte Li$_3$PS$_4$ was directly produced on the cathode active materials LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) using the SEED method which was a new liquid-phase process developed by applying liquid-phase shaking method. The generation of PS$_4^{3-}$ unit in the SEED process was confirmed by in-situ Raman spectroscopy measurement. The generation of β-Li$_3$PS$_4$ on NMC was shown using X-ray elemental mapping, transmission electron microscope observation and electron diffraction analysis. An all-solid-state cell composed of [90NMC·10Li$_3$PS$_4$ by SEED composite $|$ Li$_3$PS$_4$ $|$ In] was fabricated. It showed promising charge–discharge cycle performance, which could be ascribed to good retention of electrochemical contact at the interface between NMC and the electrolyte during the cycling.

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1. Introduction

For all-solid-state lithium batteries, the electrochemical contact of the interface between active materials and solid electrolytes is one of the most important themes. It is difficult to coat the active material uniformly with the solid electrolyte. The sulfide-based solid electrolytes are currently well known as excellent candidates for all-solid-state battery and extensively studied because of their high lithium ionic conductivity comparable to organic electrolytes and suitable plasticity for good contact at the interface. The various methods for composite fabrication of cathode active materials and solid electrolytes have been extensively studied. The tightly packed composites were prepared using cold-pressing at room temperature or hot-pressing at relatively low temperature. However, volume change in the composite during charge–discharge cycles causes an increase in vacancy between active materials and electrolytes, which results in a decrease in the capacity of the all-solid-state battery. Thus, it is essential to develop a new concept to design the composite electrodes which can be following up such a volume change during the charge–discharge cycling.

Recently we have developed a new process, liquid-phase shaking (LS) method, to prepare electrolytes in the Li$_2$S–P$_2$S$_5$ system. The electrolyte prepared by LS method can be mixed homogeneously with active materials because the particles of the resultant electrolyte are very fine. In this study, we propose a new preparation method of active materials and solid electrolytes composite based on the liquid phase process, which is named “SEED method”. In the SEED method, the solid electrolyte is prepared from the seed materials, which are nuclei precipitated on the surface of the active material and act as scaffold to prepare the electrode composite as shown in Fig. 1. Li$_3$PS$_4$ (LPS) solid electrolyte with excellent plasticity was prepared by the SEED method on the surface of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) positive electrode active material with high-potential. The structure of the NMC–LPS composite thus obtained and its battery characteristics were also evaluated in the present study.

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2. Experimental

First, Li$_2$S (99.9%, Mitsuwa) was added to ethanol [EtOH, Super Dehydrated (99.5%), Wako] and dissolved by stirring treatment for 30 min. NMC (1 wt% LiNbO$_3$ coated, JST-ALCA-SPRING) was immersed in the obtained Li$_2$S EtOH solution and then evacuated at 170°C for 2 h to evaporate EtOH to prepare the NMC–Li$_2$S composite. Retention of Li$_2$S after EtOH evaporation was confirmed by using X-ray diffraction (XRD) measurement (Ultima IV, Rigaku). Second, Li$_2$S and P$_2$S$_5$ (99%, Merck) were mixed at a molar ratio of Li$_2$S:P$_2$S$_5$ = 1:1 and dissolved in ethyl propionate (EP) by ultrasonic treatment (500 W, 23 Hz) for 1 h to obtain a transparent yellow solution. The NMC–Li$_2$S composite was added to the obtained transparent yellow Li$_2$S–1P$_2$S$_5$ EP solution, and agitation treatment (stirring 500 rpm at 50°C) was carried out for 6 h. Li$_2$S added to EtOH was fixed to be twice as much as the total amount of P$_2$S$_5$ in the EP solution (total Li$_2$S:P$_2$S$_5$ molar ratio in the EP solution was 3:1), and NMC: LPS weight ratio was expected as 90:10. The NMC coated with LPS precursor was heat treated at 170°C for 2 h under reduced pressure after evaporating the solvent EP at room temperature under reduced pressure. The gray powders of NMC–LPS composites were obtained.

To confirm the formation reaction of LPS from Li$_2$S and Li$_2$P$_2$S$_6$ in EP during SEED process, in-situ observation of suspensions using Raman spectroscopy (NRS-3100, Jasco) was carried out. Twice amount of Li$_2$S in molar ratio was added to the solution of ‘Li$_2$S:P$_2$S$_5$ = 1:1 (Li$_2$P$_2$S$_6$) in EP’ in the quartz sealed container with a cap. The Raman spectra were detected each time during stirring from 0 to 6 h. The prepared composites were characterized using scanning electron microscopy (SEM; S4800, Hitachi). X-ray elemental maps were taken using an energy dispersive X-ray spectroscopy (EDXS, Horiba) detector attached to the SEM system. The transmission electron microscope (TEM) image and the electron diffraction patterns were obtained using JEM-2100F field-emission-type TEM (JEOL). The XRD pattern of LPS was also obtained.

