Preparation of cubic Na$_3$PS$_4$ by liquid-phase shaking in methyl acetate medium

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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$_3$PS$_4$ by heating Na$_2$S–P$_2$S$_5$ 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$_3$PS$_4$ (c-Na$_3$PS$_4$) was successfully stabilized at room temperature by crystallization from a glass. Inspired by this innovation, modified forms of Na$_3$PS$_4$ have also been prepared by either cation substitution, Na$_3$PS$_4$–Na$_2$SiS$_4$ and Na$_3$P$_1$–As$_2$S$_6$, or anion substitution, Na$_3$PSe$_4$–S$_2$ [3, 4, 5].

One of the most interesting points from the report by Hayashi et al. was the stabilization of c-Na$_3$PS$_4$ 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$_3$PS$_4$, a high temperature phase of Li$_3$PS$_4$, was also successfully stabilized at room temperature either embedded in a Li$_3$PO$_4$ matrix or in a nanoporous structure [6, 7]. It is also worth mentioning that nanoporous β-Li$_3$PS$_4$ was synthesized using a liquid-phase synthesis from reaction of Li$_2$S and P$_2$S$_5$ in tetrahydrofuran. We also studied the reaction of the Li$_2$S–P$_2$S$_5$–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$_3$PS$_4$ using an ester solvent, to determine if c-Na$_3$PS$_4$ could be synthesized through a suspension route, as we demonstrated with β-Li$_3$PS$_4$–LiI solid electrolytes. Yubuchi et al. also succeeded in the preparation of c-Na$_3$PS$_4$ by dissolution of Na$_2$S and P$_2$S$_5$ 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$_2$S and P$_2$S$_5$ 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$_3$PS$_4$ was obtained. In a previous publication, we hypothesized that the reactions between Li$_2$S and P$_2$S$_5$ in organic solvents were strongly related to the solubility parameters and donor numbers of the employed solvents [13]. In consideration that Na$^+$...
ion in Na$_2$S has a bigger diameter than that of Li$^+$ in Li$_2$S, which results in a lower charge density on the Na$^+$-ion surface, the solvents employed for promoting the reaction between Na$_2$S and P$_2$S$_5$ should have a higher donor number value than those used for the reaction between Li$_2$S and P$_2$S$_5$. 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$_2$S and P$_2$S$_5$ (Fig. 1).

2. Experimental

Na$_2$S (99%) and P$_2$S$_5$ (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$_2$S$_5$ was fixed for all runs and the amount of Na$_2$S was changed to obtain the following molar ratios Na$_2$S: P$_2$S$_5$ = 75, 76, 77, 78 : 25, since it has been reported that the purity of Na$_2$S a critical point to obtain c-Na$_3$PS$_4$ 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$_2$S: P$_2$S$_5$ = 75 : 25. The reaction product was then collected from the suspension by centrifugation at 10000 rpm for 5 min and decanted. The obtained solid...
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 Na₂S: P₂S₅ = 75 : 25 using different amounts of MA after being dried at room temperature (a) and 220 °C for 2 h (b). Typical peaks of Na₂S were undetected in either sample dried at RT or 220 °C, which indicated that all the Na₂S 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 Na₃PS₄ and MA as reported elsewhere, this result pointed out that the structures of products obtained from the reaction between Na₂S and P₂S₅ 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-Na₃PS₄ and an unknown phase, where the unknown phase seemed to be the main phase; whilst c-Na₃PS₄ was clearly detected in the sample prepared with 4.0 mL of MA with the relative intensity ratio between the main peaks of c-Na₃PS₄ 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-Na₃PS₄ 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 Na₂S affects the ionic conductivity of glass–ceramic c-Na₃PS₄, which motivated us to investigate the effect of the amount of Na₂S on the formation of c-Na₃PS₄ prepared using 4.0 mL of MA.

Fig. 3. XRD patterns of the prepared 75, 76, 77, 78Na₂S·25P₂S₅ samples dried at (a) RT for 1 h and (b) 220 °C for 2 h.

