

# Composite Cathode of NCM Particles and $\text{Li}_3\text{PS}_4\text{-LiI}$ Electrolytes Prepared using the SEED Method for All-Solid-State Lithium Batteries

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**Abstract.**  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$  (LPSI) electrolytes were directly produced on a cathode active material  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) using the new liquid process which is named 'SEED method'. The formation of electrolytes on NMC was confirmed using scanning electron microscopy and energy dispersive X-ray mapping. The ionic conductivities of the LPSI electrolyte prepared by the SEED method were evaluated and the LPSI electrolyte showed  $2.5 \times 10^{-4} \text{ Scm}^{-1}$  at room temperature which is almost equal to that of the LPSI electrolyte prepared by the previous liquid-phase shaking process. All-solid-state cells composed of [90MNC • 10LPSI composite |  $\text{Li}_3\text{PS}_4$  | In-Li] were fabricated and the electrochemical properties of the cells were evaluated. The cell fabricated using this composite as cathode material exhibited enhanced performance in comparison with the cell using the cathode material prepared by hand mixing LPSI with NMC.

## 1. Introduction

Design of high ion conducting paths and good electrochemical contacts between active materials and the solid electrolytes is crucial for fabrication of all-solid-state lithium batteries. The sulfide-based solid electrolytes are currently well known as a promising candidate for all-solid-state batteries and extensively studied due to their high lithium ionic conductivities and suitable plasticity for good contacts at the interface.[1,2] Various methods for composite fabrication of cathode active materials and solid electrolytes have been extensively studied.[3,4,5] However, the volume change in the composites during charge-discharge cycles causes in the gap increment between active materials and electrolytes, which results in a decrease in the capacity of the all-solid-state battery. Thus, it is essential to design the composite electrodes which can adjust and/or follow the gap accordingly to the volume change during the charge-discharge cycling.

Recently our group had developed a new process, liquid-phase shaking (LS) method [6] for preparation of electrolytes used in the  $\text{Li}_2\text{S-P}_2\text{S}_5$  system. The electrolytes prepared by LS method can be mixed with active materials homogeneously due to the fine particle sizes of the resultant electrolytes. [6] We propose a new preparation method named as 'SEED method' to fabricate composites of active materials and solid electrolytes based on the liquid-phase process. In this method, the solid electrolytes were prepared from  $\text{Li}_2\text{S}$  using as a seed materials, which are nuclei precipitated on the surface of the active materials that act as scaffold for the composites preparation. The composite



of electrolyte  $\text{Li}_3\text{PS}_4$  (LPS) and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  positive electrode active material (NMC) which is a high-potential oxide active material was obtained using the SEED method [7]. In this study,  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$  (LPSI) solid electrolyte in the  $\text{Li}_3\text{PS}_4$ - $\text{LiI}$  system, which shows higher ionic conductivities than LPS[8], [9], was prepared by the SEED method on the surface of NMC. The NMC-LPSI composites were obtained and their battery characteristics were evaluated.

## 2. Experimental

Figure 1 shows the preparation procedure of NMC-LPSI composite by the SEED method.  $\text{Li}_2\text{S}$  coating on active material NMC reacts with  $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  ethyl propionate (EP) solution and then the composites of NMC and electrolyte LPSI with molar ratio of  $\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiI} = 3:1:1$  were obtained. The illustration shown in Figure 1 is the concept of the SEED method. Two-thirds of  $\text{Li}_2\text{S}$  that was required for preparation of LPSI was coated on active materials NMC while the remaining required one-third of  $\text{Li}_2\text{S}$  was dissolved in the solution to containing ' $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  with a molar ratio of  $\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiI} = 1:1:1$ . The resultant solution was transparent and homogeneous.<sup>[10]</sup>

