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Liquid-phase synthesis of $\text{Li}_6\text{PS}_5\text{Br}$ using ultrasonication and application to cathode composite electrodes in all-solid-state batteries

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Abstract

Lithium-ion conductive $\text{Li}_6\text{PS}_5\text{Br}$ is prepared using ultrasonication of Li_2S , P_2S_5 and LiBr in ethyl propionate-ethanol solution and subsequent heating at 453 K. The main phase of the synthesized product is $\text{Li}_6\text{PS}_5\text{Br}$ and its lithium ion conductivity is $3.4 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The cathode composite of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{Li}_6\text{PS}_5\text{Br}$ and vapor grown carbon fiber (VGCF) is prepared via ultrasonication of the $\text{Li}_6\text{PS}_5\text{Br}$ precursor solution containing $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and VGCF, and the all-solid-state lithium battery using this cathode composite is fabricated. The cell exhibits the discharge capacity of 109 mAh g^{-1} for the first cycle and its capacity of 87 mAh g^{-1} after 10 cycles.

1. Introduction

Lithium ion batteries have been widely used in electronic devices and transportation, which are key devices for current and future society. However, their flammable organic electrolytes bring about safety issues [1], and all-solid-state lithium secondary batteries using nonflammable solid electrolyte have received a great attention [2,3]. The challenge for all-solid-state lithium secondary batteries is lithium ion path in solids; high lithium ion conductivity of solid electrolyte as well as large contact area between electrolyte and electrode powders are essential [4,5]. Inorganic solid electrolytes for all-solid-state lithium secondary batteries application include oxide-based [6,7,8] and sulfide-based compounds [9,10]. Oxide-based solid electrolytes have advantages of stability in air in contrast to sulfide-based ones. Nevertheless, it is difficult to form lithium ion path in the composite electrodes without high temperature sintering because of its high grain boundary resistance [11,12]. While sulfide-based solid electrolytes are unstable in air, their grain boundary resistance is small without high temperature sintering due to their softness [10,12]. Sulfide-based solid electrolytes, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_7\text{P}_3\text{S}_{11}$ and $\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5$ glasses, are promising solid electrolytes for all solid state battery with high lithium ion conductivity of 10^{-2} - 10^{-4} S cm^{-1} [6,7,8,13,14,15]. Among them, $\text{Li}_6\text{PS}_5\text{X}$ (X=Cl, Br, I) with argyrodite structure exhibits rather high lithium ion conductivity of 10^{-2} - 10^{-3} S cm^{-1} [16,17].

$2\cdot 10^{-3} \text{ S cm}^{-1}$ at room temperature [16,17]. Electrode composites containing active material and solid electrolyte are useful to reduce internal resistivity of all-solid-state lithium secondary batteries. Nonetheless, it is difficult to prepare the composite materials with large contact area between electrode and solid electrolyte powders by a solid process via mixing these powders. In contrast, a solution process has the advantages to prepare the composite by formation of a solid electrolyte layer on electrode powder using precursor solution of solid electrolyte. Thus, high contact area between the powders can be achieved. Additionally, solid electrolyte layer on electrode powder can bring large contact area even when the weight ratio of electrode powder in electrode composite increases. Hence, an increase of capacity can be expected by solution process [18]. Teragawa et al. have reported the coating of $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ on LiCoO_2 powder using a solution process [5]. The all-solid-state cell using $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ coated LiCoO_2 prepared by solution process shows a higher charge-discharge capacity than the cell using mixture of $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass and LiCoO_2 prepared via the solid process. Yubuchi et al. have reported the synthesis of $\text{Li}_6\text{PS}_5\text{Br}$ and $\text{Li}_6\text{PS}_5\text{Cl}$ with high lithium ion conductivity by a solution process using ethanol [19,20]. This solution process includes three steps. First, the solid electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$ or Li_3PS_4) is synthesized by the mechanical milling method using planetary ball mill apparatus. Second, synthesized solid electrolyte is dissolved in

