High Ionic Conductivity with Improved Lithium Stability of CaS- and CaI2-Doped Li7P3S11 Solid Electrolytes Synthesized by Liquid-Phase Synthesis

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ABSTRACT: Li7P3S11 solid electrolytes (SEs) subjected to liquid-phase synthesis with CaS or CaI2 doping were investigated in terms of their ionic conductivity and stability toward lithium anodes. No peak shifts were observed in the XRD patterns of CaS- or CaI2-doped Li7P3S11, indicating that the doping element remained at the grain boundary. CaS- or CaI2-doped Li7P3S11 showed no internal short circuit, and the cycling continued, indicating that not only CaI2 including I− but also CaS could help increase the lithium stability. These results provide insights for the development of sulfide SEs for use in all-solid-state batteries in terms of their ionic conductivity and stability toward lithium anodes.

INTRODUCTION

Sulfide-type solid electrolytes (SEs) are promising candidates owing to the higher polarizability of S2−, resulting in a high ionic conductivity and superior mechanical properties compared with oxide SEs for all-solid-state lithium batteries.1,2 Sulfide-type SEs have been extensively investigated, including thio-LISICON (2.2 mS cm−1 at 25 °C),3−5 Li7P3S11 glass ceramics (17 mS cm−1),6 Li10GeP2S12 (12 mS cm−1),8 and Li0.3S1.7P1.4S11.7Cl0.3 (25 mS cm−1).9 Although Li7P3S11 has a high ionic conductivity of more than 10 mS cm−1 at room temperature (approximately 25 °C) as above, Li7P3S11 SEs are synthesized by solid-state reactions such as mechanical milling and heat treatment. Solid-state reactions have several disadvantages, such as high energy consumption, which inhibits their use for mass production. On the other hand, liquid-phase synthesis is a viable method for the mass production10 and preparation of electrode composites used in all-solid-state batteries.11

There have been more reports related to the liquid-phase synthesis of Li7P3S11 SEs than solid-state methods. For example, dimethoxy ether (0.27 mS cm−1),12 acetonitrile (ACN, 1 mS cm−1),13,14 and tetrahydrofuran (0.97 mS cm−1)15 have been used for the synthesis of Li7P3S11. Various solvents were investigated, and their highest conductivity was found to be 1 mS cm−1 for ACN.16 Thus, the ionic conductivity of Li7P3S11 synthesized using the liquid-phase method is typically lower than that of the samples synthesized using solid-state methods. Liquid-phase synthesis faces significant challenges because the liquid-phase synthesis itself is complicated because of, for example, the variety of solvents, solvent residue, and drying conditions. To improve the ionic conductivity, several previous reports have focused on doping with other elements. The aliovalent substitution of P5+ with other cations and S2− with other anions was investigated. Nb/O-,17 Mn/I-,18 Sb/I-,19 and Sb/O-substituted20 Li7P3S11 SEs have high ionic conductivities of 2.8, 5.6, 2.55, and 1.66 mS cm−1 at room temperature, respectively. Ce2S3- and LiCl-doped...
Li₇P₃S₁₁ (Li₇P₃S₁₁(Ca₀₂S₁₀Cl₀₃)) have also been reported to exhibit an ionic conductivity of 3.2 mS cm⁻¹. Recently, lithium halogen-doped Li₇P₃S₁₁ was also investigated; 80Li₇P₃S₁₁:20LiBr showed an ionic conductivity of 3.77 mS cm⁻¹, and the lithium stability was improved. Thus, most approaches have focused on the oligomeric substitution of S²⁻ and/or Br⁻ by other cations. However, the effect on ionic conductivity and stability of lithium owing to the introduction of other alkali earth metals into Li₇P₃S₁₁ has not been investigated. Previously, we investigated alkali earth metal-doped Li₇PS₄ and Li₆PS₅Cl SEs. The ionic conductivity at temperatures above 50 °C drastically increased with the addition of either Ca²⁺ or Mg²⁺ into Li₆PS₅Cl. Adelì et al. also reported that multivalent cation substitution improved the ionic conductivity of Li₆₋ₓ₋₃₋ₓ₋₅₋ₓ₋₃₋ₓ₋₅₋ₓ₋₁₋ₓ at room temperature. Therefore, the introduction of other cations, such as Ca²⁺, into Li₇P₃S₁₁ SEs has the possibility of improving the ionic conductivity. In addition, doping with other elements can help improve the stability of the lithium anode, although Li₇P₃S₁₁ SEs are unstable toward the lithium anode.

