



Preparation of lithium ion conductive $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte from solution for the fabrication of composite cathode of all-solid-state lithium battery

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Abstract

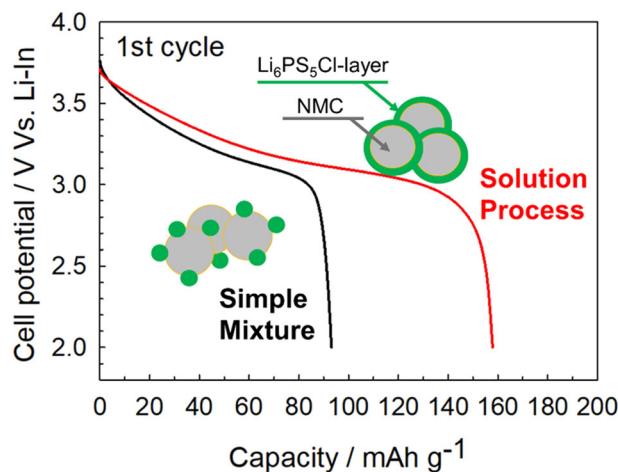
An argyrodite type $\text{Li}_6\text{PS}_5\text{Cl}$ was prepared by the solution process using a mixture of solvents with a fast evaporation rate. The crystal phase and ionic conductivity of the $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte were examined by X-ray diffraction and electrochemical impedance spectroscopy, respectively. $\text{Li}_6\text{PS}_5\text{Cl}$ derived from solution process shows an argyrodite structure with an ionic conductivity of $6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. Composite cathode was directly prepared by dispersing $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (84 wt%) and a conductive additive (2 wt%) into a $\text{Li}_6\text{PS}_5\text{Cl}$ precursor solution (14 wt%), with subsequent heating at 150 °C. Morphology of the composite cathode was evaluated by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The formation of $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on the active material particles was observed. A bulk-type all-solid-state cell was fabricated with composite cathode derived from the solution process, achieving an initial discharge capacity of 160 mAh g^{-1} and capacity retention of ~80% after 20 cycles with a capacity efficiency of 100%.

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Graphical Abstract

Argyrodite type $\text{Li}_6\text{PS}_5\text{Cl}$ prepared by solution process and its application to prepare composite cathode for an all-solid-state lithium battery.



Highlights

- An argyrodite type $\text{Li}_6\text{PS}_5\text{Cl}$ was prepared by solution process using a mixture solvents with a fast evaporation rate.
- Composite cathode for all solid state battery was directly prepared by dispersing a cathode material in the precursor solution.
- The cell worked as a rechargeable battery with good cycle performance.

Keywords All solid state lithium battery · Solid electrolyte · Composite electrode · Argyrodite type

1 Introduction

All-solid-state lithium secondary batteries (ASLBs) using inorganic solid electrolytes have been predicted as next generation batteries with having higher energy density, safety and reliability. Sulfide-based solid electrolytes (SSE), such as glassy or glass-ceramic $\text{Li}_2\text{S-P}_2\text{S}_5$ or $\text{Li}_2\text{S-P}_2\text{S}_5\text{-GeS}_2$ systems, have been widely used to fabricate bulk-type ASLBs [1–4], not only because of their high lithium ion conductivity (10^{-2} – 10^{-4} S cm^{-1}), but also because of their mechanical properties that allow an intimate contact between electrode and electrolyte [5]. Usually, composite cathode is prepared by a simple mixture of active material, solid electrolyte, and/or carbon additives [1–4]. In general terms, the solid electrolyte content in the composite cathode obtained by simple mixture may vary from 30 to 60 wt% achieving up to 70% of the total theoretical discharge capacity (e.g., circa of 100 mAh g^{-1} for LiCoO_2 [1, 2]). To obtain superior electrochemical performance in ASLBs, it is necessary to prepare favorable interfaces between electrodes and solid electrolytes with large contact areas. As liquids easily cover the surface of a solid, the favorable interfaces between electrodes and solid electrolytes can be prepared by the coating of a liquid precursor of the solid electrolyte on the electrode material by solution phase process and