ethanol for producing precursor solution. Finally, the precursor solution is heated and solid electrolyte is precipitated. However, mechanical milling process using planetary ball mill apparatus often produces only gram-scale powders and takes a few tens of hours, thus large-scale synthesis is still challenging. Recently, solid electrolytes have been synthesized without mechanical milling process. Liu et al. have reported the synthesis of β -Li₃PS₄ by reacting Li₂S and P₂S₅ in tetrahydrofuran and then heat treatment [21]. Ito et al. have reported Li₇P₃S₁₁ prepared by stirring Li₂S and P₂S₅ in 1,2-dimethoxyethane and heating [22]. The lithium ion conductivity of this Li₇P₃S₁₁ is 2.7×10^{-4} S cm⁻¹. Xu et al. have showed the preparation of Li₇P₃S₁₁ by dissolution-evaporation method using acetonitrile [23]. The Li₇P₃S₁₁ has lithium ion conductivity of 9.7×10^{-4} S cm⁻¹. Park et al. have reported that the synthesis of 0.4LiI-0.6Li₄SnS₄ with high lithium ion conductivity of 4.1×10^{-4} S cm⁻¹ and its stability in air [24]. The all-solid-state battery using cathode active material coated with 0.4LiI-0.6Li₄SnS₄ shows stable charge-discharge behavior. Recently, some of the authors have reported a shaking process to produce Li₃PS₄ solid electrolyte [25,26]. The suspension of Li₃PS₄ precursor is prepared by shaking the starting materials of Li₂S and P₂S₅ powders in dimethyl carbonate as well as by ultrasonication of these same powders in ethyl propionate. The conductivity of Li₃PS₄ is 2.0×10^{-4} S cm⁻¹ and the synthesized Li₃PS₄ is applied to all-solid-state batteries. The

ultrasonication process has advantage of simple experimental manipulation and short synthesis time.

In this study, $\text{Li}_6\text{PS}_5\text{Br}$ was prepared as a powder and coating on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders by the solution process using ultrasonication treatment but without mechanical-milling process. The cathode electrode composite composed of $\text{Li}_6\text{PS}_5\text{Br}$ -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders and vapor grown carbon fiber was prepared by ultrasonication process, and evaluated as cathode material in an all-solid-state battery by the charge-discharge characteristics.

2. Experimental

All the synthesis processes and characterization except heat treatment were performed under a dry Ar atmosphere not to expose to air and moisture. $\text{Li}_6\text{PS}_5\text{Br}$ powder was prepared by two steps: ultrasonication of starting materials of $\text{Li}_6\text{PS}_5\text{Br}$ in ethyl propionate (EP), and subsequent reaction involved with ethanol solution. First, Li_2S (Mitsuwa Chemical, 99.9%), P_2S_5 (Aldrich, 99%) and LiBr (Aldrich, 99.9%) powders were weight in the molar ratio of $\text{Li}_2\text{S} : \text{P}_2\text{S}_5 : \text{LiBr} = 5 : 1 : 1.5$. These powders were put into EP (Kishida, 98%) in the mass ratio of starting material powders : EP = 1 : 19. The sample contained starting materials in EP was ultrasonicated at 333 K for 1 h under 28

