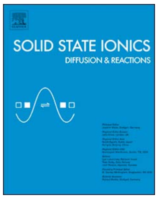
Solid State Ionics 320 (2018) 33–37

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Preparation of Na_3PS_4 electrolyte by liquid-phase process using ether

Miwa Uematsu, So Yubuchi, Kousuke Noi, Atsushi Sakuda, Akitoshi Hayashi[*],
Masahiro Tatsumisago

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

ARTICLE INFO

Keywords:
Solid electrolyte
Liquid-phase synthesis
Sodium ion conductor
Sulfide
Ether

ABSTRACT

Na_3PS_4 solid electrolytes were synthesized by liquid-phase reactions of Na_2S and P_2S_5 in 1,2-dimethoxyethane or diethyl ether. After stirring of the starting materials, white suspensions were obtained. The suspensions were dried at room temperature and heated at 270 °C under vacuum to obtain powders. The crystalline phases of the powders were cubic Na_3PS_4. The pelletized Na_3PS_4 prepared using 1,2-dimethoxyethane or diethyl ether showed conductivities of 2.6×10^{-5} S cm^{-5} or 1.8×10^{-5} S cm^{-1} at 25 °C, respectively.

1. Introduction

All-solid-state batteries using nonflammable inorganic solid electrolytes are safer and more reliable than ordinary batteries using organic electrolytes [1]. In addition, sodium secondary batteries are attracting attention because sodium is an abundant and inexpensive resource [2]. In order to realize all-solid state batteries, solid electrolytes have been actively studied. We have reported that sulfide glass-ceramics of cubic Na_3PS_4 prepared by a mechanical milling (MM) technique show a high sodium-ion conductivity of over 10^{-4} S cm^{-1} at room temperature. The all-solid-state batteries using Na_3PS_4 electrolyte with TiS_2 [3], TiS_3 [4], $NaCrO_2$ [5], and S [6,7] electrode active materials successfully worked as a secondary battery at room temperature.

For a practical realization of the all-solid-state batteries, the simpler preparation methods of the sulfide-based solid electrolytes are required. Recently, a liquid-phase synthesis of the solid electrolytes has been attracting attention. In the method, raw materials are stirred in organic solvents, and the obtained suspensions [8–10] or solutions [11,12] are dried and heated to obtain the solid electrolytes. This method is suitable for practical application because it is highly versatile and particle morphology can be controlled. There are several reports on liquid-phase syntheses of lithium-ion conductive sulfide solid electrolytes. Liu et al. reported the liquid-phase synthesis of β-Li_3PS_4 electrolyte using tetrahydrofuran [8]. Additionally, there have been several attempts to prepare lithium-ion conductors such as Li_2S-P_2S_5 solid electrolytes using ethers, esters or other organic solvents. Ito et al. synthesized $Li_7P_3S_{11}$ electrolyte using 1,2-dimethoxyethane (DME) [9]. Phuc et al. prepared β-Li_3PS_4 electrolyte using ethyl acetate [10]. On the other hand, there is only one report on the subject of sulfide sodium-ion conductor prepared from raw materials by the liquid-phase method [13]. We first reported that cubic Na_3PS_4 synthesized using *N*-methylformamide (NMF). Its ionic conductivity was 2.6×10^{-6} S cm^{-1} which is two orders of magnitude lower than the conductivity of cubic Na_3PS_4 prepared by an MM technique [3,5]. Co-precipitation of an impurity of Na_3POS_3 is a possible reason for the lower conductivity. Moreover, due to the high boiling point of NMF (183 °C), heat treatment at high temperature is needed to remove the solvent.

In this study, Na_3PS_4 solid electrolytes with high ionic conductivities were prepared by the liquid-phase method using ethers. As reaction media, 1,2-dimethoxyethane (DME) and diethyl ether (DEE), which are conventional solvents for organic synthesis and liquid electrolytes, were used. These can be removed easily because the boiling points are less than 100 °C. The structure, morphology and conductivity of the obtained solid electrolytes were evaluated.

