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# Organic-inorganic hybrid solid electrolytes for solid-state lithium cells operating at room temperature



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#### 1. Introduction

Recently, significant attention has been paid to rechargeable lithium-ion batteries with high energy density and long cycle life for applications in portable electronic devices, electric vehicles and energy storage systems [1–6]. However, since these batteries use flammable liquid electrolytes, there have been safety concerns, especially for large capacity applications. For this reason, solidstate lithium batteries with solid electrolytes have been developed to improve the safety of conventional lithium-ion batteries with liquid electrolyte [7–13]. As a solid-state electrolyte, ceramic electrolytes and polymer electrolytes have been studied for all solid-state lithium battery applications. Ceramic electrolytes usually exhibit relatively high ionic conductivity ( $\sim 10^{-4} \, \mathrm{S \, cm^{-1}}$ ) at room temperature, wide electrochemical stability window (>5.0 V vs. Li/Li<sup>+</sup>) and good chemical stability in contact with lithium metal. However, their hard and brittle mechanical properties do not allow easy construction of large-scale solidstate lithium batteries. In addition, there is a lack of flexibility results in high interfacial resistance and poor interfacial contacts with electrodes in the cell. On the other hand, solid polymer electrolytes have advantages such as a flexible battery shape and good interfacial contacts with the electrodes [14-16]. However,

#### ABSTRACT

Organic-inorganic hybrid solid electrolytes composed of Li<sup>+</sup>-conducting lithium aluminum germanium phosphate (LAGP), poly(ethylene oxide) (PEO), lithium perchlorate and succinonitrile (SN) were prepared in the form of flexible thin film, and their electrochemical properties were investigated. The hybrid solid electrolytes showed high ionic conductivities ranging from  $3.0 \times 10^{-5}$  to  $1.1 \times 10^{-4}$  S cm<sup>-1</sup> at room temperature and exhibited good electrochemical stability. A solid-state Li/LiFePO<sub>4</sub> cell assembled with hybrid solid electrolyte composed of 70 wt.% LAGP, 21 wt.% PEO-LiClO<sub>4</sub> and 9 wt.% SN delivered a high discharge capacity and exhibited good capacity retention at ambient temperature. Good cycling performance of the cell resulted from the high ionic conductivity of the solid electrolyte and its good interfacial contacts with electrodes.

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most solid polymer electrolytes show poor room temperature ionic conductivity, which limits their practical application at ambient temperature. Moreover, their poor mechanical properties at high temperatures may cause short circuits between two electrodes in cases where unexpected heat is generated. To overcome the disadvantages of ceramic and polymer electrolytes, hybrid solid electrolytes composed of ceramic and polymer have been studied [17–23]. These hybrid electrolytes improved the interfacial contact between electrolyte and electrodes in the cell during charge and discharge cycling due to the presence of flexible and adhesive polymer materials. The hybrid solid electrolytes synergistically could combine the beneficial properties of both ceramic electrolytes and polymer electrolytes. However, their ionic conductivities were not sufficiently high to allow the cell to operate at ambient temperature. Therefore, developing a hybrid solid electrolyte with high ionic conductivity at room temperature is an attractive and urgent work for solid-state lithium batteries operating at ambient temperature.

In this study, we prepared a flexible and highly conductive hybrid solid electrolyte composed of lithium aluminum germanium phosphate (LAGP), poly(ethylene oxide) (PEO)-LiClO<sub>4</sub> and succinonitrile (SN), and their electrochemical properties were investigated. The NASICON-type LAGP was used as the Li<sup>+</sup>conducting ceramic electrolyte in the hybrid solid electrolytes because it exhibited high ionic conductivity and superior stability in contact with lithium metal [24–26]. SN has been known as a plastic crystal that remains in the plastic phase until it melts at

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Composition, glass transition temperatures (Tg) and activation energies (Ea) for ionic conduction in different hybrid solid electrolytes.

