Supporting information

Electrochemical and Microstructural Analysis of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Cathode Composites Prepared using SEED Method

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Experimental

Synthesis

A detailed flowchart of the preparation of $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (1wt% $LiNbO_3$ coated, TODA KOGYO)-$10Li_7P_2S_8I$ (Li_2S:P_2S_5:LiI = 3:1:1 as the chemical composition) (wt%) using the SEED method is shown in Fig. S1. First, 25 mg of Li_2S (Mitsuwa, 99%) was weighed and mixed with 1 ml of ethanol (EtOH (Wako, 99.5%)) for 5 min to prepare a Li_2S-EtOH solution with a concentration of 0.025 g/ml. Next, 450 mg of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was weighed, and 0.372 ml of the Li_2S-EtOH solution was added, followed by the dispersion of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in the solution at 28 kHz for 5 min. Li_2S seeds were deposited on the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles by drying under vacuum at room temperature for 1 h on a 50 °C hot plate for 30 min and 150 °C hot plate for 2 h. Next, 12.8 mg Li_2S and 62.4 mg P_2S_5 (Aldrich, 99%) were weighed, and 1 ml of ethyl propionate (EP (Aldrich, 99.8%)) was added while stirring for 30 min to form a $Li_2P_2S_6$-EP solution with a concentration of 0.074 g/ml. A LiI-EP solution with a concentration of 0.1 g/ml was prepared by adding 1 ml of EP to 100 mg of LiI (Aldrich, 99%) and stirring for 5 min. Additionally, 0.365 ml $Li_2P_2S_6$ and 0.135 ml LiI-EP solutions were added to the pre-prepared $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$Li_2S$ seed composite, and a 28-kHz ultrasonic wave was applied for 1 min to disperse the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$Li_2S$ seed composite in the solution. This mixture was stirred at 250 rpm for 4.5 h. The $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$10Li_7P_2S_8I$ (wt%) was then prepared by drying under vacuum at room temperature for 1 h on a hot plate at 70 °C for 30 min and at 170 °C for 2 h. In addition, $Li_7P_2S_8I$ was similarly synthesised without using a cathode-active material. For comparisons with the SEED cathode composite, a hand-mixed $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$10Li_7P_2S_8I$ (wt%) composite was also prepared by weighing $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

and $Li_7P_2S_8I$ powders in a 90:10 (wt%) ratio and mixing them with mortar for 10 min. The $Li_7P_2S_8I$ utilised here was synthesised using the liquid-phase shaking (LS) method.[1-2]

Characterization

The crystal structures of the prepared cathode composites were evaluated through X-ray diffraction (XRD; Ultima IV and Smartlab SE, Rigaku Co., Ltd.). The samples were sealed in specialised holders (Rigaku Co., Ltd.) in an Ar-filled glove box to prevent exposure to humid air. The morphologies of the solid electrolytes were evaluated using field-emission scanning electron microscopy (FE-SEM; S-4800, Hitachi High-Tech Co., Ltd.). Additionally, cross-sectional SEM with energy dispersive X-ray spectroscopy (EDX) was conducted using a FE-SEM instrument (Hitachi High-Tech; SU8220) equipped with an EDX (HORIBA; EMAX). The cross-section of the cut pellet was flattened by ion milling (Hitachi High-Tech, IM4000), which was conducted under cryogenic conditions using an Ar ion beam. The SEM and EDX observations were conducted at electron beam acceleration voltages of 2 and 7.5 kV, respectively.