An all-solid-state cell using the prepared 90 NMC–10LPS composite as a positive electrode, LPS prepared by the liquid-shape mixing method invented by our laboratory as an electrolyte layer and Indium foil (In, 99.99%, Nilaco) as a counter electrode was fabricated. The composed electrodes for electrochemical measurements were prepared by uniaxial pressing (about 80 mg of sample dried at 170°C) into pellets of about 0.6 mm in thickness and 10.0 mm in diameter at a pressure of 330 MPa (at room temperature). The prepared pellet was placed in a holder made from polyetheretherketon with two stainless steel rods. The charge–discharge test of the cells was conducted at a constant current at 0.1 C. In order to verify the effect of composite by the SEED method, the same test was also carried out on all-solid-state cell using a positive electrode composite prepared by hand mixing. All processes for preparing the composites and fabricating the all-solid-cells were performed in an Ar-filled dry box. The cell was placed in a glass tube filled with Ar when the electrochemical characterizations were performed.

3. Results and discussion

Figure 1 shows the concept of the preparation procedure of NMC–LPS composite by SEED method. Li$_2$S, as a seed material, coated on active materials NMC reacts with the ‘Li$_3$P$_2$S$_6$ in EP’ solution and finally LPS (molar ratio Li$_2$S:P$_2$S$_5$ = 3:1) is formed on the surface of NMC. The solution of ‘Li$_2$P$_2$S$_6$ in EP’ prepared with Li$_2$S and P$_2$S$_5$ (molar ratio Li$_2$S:P$_2$S$_5$ = 1:1) in EP is transparent and homogeneous. In the case of other ratios, some sediments were precipitated at Li$_2$S:P$_2$S$_5$ = 6:4, and the solution was separated into two layers at Li$_2$S:P$_2$S$_5$ = 3:7. It is consequently suggested that Li$_2$S:P$_2$S$_5$ ratio in the EP solution is quite important to induce uniform reaction with Li$_2$S on NMC.

To confirm the formation of LPS without NMC, Li$_2$S was added solely to the solution of ‘Li$_3$P$_2$S$_6$ in EP’ and the changes in profile of the suspension were examined with in-situ Raman spectroscopy. Figure 2 shows Raman spectra of the suspensions after Li$_2$S was added to ‘Li$_2$P$_2$S$_6$ in EP’ and EP. The intensity of all suspension’s spectra was normalized with the highest peak intensity at around 2940 cm$^{-1}$ assigned to the vibration of CH$_3$ group in EP.$^{[10]}$ All of the suspensions and EP solvent have bands at around 369 cm$^{-1}$ assigned to EP in their spectra. The spectrum immediately obtained after adding Li$_2$S (0 h) shows a band at around 389 cm$^{-1}$, which is assigned to P$_2$S$_6^{2-}$ ions$^{[8,11]}$ and gradually dwindles. It is considered that the dimer of phosphorus sulfides such as P$_2$S$_6^{2-}$ ions and P$_2$S$_7^{4-}$ ions have been generated in the ‘Li$_2$P$_2$S$_6$ in EP’ before adding Li$_2$S. Because the generated dimeric phosphorus sulfide ions have higher solubility in EP, the solution of ‘Li$_2$P$_2$S$_6$ in EP’ is homogeneous and the ions easily react with Li$_2$S added into the solution to form PS$_4^{3-}$ ions. With the

![Fig. 1. The concept of the preparation procedure of NMC–LPS composite by the SEED method. NMC: LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, EP: ethyl propionate, LPS: Li$_3$PS$_4$.](image)
spectrum of 3 h after the addition of Li$_2$S, a band located at around 419 cm$^{-1}$ appeared and gradually increased. This band is assigned to PS$_4^{3-}$ ions, indicating that the dimer ions cleaved with Li$_2$S to form the monomer ions and then LPS was finally generated in 6 h. That should be an important reason for the formation of LPS under mild conditions without high temperature or high mechanical impact.

**Figure 3** shows an SEM image and EDXS elemental mappings of P and S of the prepared active material NMC-electrolyte LPS composite produced by SEED method. There are some sheet-like solid particles on the center of NMC particle surface and some thin scale-like precipitates are seen on the both sides of the NMC. According to the EDXS mappings, P and S are dispersed on the whole particle surface. This indicates that the thin film of LPS electrolyte was generated on the surface of the particles and then thin scale-like solid LPS grew on the NMC composite as illustrated in Fig. 1.

