Heliyon 5 (2019) e02760

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.heliyon.com

Research article

Preparation of cubic Na_3PS_4 by liquid-phase shaking in methyl acetate medium

Matsuda Atsunori *, Gamo Hirotada, Nguyen Huu Huy Phuc **

Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan

ARTICLE INFO

Keywords:
Materials chemistry
Inorganic chemistry
Na_3PS_4
Liquid phase synthesis
Solid electrolyte
Sulfide-based solid electrolyte

ABSTRACT

Cubic Na_3PS_4 (c-Na_3PS_4), a high temperature phase of Na_3PS_4, is successfully prepared by liquid-phase shaking from Na_2S and P_2S_5 in methyl acetate medium. The effects of the amount of solvents, Na_2S and heat treatment on the formation of c-Na_3PS_4 are carefully investigated. In addition to c-Na_3PS_4, an unknown phase is also detected in the sample containing an excess amount of Na_2S in the starting materials mixture.

1. Introduction

Rechargeable sodium-ion batteries (SIBs) show great potential as stationary energy storage systems because of the high abundance of sodium and its suitable redox potential ($E_{Na+/Na} = -2.71$ V vs. SHE), which is just above that of lithium ($E_{Li+/Li} = -3.04$ V vs. SHE). Investigation of SIBs began in 1970s, along with lithium-ion batteries (LIBs), but was almost completely obscured by LIBs with the successful commercialization of LIBs by Sony in the 1990s [1]. In fact, while LIBs are mostly installed in personal portable devices or recently-developed electric vehicles (EVs), Na–S cells are currently being employed for megawatt-scale grid storage and Na–$NiCl_2$ ZEBRA (Zero Emission Batteries Research Activities) are being applied in EVs, both of which employ highly conductive sodium beta-alumina ceramics at high temperature (*ca.* 300 °C). Therefore, with the knowledge obtained from Li-ion technology, a room or moderate temperatures operation of Na-ion cells is an expected and a realistic target.

Solid electrolytes, such as oxide based and sulfide based, have also been receiving much interest from researchers. Hayashi and his group reported the formation of cubic and tetragonal Na_3PS_4 by heating Na_2S–P_2S_5 glass, which was synthesized by the planetary ball-milling method, to 270 °C and 420 °C, respectively [2]. It is worth noting that the high temperature cubic Na_3PS_4 (c-Na_3PS_4) was successfully stabilized at room temperature by crystallization from a glass system. Inspired by this innovation, modified forms of Na_3PS_4 have also been prepared by either cation substitution, Na_3PS_4–Na_4SiS_4 and $Na_3P_{1-x}As_xS_4$, or anion substitution, $Na_3PSe_{4-x}S_x$ [3, 4, 5].

One of the most interesting points from the report by Hayashi et al. was the stabilization of c-Na_3PS_4 at room temperature, which resulted in a high ionic conductivity of 2×10^{-4} S cm^{-1} [2]. On revisiting the Li-ion conductors, β-Li_3PS_4, a high temperature phase of Li_3PS_4, was also successfully stabilized at room temperature either embedded in a Li_3PO_4 matrix or in a nanoporous structure [6, 7]. It is also worth mentioning that nanoporous β-Li_3PS_4 was synthesized using a liquid-phase synthesis from reaction of Li_2S and P_2S_5 in tetrahydrofuran. We also studied the reaction of the Li_2S–P_2S_5–LiI system by liquid-phase shaking using a variety of ester-group-containing solvents and obtained nanosized solid electrolytes, which were useful to increase the active material loading in the electrode composite [8, 9, 10]. These results motivated us to attempt to prepare c-Na_3PS_4 using an ester solvent, to determine if c-Na_3PS_4 could be synthesized through a suspension route, as we demonstrated with Li_2S–P_2S_5–LiI solid electrolytes. Yubuchi et al. also succeeded in the preparation of c-Na_3PS_4 by dissolution of Na_2S and P_2S_5 in *N*-methylformamide and different solvents containing ether groups, such as 1, 2-dimethoxy ether (DME) or diethyl ether (DEE) [11, 12].