In this study, the ionic conductivity of Li₇P₃S₁₁ SEs subjected to liquid-phase synthesis was improved by optimizing the stirring, drying, and crystallization conditions. The Li₇P₃S₁₁ SEs synthesized at 50 °C for 72 h with stirring, 80 °C for drying, and 270 °C for 1 h for crystallization.

**EXPERIMENTAL SECTION**

**Solid Electrolyte Synthesis.** Li₂S (99.9%, Mitsuwa), P₂S₅ (Merck, 99%), CaS (99.99%, Kojundo Laboratory), CaI₂ (99.99%, Aldrich), and ACN (Wako FUJIFILM) were used as received without any further treatment. We weighed 1.5 g of Li₂S and P₂S₅ (molar ratio of 7:3) and placed them in a screw vial along with 40 mL of ACN. The mixture was stirred at 400 rpm and 50 °C for 24 h. The solvent was then evaporated at 80 °C. The residue was carefully ground using an agate mortar prior to heat treatment to obtain the Li₇P₃S₁₁: CaS- and CaI₂-doped Li₇P₃S₁₁ were prepared in the same manner.

**Characterization.** The crystal structure of the SEs was characterized by X-ray diffraction (XRD) (Ultima IV, Rigaku Co., Ltd., Japan). The samples were sealed in specialized holders equipped with a Be window (Rigaku Co., Ltd., Japan) in an Ar-filled glovebox to avoid exposure to humidity. The XRD measurements were partly conducted using a 1D silicon strip detector (D/teX Ultra 250, Rigaku Co., Ltd., Japan) instead of a conventional scintillation counter (SC, Rigaku Co., Ltd., Japan). Thermogravimetric differential thermal analysis (TG-DTA) (EVO II, Rigaku Co., Ltd., Japan) was conducted in an Ar-filled glovebox to avoid exposure to humidity and evaluate the thermal properties of the SEs.

**Electrochemical Properties.** The relationship between the temperature and the total conductivity of the SEs was investigated using alternating-current electrochemical impedance spectroscopy (EIS) (SI 1260, Solartron Analytical for Li₇P₃S₁₁ and CaI₂-doped Li₇P₃S₁₁, HZ-Pro, Hokuto for CaS-doped Li₇P₃S₁₁) in the frequency range from 1 MHz to 10 Hz under dry Ar flow. The EIS samples were prepared by uniaxially pressing the samples (~100 mg) into pellets with a diameter of ~10 mm at a pressure of 254 MPa and room temperature. The pellets were placed in a poly(ether ketone) (PEEK) holder with two pieces of carbon paper used as the blocking electrodes. The cell was placed under an Ar flow in a glass tube for temperature dependence measurements. Galvanostatic cycling tests were conducted using lithium metal sheets as nonblocking electrodes. The pelleted sample (diameter of 10 mm) was prepared by cold pressing at 254 MPa in a cell mold made of a PEEK cylinder. Lithium-metal sheets (Li 99.99%, Honjo Metal) (diameter of approximately 9 mm and thickness of approximately 0.1 mm) were attached to both faces of the pellet at room temperature. SUS rods were employed as current collectors. The prepared cells were then...
cycled at ±0.1 mA cm$^{-2}$ using a charge–discharge device (BST-2004H, Nagano) under a dry Ar atmosphere.