2. Experimental

Na_3PS_4 solid electrolytes were synthesized from Na_2S (Nagao Co., 99.1%) and P_2S_5 (Aldrich, 99%) powders. The Na_2S and P_2S_5 were mixed in a mortar and then the mixture was stirred in 15 mL of DME or DEE at room temperature (25 °C) for over 60 h. The molar ratio of Na_2S and P_2S_5 was 3:1 and the total weight of the mixture was 1.5 g. In general, the amount of reaction media affects particle morphology and properties of solid electrolytes. In this study, since both Na_2S and P_2S_5 are almost insoluble in DME and DEE, we consider that the amount of reaction medium may have little effect on them. After stirring, the obtained white suspensions were dried under vacuum at room temperature to obtain the precursor powders. The powders were heated at

---

[*] Corresponding author.
E-mail address: hayashi@chem.osakafu-u.ac.jp (A. Hayashi).

https://doi.org/10.1016/j.ssi.2017.12.021
Received 20 August 2017; Received in revised form 3 December 2017; Accepted 18 December 2017

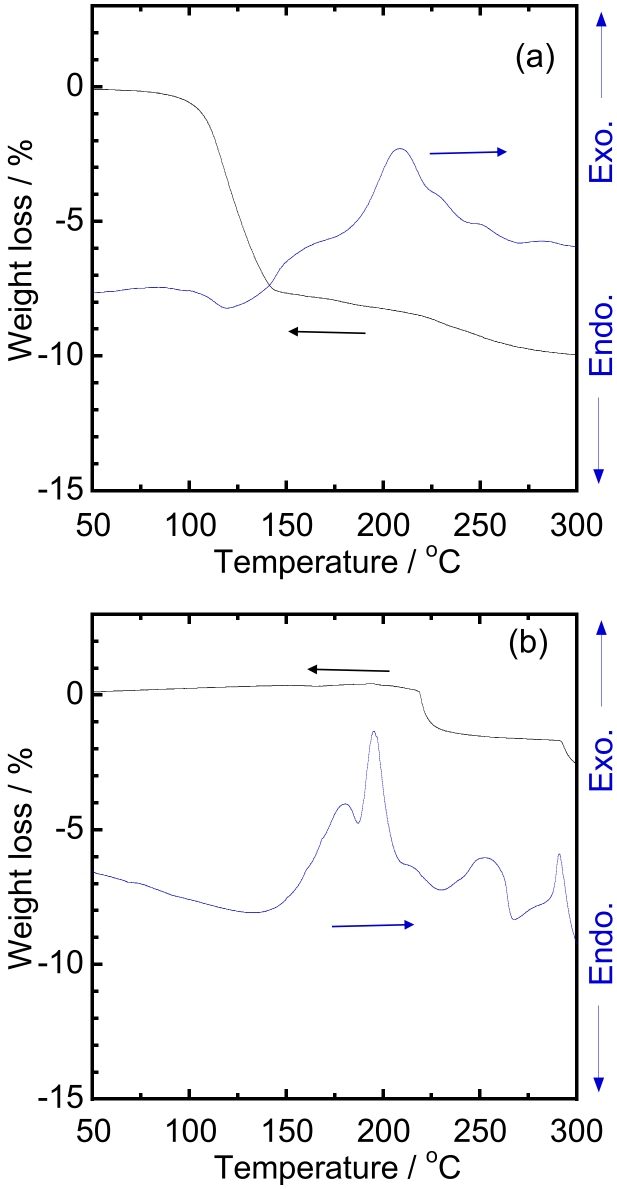


Fig. 1. TG-DTA curves of Na_3PS_4 electrolytes prepared using DME (a) and DEE (b) before heat treatment.

270 °C under vacuum to form the Na_3PS_4 electrolytes.

For comparison, the Na_3PS_4 electrolyte was also prepared by an MM technique using a planetary ball milling (Fritsch, Pulverisette 7) [5]. A milled powder was heated and then pressed into a pellet at 720 MPa at room temperature (25 °C).