subsequent drying and heating to form solid electrolyte from the precursor. Recently, SSEs have been prepared by solution process achieving high ionic conductivities of 10^{-4} – 10^{-5} S cm^{-1} . Some examples include Li_3PS_4 (2.3×10^{-6} S cm^{-1}) [6], $\text{LiI-Li}_4\text{SnS}_4$ (4.1×10^{-4} S cm^{-1}) [7], Li_4SnS_4 (1.4×10^{-4} S cm^{-1}) [8], $\text{Li}_6\text{PS}_5\text{Br}$ (3.4×10^{-5} S cm^{-1}) [9], $\text{Li}_6\text{PS}_5\text{Cl}$ (1.4×10^{-5} S cm^{-1}) [10, 11], from different solvents such as N-methylformamide [6], methanol [7], water [8], ethanol [10] or solvent mixtures, ethanol, and ethyl propionate [9]. The composite cathodes were obtained after the solvent removal at relative low temperatures of 80–200 °C [7, 9] or higher temperature up to 320 °C [8] to promote higher ionic conductivity of SSE-layer. The formation of an adequate interface between SSE-layer and active material has been verified by the good electrochemical performance of the bulk-type ASLBs. Composite cathodes with ca. 15 wt% SSE-layer have achieved high initial discharge capacities of 110 mAh g^{-1} ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) [9] and 140 mAh g^{-1} (LiCoO_2) [7, 8].

Based on these positive achievements, in the present work, we studied a new solvent medium to prepare a SSE-layer and promote a better interface between active material and sulfide solid electrolyte for a bulk-type ASLB. In the formulation of the coating, the selection of solvents is based on their evaporation rate because the evaporation rate plays

an important role in obtaining adequate coating properties such as density, covering degree, and homogeneity [12]. In a previous study, $\text{Li}_6\text{PS}_5\text{Cl}$ was dissolved in ethanol and it was used to produce a SSE-layer [10, 11]. Here, a solvent medium combining ethyl acetate and ethanol is proposed to control the properties of the sulfide electrolyte layer since both solvents are fairly volatile [12] with low boiling points around 78 °C. In addition, both solvents have relatively low toxicity and low cost making them suitable for a further industrial application. To evaluate the effectivity of the solvent medium to form an appropriate SSE-layer, a composite cathode was prepared using $\text{Li}_6\text{PS}_5\text{Cl}$ and high voltage cathode $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$.

2 Experimental

All of the experiments in this study were conducted under an argon atmosphere ($\text{H}_2\text{O} \leq 5$, $\text{O}_2 \leq 1$ p.p.m).

2.1 Synthesis of composite cathode

The composite cathodes were prepared by solution process using LiNbO_2 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) [13, 14], $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte and vapor grown carbon fiber (VGCF, Showa Denko, Japan) as the active material, ionic, and electronic conductor additives, respectively. Super-dehydrated ethanol (99.5%, Wako Pure Chemical, Japan) and super-dehydrated ethyl acetate (99.5%, Wako Pure Chemical, Japan) were used as solvents. The weight ratio of NMC: $\text{Li}_6\text{PS}_5\text{Cl}$:VGCF of 84:14:2 was evaluated.

$\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte was firstly prepared by a mechanical milling process following the procedure reported previously [11]. Typically, 0.5 g of stoichiometric proportions of Li_2S (Mitsuwa's Purity Chemicals, 99.9%), P_2S_5 (Sigma Aldrich, 99%), and LiCl (Sigma Aldrich, 99.9%) were milled with 15 zirconia balls (10 mm diameter) in a zirconia pot (45 mL) using a planetary ball mill (PULVERISETTE, Fritsch, Germany) for 40 h at 600 r.p.m. The as-synthesized $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte powder with an ionic conductivity of 4×10^{-5} S cm^{-1} was then used to prepare the SSE-solution and further, $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on active material. $\text{Li}_6\text{PS}_5\text{Cl}$ powder was dissolved in a mixture of ethanol and ethyl acetate (molar ratio of 4:6), the concentration of $\text{Li}_6\text{PS}_5\text{Cl}$ solution was 0.1 g mL^{-1} . The composite cathode was finally prepared by solution process dispersing NMC and VGCF in the $\text{Li}_6\text{PS}_5\text{Cl}$ -solution. A vortex mixer at 2800 r.p.m. (AS ONE test tube shakers, Japan) was used to homogenize the slurry and the solvents were then removed by heating at 150 °C under vacuum.