In this study, methyl acetate (MA) was employed as the reaction medium. The reaction between Na_2S and P_2S_5 occurred and was completed in MA; then the reaction product was precipitated from solution and was collected by centrifugation. Upon heating the reaction product under reduced pressure, c-Na_3PS_4 was obtained. In a previous publication, we hypothesized that the reactions between Li_2S and P_2S_5 in organic solvents were strongly related to the solubility parameters and donor numbers of the employed solvents [13]. In consideration that Na^+

* Corresponding author.
** Corresponding author.
E-mail addresses: matsuda@ee.tut.ac.jp (M. Atsunori), phuc@ion.ee.tut.ac.jp (N.H.H. Phuc).

https://doi.org/10.1016/j.heliyon.2019.e02760
Received 22 December 2018; Received in revised form 10 October 2019; Accepted 28 October 2019

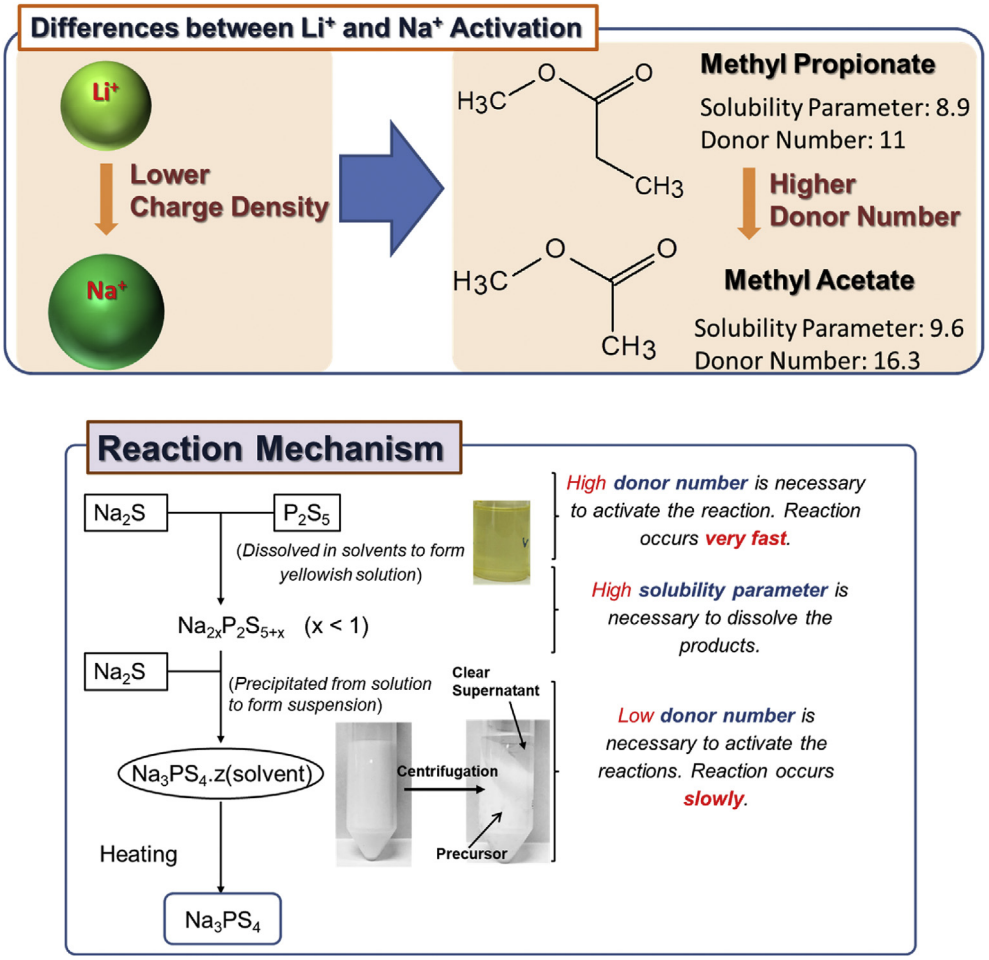

Fig. 1. Strategy of solvent choice for Na_3PS_4 synthesis through the liquid-phase route.

ion in Na_2S has a bigger diameter than that of Li^+ in Li_2S, which results in a lower charge density on the Na^+-ion surface, the solvents employed for promoting the reaction between Na_2S and P_2S_5 should have a higher donor number value than those used for the reaction between Li_2S and P_2S_5. We then found that MA had a donor number value of approximately 16.3 kcal mol^{-1}, which was slightly higher than the donor number value (11.0 kcal mol^{-1}) of methyl propionate (MP), which is one of the best solvents for mediating the reaction between Li_2S and P_2S_5 (Fig. 1).