Solid electrolyte	LAGP (wt.%)	PEO-LiClO <sub>4</sub> (wt.%)	SN (wt.%)	T <sub>g</sub> (°C)	$E_a$ (kJ mol <sup>-1</sup> )
PEO-LiClO <sub>4</sub>	-	100	-	-42.6	179.5
LAGP70-SN0	70	30	0	-55.2	97.0
LAGP70-SN3	70	27	3	-59.2	67.0
LAGP70-SN6	70	24	6	-61.7	54.2
LAGP70-SN9	70	21	9	-62.5	41.1

around 60 °C [27–29]. In these electrolytes, a small amount of SN with high polarity was added into the hybrid solid electrolyte because of its ability to dissolve lithium salts. The effect of SN composition was investigated to provide hybrid solid electrolytes with high ionic conductivity and good mechanical stability. The hybrid solid electrolytes were then applied to the solid-state Li/LiFePO<sub>4</sub> cells, and their cycling performance was evaluated at room temperature. The cycling results of the cells revealed that the hybrid solid electrolytes allowed successful operation of the solid-state Li/LiFePO<sub>4</sub> cell at room temperature.

#### 2. Experimental

## 2.1. Preparation of the hybrid solid electrolyte

LAGP (Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub>) was synthesized by a conventional solid solution method [30]. Stoichiometric amounts of lithium carbonate, aluminum oxide, germanium oxide and ammonium dihydrogen phosphate were used as the starting materials. The mixture was thoroughly dispersed in isopropyl alcohol by ball milling and dried at 25 °C for 24 h to evaporate the solvent. The powder mixture was heated to 700°C at a heating rate of 5°C min<sup>-1</sup> in a tube furnace and held at that temperature for 2h to release any volatile compounds. The powders were then reground followed by heating to 850°C with a heating rate of  $5 \,^{\circ}$ C min<sup>-1</sup> and calcinated at the same temperature for 12 h in an argon atmosphere. PEO  $(M_n = 200,000)$  and lithium perchlorate (LiClO<sub>4</sub>) were purchased from Sigma-Aldrich, and the salt was used after vacuum drying at 100°C for 24h. Hybrid solid electrolytes were prepared by a solution casting method. Appropriate amounts of PEO and LiClO<sub>4</sub> to give [EO]:[Li] ratio of 18:1 were dissolved in anhydrous acetonitrile, and the solution was stirred at 60°C for 12 h. A predetermined amount of LAGP powder and SN was added into the solution and the resulting solution was mixed using ballmilling for 24 h. The detailed compositions of LAGP, PEO-LiClO<sub>4</sub> and SN in the hybrid solid electrolytes are given in Table 1. When complete homogenization of a mixture had occurred, the solution was cast on a flat Teflon plate using a doctor blade by allowing evaporation of solvent in an argon-filled glove box. Residual solvent was completely removed by heating the hybrid solid electrolyte at 40°C under vacuum. The resulting hybrid solid electrolyte was obtained as a flexible thin film, and its thickness ranged from 40 to 50 µm. It should be noted that the amount of SN was not increased above 9 wt.%, because the hybrid solid electrolyte could not be obtained as a self-standing thin film.

#### 2.2. Electrode preparation and cell assembly

The LiFePO<sub>4</sub> composite positive electrode was prepared by coating an acetonitrile-based slurry containing LiFePO<sub>4</sub> (Hanwha Chemical), PEO, LiClO<sub>4</sub>, SN and Super P carbon (MMM Co.) (50: 30.86: 4.14: 5: 10 by weight) onto Al foil. PEO was used as a Li<sup>+</sup> ion conductor as well as a binder in the positive electrode. The electrode was dried under vacuum for 12 h at 40 °C, and then roll pressed to enhance particulate contact and adhesion to the current

collector. The active mass loading in the positive electrode was about 8.0 mg cm<sup>-2</sup>. The lithium negative electrode consisted of a 200- $\mu$ m-thick lithium foil (Honjo Metal Co., Ltd.) that was pressed onto a copper current collector. A solid-state Li/LiFePO<sub>4</sub> cell was then assembled by sandwiching the hybrid solid electrolyte between the lithium negative electrode and the LiFePO<sub>4</sub> positive electrode. After cell assembly, the cells were kept at 55 °C for 24 h in order to promote interfacial contacts between the hybrid solid electrolyte and the LiFePO<sub>4</sub> positive electrode. All cells were assembled in a dry box filled with argon gas.