kHz using an ultrasonic bath (Shimadzu RIKA, 100W). This ultrasonication process formed white suspension. Second, absolute ethanol(Wako, 99.5%) in the same amount of EP was added to the suspension, resulting in the formation of green transparent precursor solution. Then, the solution was heated at 423 K or 453 K for 3 h under vacuum to remove solvents. For comparison, the sample without adding ethanol and subsequent heating was prepared in order to examine the effect of ethanol addition. X-ray diffraction (XRD) patterns were measured by a XRD diffractometer using $\text{CuK}\alpha$ radiation of 1.5418 Å (Rigaku: Miniflex600). XRD data were recorded in the range of $2\theta = 10^\circ - 40^\circ$. Lithium ionic conductivity was estimated by AC impedance spectra measured using impedance analyzer (Solartron: 1260 Impedance Analyzer) in room temperature, in a frequency range from 0.1 Hz to 10^7 Hz. Cyclic voltammetry was measured to evaluate electrochemical stability of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by ultrasonication and subsequent heating at 453 K. For the measurement, the collector cell of Li-In/ $\text{Li}_6\text{PS}_5\text{Br}$ /stainless steel was constructed and its current was measured by potentiostat/galvanostat (Solartron: 1287 Electrochemical interface).

In order to prepare cathode composite electrodes, LiNbO_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Toda Kogyo) and Vapor Grown Carbon Fiber (VGCF, Showa Denko) were used as cathode active material and conductive additives, respectively. The cathode electrode

composite was prepared with the process based on the preparation of $\text{Li}_6\text{PS}_5\text{Br}$. First, the suspension was prepared from Li_2S , P_2S_5 , LiBr and EP by ultrasonication treatment at 333 K for 1 h under 28 kHz. Then, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, VGCF and ethanol were added to the suspension; the mass ratio of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$: the electrode components (Li, P, S, Br) : VGCF = 84 : 14: 2; this is relatively high mass ratio of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ against solid electrolyte to achieve high capacity when it is compared with the composite prepared by solid process [5]. Then, the ultrasonication was performed at 300 K for 5 minutes to disperse the active materials and VGCF in the suspension, and then heated at 453 K for 3 h under vacuum to remove solvents. Morphology and compositional distribution of the prepared cathode composites was studied by scanning electron microscopy (SEM) equipping energy-dispersive X-ray spectroscopy (EDX).

Laboratory-scale bulk-type all-solid-state cells [10] of $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were assembled. In brief, the cathode composites (10 mg) and the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ solid electrolyte glass (80 mg) were pressed under 320 MPa in a polycarbonate tube ($\phi=10$ mm). Subsequently, In foil (thickness: 0.1 mm) was pressed under 240 MPa on the prepared two layer pellet. The three-layered pellet was sandwiched by two stainless-steel dies as current collectors. $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ was prepared by mechanochemical process, following a previous report[15]. Charge-discharge

performance of the cell was evaluated under a constant current of 0.1 mA at room temperature using a charge-discharge measuring device (Scribner Associates, 580 battery type system): a current density of 0.13 mA cm^{-2} and ca. 0.07 C assuming 168 mAhg^{-1} of the theoretical capacity of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

For comparison with the solution process, $\text{Li}_6\text{PS}_5\text{Br}$ was prepared by mechanical milling of Li_2S and P_2S_5 , LiBr powders [27]. For mechanical milling condition, total mass of these powders was 2.0 g, a rotating speed was 600 rpm and a milling time was 20 h. The cathode composite was prepared by mixing $\text{Li}_6\text{PS}_5\text{Br}$ powder synthesized by ball milling, LiNbO_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, VGCF in an agate mortar with the same mass ratio of the above solution process.

3. Results and Discussion

The ultrasonication of Li_2S , P_2S_5 and LiBr in EP resulted in formation of white suspension. Subsequent addition of ethanol to the suspension produced green transparent solution, suggesting that the addition of polar solvent resulted in dissolution of white powder to form ion species.

The XRD patterns of the powder prepared by ultrasonication and further addition of ethanol and subsequent heat treatment at 453K and 423 K are shown in Fig . 1 (a,b).

The main peaks were indexed as $\text{Li}_6\text{PS}_5\text{Br}$, and the minor peaks from LiBr were also detected. Heat treatment temperature between 423 K and 453 K had no effect on the product phase. The calculated lattice parameter of cubic $\text{Li}_6\text{PS}_5\text{Br}$ was 10.0 Å, which was close to the reported one (9.9689 Å [28]). The average crystalline size was 28.7 nm from 220, 311 and 222 diffraction peaks.

