Preparation of Li₃PS₄ Solid Electrolyte Using Ethyl Acetate as Synthetic Medium

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Abstract:

A precursor for Li₃PS₄ solid electrolyte was successfully prepared by reaction of Li₂S and P₂S₅ in ethyl acetate. The precursor was composed of Li₃PS₄ and ethyl acetate in a molar ratio of 1:2, as determined by thermogravimetry-differential thermal analysis (TG-DTA). Upon drying at 160 °C, the precursor decomposed to form crystalline Li₃PS₄ with a high ionic conductivity of $3.3 \times 10^{-4} \text{ S cm}^{-1}$ and low activation energy of about 31 kJ mol⁻¹.

Keywords: Lithium thiophosphate; Ethyl acetate; Solid-state electrolyte

1. Introduction:

The blooming of mobility electrochemical systems with high energy density based on lithium ion intercalation requires improvements in safety and durability because of their use of organic liquid electrolytes. This has raised a demand for suitable solid electrolytes or quasi-solid electrolytes. Among the solid state electrolytes, sulfides based on Li₂S–P₂S₅ have been proven to exhibit high ionic conductivity of up to $1.7 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C, which is equal to that of the currently employed liquid electrolytes [1]. Additionally, Kamaya et al. found the new crystal structure Li₁₀GeP₂S₁₂, which showed an ionic conductivity of about $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at 27 °C [2]. As well as high ionic conductivity, sulfide-based solid electrolytes are also reported to have excellent mechanical properties that favor the formation of the interface between the active material and electrolyte particles [3].

Such sulfide-based solid electrolytes were mainly prepared by planetary ball-milling or melt-quenching methods [1, 4, 5]. Solid electrolytes obtained from these conventional methods exhibit excellent Li⁺ ionic conductivity but with the disadvantages of high energy consumption and difficulties in scale up. Recently, liquid phase synthesis methods are being reported as a potential way to synthesize solid electrolytes. Many kinds of organic solvents have been employed as the synthetic media, including tetrahydrofuran, N-methylformamide, hydrazine, dimethoxyethane, and

dimethyl carbonate [6-9]. Although the use of organic solvents makes the preparation of solid electrolytes easier there are still many problems to be solved, such as the low ionic conductivities of the obtained materials, the presence of residual organic substances, and the toxicity of the solvents. Therefore, the discovery of new solvents for solid electrolyte synthesis is still of interest. The chosen solvent must satisfy the requirements of safety to humans and the environment, a short preparation time, and a high ionic conductivity of the product solid electrolytes.

In this study, precursor for Li_3PS_4 solid electrolyte was successfully prepared from the reaction of Li_2S and P_2S_5 in ethyl acetate medium. Upon drying at 160°C , the precursor decomposed to form crystalline Li_3PS_4 with a high ionic conductivity of $3.3 \times 10^{-4} \text{ S cm}^{-1}$ and low activation energy of about 31 kJ mol^{-1} .

2. Experimental:

Li_2S (99.9%) and P_2S_5 (99%) were purchased from Mitsuwa and Aldrich, respectively, and used without purification. Ethyl acetate (EA), obtained from Aldrich, was dehydrated with 3A molecular sieves prior to use. In a typical batch, Li_2S (0.3827 g), P_2S_5 (0.6170 g; molar ratio $\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 3:1$), and EA (20 mL) were mixed in a 45 mL centrifugation tube (polypropylene, Labcon) and shaken in a dry Ar atmosphere for 1 day 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 solid phase was evacuated at room temperature then 110 and 160°C overnight at low pressure (about -100 kPa).

Structure of the prepared powder was characterized using X-ray diffraction (XRD; Ultima IV, Rigaku), thermogravimetry-differential thermal analysis (TG-DTA; TG 8121, Rigaku), and Raman spectroscopy (NRS-3100, Jasco). Samples were sealed in special holders in an Ar-filled glove box to protect them from exposure to air humidity prior to their characterization by XRD, TG-DTA, and Raman spectroscopy. TG-DTA studies were performed in a dry Ar flow.