#### 2.3. Characterization and measurements

The particle size distribution of LAGP powders was obtained by using particle size analyzer (PSA, CILAS). The cross-sectional morphology of hybrid solid electrolyte was examined using a fieldemission scanning electron microscope (FE-SEM, JEOL JSM-7001F). The elemental distribution on the cross-sectional area of the hybrid solid electrolyte was examined using energy dispersive Xray spectroscopy (EDXS). X-ray diffraction (XRD) patterns of various samples were obtained using an X-ray diffractometer (Rigaku M2500) with Cu K $\alpha$  radiation. Differential scanning calorimetry (DSC) measurements were performed using TA instrument (SDT Q600/DSC Q20) with a heating rate of 5 °C min<sup>-1</sup> from -80 to 100 °C under the dry nitrogen atmosphere. For ionic conductivity measurements, the hybrid solid electrolyte was sandwiched between two disk-like stainless steel electrodes (12 mm in diameter). AC impedance measurements were carried out using a Zahner Electrik IM6 impedance analyzer over the frequency range from 10 Hz to 1 MHz with an amplitude of 10 mV at different temperatures. Each sample was allowed to equilibrate for 1 h at the required temperature before measurements. Linear sweep voltammetry (LSV) experiments were performed to investigate the electrochemical stability of the hybrid solid electrolytes on a platinum working electrode, with counter and reference electrodes of lithium metal, at a scanning rate of  $1.0 \text{ mV s}^{-1}$  and  $55 \circ C$ . Galvanostatic lithium plating/stripping measurements of symmetric Li/hybrid solid electrolyte/Li cells were performed at a constant current density of 0.2 mA cm<sup>-2</sup> and 55 °C. Charge and discharge cycling tests of the solid-state Li/ LiFePO<sub>4</sub> cells were conducted at a current rate of 0.2C in the voltage range of 2.6–4.0 V using battery testing equipment (WBCS 3000, Wonatech) at 25 °C.

## 3. Results and discussion

Fig. 1(a) shows an SEM image of the synthesized LAGP powders, showing that fine powders without agglomeration are obtained. As depicted in Fig. 1(b), the particle size ranged from 0.7 to 36.0  $\mu$ m, and the average particle size (D<sub>50</sub>) was about 10.6  $\mu$ m. The X-ray diffraction pattern of LAGP shown in Fig. 1(c) matched well with the standard pattern of the NASICON-type LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (JCPDS 80-1924), with a minor impurity peak corresponding to Li<sub>2</sub>O [30]. The lattice parameters for the LAGP crystalline phase were calculated to be a = 8.286 ± 0.002 Å and c = 20.535 ± 0.036 Å from



**Fig. 1.** (a) SEM image and (b) particle size distribution of the synthesized LAGP powders. (c) XRD patterns of the synthesized LAGP powder and the standard NASICON-type LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (JCPDS 80-1924).

a least-squares fitting, respectively. These values are consistent with those (a = 8.250 Å and c = 20.460 Å) previously reported for LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [31].

The hybrid solid polymer electrolytes composed of LAGP, PEO-LiClO<sub>4</sub> and SN were prepared. As shown in Fig. 2(a) and (b), the hybrid solid electrolyte (LAGP70-SN3) was obtained in the form of a flexible thin film. In contrast, the ceramic electrolyte prepared with LAGP was a brittle and rigid thick pellet with a thickness of 500 µm, as depicted in Fig. 2(c) and (d). A cross-sectional SEM image of the representative hybrid solid electrolyte (LAGP70-SN9) is presented in Fig. 3(a). It was found that the LAGP powders are well embedded in the hybrid solid electrolyte. Fig. 3(b)–(d) show the EDXS mapping images of various elements (P, C and N) on the cross section of the hybrid solid electrolyte shown in Fig. 3(a). The elemental mappings of the hybrid solid electrolyte show the overall distributions of phosphorus, carbon and nitrogen across the image, indicating that LAGP powders, PEO and SN are well distributed in the hybrid solid electrolyte.