The crystal phase, morphology, and ionic conductivity of the $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte obtained by dissolution-

recipitation process were examined to elucidate the effect of the solvents on the properties of the sulfide electrolyte. The crystal phase evaluated by X-ray diffraction (XRD) was carried out with an X-ray diffractometer (MultiFlex600, Rigaku) using $\text{CuK}\alpha$ radiation. In XRD measurements, a stainless-steel background holder covered with a protective Kapton film was used to prevent reaction of solid electrolyte with moisture. The ionic conductivity of pelletized samples was determined by electrochemical impedance spectroscopy (EIS) using an impedance analyzer (SI 1260, Solartron) in the frequency range of 0.1 MHz to 200 Hz at the amplitude of 10 mV. The solid electrolyte powders (110 mg, thickness of ~ 0.9 mm) were pressed under 360 MPa (at room temperature) in a polycarbonate tube, 10 mm of diameter and two stainless steel (SS) disks were used as current collectors. The sample was placed in a sealed glass container with terminals in a glove box. The impedance was measured under the inert conditions. Morphology and compositional distribution of the prepared composite cathode were studied by scanning electron microscopy (SEM), performed on a JIB-4600F Multibeam SEM-FIB Scanning Electron Microscope.

2.2 Cell assembly and electrochemical measurements

The all-solid-state battery was constructed using $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol%) glass and indium metal (99.99% 0.1 mm thickness) as solid electrolyte and anode, respectively. The $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ solid electrolyte was prepared by mechanical milling using 1 g of stoichiometric proportions of Li_2S and P_2S_5 and 4 mm diameter zirconia balls (500 balls) in a zirconia pot (45 mL) at 510 r.p.m. for 10 h. The composite cathode (10 mg) and the solid electrolyte powder (80 mg) were pressed under 360 MPa in a polycarbonate tube ($\phi = 10$ mm). The indium metal (40 mg) was pressed under 240 MPa on the prepared pellet. The three-layered pellet was sandwiched between two stainless-steel disks as current collectors to fabricate two electrode cells. The all-solid-state cells were placed in a sealed glass container with terminals, in a glove box. The all-solid-state cells were evaluated under the inert conditions. The electrochemical performance of the cell was evaluated under a constant current density of 0.13 mA cm^{-2} in the voltage range from 2.0 V to 3.8 V vs. Li-In at room temperature, using a charge/discharge measuring device (Scribner Associates, 580 battery type system).

An all-solid-state battery fabricated with composite cathode prepared by a simple mixture of NMC, $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by mechanical milling and VGCF was used as a comparison. NMC, $\text{Li}_6\text{PS}_5\text{Cl}$, and VGCF were mixed using a vortex mixer with the same mass ratio of the composite cathode prepared by solution process.