2. Experimental

Na_2S (99%) and P_2S_5 (98%) were obtained from Kojundo Laboratory and Merck, respectively, and used without any further purification. Methyl acetate (99%; MA) was purchased from Aldrich and dehydrated using a 3-Å molecular sieve prior to use. The synthesis process was similar to our previous report [9]. In this study, slightly modified conditions were applied, 0.617 g of P_2S_5 was fixed for all runs and the amount of Na_2S was changed to obtain the following molar ratios Na_2S: P_2S_5 = 75, 76, 77, 78 : 25, since it has been reported that the purity of Na_2S a critical point to obtain c-Na_3PS_4 with high ionic conductivity [14]. The shaking time was fixed at 24 h. The amount of MA was investigated using a starting material with a molar ratio of Na_2S: P_2S_5 = 75 : 25. The reaction product was then collected from the suspension by centrifugation at 10000 rpm for 5 min and decanted. The obtained solid

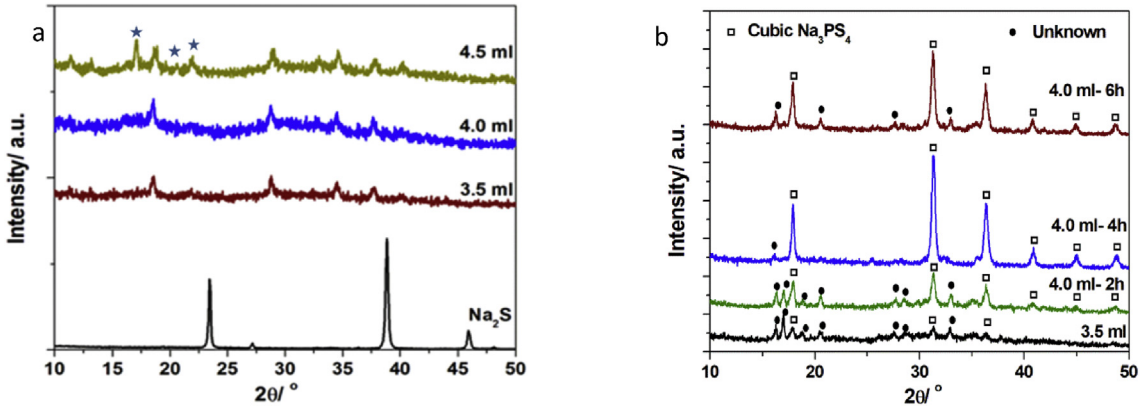

Fig. 2. XRD patterns of the prepared $75Na_2S{\cdot}25P_2S_5$ samples dried at (a) RT for 1 h and (b) 220 °C prepared using different amounts of MA.

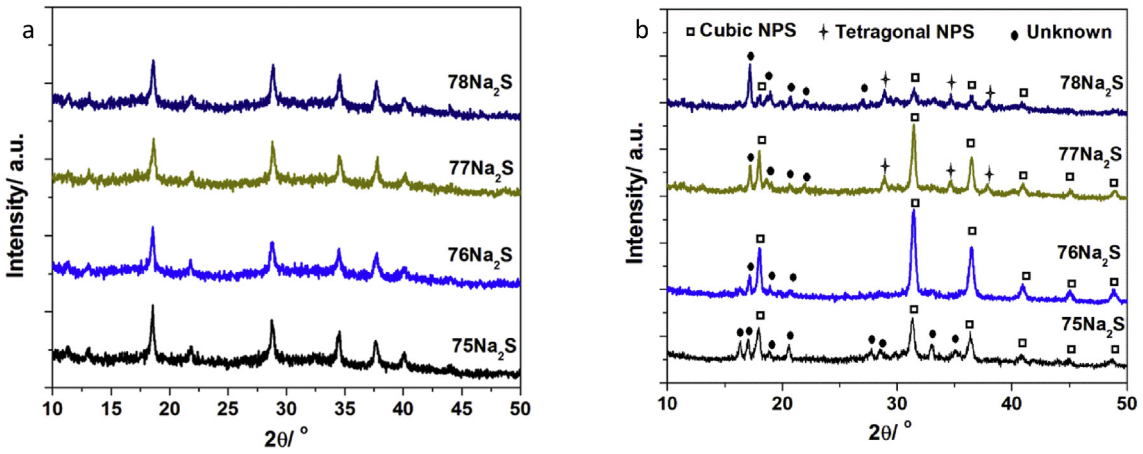

Fig. 3. XRD patterns of the prepared 75, 76, 77, 78Na_2S·25P_2S_5 samples dried at (a) RT for 1 h and (b) 220 °C for 2 h.

matter was then evaporated at RT and 220 °C under reduced pressure using a rotary pump.