## RESULTS AND DISCUSSION

**Optimized Synthesis Conditions.** Figure 1a shows the XRD patterns of the Li$_7$P$_3$S$_11$ SEs obtained under several stirring conditions for three days (72 h) of stirring time. The drying conditions and crystallization conditions were 170 °C for 1 h and 270 °C for 1 h, respectively. All samples showed the existence of Li$_2$S and β-Li$_4$P$_2$S$_6$ because the diffraction peaks at 2θ ≈ 27 and 28° were attributed to Li$_2$S (ICSD #196932) and β-Li$_4$P$_2$S$_6$ (ICSD #180319), respectively. The intensity ratio of the diffraction peaks of the starting materials (Li$_2$S) at 2θ ≈ 27° and second phase (β-Li$_4$P$_2$S$_6$) at 2θ ≈ 28° to that of the Li$_7$P$_3$S$_11$ phase at 2θ ≈ 30° was lower (0.36 and 0.31 for Li$_7$S/Li$_7$P$_3$S$_11$ and β-Li$_4$P$_2$S$_6$/Li$_7$P$_3$S$_11$, respectively) in the samples under the stirring condition of 50 °C for 3 days than in those under the stirring condition of 70 °C for 3 days (0.37 and 0.40, respectively) and 80 °C for 3 days (0.37 and 0.46, respectively). In addition, Figure S1 shows the XRD patterns of the Li$_7$P$_3$S$_11$ SE precursors obtained at various stirring times and a stirring temperature of 50 °C. The XRD patterns of the precursor samples after vacuum drying with stirring for 1 and 2 days indicated the existence of Li$_2$S as the starting material. Therefore, stirring was conducted at 50 °C for 3 days, which is the shortest stirring time required for the efficiency of these experiments.

Figure S2 shows the XRD patterns of the Li$_7$P$_3$S$_11$ SE precursors obtained under several drying conditions with a crystallization temperature of 270 °C for 1 h. The XRD patterns of the samples dried at 130 °C for 2 h and 170 °C for 1 h indicate the existence of Li$_2$S as the starting material after vacuum drying. Figure S3a–c show the TG-DTA curves of the precursor powders obtained under several drying conditions with a crystallization temperature of 270 °C for 1 h for the evaluation of the amount of organic solvent elements. The weight loss was observed to be 1.83, 0.02, and 0.08% for the samples dried at 80 °C for 6 h, 130 °C for 2 h, and 170 °C for 1 h until 100 °C, respectively. The DTA curve exhibited endothermic peaks centered at 200 and 250–270 °C that depended on the drying conditions. The former peak corresponded to the dissociation of the solvent—thiophosphate complex, and the latter peak originated from several reactions, namely, the formation of Li$_7$P$_3$S$_11$ and the decomposition of Li$_7$P$_3$S$_11$ into Li$_3$PS$\_4$, Li$_4$P$_2$S$_6$, and sulfur, which is still unclear. Therefore, little free solvent in the Li$_7$P$_3$S$_11$ SE precursor dried under all the conditions remained and the weight loss for the samples dried at 80 °C for 6 h could represent the solvent in the complex. In addition, slight changes were observed depending on the drying time at 80 °C (Figure S3d). Based on the XRD patterns and TG analysis, the drying conditions were fixed at 80 °C above 6 h.

Figure S4 shows the XRD patterns of the Li$_7$P$_3$S$_11$ SEs obtained under several crystallization conditions. Based on the DTA curves, a crystallization temperature of around 260 °C was considered. The sample at a crystallization temperature of 260 °C for 1 h exhibited Li$_2$S and β-Li$_4$P$_2$S$_6$. On the other hand, at crystallization temperatures above 280 °C, β-Li$_4$P$_2$S$_6$ formed as the stable phase. Therefore, the crystallization conditions were fixed at 270 °C for 1 h. In summary, the optimized synthesis conditions for Li$_7$P$_3$S$_11$ were determined to be at 50 °C for 72 h under stirring, 80 °C for 6 h for drying and 270 °C for 1 h for crystallization. Figure 1b shows the temperature dependence of the ionic conductivities of the Li$_7$P$_3$S$_11$ SEs. The ionic conductivity of Li$_7$P$_3$S$_11$ was 0.70 mS cm$^{-1}$ at 22 °C with an activation energy of 35 kJ mol$^{-1}$, resulting in a high ionic conductivity similar to that reported previously. Finally, the SEM images of the Li$_7$P$_3$S$_11$ SEs revealed particle sizes of approximately 100 nm (Figure S5).