Electrochemical properties

The ionic conductivities of the solid electrolyte and cathode composite were calculated using AC impedance measurements with the cell shown in Fig. S2a. The solid electrolyte (80 mg) was placed in a PEEK cell and pressed at 255 MPa for 10 min. The electronic conductivity of the cathode composite was determined using a DC polarisation test using the evaluation cell shown in Fig. S2b. The cathode composite (100 mg) was placed in the PEEK cell and pressed at 255 MPa for 10 min to construct the cell used to evaluate electronic conductivity. Five 50 mV steps from 100 to 300 mV were applied for 30 s. Electronic conductivity was calculated using the stabilised current, sample thickness, and cross-sectional area. The ionic conductivity of the cathode composite was measured by AC impedance measurements using the cell shown in Fig. S2c. Pellets of the cathode composite were prepared by pressing 100 mg of the composite at 255 MPa for 10 min. These pellets were then placed in a PEEK cell, and 40 mg of the mechanochemically prepared $Li_{5.5}PS_{4.5}Cl_{1.5}$ were added between the pellets of the cathode composite and pressed at 255 MPa for 10 min to assemble the cell. The AC impedance measurements were performed at a constant voltage of 50 mV in the frequency range of 100 Hz to 10 MHz at 298 K. The ionic conductivity of the cathode composite was calculated by subtracting the resistance of $Li_{5.5}PS_{4.5}Cl_{1.5}$ from the total resistance obtained using the Nyquist plot.

Battery Performance

The ASSB was assembled by uniaxially pressing the $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-10 $Li_7P_2S_8I$ (wt%) cathode composite for the positive electrode, the mechanochemically prepared $Li_{5.5}PS_{4.5}Cl_{1.5}$ for the solid electrolyte

layer, and Li-In for the negative electrode. The solid electrolyte (80 mg) was placed in a PEEK cell and pressed at 255 MPa. Subsequently, 5 mg of the cathode composite was added (The mass loading ratio is 6.3 mg/cm^2), and the mixture was pressed under the same pressure for 10 min. Thereafter, indium foil (Φ8, Nilako) and lithium foil (Φ3, Honjo Metal) were placed on a solid electrolyte layer and pressed at the same pressure. Charge–discharge measurements were conducted at a constant current of 0.1 C (0.072 mA) in the voltage range 2.0–3.6 V at a temperature of 30 °C.