The structure of the prepared powder was characterized using X-ray diffraction (XRD; Ultima IV, Rigaku). Samples were sealed in special holders in an Ar-filled glove box to protect them from exposure to humidity prior to their characterization by XRD.

The temperature dependences of the total conductivity of the prepared samples were investigated using alternating-current impedance spectroscopy (SI 1260, Solatron) from 1 MHz to 10 Hz in a dry Ar flow. The samples for impedance measurements were prepared by uniaxial pressing (approximately 100 mg of sample) into pellets of approximately 10.0 mm in diameter at a pressure of 550 MPa (at room temperature). The prepared pellet was placed in a holder made from polyetheretherketone (PEEK) with two stainless steel rods used as blocking electrodes. The cell was then placed in an Ar stream in a glass tube for the temperature dependence measurements. The temperature was gradually increased from room temperature to 170 °C. The sample was held at each temperature for 1 h prior to the impedance measurement.

3. Results and discussion

Fig. 2 shows the XRD patterns of the samples prepared with a molar ratio of Na_2S: P_2S_5 = 75 : 25 using different amounts of MA after being dried at room temperature (a) and 220 °C for 2h (b). Typical peaks of Na_2S were undetected in either sample dried at RT or 220 °C, which indicated that all the Na_2S in the starting material mixture was consumed and changed into the reaction products. XRD patterns of the samples prepared with 3.5 and 4.0 mL of MA after drying at RT exhibited similar features, though all peaks were unknown. Interestingly, slightly increasing the amount of MA from 4.0 to 4.5 mL resulted in the appearance of new peaks in the 2θ range from 10 to 17° and one at approximately 22° (marked with stars) in addition to those detected in the samples prepared using smaller amounts of MA. This observation showed that a new phase formed in addition to those observed in the samples obtained with 3.5 and 4.0 mL of MA. Although this phase was the co-crystalline of Na_3PS_4 and MA as reported elsewhere, this result pointed out that the structures of products obtained from the reaction between Na_2S and P_2S_5 in MA were strongly dependent on the amount of this solvent. Despite the similarity in XRD patterns of the samples obtained using 3.5 and 4.0 mL of MA after being dried at RT, the products obtained from heating these samples at 220 °C for 2 h exhibited differences in the XRD patterns (Fig. 1b). The sample prepared with 3.5 mL of MA exhibited the existence of both c-Na_3PS_4 and an unknown phase, where the unknown phase seemed to be the main phase; whilst c-Na_3PS_4 was clearly detected in the sample prepared with 4.0 mL of MA with the relative intensity ratio between the main peaks of c-Na_3PS_4 and the unknown phase becoming higher than 1 [2]. Inspired by this result, the heat treatment duration of this sample was varied to 4 and 6 h to investigate its change in structure, that is, the disappearance of the unknown phase. Upon prolonging the heat treatment time, c-Na_3PS_4 crystallization was improved with the increase of the relative peak intensity ratios, in comparison with that of the unknown phase, but the unknown phase was still detected. It has also been reported that the purity of Na_2S affects the ionic conductivity of glass–ceramic c-Na_3PS_4, which motivated us to investigate the effect of the amount of Na_2S on the formation of c-Na_3PS_4 prepared using 4.0mL of MA.