The detailed preparation procedure of NMC-LPSI composite is as follow. Firstly, the NMC was coated with  $\text{Li}_2\text{S}$ .  $\text{Li}_2\text{S}$  (99.9%, Mitsuwa) was added to ethanol (EtOH, Super Dehydrated (99.5%, Wako) and dissolved by stirring treatment for 1 h. NMC (1 wt%  $\text{LiNbO}_3$  coated) was immersed in the as-obtained  $\text{Li}_2\text{S}$  EtOH solution and then EtOH was evacuated at  $170^\circ\text{C}$  for 2 h under reduced pressure to form the NMC- $\text{Li}_2\text{S}$  composite. Secondly,  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$  (99%, Merck) and  $\text{LiI}$  (99%, Aldrich) were mixed and dissolved in EP by stirring treatment for 30 min. The obtained EP solution ( $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  in EP) was transparent and pale yellow. The NMC- $\text{Li}_2\text{S}$  composite was then added to the ' $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  in EP' and agitation treatment with stirring was carried out for 6 h at  $50^\circ\text{C}$ . The precursor of NMC-LPSI was heat treated at  $170^\circ\text{C}$  for 2 h under reduced pressure after evaporated the solvent EP at room temperature. The gray powders of NMC-LPSI composites were obtained.

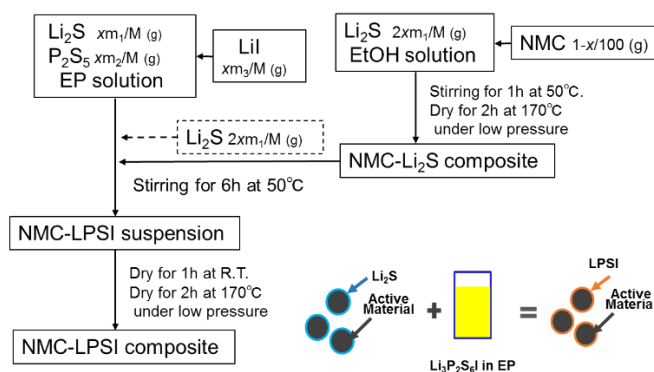


Figure 1: The preparation procedure of NMC-LPSI composites. The weight ratio of NMC: LPSI is  $(100-x):x$ . In the Figure,  $m_1$ ,  $m_2$ ,  $m_3$  and  $M (=3m_1+m_2+m_3)$  are the molar weight of  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$ ,  $\text{LiI}$  and LPSI, respectively.

The prepared composite was characterized using scanning electron microscopy (SEM; S4800, Hitachi). Elemental mapping was taken using an energy dispersive X-ray spectroscopy (EDXS, Horiba) detector attached to the SEM system. The X-ray diffraction patterns of LPSI were obtained using Ultima IV (Rigaku).

All-solid-state cells were fabricated using the prepared composite as a cathode material, LPS prepared by the liquid-phase shaking method [6] as an electrolyte layer and indium foil (diameter about 8 mm) as a counter electrode. To form electronic conducting paths to the composites, vapor grown carbon fiber (VGCF) was hand mixed with the composites. The cathode composites consist of 90NMC-10LPSI-3VGCF (wt. %). The composite electrodes for electrochemical measurements were

prepared by uniaxial pressing (about 80 mg of sample dried at 170°C) into pellets of approximately 0.6 mm in thickness and 10.0 mm in diameter at a pressure of 330 MPa at room temperature. The prepared pellet was then placed in a holder made from polyetheretherketon (PEEK) and switched between two stainless steel rods. The charge-discharge tests of the cells were conducted at a constant current at 0.1 C. In order to compare the effect of composite by the SEED method, the similar tests were also carried out on all-solid-state cells fabricated using positive electrodes composite prepared by hand mixing of NMC and LPSI. All processes for preparation the composites and fabrication the all-solid-cells were performed in an Ar-filled dry box. The cells were placed in a glass tube filled with Ar during the electrochemical characterization measurements.