**CaS Doping.** Figure S6a shows the TG-DTA curves of the CaS doped-Li$_7$P$_3$S$_11$ precursor. The DTA curve of the CaS doped-Li$_7$P$_3$S$_11$ precursor exhibited endothermic peaks at 200 and 250 °C, which were similar to those of nondoped Li$_7$P$_3$S$_11$. Thus, CaS-doped Li$_7$P$_3$S$_11$ was also crystallized at 270 °C for 1 h, which was the same as that for nondoped Li$_7$P$_3$S$_11$. Figure 2a shows the XRD patterns of the CaS-doped Li$_7$P$_3$S$_11$ SEs. The XRD pattern of the Li$_7$P$_3$S$_11$-0.56CaS SE was measured using a 1D silicon strip detector (D/teX Ultra 250).

![Figure 2](https://example.com/f2.png)

**Figure 2.** (a) XRD patterns and (b) temperature dependence of the ionic conductivity of the Li$_7$P$_3$S$_11$-xCaS (where 0 ≤ x ≤ 0.7) SEs. The XRD pattern of the Li$_7$P$_3$S$_11$-0.56CaS SE was measured by using a 1D silicon strip detector (D/teX Ultra 250).
our previous study on CaS-doped Li6PS5Cl SEs synthesized using the mechanical milling method; hence, the doped element could remain at the grain boundary. Figure 2b shows the temperature dependence of the ionic conductivities of the CaS-doped Li7P3S11 SEs. The ionic conductivity of the sample of Li6.35Ca0.35P3S11 was 0.95 mS cm$^{-1}$ at 30 °C, while those of Li6.25Ca0.25P3S11 and Li6.08Ca0.42P3S11 SEs were 0.84 and 0.25 mS cm$^{-1}$ at 30 °C, respectively. The activation energy (34 kJ mol$^{-1}$) of Li6.72Ca0.14P3S11 was relatively lower than those of Li6.38Ca0.35P3S11 and Li5.88Ca0.56P3S11 (36 and 38 kJ mol$^{-1}$, respectively). Therefore, the samples with Li6.72Ca0.14P3S11 SEs exhibited the highest ionic conductivity, although Li6.38Ca0.35P3S11 SEs also showed similar ionic conductivities.

**Cal2 Doping.** Figure 3b shows the TG-DTA curves of the CaI2-doped Li7P3S11 precursor. The DTA curve of the CaI2-doped Li7P3S11 precursor exhibited endothermic and exothermic peaks at 203 and 250 °C similar to that of nondoped Li7P3S11. Therefore, CaI2-doped Li7P3S11 was also crystallized at 270 °C for 1 h, the same as that for nondoped Li7P3S11. Figure 3a shows the XRD patterns of the CaI2-doped Li7P3S11 SEs obtained using several synthesis processes. All samples indicated the existence of Li2S and β-Li4PS4I w with a starting voltage of 7 mV, which is lower than those of 0.98Li7P3S11-0.02CaI2 and 0.95Li7P3S11-0.05CaI2 SEs. The ionic conductivity of the 0.98Li7P3S11-0.02CaI2 was 0.78 mS cm$^{-1}$ at 29 °C while those of the 0.95Li7P3S11-0.05CaI2 and 0.93Li7P3S11-0.07CaI2 SEs were 0.59 at 27 °C and 0.30 mS cm$^{-1}$ at 29 °C, respectively. The activation energy (36 kJ mol$^{-1}$) of 0.98Li7P3S11-0.02CaI2 was similar to that of 0.95Li7P3S11-0.05CaI2 (33 kJ mol$^{-1}$). On the other hand, the activation energy of 0.93Li7P3S11-0.07CaI2 (22 kJ mol$^{-1}$) was lower than those of 0.98Li7P3S11-0.02CaI2 and 0.95Li7P3S11-0.05CaI2. Thus, the introduction to CaI2 could cause the lower ionic conductivity and the increment of the activation energy than nondoped Li7P3S11.