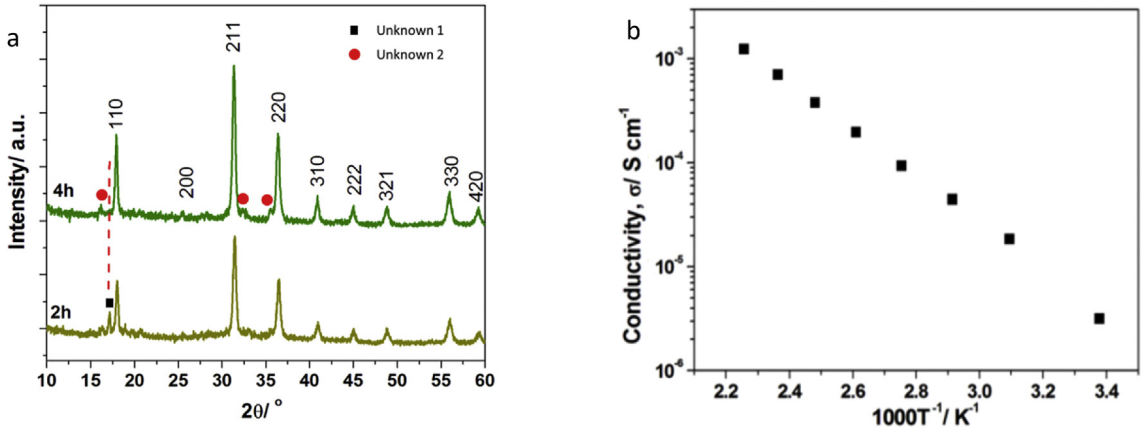

Fig. 4. (a) XRD patterns of the prepared 76Na_2S·25P_2S_5 samples heated at 220 °C for 2 and 4 h and (b) temperature dependence of ionic conductivity of sample obtained after heat treatment for 4h.

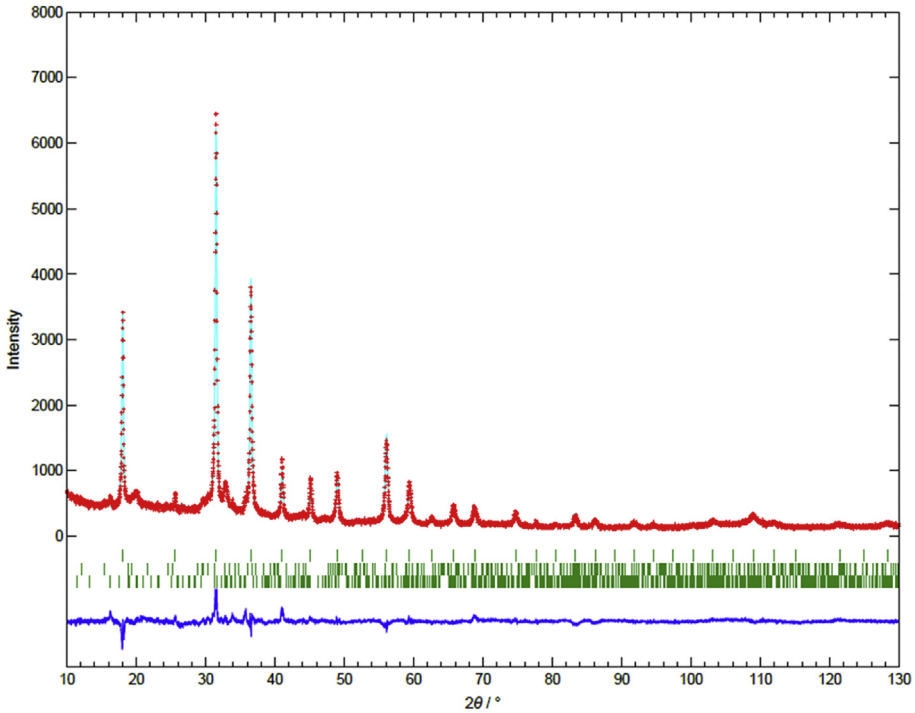

Fig. 5. X-ray Rietveld refinement profile of the prepared Na_3PS_4.

Fig. 3 shows the XRD patterns of the samples prepared with different molar ratios Na_2S: P_2S_5 = 75, 76, 77, 78 : 25 when the amount of P_2S_5 and MA were fixed at 0.617 g and 4.0 mL after being dried at RT (a) and 220 °C for 2 h. The samples dried at RT exhibited similar XRD patterns and all the observed peaks were unknown. The samples after being heated at 220 °C possessed different XRD patterns depending on the amount of Na_2S in the starting material mixture. Among them, the sample with Na_2S: P_2S_5 = 76 : 25 showed a nearly pure c-Na_3PS_4 phase with the impurity unknown phase detected with peaks in the 2θ range from 15 to 17°. A slight increase of Na_2S resulted in the formation of tetragonal Na_3PS_4 (Na_2S: P_2S_5 = 77 : 25) or even the new unknown phase when Na_2S: P_2S_5 = 78 : 25. This result proved that the amount of Na_2S was also a critical factor that affected the formation of c-Na_3PS_4 in addition to the amount of MA, as was discussed. We noticed that the Na_3PS_4 precursor, co-crystal of Na_3PS_4 and MA had different crystal structures to those prepared by either DME or DEE [12].