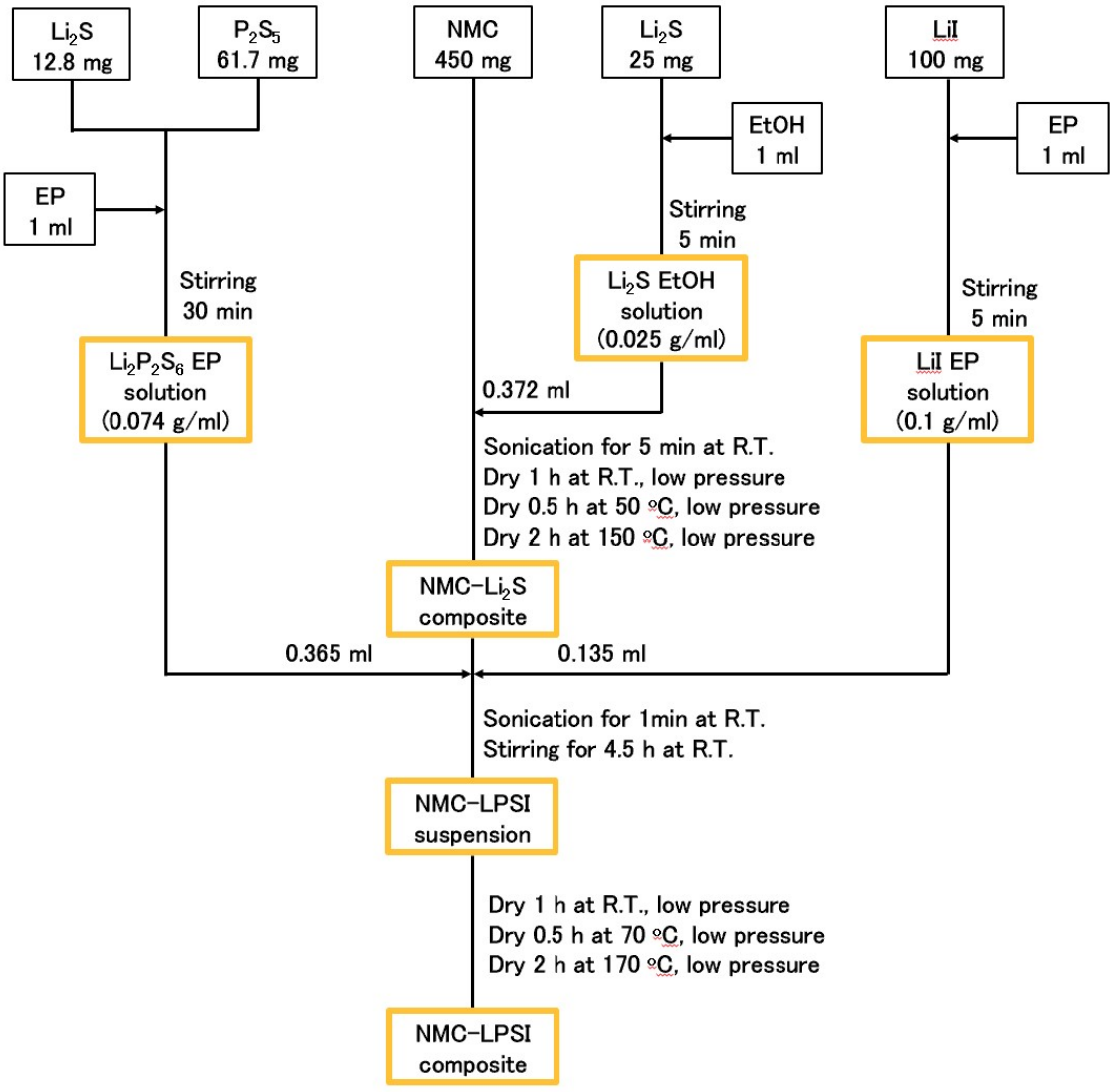

Figure S1 Flowchart for the preparation of $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$10Li_7P_2S_8I$ (wt%) using the SEED method.