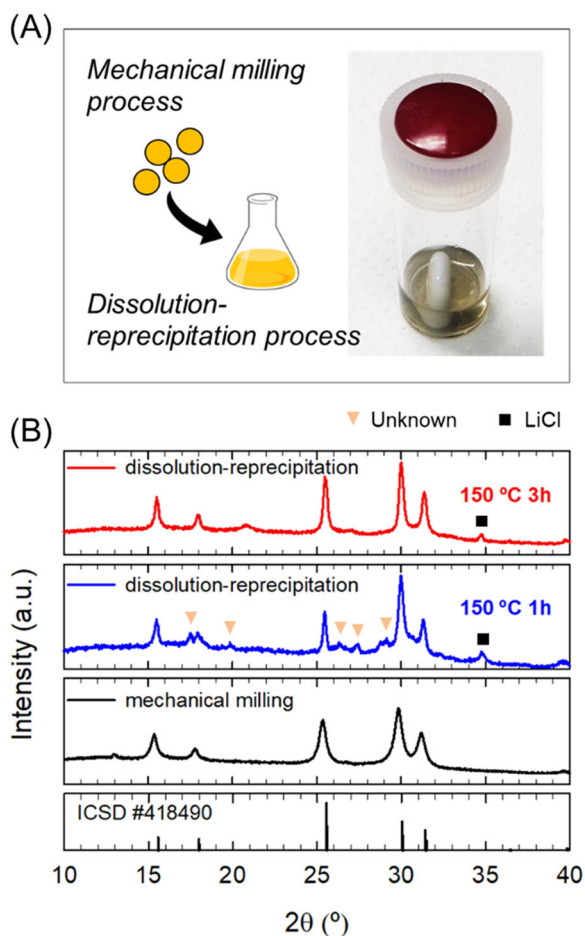


Fig. 1 **a** Photography of $\text{Li}_6\text{PS}_5\text{Cl}$ SSE-solution. **b** XRD of the $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by mechanical milling and dissolution-precipitation process after drying at 150°C

3 Results and discussion

Figure 1a shows a photography of $\text{Li}_6\text{PS}_5\text{Cl}$ solution. Homogeneous yellow solution was obtained after full dissolution of $\text{Li}_6\text{PS}_5\text{Cl}$ prepared by mechanical milling in a mixture of ethanol and ethyl acetate solvents. Figure 1b displays the X-ray diffraction (XRD) patterns of the $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte obtained by mechanical milling and dissolution-precipitation procedures. The precipitation of $\text{Li}_6\text{PS}_5\text{Cl}$ powder from $\text{Li}_6\text{PS}_5\text{Cl}$ -SSE-solution was promoted at 150°C . The XRD patterns at two different period times of heat treatment were included. The indexed XRD pattern of the $\text{Li}_{6.2}\text{PS}_5\text{Cl}$ (ICDD #418490) phase was also included for comparison. The $\text{Li}_6\text{PS}_5\text{Cl}$ phase is clearly observed in the XRD pattern of the powder obtained by mechanical milling, indicating a complete reaction of raw materials. The XRD pattern of the $\text{Li}_6\text{PS}_5\text{Cl}$ powder obtained by dissolution-precipitation process shows the $\text{Li}_6\text{PS}_5\text{Cl}$ phase as the major phase, a small peak around 35° is attributed to the LiCl . Small additional reflections are

observed in the XRD pattern of the $\text{Li}_6\text{PS}_5\text{Cl}$ powder obtained after heating at 150°C for 1 h. These reflections could not be indexed by the structure of the starting precursor materials, however, they disappear when the heat treatment was extended to 3 h. The formation of complex between solid electrolyte and solvents could produce these additional reflections [15]. The XRD results indicate that the solvents do not produce significant changes in the structure of $\text{Li}_6\text{PS}_5\text{Cl}$ crystal phase obtained by dissolution-precipitation process.

Figure 2 shows the impedance plot of $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by the dissolution-precipitation process. The Nyquist plot consists in a semicircle at high frequency and a capacitive tail at low frequency due to the interface between the ionic conductor and blocking stainless steel electrodes. The total resistance (bulk and grain boundary resistances) used to calculate the ionic conductivity was estimated at the intersection point, Z' axis, between semicircle and capacitive tail ($3 \times 10^4 \text{ Hz}$). Ionic conductivity of the $\text{Li}_6\text{PS}_5\text{Cl}$ attains $6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The high crystallinity of $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by the dissolution-precipitation process, verified by XRD patterns (Fig. 1b), make it difficult to pelletize the sample leading to a possible underestimated ionic conductivity. The ionic conductivity of the $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by dissolution-precipitation process was lower than that obtained by mechanical milling and heated at 550°C ($1 \times 10^{-3} \text{ S cm}^{-1}$ [16, 17]), and slightly higher to the $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by solution process from ethanol solution ($\sim 2 \times 10^{-5} \text{ S cm}^{-1}$) [10, 11]. In crystallized samples, the high thermal treatment is used to create a better grain boundary contact between particles [17]. The lower ionic conduction of SSE derived from solution process has been attributed to an increase of the grain boundary resistance produced most likely by the remaining organic compounds on the surface of SSE particles [10, 15]. In this sense, the unassigned peaks observed in the XRD pattern of $\text{Li}_6\text{PS}_5\text{Cl}$ crystal derived from $\text{Li}_6\text{PS}_5\text{Cl}$ solution at 150°C for 1 h (Fig. 1b), suggest that the presence of remaining organic phases in the $\text{Li}_6\text{PS}_5\text{Cl}$ are promoted by insufficient thermal treatment. In our previous results [11], a $\text{Li}_6\text{PS}_5\text{Cl}$ crystal derived from ethanol showed a well crystallized argyrodite phase without any additional peak after solvent evaporation at lower temperature of 80°C . The boiling point and vapor pressure of both, ethanol ($\sim 5.95 \text{ kPa}$ at 20°C) and ethyl acetate ($\sim 9.73 \text{ kPa}$ at 20°C), are low and quite similar, therefore these should be evaporating at low temperature around 80°C . However, a higher temperature of 150°C was needed to completely remove ethanol and ethyl acetate, used to prepare the $\text{Li}_6\text{PS}_5\text{Cl}$ crystal reported in this work, evidencing a different reactivity of $\text{Li}_6\text{PS}_5\text{Cl}$ with the solvents. The chemical interactions between the $\text{Li}_6\text{PS}_5\text{Cl}$ and organic solvent medium is still not understood and further studies will be carried out to elucidate this behavior.