**CaS and Cal Doping Effects.** The ionic conductivities of CaS- and Cal-doped Li7P3S11 are in the range of 0.7–1.0 mS cm$^{-1}$ at room temperature, which is not a wide range even for liquid-phase-synthesized Li7P3S11. The previous report reported that multivalent cation substitution into argyrodite SEs (Li3.5Ca1.0PS4.5Cl1.55) improved the ionic conductivity at room temperature. This study confirmed the presence of an aloivalent dopant (Ca) on the Li sites in the cubic structure. However, Ca$^{2+}$ was not incorporated into the Li7P3S11 crystal lattice and no solid solution was formed in this study. In addition, the ionic conductivity at room temperature was not improved. The different synthesis methods consisting of mechanical milling and liquid-phase techniques may have contributed to this lack of improvement. Further research is needed on solvents and doping materials for sulfide-type SEs doped with other elements and synthesized by liquid-phase methods. Moreover, Li3PS11 was observed in Cal-doped Li7P3S11. This Li3PS11 phase has an ionic conductivity of 0.1 mS cm$^{-1}$ at room temperature. Therefore, Cal-doped Li7P3S11 displayed an ionic conductivity similar to those of Li3PS11 and CaS-doped Li7P3S11. Thus, the doping including I in LiI and Cal, for example, slightly improved the ionic conductivity.

Furthermore, galvanostatic cycling tests were conducted for Li7P3S11, Li6.72Ca0.14P3S11, and 0.98Li7P3S11-0.02CaI2 SEs synthesized under optimal conditions. Before cycling non-doped Li7P3S11 exhibited a starting voltage of 7 mV, which is similar to those of Li6.72Ca0.14P3S11 (7 mV) and 0.98Li7P3S11-0.02CaI2 (9 mV). The overvoltages at the starting point are in

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**Figure 3.** (a) XRD patterns and (b) temperature dependence of the ionic conductivity of the (1 - x)Li7P3S11-xCaI2 (where 0 ≤ x ≤ 0.07) SEs. The XRD pattern of Li4PS4I was measured by VESTA software. 

**Figure 3b** shows the temperature dependences of the ionic conductivities of the Cal-doped Li7P3S11 SEs. The ionic conductivity of the sample of 0.98Li7P3S11-0.02 CalI2 was 0.78 mS cm$^{-1}$ at 29 °C while those of the 0.95Li7P3S11-0.05CalI2 and 0.93Li7P3S11-0.07CalI2 SEs were 0.59 at 27 °C and 0.30 mS cm$^{-1}$ at 29 °C, respectively. The activation energy (36 kJ mol$^{-1}$) of 0.98Li7P3S11-0.02CalI2 was similar to that of 0.95Li7P3S11-0.05CalI2 (33 kJ mol$^{-1}$). On the other hand, the activation energy of 0.93Li7P3S11-0.07CalI2 (22 kJ mol$^{-1}$) was lower than those of 0.98Li7P3S11-0.02CalI2 and 0.95Li7P3S11-0.05CalI2. Thus, the introduction to CalI2 could cause the lower ionic conductivity and the increment of the activation energy than nondoped Li7P3S11.
good agreement with the ionic conductivity results, in which Li₇P₃S₁₁, Li₆.₇₂Ca₀.₁₄P₃S₁₁, and 0.₉₈Li₇P₃S₁₁-0.₀₂CaI₂ had a similar ionic conductivity of approximately 1.0 mS cm⁻¹. During cycling, nondoped Li₇P₃S₁₁ became unstable at approximately 900 h and finally ended up with an internal short circuit at 930 h. In addition, nondoped Li₆.₇₂Ca₀.₁₄P₃S₁₁ reached 30 mV (429% of the first cycle). On the other hand, Li₆.₇₂Ca₀.₁₄P₃S₁₁ and 0.₉₈Li₇P₃S₁₁-0.₀₂CaI₂ maintained stable cycling until 1050 h, respectively, although Li₆.₇₂Ca₀.₁₄P₃S₁₁ and 0.₉₈Li₇P₃S₁₁-0.₀₂CaI₂ reached 22 mV at 1050 h (Figure 4). In addition, CaS- or CaI₂-doped Li₇P₃S₁₁ showed no internal short circuit until 1150 and 2600 h, respectively (Figure S8) and the increment in the overvoltage of 0.₉₈Li₇P₃S₁₁-0.₀₂CaI₂ during cycling was lower than that of Li₆.₇₂Ca₀.₁₄P₃S₁₁. Therefore, the order of the lithium stability is 0.₉₈Li₇P₃S₁₁-0.₀₂CaI₂, Li₆.₇₂Ca₀.₁₄P₃S₁₁, and Li₇P₃S₁₁. In summary, CaS and CaI₂ doping have effects on lithium stability, although they slightly affect the ionic conductivity and activation energy.