For comparison, the XRD pattern of the powder prepared without addition of ethanol and heated at 453 K is shown in Fig. 1 (c). The peaks of $\alpha\text{-Li}_3\text{PS}_4$, Li_2S and LiBr were detected and peaks of $\text{Li}_6\text{PS}_5\text{Br}$ were not observed. The reactions of Li_2S , P_2S_5 and LiBr in EP by ultrasonication, ethanol addition, subsequent heating are considered as follows. First, Li_2S , P_2S_5 and LiBr powders were dispersed in EP. The ultrasonication causes the reaction between Li_2S and P_2S_5 to form PS_4^{3-} unit and produces $\alpha\text{-Li}_3\text{PS}_4$ precursor in white suspension; this is confirmed by the XRD peaks of $\alpha\text{-Li}_3\text{PS}_4$, Li_2S and LiBr observed in the precipitate produced by heating of the white suspension (Fig. 1 (c)). Then, the addition of ethanol to the white suspension results in the dissolution of $\alpha\text{-Li}_3\text{PS}_4$ precursor, Li_2S and LiBr , and form PS_4^{3-} , Li^+ , S^{2-} and Br^- ion species. Heat treatment of this solution brings precipitation of $\text{Li}_6\text{PS}_5\text{Br}$ powder by evaporation of EP-ethanol solvent (Fig. 1 (a,b)).

Figure 2 shows the impedance plots of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by (a) ultrasonication process

heated at 453K (b) ultrasonication process heated at 423K and (c) mechanical-milling process. The conductivity of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by the ultrasonication process heated at 453 K and 423 K are $3.4 \times 10^{-5} \text{ S cm}^{-1}$ and $1.5 \times 10^{-5} \text{ S cm}^{-1}$, respectively. Because of this result, in the cathode material synthesis, heat treatment was carried out at 453 K. which The conductivity of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by the ultrasonication process is approximately one-third lower ion conductivity than $\text{Li}_6\text{PS}_5\text{Br}$ prepared by mechanical milling ($1.0 \times 10^{-4} \text{ S cm}^{-1}$). The higher resistivity of that prepared by solution process than that prepared by mechanical milling can be attributed to rather large grain boundary resistance. The conductivity of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by ultrasonication is lower than $\text{Li}_7\text{P}_3\text{S}_{11}$ ($9.7 \times 10^{-4} \text{ S cm}^{-1}$) and $0.4\text{LiI}-0.6\text{Li}_4\text{SnS}_4$ ($4.1 \times 10^{-4} \text{ S cm}^{-1}$) prepared by liquid phase synthesis [23,24]. However, one order higher than $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass ($2.6 \times 10^{-6} \text{ S cm}^{-1}$) prepared via solution process [5]. Thus, $\text{Li}_6\text{PS}_5\text{Br}$ powder with moderate ion conductivity can be prepared by this ultrasonication process in a short time.

Figure 3 shows the CV plots of a Li-In/ $\text{Li}_6\text{PS}_5\text{Br}$ /stainless steel cell. The metallic lithium deposition ($\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$) and stripping ($\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$) were observed around 0 V. Nonetheless, small oxidation and reduction currents were observed in the range between 0 and 2 V, in contrast to the sample prepared by ball milling [28].

Figure 34 shows the XRD pattern of the cathode composite prepared by ultrasonication.

The diffraction peaks of $\text{Li}_6\text{PS}_5\text{Br}$ were observed with the strong peaks of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. This indicates that $\text{Li}_6\text{PS}_5\text{Br}$ phase is formed in the suspension of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and VGCF. Figure 5 shows SEM and EDX images of the cathode composite prepared by ultrasonication. The elemental mappings of P, S and Br overlap with the mapping of Co, suggesting $\text{Li}_6\text{PS}_5\text{Br}$ coating on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles. Thus, XRD and EDX results indicate that this process enables us to prepare solid electrolyte coating of $\text{Li}_6\text{PS}_5\text{Br}$ on the active material, based on the solution synthesis of $\text{Li}_6\text{PS}_5\text{Br}$.