Fig. 4 shows the XRD patterns of the Na_2S: P_2S_5 = 76 : 25 samples after heat treatment at 220 °C for 2 and 4 h (a) and temperature dependence of ionic conductivity of the sample being heated for 4 h. As shown in Fig. 3a, the unknown phase was still detected in the sample after 2 h of heat treatment at 220 °C but nearly pure c-Na_3PS_4 was obtained in the sample being treated for 4 h and this phase was stabilized at room temperature. Fig. 3b shows the temperature dependence of the ionic conductivity of the sample after heat treatment for 4 h, the conductivity obeyed Arrhenius law; the conductivity at room temperature $\sigma_{25} = 4.1 \times 10^{-6}$ S cm^{-1} and activation energy was approximately 43 kJ mol^{-1}. The ionic conductivity of the sample obtained in this study was approximately two orders of magnitude lower than that of glass–ceramic c-Na_3PS_4 [2,14]. The low ionic conductivity of the sample prepared in this study may arise from the following reasons: 1) the formation of an unknown phase (unknown 2 in Fig. 3b), which was indicated as Na_3POS_3 in Ref. [11]; 2) solvent elimination would have contributed to the disorder of c-Na_3PS_4 prepared in this study, which then affected its ionic conductivity since the Na^+ ion moves in 3D conduction pathways and any blocking of these pathways will also lower the ionic conductivity [15]; 3) solvent elimination would also have an effect on the surface structure of the particle prepared in this study, which then increased the grain boundary resistance, as discussed in Ref. [11]. Although the ionic conductivity of c-Na_3PS_4 prepared in this study is lower than that of glass–ceramic c-Na_3PS_4, it is close to the values of c-Na_3PS_4 prepared by a liquid-phase synthesis reported so far [11, 12].

Fig. 5 illustrated the X-ray Rietveld refinement profile of the prepared Na_3PS_4 using the computer program RIETAN-FP [16]. The formation of cubic Na_3PS_4 (phase 1) was confirmed. However, trace of Na_3PS_3O (phase 2) and $Na_4P_2O_7$ (phase 3) were found to be co-existed with the main phase Na_3PS_4 [17, 18, 19]. Reliability factors were calculated to be Rwp = 8.581 (S = 1.532), Rp = 6.671, Re = 5.600 and lattice parameters of Na_3PS_4 were a = 6.9528 (4) Å and V = 336.12 (3) Å^3. The space groups of the three phases were determined to be: I -4 3 m (A-217), C m c 21 (A-36) and P 21 21 21 (A-19), respectively. Mass fractions of the three components were about 81.0% (Na_3PS_4), 6.9% (Na_3PS_3O) and 12.1% ($Na_4P_2O_7$). The low mass fraction of main component (81.0%) might be one of the reasons for the low ionic conductivity of the samples prepared in this study. Moreover, the reason for high fraction of $Na_4P_2O_7$ still remained for further investigated.

4. Conclusion

In summary, c-Na_3PS_4 was successfully prepared in this study by liquid-phase shaking using methyl acetate as the reaction medium to promote the reaction between Na_2S and P_2S_5. This study also showed that the relative amount of solvent to reactant was a critical factor in the liquid-phase synthesis of c-Na_3PS_4. To obtain high ionic conductivity sulfide-based solid electrolytes from the liquid phase, a detailed investigation and optimization of the relative amounts and heat treatment conditions are required—the same as those prepared by conventional methods.

Declarations

Author contribution statement

Nguyen Phuc: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed

reagents, materials, analysis tools or data; Wrote the paper.