Thermogravimetric and differential thermal analysis (TG-DTA) was conducted using a thermal analyzer (Rigaku, Thermo plus EVO 2 TG8121) from 25 °C to 500 °C at 10 °C min^{-1} under N_2 gas flow. A powder X-ray diffraction (XRD) was measured using an X-ray diffractometer (CuKα, Rigaku, SmartLab) to determine the crystalline phases of the obtained powders. Raman spectra were obtained using a Raman spectrophotometer (HORIBA jobin Yvon, Lab-Ram HR-800) to identify the structural units in the obtained samples. The temperature dependence of the conductivity of the obtained powders was measured using an impedance analyzer (Solartron, 1260) in the frequency range of 1 Hz to 4 MHz. For the AC impedance measurements, the samples were uniaxially pressed into pellets of 10 mm in diameter at 360 MPa or 720 MPa. Densities of the pellets (ρ_{bulk}) were calculated from their mass, area and thickness. The densities of the powders were determined by an Ar gas pycnometer (Shimadzu, AccuPyc II 1340) placed in an Ar-filled glove box and used as true densities of the electrolyte (ρ_{true}) [14]. Relative densities were defined as ρ_{bulk}/ρ_{true}. The morphology of the obtained powders and the microstructure of the pellets were observed by scanning electron microscopy (SEM, HITACHI, SU8200). All the processes were performed in a dry Ar atmosphere.

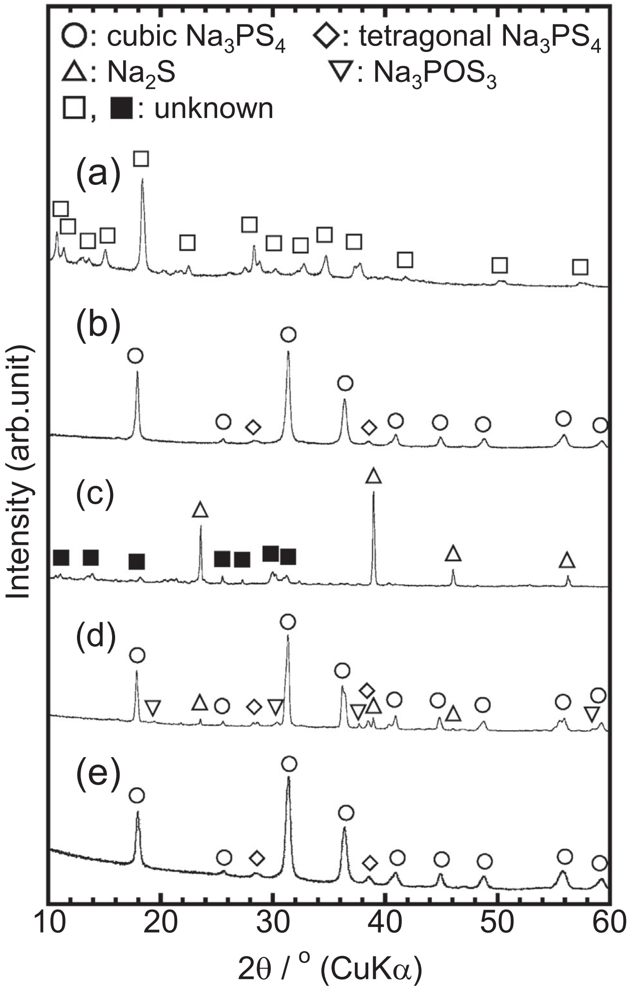


Fig. 2. XRD patterns of Na_3PS_4 electrolytes prepared using DME dried at room temperature (a), heated at 270 °C (b), using DEE dried at room temperature (c) and heated at 270 °C (d). The pattern of Na_3PS_4 prepared by mechanical milling is also shown in (e).

3. Results and discussion

Fig. 1 shows the TG-DTA curves of the powders synthesized using DME (a) and using DEE (b) after drying at room temperature. The TG curve of the sample prepared using DME showed about 10 wt% loss from the sample. In the sample prepared using DEE, little weight loss was observed. The slight weight loss at 220 °C was presumed to be due to volatilization of sulfur.

Fig. 2 shows XRD patterns of the powders prepared by using DME after drying at room temperature (a) and heat treatment at 270 °C (b). Those prepared by using DEE after drying at room temperature (c) and heat treatment at 270 °C (d) are also shown. The diffraction pattern of