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Chemical synthesis of Li_3PS_4 precursor suspension by liquid-phase shaking

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ABSTRACT

A suspension of a submicron Li_3PS_4 (LPS) precursor in dimethyl carbonate was successfully prepared by shaking the mixture of starting materials and dimethyl carbonate with the presence of zirconia balls. LPS precursor formation from Li_2S and P_2S_5 was complete after shaking for 5 h. Amorphous LPS was obtained from the precursor by drying at 190 °C; the ionic conductivity was 6.4×10^{-6} S cm^{-1}, which is lower than that of glassy LPS prepared by planetary ball-milling method. The reason for the lower ionic conductivity of the prepared LPS is that undefined organic substances formed and remained in the prepared samples even after heating up to 260 °C in vacuum for 4 h. The LPS powder appeared to have uncertain morphology with the particle sizes smaller than 500 nm after being evacuated at 190 °C.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have been widely used since their introduction in 1991 [1]. For safety, instead of flammable organic solvents, highly flame-retardant organic solvents, gels, or solid-state ionic conductors should be used as ion-conducting media [2–8]. The use of sulfide-based solid-state electrolytes, which have high ionic conductivities, and favorable mechanical and nonflammable properties, has increased the demand for all-solid-state LIBs [8,9]. The glass–ceramic Li_2S–P_2S_5 (70:30 M ratio) has a reasonably high ionic conductivity, 3.2×10^{-3} S cm^{-1} at room temperature, and the introduction of Ge into Li_2S–P_2S_5 increases the conductivity to 1.2×10^{-2} S cm^{-1}, which is equivalent to those of organic solvents containing supporting electrolytes [10].

Electrolytes with high ionic conductivities are needed for LIBs, but the interfaces between the electrolytes and active materials are also very important. In conventional LIB cells, interfaces between active materials and liquid electrolytes are easily formed, but in all-solid-state cells, continuous ionic and electrical conduction paths must be designed at solid–solid interfaces, because of the low fluidity and insufficient wettability of solid electrolytes. No matter how high the ionic conductivity of the solid electrolyte is, the distribution of active materials, solid electrolytes, and electrical conductive materials must be homogeneous in the cathode to obtain solid-state cells with high levels of performance.

In most work on all-solid-state LIBs using Li-conductive sulfide glass electrolytes, the ball-milling (BM) method is used for electrolyte preparation and the composite cathode is prepared via hand-mixing in a mortar with agate [9,11]. It is therefore difficult to control the distribution of the components in the mixture. Furthermore, the BM method consumes large amounts of time and energy, and its use for large-scale production may be difficult. Recently, there have been reports on the preparation of Li_3PS_4 (LPS) using a wet chemical method by dissolving the starting sulfide materials like Li_2S and P_2S_5 in various organic solvents such as tetrahydrofuran, *N*-methylformamide, and dimethoxyethane [12–14]; however, none of these methods involved preparation of a suspension containing LPS precursor colloid particles, which is very important for the fabrication of cathode composites, as reported elsewhere [15].

In this study, a suspension of LPS precursor was successfully prepared using a new liquid-phase shaking (LS). The suspension, which was prepared without the addition of a dispersant, was stable for 1 week, without any noticeable sedimentation. The particle size, after drying at 110 °C, was 100–500 nm. Similar results have not been previously reported. The usage of nanosize solid electrolyte will result in the increase of the loading amount of active materials in the electrodes; thus the specific energy of the batteries will be increased.