Fig. 4(a) shows the XRD patterns of PEO-LiClO<sub>4</sub>, SN, LAGP and hybrid solid electrolytes. The XRD pattern of PEO-based solid polymer electrolyte (PEO-LiClO<sub>4</sub>) presents two broad crystalline peaks at  $2\theta = 19^{\circ}$  and  $23^{\circ}$ , which are due to the ordering of PEO chains [32,33]. The XRD pattern of SN exhibits two crystalline peaks at  $2\theta = 20^{\circ}$  and  $28^{\circ}$ , which can be ascribed to its plastic crystalline phase [27,28]. The intensity of crystalline peaks in PEO and SN was significantly reduced by hybridizing them with LAGP. This result can be attributed to the destructive effect of LAGP on the ordered arrangement of PEO chains as well as physical interaction between SN and PEO, resulting in an increase of the amorphous phase in the solid polymer electrolyte (PEO-LiClO<sub>4</sub>). The reduction in crystalline phase PEO due to the introduction of LAGP powders and SN is expected to increase the ionic conductivity in the solid polymer electrolyte. Compared to pure LAGP powder, the crystalline peaks of LAGP in hybrid solid electrolytes were almost the same without any broadening or shifting. This result supports the idea that the LAGP powder maintains its crystalline structure without any degradation in the hybrid solid electrolytes. Similarly, the intensity of crystalline peaks in PEO was also reduced in the composite solid electrolyte by incorporation of Al<sub>2</sub>O<sub>3</sub> into PEO-LiClO<sub>4</sub>, as shown in Fig. 4(b). These results suggest that the addition of ceramic particles (LAGP and Al<sub>2</sub>O<sub>3</sub>) is effective in reducing the crystallinity of PEO.

Temperature dependence of ionic conductivities for hybrid solid electrolytes with different compositions is shown in Fig. 5(a). For comparison, the ionic conductivities of solid polymer electrolyte (PEO-LiClO<sub>4</sub>) are also given in the figure. As expected, the ionic conductivities increased with increasing temperature for all the solid electrolytes, due to the faster movement of ions and increased flexibility of polymer chains. The PEO-based solid polymer electrolyte exhibited ionic conductivities ranging from  $10^{-7}$  to  $10^{-4}$  S cm<sup>-1</sup> in the temperature range of 25 to 75 °C, which are in good agreement with previous results [34]. The ionic conductivities of hybrid solid electrolyte composed of PEO-LiClO<sub>4</sub> and LAGP without SN (LAGP70-SN0) were higher than those of solid polymer electrolyte prepared with PEO and LiClO<sub>4</sub> at all temperature ranges investigated. This result implies that ion conduction in Li+conducting LAGP enhances the ionic conductivity of the hybrid solid electrolyte. In order to confirm this presumption, we measured the ionic conductivities of hybrid solid electrolytes containing 70 wt.% LAGP powder (LAGP-70) and 70 wt.% Al<sub>2</sub>O<sub>3</sub> particle (Al<sub>2</sub>O<sub>3</sub>-70), respectively. As a result, the LAGP-70 exhibited much higher ionic conductivity  $(1.0 \times 10^{-5} \, \text{S \, cm}^{-1})$  compared to  $Al_2O_3\mbox{-}70\mbox{}$  (7.2  $\times\,10^{-7}\,S\,cm^{-1}$  ). Accordingly, the enhanced ionic conductivity in the LAGP-based hybrid solid electrolyte can be attributed to the incorporation of ionic conductive LAGP powder. The increase of ionic conductivity in the hybrid solid electrolyte as compared to that of PEO-based solid polymer electrolyte also arises from the reduction in crystallinity of the PEO phase by adding glass ceramic powders (LAGP), as explained in Fig. 4. Ionic conductivities of hybrid solid electrolytes are further increased with the addition of SN into the hybrid solid electrolytes. The enhanced ionic conductivity can be attributed to an increase in solvating power for dissolving lithium salts and with a reduction in crystallinity of the PEO phase by incorporation of SN [27]. The activation energies  $(E_a)$ 



Fig. 2. Photographs of hybrid solid electrolyte (LAGP70-SN3) (a,b) and ceramic electrolyte prepared with LAGP (c,d).



Fig. 3. Cross-sectional SEM image of the hybrid solid electrolyte (LAGP70-SN9), and EDXS mapping images of (b) P, (c) C and (d) N on the cross section of the hybrid solid electrolyte.