Figure 6 shows the charge-discharge curves of the all-solid-state battery of $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5/\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell using the prepared composite via ultrasonication. The cell was first charged to 3.8 V, and the cutoff voltage for discharge was 2.0 V. For the first cycle, the discharge capacity is 109 mAh g^{-1} . The retention rate of discharge capacity after 10 cycles is ca. 80 % for the cell. The degradation of the capacity can be related to instability in the prepared $\text{Li}_6\text{PS}_5\text{Br}$ suggested in the above CV curve and/or the reaction between solid electrolyte and active material [29]. On the other hand, as shown in Fig. 67, the cell using the composite prepared by mechanical- milling process shows lower capacity than that prepared by the ultrasonication process. In the first cycle, the discharge capacity was 55 mAh g^{-1} . Although the ion conductivity of $\text{Li}_6\text{PS}_5\text{Br}$

prepared by ultrasonication is lower than that prepared by mechanical milling, the cell using cathode composite via ultrasonication showed a higher charge-discharge capacity than the cell using cathode composite prepared by mechanical milling process. This would be attributed to large contact area between $\text{Li}_6\text{PS}_5\text{Br}$ and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ prepared by solution process; the coating of $\text{Li}_6\text{PS}_5\text{Br}$ thin layer on $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle effectively form lithium ion path. In contrast, SEM-EDX analysis showed more aggregated $\text{Li}_6\text{PS}_5\text{Br}$ in the cathode composite prepared only by the solid process (See supporting document); the aggregated $\text{Li}_6\text{PS}_5\text{Br}$ would not produce the effective lithium ion path between $\text{Li}_6\text{PS}_5\text{Br}$ and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Thus, the solution process can form the composite in which the active materials can be effectively utilized and has therefore the advantage to achieve high energy density of the cell.

4. Conclusion

A new synthesis process of $\text{Li}_6\text{PS}_5\text{Br}$ was developed by using ultrasonication of Li_2S , P_2S_5 and LiBr in EP-ethanol solution and subsequent heating at 453 K. The synthesized $\text{Li}_6\text{PS}_5\text{Br}$ showed rather high lithium ion conductivity of $3.4 \times 10^{-5} \text{ S cm}^{-1}$. The conductivity of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by the ultrasonication process was lower than the conductivity of that prepared by mechanical milling process. However, this process has

the advantages of simple synthesis condition applicable for the coating on active materials to produce cathode composite by adding active materials. The cell using the cathode composite electrodes prepared by this process exhibited the capacity of 109 mAh g⁻¹ for the first discharge and its capacity of 87 mAh g⁻¹ after 10 cycles. The future challenges are to improve conductivity and electrochemical stability of Li₆PS₅Br, which would enhance the performance of the all-solid state battery.

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Reference

- [1] J. M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* 414(6861):359-367.
- [2] M. Tatsumisago, M. Nagao, A. Hayashi, Recent development of sulfide solid electrolytes and interfacial modification for all-solid-state rechargeable lithium batteries, *Journal of Asian Ceramic Societies* 1 (2013) 17–25.
- [3] M. Tatsumisago, S. Hama, A. Hayashi, H. Morimoto, T. Minami, New lithium ion conducting glass-ceramics prepared from cechanochemical Li₂S-P₂S₅ glasses, *Solid State Ionics* 154-155 (2002) 635-640.
- [4] H. Kitaura, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, Fabrication of electrolyte-electrolyte interfaces in all-solid-state rechargeable lithium batteries by

using a supercooled liquid state of the glassy electrolytes, *J. Mater. Chem.* 2011, 21, 118-124.