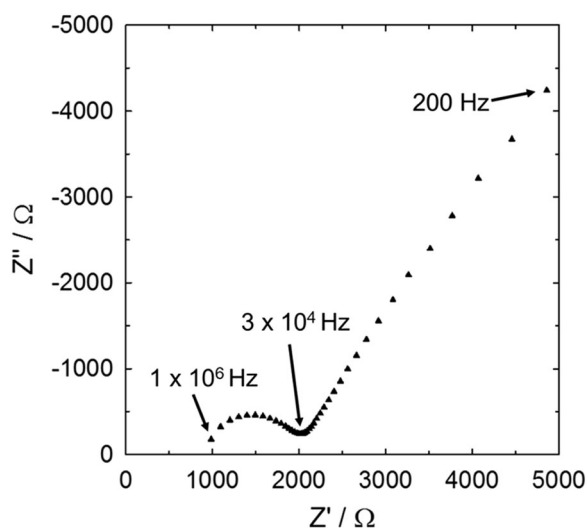


Fig. 2 Nyquist plot at room temperature of $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by dissolution-reprecipitation process after drying at 150°C

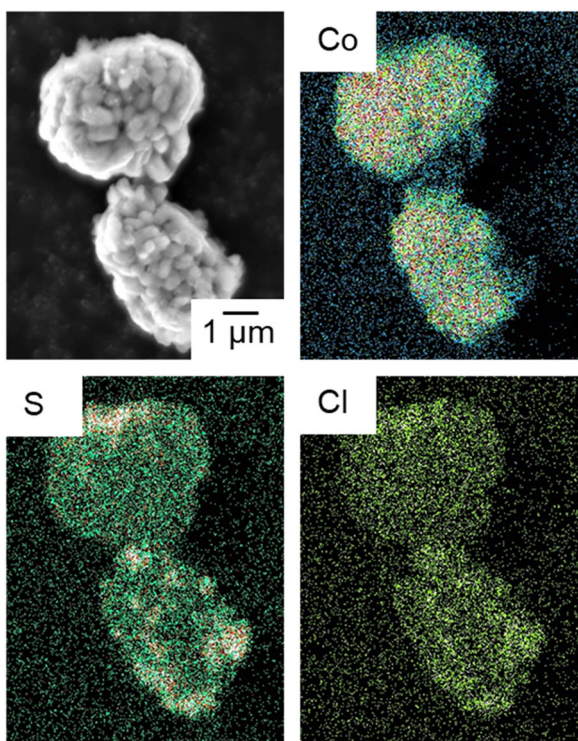


Fig. 3 SEM-EDS analysis of composite cathode prepared by liquid phase process

A heat treatment at relative low temperature of 150°C during a short period time of 3 h is suitable to promote the entire solvents removal to prepare $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on NMC particles with moderate-high ionic conductivity.