Fig. 4. XRD patterns of (a) LAGP-based hybrid solid electrolytes and (b) Al<sub>2</sub>O<sub>3</sub>-based composite electrolytes.

of the various hybrid solid electrolytes were calculated from the linear-least-square fit of the data from  $\log \sigma$  versus 1/T plots in the lower temperature region showing a linear relationship. As given in Table 1, the activation energy was significantly reduced by hybridizing PEO-LiClO<sub>4</sub> with LAGP. The values of E<sub>2</sub> were further decreased with increasing the content of SN in the hybrid electrolytes. This result is due to the enhanced mobility of polymer segments and faster movement of carrier ions by addition of SN. It could be confirmed by decrease of glass transition temperature  $(T_{\sigma})$ with increasing SN content in the hybrid solid electrolytes (Table 1). At the high temperatures at which PEO melts, the PEO-based solid polymer electrolyte exhibited relatively high ionic conductivities due to the melting of the crystalline PEO phase; however, its dimensional stability was not good at high temperatures. The ionic conductivity reached  $1.1 \times 10^{-4} \,\text{S cm}^{-1}$  for LAGP70-SN9 at room temperature. Although its room temperature ionic conductivity was lower than that of LAGP in the form of a sintered pellet  $(1.9 \times 10^{-4} \,\mathrm{S \, cm^{-1}})$ , the hybrid solid electrolyte could be prepared with a flexible thin film ( $\sim$ 45  $\mu$ m). The electrochemical stability of the hybrid solid electrolytes was evaluated by linear sweep voltammetry, and the resulting LSV curves are shown in Fig. 5(b). The experiments were conducted at 55°C because the ionic conductivity of PEO-based solid polymer electrolyte was too low to measure the oxidative current with linear sweep voltammetry at 25 °C. In the PEO-based solid polymer electrolyte, the oxidation current started to increase around 4.5 V vs. Li/Li<sup>+</sup> due to the oxidative decomposition of PEO. On the other hand, the hybrid solid electrolytes exhibited enhanced oxidative stabilities higher than 5.0V. The enhanced oxidative stabilities of hybrid solid electrolytes arise from the addition of a large amount of LAGP with good oxidative stability at high potential [26]. These results reveal



Fig. 5. (a) Temperature dependence of ionic conductivity and (b) linear sweep voltammograms of various solid electrolytes with different compositions at  $55 \,^{\circ}$ C.

that the hybrid solid electrolyte can be safely applied to a Li/LiFePO<sub>4</sub> cell that is cycled in the voltage range of 2.5-4.0 V.

To investigate the interfacial behavior between lithium electrode and solid electrolyte under dynamic conditions, the symmetrical Li/electrolyte/Li cells with different solid electrolytes were subjected to galvanostatic plating and stripping cycles at a current density of 0.2 mAh cm<sup>-2</sup> at 55 °C. Fig. 6(a) and (b) show the voltage profiles, which are obtained from the galvanostatic lithium plating and stripping tests performed using PEO-based solid polymer electrolyte and hybrid solid electrolytes in the symmetrical cells. The cell with PEO-based solid polymer electrolyte exhibited an unstable high voltage profile and intermittent short circuit behavior, due to the formation of a dendritic short circuit and its poor dimensional stability at 55 °C. In contrast, the cells employing hybrid solid electrolytes showed more stable voltage profiles. These results indicate that inorganic LAGP particles in the hybrid solid electrolytes reinforce dimensional stability and inhibit the growth of lithium dendrite. The cells with hybrid solid electrolyte showed much lower voltage profiles compared to the PEO-based cell, and the overpotential decreased with increasing SN, which could be ascribed to the enhanced ionic conductivity of solid electrolytes and favorable interfacial properties. Accordingly, it is expected that the use of a hybrid solid electrolyte composed of LAGP, PEO-LiClO<sub>4</sub> and SN reduces the internal resistance of the cell and allows the safe operation of lithium metal-based cells.