**Figure 4** shows a TEM image and selected area electron diffraction patterns of the prepared active material NMC-electrolyte LPS composite produced by SEED method. The center part of TEM image, which looks dark, is NMC. The translucent parts ① and ② are considered to be precipitated LPS electrolytes. The right side ring patterns ① and ② are corresponding to the parts of ① and ② on the TEM image. Part ① seems to be amorphous because of the halo pattern without spots. Part ② shows clear spots in the pattern, indicating this part is crystalline. Therefore, the prepared electrolyte is a mixture of amorphous part and crystalline part.

The intensity profile of the electron diffraction pattern for the composite is shown in **Fig. 5**, and the XRD intensities of β-Li$_3$PS$_4$ listed in the ICDD file (No. 01-076-0973) are also shown. These peaks of the profile are broad but each one is identified from the strong lines of the β-Li$_3$PS$_4$. This result shows that β-Li$_3$PS$_4$ was generated on the NMC by SEED method.

The all-solid-state cells were fabricated with the active material NMC-electrolyte LPS composite obtained by SEED method. The weight ratio of the composite is NMC: LPS = 90:10. The cell with hand-mixed active material, which was made of NMC and LPS, was also fabricated for comparison. The weight ratio is the same to that of the composite by SEED method. LPS used in hand-
mixing was prepared by the liquid-phase shaking method. **Figure 6** shows the charge–discharge curves of the cells at the current of 0.1 C. Both cells of hand-mixing and SEED method show high capacity more than 100 mAhg⁻¹ though the amounts of electrolyte content are low. Because LPS particles by the liquid-phase method are very fine, LPS can be easily mixed with active materials.⁸) The cell with the composite by SEED method shows small IR-drop and keeps 3 V until 83 mAhg⁻¹ (NMC) at first discharge, while the hand-mixing cell does not keep 3 V in the region higher than 56 mAhg⁻¹ as indicated with dotted lines.

**Figure 7** shows the cycle performance of capacities and coulomb efficiencies of the corresponding cells in Fig. 6. The capacity of the cell using prepared composite by
SEED method is 95 mAh g⁻¹ at 9th cycle and higher than that of the cell using hand-mixed active material (80 mAh g⁻¹). The coulomb efficiency of the cell by SEED method was constantly higher than those of the cell by hand-mixing. Complex impedance plots for the fabricated all-solid-state cells after the first and 10th charges are shown in Fig. 8. In the figure, (A) and (C) are the cell by hand-mixing, and (B) and (D) are those of the cell by the SEED method. All plots are composed of three semicircles divided by frequency into low area (<100 Hz) assigned to anode resistance, medium area (<10 kHz) assigned to boundary resistance of the cell, and high area (>10 kHz) assigned to bulk resistance of electrolyte shown in Fig. 8(a). In the area of medium frequency, both plots of cells by the SEED method first (B) and 10th (D) charge show smaller semicircles than the cells by hand-mixing (A) and (C). This indicates that the boundary resistance of the cells by SEED method is lower, and it maintains better contact between NMC and electrolyte in comparison with that of the cells prepared by hand-mixing.

To further analysis of boundary resistance of the cells, the results of complex impedance plots were applied to fitting analysis using the equivalent circuit model shown in Fig. 8(b). Figure 8(a) shows an example of fitting analysis corresponding the plots data in Fig. 8(A). The semicircle of plots in the medium frequency area is divided by fitting into grain boundary resistance of electrolyte (RSE,gb) shown in an orange colored semicircle and interfacial resistance between the electrolyte and active materials (RSE/cathode) shown in a red colored semicircle. In the results of the fitting corresponding all data in Figs. 8(A)–8(D), the values of RSE/cathode are shown in Table 1. Focusing on RSE/cathode after 10th charging, the RSE/cathode of the cell by using SEED method is smaller than that of the cell by hand-mixing. In comparison by the increasing rate, these values of the cell using SEED method is not so high against the cell by hand-mixing. This can be ascribed to good retention of electrochemical contact at the interface between NMC and LPS in the cell by SEED method during 10th charge–discharge cycles.

### Table 1. Comparison of RSE/Cathode after 1st and 10th charging to 3.8 V vs. In-Li at 0.1 C and RSE/Cathode growth rate for the all-solid-state 90NMC–10LPS/LPS (LS method) cells obtained by hand mixing and SEED method

| Method          | RSE/cathode (Ω cm⁻²) | Growth rate of RSE/cathode (%) |
|-----------------|----------------------|--------------------------------|
| Hand Mixing     | 23.8                 | 38.3                           |
| SEED method     | 18.3                 | 20.7                           |

### 4. Conclusions

The cathode composite was successfully prepared using the SEED method. Li₃PS₄ was directly produced on the active material NMC on the basis of the liquid-phase shak-
ing process. The impedance profiles showed that the composite interface between Li$_3$PS$_4$ and the active material by the SEED method maintained good contacts after the 10th charge–discharge cycles.

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