2. Materials and method

Li_2S and P_2S_5 were purchased from Mitsuwa and Sigma, respectively, and used without purification. Dimethyl carbonate (DMC) (battery grade), obtained from Wako Pure Chemical Industries, Ltd., was dehydrated with 3A molecular sieves prior to use. In a typical batch, Li_2S (0.1149 g), P_2S_5 (0.1852 g; molar ratio Li_2S:P_2S_5 = 3:1), DMC

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(5 mL), and about 100 zirconia balls (diameter 4 mm, about 21.6 g) were mixed in a 45 mL centrifugation tube (polypropylene, Labcon) and shaken in a dry Ar atmosphere for 5 h at 1500 rpm with an amplitude of about 1 cm. The tube was then sealed and centrifuged at 10,000 rpm for 5 min and decanted. The residue was dried at room temperature, 90, 130, 150, and 190 °C at low pressure (about −100 kPa). DMC was chosen because it can form a complex with Li ion in Li_2S, which then react with P_2S_5 to form the precursor of LPS.

The prepared powder was characterized using scanning electron microscopy (SEM; S4800, Hitachi), X-ray diffraction (XRD; Ultima IV, Rigaku), thermogravimetry–differential thermal analysis (TG–DTA; TG 8121, Rigaku), and Raman spectroscopy (NRS-3100, Jasco). Samples were placed in special holders in an Ar glove box prior to characterizing by XRD, TG–DTA, and Raman spectroscopy. TG–DTA study was performed in dry nitrogen flow. The temperature dependences of the ionic conductivities 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 cold-pressing of LPS powder (about 80 mg) into pellets of thickness about 0.60 mm and diameter about 10.0 mm at a pressure of 330 MPa.

3. Results and discussion

Fig. 1 shows the Raman spectra of samples dried at different temperatures and the raw materials. The most intense peak in the Raman spectra of the prepared powders was at 417 cm^{-1}, which is characteristic of P—S bonds in PS_4^{3-} ions, as reported elsewhere [8,12]. None of the peaks originating from the raw materials (Li_2S and P_2S_5) were detected in the prepared samples; this confirmed that the reaction between the two starting materials was complete after 5 h. The Raman spectrum of DMC (Fig. 1) has peaks at 513, 912, 1449, 1744, 2841, 2881, 2960, and 3023 cm^{-1}, which are assigned to CO_2 deformation, CH_3—O stretching, CH_3 symmetric deformation, C═O stretching, CH_3 symmetric deformation, CH_3 symmetric deformation, CH_3 symmetric stretching, and CH_3 asymmetric stretching, respectively [16]. The Raman spectrum of the sample dried at room temperature had the same features as that of pure DMC, with the addition of peaks from PS_4^{3-} ions; the DMC peak at 912 cm^{-1}, generated from CH_3—O stretching, shifted to 924 cm^{-1}. This shift suggests an interaction between DMC and Li^+. In addition, the appearance of a small peak at 580 cm^{-1}, which is one of the features of the DMC second conformer, proved that the DMC structure had been changed by bond formation with Li ions [16]. When the sample was dried at or above 110 °C, these significant features of DMC disappeared and new peaks were observed at 696, 2843, 2914, and 2990 cm^{-1}, and a shoulder was observed at 568 cm^{-1}. The peaks locating from 3000 to 2800 cm^{-1} are frequently assigned as the CH_3 vibrations but the origin of the peaks at 696 and 568 cm^{-1} is still unclear. The shift of CH_3 vibration peaks associates with the disappearance of DMC features and the detection of new peaks may indicate the formation of new organic substances resulted from the decomposition of DMC.

Peaks at 2θ = 13.7°, 17.3°, 19.0°, 21.6°, and 28.8° were detected in the XRD pattern of the sample dried at room temperature, but none of these originate from the raw materials (Fig. 2). It can therefore be concluded that the formation of LPS was complete after reaction for 5 h. However, these peaks could not be indexed to any of the JCPDS cards. We also found no similarities between this and previously reported materials [12,14]. These facts suggest the co-crystallization between LPS and DMC. This is consistent with the Raman spectra described above. However, on drying up to 110 °C, these peaks disappeared and XRD showed that the powders were amorphous (Fig. 2), despite the detection of organic substances by Raman spectroscopy, as mentioned above. Further heating the sample at 260 °C in vacuum for 4 h, the Li_3PS_4 crystalline (JCPS 076-0973) appeared but the Raman features of the organic substances were still observed.