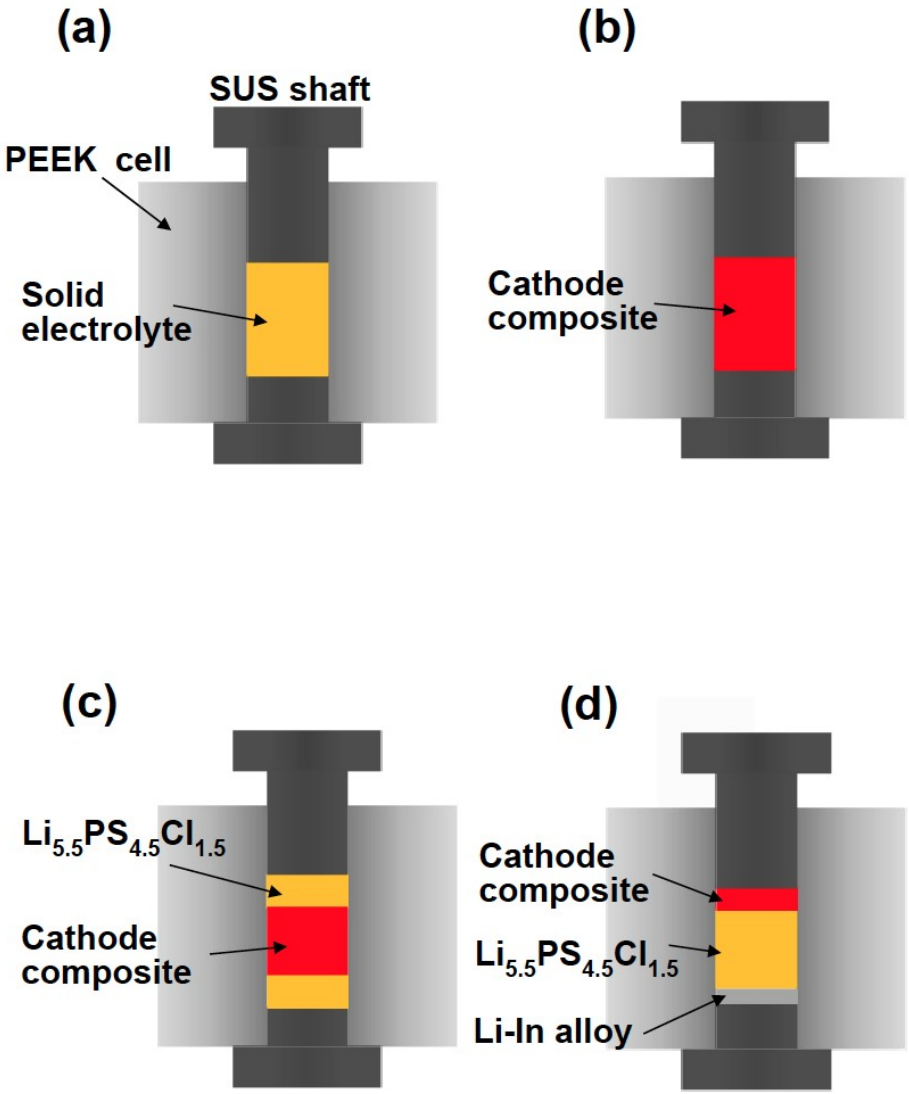

Figure S2 Schematic illustrations of the electrochemical cells for electrochemical property measurements. (a) Ionic conductivity measurement of solid electrolytes, (b) electronic conductivity measurement of cathode composite, and (c) ionic conductivity measurement of cathode composite.

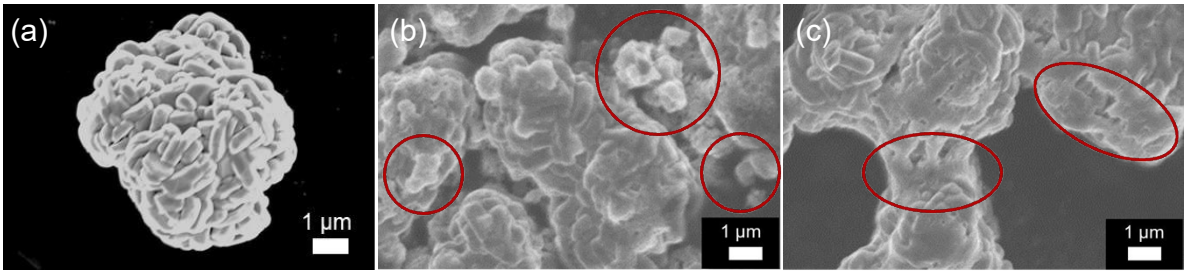

Figure S3 SEM images of (a) $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, the $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$10Li_7P_2S_8I$ cathode composite prepared by (b) hand mixing, and (c) the SEED method

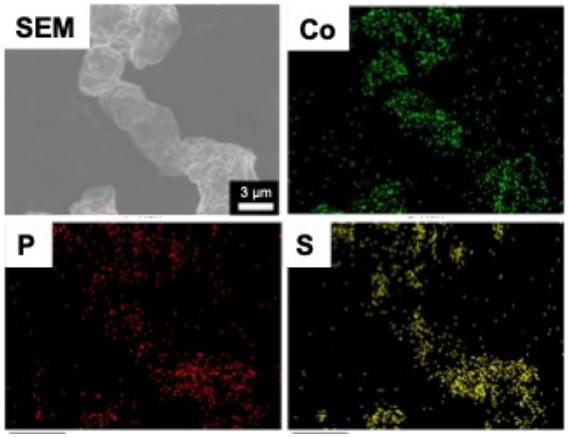

Figure S4 SEM-EDX images of the $90LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$10Li_7P_2S_8I$ cathode composite prepared by the SEED method