The solid-state Li/LiFePO<sub>4</sub> cells assembled with hybrid solid electrolytes were subjected to charge and discharge cycles in the voltage range of 2.5-4.0 V at a constant current rate of 0.2C and  $25 \,^{\circ}$ C. Fig. 7(a) shows the typical charge and discharge curves of the Li/LiFePO<sub>4</sub> cell assembled with LAGP70-SN9. The cell exhibited a



**Fig. 6.** Voltage profiles of the symmetrical Li/electrolyte/Li cells with (a) PEO-based solid polymer electrolyte and (b) hybrid solid electrolytes at a current density of 0.2 mAh cm<sup>-2</sup> at 55 °C.

potential plateau in the range of 3.4 to 3.5 V during cycling, which is a typical cycling behavior of the Li/LiFePO₄ cells [35–37]. The cell initially delivered a discharge capacity of 127.8 mAh  $g^{-1}$  based on the active LiFePO<sub>4</sub> material in the positive electrode. It is noticeable that the discharge capacity of the cell was gradually increased to 136.8 mAh  $g^{-1}$  during the initial 20 cycles and then slowly decreased with further cycling, which is similar to previous reports [28,38]. An initial increase in the discharge capacity may be due to the fact that ion transport in the hybrid solid electrolyte as well as the interfacial contacts between the electrolyte and electrodes are improved during the initial charge-discharge cycles of the cells. The coulombic efficiency of the Li/LiFePO<sub>4</sub> cell steadily increased and stabilized with the cycle number, and was maintained at>99.0% throughout cycling after the initial few cycles. Use of the electrochemically stable hybrid solid electrolyte may suppress harmful interfacial side reactions between the electrodes and the electrolyte, which results in high coulombic efficiency during cycling. The compact interfacial contacts between the hybrid solid electrolyte and the composite LiFePO<sub>4</sub> positive electrode also contributed to good cycling stability. Fig. 6(b) shows the discharge capacities of the Li/LiFePO<sub>4</sub> cells assembled with different electrolytes as a function of cycle number. It is clearly seen that the discharge capacity increased with increasing SN in the hybrid solid electrolytes. As discussed earlier, the ionic conductivity increases and the interfacial resistances decrease with increasing the content of SN in the hybrid solid electrolyte, which results in a higher discharge capacity. In the case of hybrid solid electrolyte without SN



**Fig. 7.** (a) Charge and discharge curves of the Li/LiFePO<sub>4</sub> cell assembled with LAGP70-SN9, and (b) discharge capacities of the Li/LiFePO<sub>4</sub> cells with different hybrid solid electrolytes as a function of cycle number (current rate: 0.2C, cut-off voltage: 2.5–4.0V, 25 °C). (c) Initial discharge capacities of Li/LiFePO<sub>4</sub> cells with different hybrid solid electrolytes at 0.2 and 0.5C rate.

(LAGP70-SN0), the discharge capacities are very low, which may arise from the high internal resistance of the cell due to low ionic conductivity of the hybrid solid electrolyte at room temperature. In order to examine the effect of SN content on the discharge capacity, the cells were cycled at higher current rate (0.5C). At 0.5C rate, the cells with LAGP70-SN0 and LAGP70-SN9 delivered discharge capacities of 1.8 and 94.4 mAh g<sup>-1</sup>, respectively, as shown in Fig. 7(c). These results indicate that the difference in discharge capacity is more prominent at high current rate, which is mainly caused by difference in ionic resistance of the hybrid solid electrolytes with different content of SN.

#### 4. Conclusions

Hybrid solid electrolytes composed of LAGP, PEO-LiClO₄ and SN were prepared as thin films by a solution casting process, and their electrochemical properties were investigated. Hybrid solid electrolytes showed enhanced ionic conductivities at ambient temperature when a small amount of SN was added. They showed good electrochemical stability and favorable interfacial characteristics to lithium electrode. The solid-state Li/LiFePO<sub>4</sub> cell assembled with a hybrid solid electrolyte containing 70 wt.% LAGP, 21 wt.% PEO-LiClO<sub>4</sub> and 9 wt.% SN had a high discharge capacity and exhibited good capacity retention at ambient temperature. The good cycling performance of the cells resulted from the high ionic conductivity and good electrochemical stability as well as good interfacial contacts with electrodes. Thus, it is expected that hybrid solid electrolytes composed of LAGP, PEO and SN will be useful as solid electrolytes for solid-state lithium metal cells with good cycling stability.

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