A density functional theory calculation indicated that Li₇P₃S₁₁ and other sulfide-based SEs are thermodynamically unstable against the Li metal.²⁹ The lowest lithium stability in nondoped Li₇P₃S₁₁ can be explained by the continuous formation of decomposition products, such as Li₂S, and the instability of Li₃P at the interface of Li/Li₇P₃S₁₁.³⁰

Furthermore, the resistances of CaS- and CaI₂-doped Li₇P₃S₁₁ at 18 mV saw a higher increase than nondoped Li₇P₃S₁₁ until 200 h of 14 mV. This suggested that the decomposition of Li₆.₇₂Ca₀.₁₄P₃S₁₁ at the interface of Li/Li₆.₇₂Ca₀.₁₄P₃S₁₁ was processed more than nondoped Li₆.₇₂Ca₀.₁₄P₃S₁₁. Therefore, the formation of stable layers including Ca and/or I at the interface of Li/Li₆.₇₂Ca₀.₁₄P₃S₁₁ resulted in a uniform Li deposition/dissolution reaction. In addition, previous reports mentioned that LiI-doped Li₃PS₄ was more stable as a lithium anode.³¹

The calculation results also indicated that LiI has a wide electrochemical window. Thus, CaI₂ doping in Li₇P₃S₁₁ including I⁻ can improve the stability of a lithium anode.

Therefore, CaS doping in Li₇P₃S₁₁ improved the lithium stability. These findings offer important guidance on Ca doping for the liquid-phase synthesis of Li₇P₃S₁₁ SEs with improved ionic conductivity and lithium stability.

### CONCLUSIONS

The ionic conductivity of Li₇P₃S₁₁ SEs subjected to liquid-phase synthesis was improved by optimizing the stirring, drying, and crystallization conditions. The Li₇P₃S₁₁ SEs synthesized at 50 °C for 72 h with stirring, 80 °C for drying, and 270 °C for 1 h for crystallization showed an ionic conductivity of 0.7 mS cm⁻¹. 2 and 5 wt % CaS- and CaI₂-doped Li₇P₃S₁₁ have ionic conductivities similar to that of nondoped Li₇P₃S₁₁; thus, CaS and CaI₂ doping slightly improved the ionic conductivity. Furthermore, the galvanostatic cycling test results revealed that 2 wt % CaS- or CaI₂-doped Li₇P₃S₁₁ displayed no internal short circuit and the cycling continued. CaS doping can improve the lithium stability for the first time, although previous reports mentioned that LiI including I⁻ can also help improve the lithium stability. This study provides important guidance for the liquid-phase synthesis of sulfide SEs with high ionic conductivity and lithium stability.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00546.

XRD patterns of the Li₇P₃S₁₁ precursors synthesized at 50 °C at different times; XRD patterns of the Li₇P₃S₁₁ SE precursors dried at 80 °C for 6 h, 130 °C for 2 h, and 170 °C for 1 h; TG-DTA curves of the Li₇P₃S₁₁ SE precursors dried at different conditions; XRD patterns of the Li₇P₃S₁₁ SEs synthesized by heat treatment under different conditions; SEM image of the Li₇P₃S₁₁ SEs synthesized under the optimized synthesis condition; TG-DTA curves of the CaS- and CaI₂-doped Li₇P₃S₁₁ SE precursors by drying at 80 °C for 20 h; SEM image of the 0.₉₅Li₇P₃S₁₁-0.₀₅CaI₂ SEs; and galvanostatic cycling test results of the CaS- and CaI₂-doped Li₇P₃S₁₁ SEs synthesized under the optimized conditions in a symmetric cell (PDF).

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Li2S-P2S5 Glasses.

Lithium-Ion Conducting Crystal Obtained by Crystallization of the (X=Si; Ge), Na2S-P2S5 and Li2S-GeS2 systems.

ACKNOWLEDGMENTS

The authors declare no competing financial interest.

REFERENCES

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Notes

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ACKNOWLEDGMENTS

This study was financially supported by the SOLiD-EV Project (JPNP18003) of the New Energy and Industrial Technology Development Organization (NEDO). We also thank Ms. Makiko Oshida and Mr. Keisuke Shinoda for their help for FE-SEM measurements at the National Institute for Materials Science (NIMS) Battery Research Platform.

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