### 3. Results and Discussion

Figure 2 shows an SEM image and EDXS elemental mappings of P, S and I of the composites composed of NMC and LPSI produced by the SEED method. There are some sheet-like solid on the surface of NMC particle. From the EDXS mappings, it can be observed that P, S and I are dispersed on the whole particle surface. This indicates that the thin film of LPSI electrolyte was generated on the surface of the particle and followed by growth of sheet-like solid LPSI grew on the NMC.

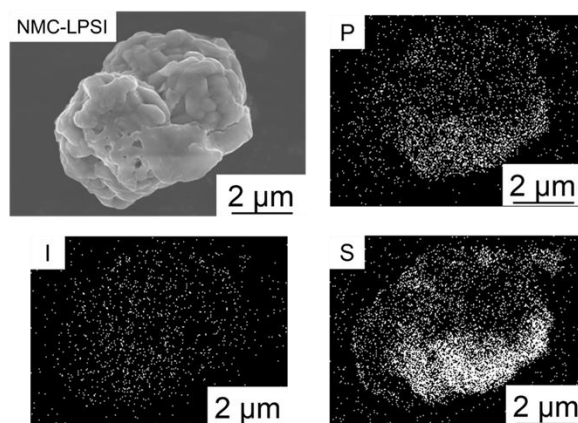


Figure 2: An SEM image of the NMC-LPSI composite particle and corresponding EDXS elemental mappings of P, S and I.

According to the procedure shown in Figure 1, the LPSI electrolyte was prepared using the SEED method without NMC particles to confirm the properties of the composite electrolytes obtained by this method. The  $\text{Li}_2\text{S}$  was added to the  $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  EP solution instead of the NMC- $\text{Li}_2\text{S}$  composite that is shown with dotted line in Figure 1. Figure 3 shows XRD patterns and SEM images of electrolytes prepared by SEED method and the LS method. Both electrolytes are exhibited almost similar XRD patterns assigned to the crystalline  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ . It is noteworthy that  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$  crystals were precipitated from the  $\text{Li}_3\text{P}_2\text{S}_6\text{I}$  in EP by adding  $\text{Li}_2\text{S}$  where a molar ratio of  $\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiI}$  was 3:1:1. The SEM image of the electrolyte obtained by SEED method shows sheet-like structure and irregular-shaped particles compared with the electrolyte formed by the LS method. This electrolyte formed by SEED method exhibited almost same profile of the temperature dependence of ionic conductivities as shown in Figure 4. The ionic conductivity of the electrolyte formed by SEED method at room temperature was  $2.5 \times 10^{-4} \text{ Scm}^{-1}$  which is higher than the ionic conductivity of LPS but it still slightly lower than that of LPSI formed by conventional LS method. Thus described that the LPSI on the active material composite produced by SEED method is considered to possess almost similar properties as the LPSI prepared by the previous method.

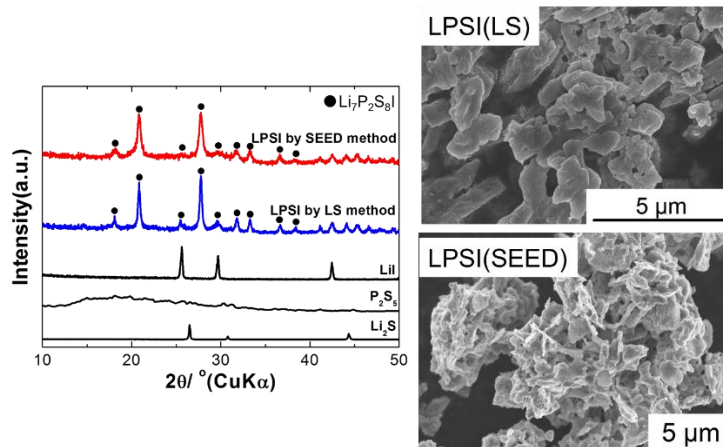


Figure 3: XRD patterns and SEM images of  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$  prepared by the SEED method and the LS method.