Hirotada Gamo, Atsunori Matsuda: Analyzed and interpreted the data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We thank Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

References

[1] M. Yoshio, R.J. Brodd, A. Kozawa, Lithium-Ion Batteries, Springer, 2009.
[2] A. Hayashi, K. Noi, A. Sakuda, M. Tatsumisago, Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries, Nat. Commun. 3 (2012) 856.
[3] N. Tanibata, K. Noi, A. Hayashi, M. Tatsumisago, Preparation and characterization of highly sodium ion conducting Na_3PS_4–Na_4SiS_4 solid electrolytes, RSC Adv. 4 (2014) 17120.
[4] Z. Yu, S.L. Shang, J.H. Seo, D. Wang, X. Luo, Q. Huang, S. Chen, J. Lu, X. Li, Z.K. Liu, D. Wang, Exceptionally high ionic conductivity in $Na_3P_{0.62}As_{0.38}S_4$ with improved moisture stability for solid-state sodium-ion batteries, Adv. Mater. (2017) 1605561.
[5] L. Zhang, K. Yang, J. Mi, L. Lu, L. Zhao, L. Wang, Y. Li, H. Zeng, Na_3PSe_4: a novel chalcogenide solid electrolyte with high ionic conductivity, Adv. Energy Mater. 5 (2015) 1501294.
[6] K. Takada, M. Osada, N. Ohta, T. Inada, A. Kajiyama, H. Sasaki, S. Kondo, M. Watanabe, T. Sasaki, Lithium ion conductive oxysulfide, Li_3PO_4–Li_3PS_4, Solid State Ion. 176 (2005) 2355–2359.
[7] Z. Liu, W. Fu, E.A. Payzant, X. Yu, Z. Wu, N.J. Dudney, J. Kiggans, K. Hong, A.J. Rondinone, C. Liang, Anomalous high ionic conductivity of nanoporous beta-Li_3PS_4, J. Am. Chem. Soc. 135 (2013) 975–978.
[8] A. Matsuda, H. Muto, N.H.H. Phuc, Preparation of Li_3PS_4 solid electrolyte by liquid-phase shaking using organic solvents with carbonyl group as complex forming medium, J. Jpn. Soc. Powder Powder Metall. 63 (2016) 976–980.
[9] N.H.H. Phuc, K. Morikawa, T. Mitsuhiro, H. Muto, A. Matsuda, Synthesis of plate-like Li_3PS_4 solid electrolyte via liquid-phase shaking for all-solid-state lithium batteries, Ionics 23 (2017) 2061–2067.
[10] N.H.H. Phuc, E. Hirahara, K. Morikawa, H. Muto, A. Matsuda, One-pot liquid phase synthesis of $(100-x)Li_3PS_4$–$xLiI$ solid electrolytes, J. Power Sources 365 (2017) 7–11.
[11] S. Yubuchi, A. Hayashi, M. Tatsumisago, Sodium-ion conducting Na_3PS_4 electrolyte synthesized via a liquid-phase process using N-methylformamide, Chem. Lett. 44 (2015) 884–886.
[12] M. Uematsu, S. Yubuchi, K. Noi, A. Sakuda, A. Hayashi, M. Tatsumisago, Preparation of Na_3PS_4 electrolyte by liquid-phase process using ether, Solid State Ion. 320 (2018) 33–37.
[13] N.H.H. Phuc, A. Matsuda, Advances in Chemistry Research 42, 2018. Chapter 8.
[14] A. Hayashi, K. Noi, N. Tanibata, M. Nagao, M. Tatsumisago, High sodium ion conductivity of glass–ceramic electrolytes with cubic Na_3PS_4, J. Power Sources 258 (2014) 420–423.
[15] N. Tanibata, K. Noi, A. Hayashi, N. Kitamura, Y. Idemoto, M. Tatsumisago, X-ray crystal structure analysis of sodium-ion conductivity in 94 Na_3PS_4·6 Na_4SiS_4 glass-ceramic electrolytes, ChemElectroChem 1 (2014) 1130–1132.
[16] F. Izumi, K. Momma, Three-dimensional visualization in powder diffraction, Solid State Phenom. 130 (2007) 15–20.
[17] P.K. Jha, O.P. Pandey, K. Singh, Structural and thermal properties of Na_2S–P_2S_5 glass and glass ceramics, J. Non-Cryst. Solids 379 (2013) 89–94.
[18] A. Petrov, I. Sokolov, V.A. Markov, Electronic structure and ionic transport in phosphate glass with pyrophosphate structural elements, Key Eng. Mater. 822 (2019) 864–870.
[19] M. Pompetzki, M. Jansen, Natriumtrithiophosphat(V): Kristallstruktur und Natriumionenleitfähigkeit, Z. Anorg. Allg. Chem. 629 (2003) 1929–1933.