Figure 3 displays the SEM morphology of composite cathode obtained by liquid phase process. EDS mapping images of cobalt, sulfur, and chlorine are also shown. The SEM image discloses NMC particles with a size around

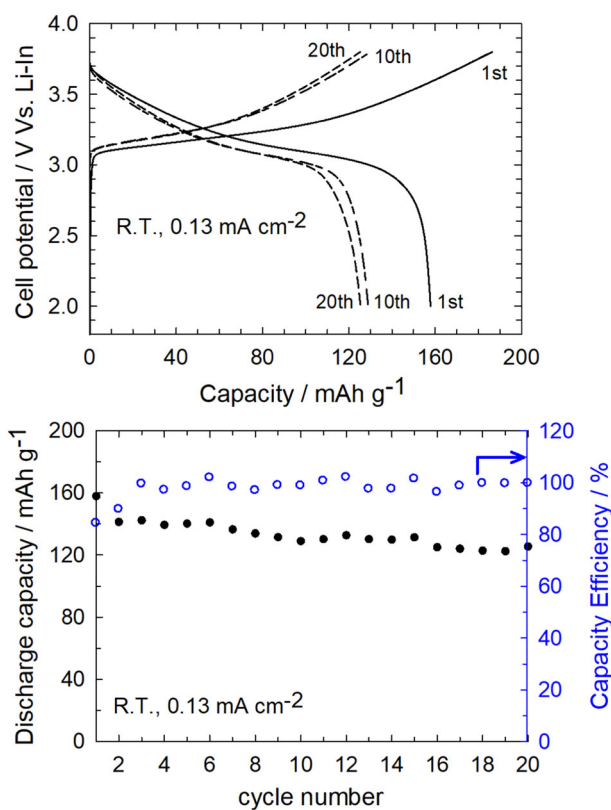


Fig. 4 Charge-discharge curves (top) and cycle performances of the all-solid-state cell using cathode composite prepared by solution process (bottom)

$5\ \mu\text{m}$. The sulfur and chlorine, elements from the sulfide solid electrolyte, were detected on the surface of active material particles. Although coating on NMC secondary particles with aggregates of primary particles is very challenging, the liquid phase process resulted to be effective to produce a good distribution of $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on them.

Figure 4 shows charge-discharge curves and cycle performance of the bulk-type ASLB cell fabricated with composite cathode prepared by the liquid phase process. The composite cathode contains a relative low content of SSE of 14 wt%. The all-solid-state cell was evaluated in a voltage range of 2 V to 3.8 V (vs. Li-In) at a current density of $0.13\ \text{mA cm}^{-2}$ at 25°C . The cell works as a rechargeable battery achieving an initial discharge capacity of $160\ \text{mAh g}^{-1}$ and capacity retention of $\sim 80\%$ after 20 cycles with a capacity efficiency of 100%. For comparison, Fig. 5 shows charge-discharge curves and cycle performance of the all-solid-state cell fabricated with composite cathode prepared by a simple mixing of solid electrolyte powder and the active material. The $\text{Li}_6\text{PS}_5\text{Cl}$ obtained by mechanical milling with an ionic conductivity of $4 \times 10^{-5}\ \text{S cm}^{-1}$ was used to prepare the composite cathode. The content of $\text{Li}_6\text{PS}_5\text{Cl}$ was 14 wt%, which is the same as that prepared by the solution process. The cell works as a rechargeable battery achieving a lower initial discharge