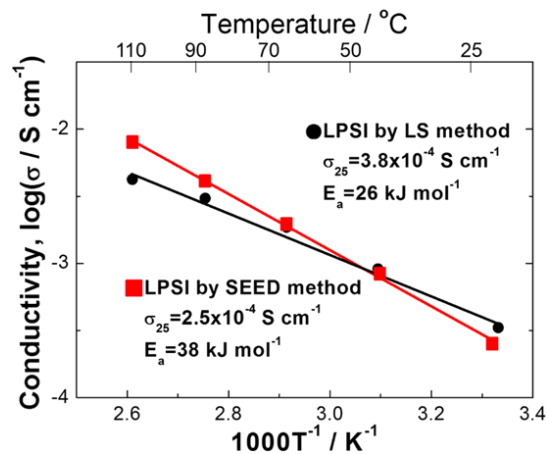


Figure 4: The temperature dependence of ionic conductivities of LPSI electrolytes prepared by SEED method(■) and LS method(●).

The all-solid-state cell using as-obtained active material NMC-electrolyte LPSI composite by SEED method was fabricated. The weight ratio of the composite used was NMC:LPSI = 90:10. The cell with hand-mixed active material consisting of NMC and LPSI was also fabricated for comparison. The weight ratio was the same as that of the composite formed by SEED method. LPSI used in the hand-mixed active material was prepared by the LS method. Figure.5 shows the initial charge-discharge curves of the cells at 0.1C. The discharge capacity of the cell using the hand mixed active material as cathode was only 27  $\text{mAhg}^{-1}$  (dash line in Figure,5) because of the amount of electrolyte content was too low to be mixed homogenously with NMC. On the other hand, the discharge capacity of the cell using NMC-LPSI composite formed by SEED method in the present study exhibited more than 90  $\text{mAhg}^{-1}$  (solid line in Figure.5) and good performance compared to the cell formed by the hand-mixing although the amount of electrolyte content was same. This result indicates that the NMC particles were coated homogenously with the LPSI electrolyte by using SEED method.

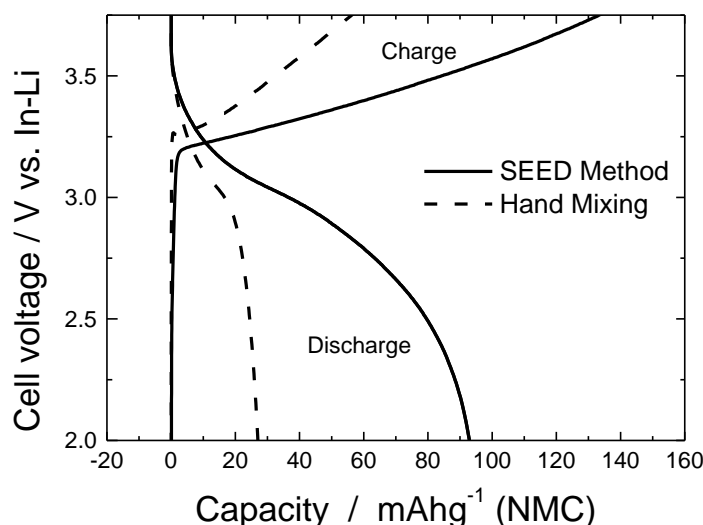


Figure 5: Charge-discharge voltage profiles in the first cycle of the all-solid-state cells fabricated using 90NMC-10LPSI-3VGCF |LPS (LS method)|In at 30°C, 0.1C. Cathode electrode composites were prepared by hand mixing (dash line) and SEED method (solid line).

#### 4. Conclusions

The cathode composite was successfully prepared using the SEED method. Crystalline  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$  electrolyte was directly produced on the active material NMC by the SEED method. The charge-discharge profiles of the all-solid-state cells show that the composite interface between LPSI and the active material formed by SEED method has good contacts. The SEED method developed in this study can be applied not only to cathode composites but also anode composites using Li metal or carbon.

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