Fig. 4. (a) XRD patterns of the prepared 76Na₂S·25P₂S₅ samples heated at 220 °C for 2 and 4 h and (b) temperature dependence of ionic conductivity of sample obtained after heat treatment for 4 h.
Fig. 3 shows the XRD patterns of the samples prepared with different molar ratios Na$_2$S: P$_2$S$_5$ = 75, 76, 77, 78:25 when the amount of P$_2$S$_5$ 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$_2$S in the starting material mixture. Among them, the sample with Na$_2$S: P$_2$S$_5$ = 76:25 showed a nearly pure c-Na$_3$PS$_4$ phase with the impurity unknown phase detected with peaks in the 2θ range from 15 to 17°. A slight increase of Na$_2$S resulted in the formation of tetragonal Na$_3$PS$_4$ (Na$_2$S: P$_2$S$_5$ = 77:25) or even the new unknown phase when Na$_2$S: P$_2$S$_5$ = 78:25. This result proved that the amount of Na$_2$S was also a critical factor that affected the formation of c-Na$_3$PS$_4$ in addition to the amount of MA, as was discussed. We noticed that the Na$_3$PS$_4$ precursor, co-crystal of Na$_3$PS$_4$ and MA had different crystal structures to those prepared by either DME or DEE [12].

Fig. 4 shows the XRD patterns of the Na$_2$S: P$_2$S$_5$ = 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$_3$PS$_4$ 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 being heated 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$_3$PS$_4$, it is close to the values of c-Na$_3$PS$_4$ prepared by a liquid-phase synthesis reported so far [11, 12].

Fig. 5 illustrates the X-ray Rietveld refinement profile of the prepared Na$_3$PS$_4$ using the computer program RIETAN-FP [16]. The formation of cubic Na$_3$PS$_4$ (phase 1) was confirmed. However, trace of Na$_3$PS$_3$O (phase 2) and Na$_4$P$_2$O$_7$ (phase 3) were found to be co-existed with the main phase Na$_3$PS$_4$ [17, 18, 19]. Reliability factors were calculated to be $R_{wp} = 8.581$ (S = 1.532), $R_p = 6.671$, $R_e = 5.600$ and lattice parameters of Na$_3$PS$_4$ 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$_3$PS$_4$), 6.9% (Na$_3$PS$_3$O) and 12.1% (Na$_4$P$_2$O$_7$). 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$_4$P$_2$O$_7$ still remained for further investigated.

4. Conclusion

In summary, c-Na$_3$PS$_4$ was successfully prepared in this study by liquid-phase shaking using methyl acetate as the reaction medium to promote the reaction between Na$_2$S and P$_2$S$_5$. This study also showed that the relative amount of solvent to reactant was a critical factor in the liquid-phase synthesis of c-Na$_3$PS$_4$. 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.

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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 Na3PS4-Na4SiS4 solid electrolytes, RSC Adv. 4 (2014) 17120.
[4] Z. Yu, S.K. 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 Na3P0.62As0.38S4 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, Na3PSe4: 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, Li3PO4-Li3PS4, 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-Li3PS4, J. Am. Chem. Soc. 135 (2013) 975–978.
[8] A. Matsuda, H. Muto, N.H.H. Phuc, Preparation of Li3PS4 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. Mitsushi, H. Muto, A. Matsuda, Synthesis of plate-like Li3PS4 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)Li3PS4–xLiI solid electrolytes, J. Power Sources 365 (2017) 7–11.
[11] S. Yubuchi, A. Hayashi, M. Tatsumisago, Sodium-ion conducting Na3PS4 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 Na3PS4 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 Na3PS4, J. Power Sources 258 (2014) 420–423.
[15] N. Tanibata, K. Noi, A. Hayashi, N. Kitamura, Y. Idenoto, M. Tatsumisago, X-ray crystal structure analysis of sodium-ion conductivity in 94 Na3PS4·6 Na4Si3S4 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 Na2S–P2S5 glasses 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.