The TG–DTA curves of the sample dried at room temperature are shown in Fig. 3a. TG showed a total weight loss of about 64%, which suggests that the sample dried at room temperature is a precursor of LPS which contains both LPS and DMC with the molar ratio of 4:7. The TG curve was composed of 5 regions, which exhibited the weight loss up to 300 °C. The DTA curve also composed of 5 exothermic peaks without any noticeable endothermic peak that is normally observed during the evaporation of solvent. At the end of the first weight loss stage, an exothermic peak centered at 110 °C was detected. Together with the changes observed from XRD and Raman results, this evidence proved the disappearance of DMC and formation of new organic substances from DMC decomposition. However, the two exothermic peaks centered at 140 and 176 °C associated with weight loss ranging from 110 to about 250 °C were not supported from Raman and XRD measurements so that they might be originated from the further decomposition of organic compounds. The strong peak at 260 °C and the partly overlapping peak at 280 °C were assigned to the formation of crystalline Li_3PS_4 as pointed out by XRD result.

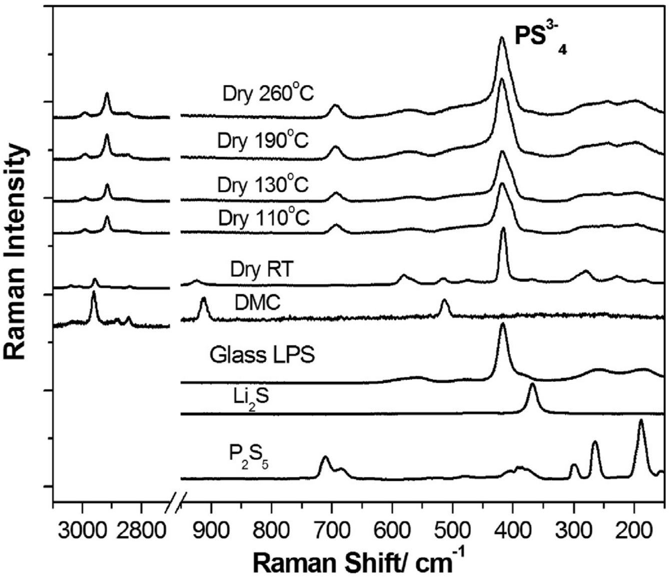

Fig. 1. Raman spectra of the LPS powder dried at different temperatures and reference materials.

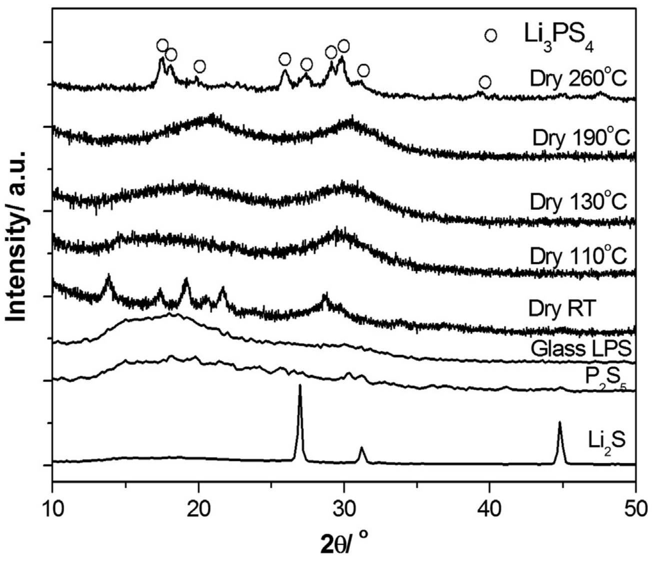

Fig. 2. XRD patterns of the LPS powders dried at different temperatures and reference materials.

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