[5] S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi, M. Tatsumisago, Preparation of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolyte from N-methylformamide solution and application for all-solid-state lithium battery, *J. Power Source* 248 (2014) 939-942.

[6] R. Murugan, V. Thangadurai, W. Weppner, Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, *Angew. Chem. Int. Ed.* 47 (2007) 7778-7781.

[7] R. Jaleem, M. J. D. Rushton, W. Manalastas, M. Nakayama, T. Kasuga, J. A. Kilner, R. W. Grimes, Effects of Gallium Doping in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Garnet-type Solid Electrolytes, *Chem. Mater.* 27 (2015) 2821-2831.

[8] E. E. Jay, M. J. Rushton, A. Chroneos, R. W. Grimes, J. A. Kilner, Genetics of superionic conductivity in lithium lanthanum titanates, *Phys. Chem. Chem. Phys.* 17 (2015) 178-183.

[9] M. Tatsumisago, A. Hayashi, Superionic glasses and glasses-ceramics in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ system for all-solid-state lithium secondary batteries, *Solid State Ionics* 225 (2012) 342-345

[10] M. Tatsumisago, M. Nagao, A. Hayashi, Recent development of sulfide solid electrolytes and interfacial modification for all-solid-state rechargeable lithium batteries, *J. Asian Ceramic Societies* 1 (2013) 17-25.

[11] I. A. Sokolov, A. A. Il'in, Y. P. Tarlakov, N. A. Valova, A. A. Pronkin, Structure and Physicochemical Properties of Glasses in the $\text{Li}_2\text{S}-\text{LiPO}_3$ System, *Glass Physics and Chemistry* 29 (2003) 282-290.

[12] A. Sakuda, A. Hayashi, M. Tatsumisago, Sulfide Solid Electrolyte with Favorable Mechanical Property for All-Solid-State Lithium Battery, *Scientific Report* 3 (2013) 2261.

[13] Y. Kato, K. Kawamoto, R. Kanno, M. Hirayama, Discharge Performance of All-Solid-State Battery Using a Lithium Superionic Conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, *Electrochemistry*

Vol. 80 (2012) No. 10 p. 749-751.

[14] H. Yamane, M. Shibata, Y. Shimane, T. Junke, Y. Seino, S. Adams, K. Minami, A. Hayashi, M. Tatsumisago, Crystal structure of a superionic conductor, $\text{Li}_7\text{P}_3\text{S}_{11}$, *Solid State Ionics* 178 (2007) 1163–1167.

[15] A. Hayashi, S. Hama, H. Morimoto, M. Tatsumisago, T. Minami, Preparation of Li_2S - P_2S_5 Amorphous Solid Electrolytes by Mechanical Milling, *J. Am. Ceram. Soc.* 84 (2001) 477-479.

[16] R.P. Rao, S. Adams, Studies of lithium argyrodite solid electrolytes for all-state-state batteries, *phys. Status Solidi A* 208, 2011, 1804-1807.

[17] H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, $\text{Li}_6\text{PS}_5\text{X}$: A Class of Crystalline Li-Rich Solids With an Unusually High Li^+ Mobility, *Angew. Chem. Int. Ed.*, 2008, 47, 755-758.

[18] Y. Wang, Z. Liu, X. Zhu, Y. Tang, F. Huang, Highly lithium-ion conductive thio-LISICON thin film processed by low-temperature solution method, *Journal of Power Sources* 224 (2013) 225-229.

[19] S. Yubuchi, S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi, M. Tatsumisago, Preparation of high lithium-ion conducting $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte from ethanol solution for all-solid-state lithium batteries, *J. Power Sources* 293 (2015) 941-945.

[20] S. Yubuchi, A. Hayashi, M. Tatsumisago, Preparation and characterization of high lithium-ion conducting $\text{Li}_6\text{PS}_5\text{Br}$ solid electrolytes using a liquid-phase technique, *The 56th Battery Symposium in Japan*, 2015, p.417.