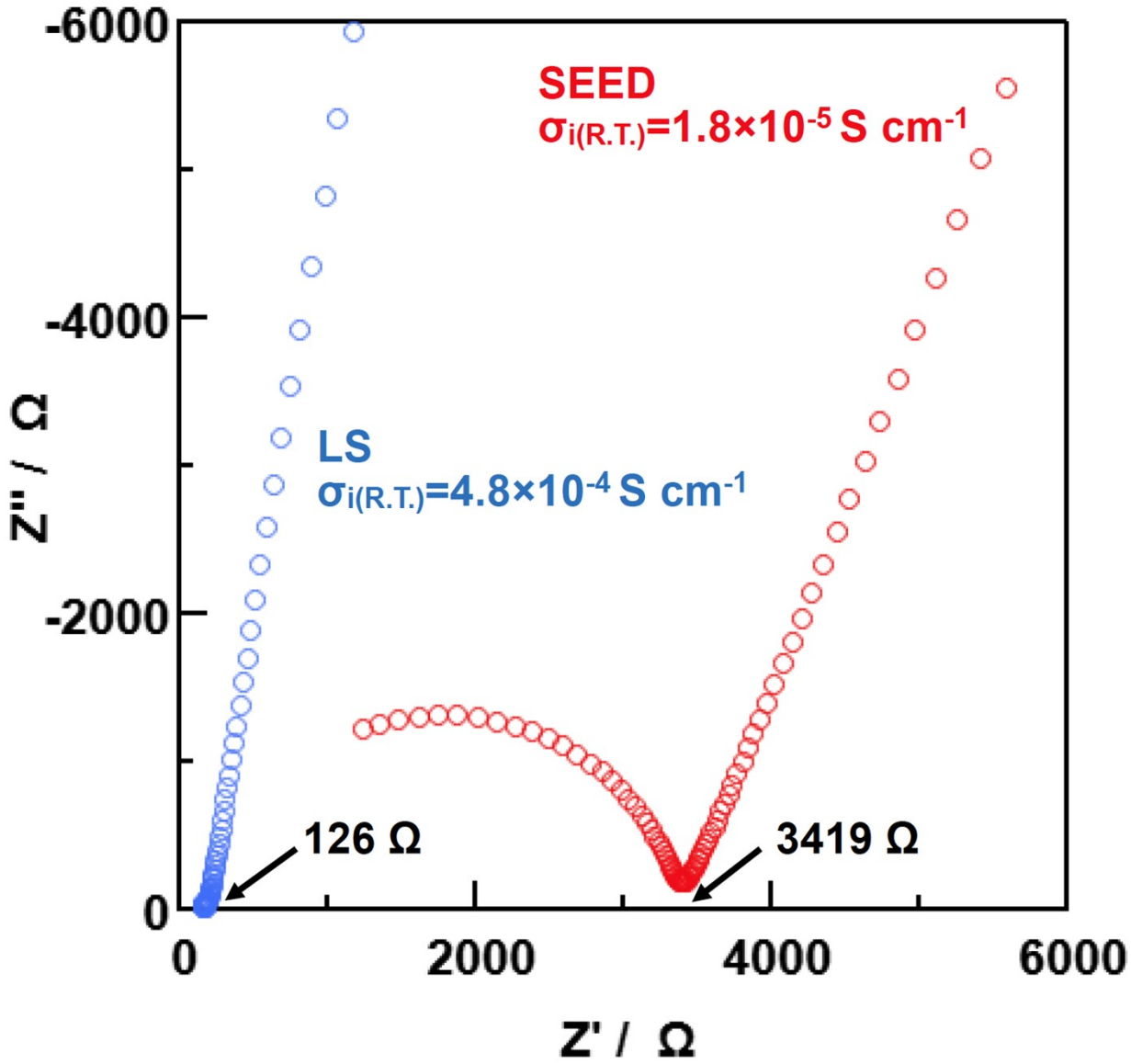

Figure S4 Nyquist plot of LPSI prepared LS method and SEED method.

Reference

[1] K. Hikima; T. Yamamoto; N. H. H. Phuc; R. Matsuda; H. Muto; A. Matsuda, *Solid State Ionics,* 354 (2020).
[2] K. Hikima; K. Ogawa; H. Muto; A. Matsuda, *Journal of the Ceramic Society of Japan,* 130 (2022) 299-302.