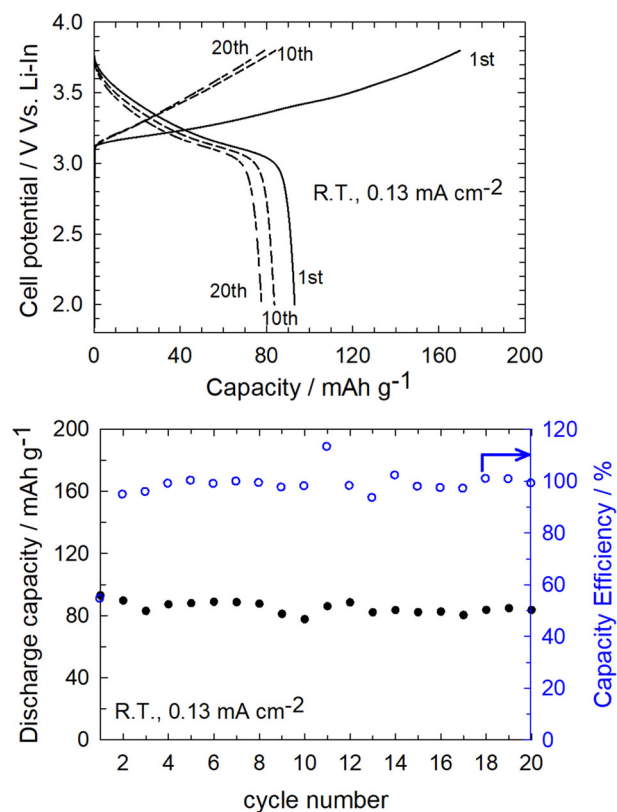


Fig. 5 Charge-discharge curves (top) and cycle performances of the all-solid-state cell using cathode composite prepared by simple mixture (bottom)

capacity of 92 mAh g^{-1} and capacity retention of $\sim 80\%$ after 20 cycles with a capacity efficiency of 100%.

The high initial discharge capacity of the bulk-type ASLB cell with the composite cathode prepared by solution process indicates that the $\text{Li}_6\text{PS}_5\text{Cl}$ -layer is well formed facilitating an adequate ionic conduction to the active material, better than using a simple mixture process. The conductivity of $\text{Li}_6\text{PS}_5\text{Cl}$ used in both composite cathodes is quite similar, $4\text{--}6 \times 10^{-5} \text{ S cm}^{-1}$, and thus the difference of their electrochemical performance is associated directly to the improvement of the interface between electrode and electrolyte obtained by solution process.

The initial discharge capacity of the bulk-type ASLB cell prepared by solution process is also higher than reported by other composite cathodes prepared by solution process with the same composition using argyrodite-type $\text{Li}_6\text{PS}_5\text{X}$ (Cl, Br) as a SSE-layer and NMC as active material and, ethanol or mixture of ethanol and ethyl propionate as solution medium [9, 11]. Composite cathode derived from ethanol solution shows an initial discharge capacity of 44 mAh g^{-1} [11], while 110 mAh g^{-1} has been reported from a solvent mixture of ethanol and ethyl propionate [9]. Although, the interaction between sulfide solid electrolyte and solvents is still unclear, the different electrochemical performance of these composite cathodes obtained by solution process

evidences that this interaction can be modified depending on the solvent or their mixture. Difficulty in removal is expected with ethyl propionate since it has a slightly high boiling point of 99°C compared with ethyl acetate.

Regarding cycle performance of the bulk-type ASLB cell with the composite cathode prepared by solution process, gradual decrease of the discharge capacity is attributed to the reaction in the interface between $\text{Li}_6\text{PS}_5\text{Cl}$ -SSE-layer and active material. In fact, the discharge capacity diminishes from 160 mAh g^{-1} to 140 mAh g^{-1} after the first and second cycle, evidencing a high reactivity during the first cycles. After the second cycle, the discharge capacity decreases slightly attaining a good capacity efficiency of 100%.

4 Conclusions

Argyrodite type $\text{Li}_6\text{PS}_5\text{Cl}$ was prepared by solution process using a mixture of ethanol and ethyl acetate as solvent medium. Crystal phase of $\text{Li}_6\text{PS}_5\text{Cl}$ was confirmed after a complete removal of the solvents at 150°C for 3 h. $\text{Li}_6\text{PS}_5\text{Cl}$ solution was used to prepare composite cathode by dispersion of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and carbon particles, followed by solvent elimination at 150°C . A bulk-type all-solid-state battery fabricated with the composite cathode obtained by solution process showed a high initial discharge capacity of 160 mAh g^{-1} . Solution process has proven to be effective to produce a good interface between $\text{Li}_6\text{PS}_5\text{Cl}$ -layer and active material. The selection of adequate solution medium could improve the electrochemical performance of composite cathode obtained by solution process.

5 Disclaimer

The material has not been published in whole or in part elsewhere; The paper is not currently being considered for publication elsewhere; All authors have been personally and actively involved in substantive work leading to the paper, and will hold themselves jointly and individually responsible for its content.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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