[21] Z. Liu, W. Fu, E. A. Payzant, X. Yu, Z. Wu, N. J. Dudney, J. Kiggans, K. L. Hong, A. J. Rondinone, C. Liang, Anomalous High Ionic Conductivity of Nanoporous β - Li_3PS_4 , *J. American Chemical Society* 135 (2013) 975-978.

[22] S. Ito, M. Nakakita, Y. Aihara, T. Uehara, N. Machida, A synthesis of crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte from 1,2-dimethoxyethane solvent, *J. Power Sources* 271 (2014) 342-345.

- [23] R. C. Xu, X. H. Xia, Z. J. Yao, X. L. Wang, C. D. Gu, J. P. Tu, Preparation of $\text{Li}_7\text{P}_3\text{S}_{11}$ glass-ceramic electrolyte by dissolution-evaporation method for all-solid-state lithium ion batteries, *Electrochimica Acta* 219 (2016) 235-240.
- [24] K. H. Park, D. Y. Oh, Y. E. Choi, Y. J. Nam, L. L. Kim, H. L. Xin, F. Lin, S. M. Oh, Y. S. Jung, Solution-Processable Glass $\text{LiI-Li}_4\text{SnS}_4$ Superionic Conductors for All-Solid-State Li-Ion Batteries, *Advanced Materials* 28 (2016) 1874-1883.
- [25] N. H. H. Phuc, K. Morikawa, M. Totani, H. Muto, A. Matsuda, Chemical synthesis of Li_3PS_4 precursor suspension by liquid-phase shaking, *Solid State Ionics* 285 (2016) 2-5.
- [26] N. H. H. Phuc, K. Morikawa, M. Totani, H. Muto, A. Matsuda, ~~in-preparation~~ Synthesis of plate-like Li_3PS_4 solid electrolyte via liquid-phase shaking for all-solid-state lithium batteries, *Ionics* 23 (2017) 2061-2067.
- [27] M. Chen, S. Adams, High performance all-solid-state lithium/sulfur batteries using lithium argyrodite electrolyte, *J. Solid State Electrochem* 19 (2015) 697-702.
- [28] S. Boulineau, M. Courty, J-M. Tarascon, V. Viallet, Mechanochemical synthesis of Li-argyrodite $\text{Li}_6\text{PS}_5\text{X}$ (X=Cl, Br, I) as sulfur-based solid electrolytes for all solid state batteries application, *Solid State Ionics* 221 (2012) 1-5.
- [29] J. Auvergniot, A. Cassel, J-B. Ledeuil, V. Viallet, V. Seznec, R. Dedryvere, Interface Stability of Argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ toward LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, LiMn_2O_4 in Bulk All-Solid-State Batteries, *Chemistry of Materials* 29 (2017) 3883-3890.

Figure Captions

Fig. 1. XRD patterns for powders (a) prepared with addition of ethanol and heated at 453 K (b) prepared with addition of ethanol and heated at 423 K (c) prepared without addition of ethanol and heated at 453 K.

Fig. 2. Nyquist plot at room temperature of $\text{Li}_6\text{PS}_5\text{Br}$ prepared by (a) ultrasonication and heating at 453 K, (b) ultrasonication and heating at 423 K and (c) mechanical milling.

Fig. 3 Cyclic voltammetry of a Li-In/ $\text{Li}_6\text{PS}_5\text{Br}$ /stainless steel cell.

Fig. 4. XRD pattern for cathode composite prepared via ultrasonication.

Fig. 5. SEM image of cathode composite prepared by ultrasonication and its corresponding EDX elemental maps.

Fig. 6. Charge-discharge curves of all-solid-state cell using cathode composite prepared by ultrasonication.

Fig. 7. Charge-discharge curves of all-solid-state cell using cathode composite prepared by mixing $\text{Li}_6\text{PS}_5\text{Br}$ synthesized by mechanical milling.

Fig.1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7