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 (about 80 mg of sample dried at 110°C) into pellets of about 0.60 mm in thickness and about 10.0 mm in diameter at a pressure of 330 MPa (at room temperature). The prepared pellet was placed in a holder made from 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 160°C and held for 1h, after which the sample was allowed to cool naturally (overnight) before being brought to temperature again for the measurements. The sample was held at each temperature for 1 h prior to the impedance measurement.

DC conductivities were carried out using blocking and non-blocking electrodes, in which the stainless steel (SUS) rods and lithium metal sheets were employed as the electrodes, respectively. The pelletized sample (diameter of 10mm and thickness of 1.3mm) was prepared by cold-pressing the powder dried at 160 °C at 360 MPa. In case of non-blocking electrodes, the Lithium metal sheets (Li) (diameter of about 8mm, thickness of about 0.1mm) were attached to both faces of the pellet at room temperature. The prepared cells were then applied 1 V (DC) and the current were measured to determine the dominant mobile ions in the sample. The experiments were carried out using potentiostat SI 1287 (Solatron).

Electrochemical compatibility was tested using Li|SE|SUS cell at a scan rate of 5 mVs⁻¹ between -0.5 and 5 V using potentiostat Si1287 (Solatron).

3. Results and discussion:

Figure 1 shows the TG-DTA curves of the sample obtained by evacuating the residue collected from the synthetic mixture at room temperature. The DTA curve was composed of only one endothermic peak ending at about 110 °C associated with the weight loss due to EA elimination. The peak was centered at 88 °C, which is higher than the boiling point of ethyl acetate. This indicates that the ethyl acetate was chemically absorbed in the sample. The TG curve showed that the sample lost about 50% of its initial weight owing to ethyl acetate elimination at high temperature. From this value, the formulation of the powder dry at room temperature could be estimated to be Li₃PS₄-2EA. The ratio of 1:2 of Li₃PS₄ to organic solvent observed in this study is different from the value of 1:3 reported in the literature [7, 10]. The DTA curve of the sample dry at room temperature showed unclear exothermic peak but the sample dry at 160°C had structure of Li₃PS₄ as confirmed by XRD. Therefore, the TG-DTA of sample dry at 90°C was carried out and the result was plotted in Fig.1 (small inset). The curves indicated that EA was nearly eliminated after evacuated at 90 °C and a small exothermic peak centered at about 150 °C was detected. This exothermic peak was associated with no weight loss so it should be originated from the structure change of the sample.

The XRD patterns of the prepared samples and raw materials were recorded and are depicted in Fig. 2. The XRD pattern of Li₃PS₄-2EA was composed of many peaks, but none originated from the raw materials. The pattern could not be assigned to any of the known phases. It was also different from the diffraction pattern of Li₃PS₄-3THF reported elsewhere [7]. The powder obtained upon evacuating Li₃PS₄-2EA at 110 °C, during which the EA was removed, was amorphous to XRD. The change in structure from crystalline to amorphous caused by EA elimination indicated that Li₃PS₄-2EA was a co-crystal of Li₃PS₄ and EA. Further heating of the amorphous powder at 160 °C caused its structure to undergo a rearrangement process to form crystalline Li₃PS₄ (JCPDS 076-0973). This observation is consistent with the TG-DTA results.

The Raman spectra of the prepared samples and raw materials are shown in Fig. 3. The spectrum of Li₃PS₄-2EA exhibited one sharp peak centered at about 420 cm⁻¹, which is

reported to be the finger-print of the PS_4^{3-} ion [7-9, 11]. The spectrum also contained peaks generated from $-\text{CH}_3$ vibrations at about 2900 cm^{-1} . Owing to the removal of EA, these peaks disappeared and only the peaks of Li_3PS_4 were detected from the samples dried at 110 and 160 °C. These results are also in consistency with the observation from X-ray diffraction.

The temperature dependence of the ionic conductivity of the sample dried at 110 °C is plotted in Fig. 4. After drying at 110 °C, the sample exhibited a Li^+ ion conductivity of about $5.0 \times 10^{-5}\text{ S cm}^{-1}$. After the temperature was increased to 160 °C and then naturally cooled to room temperature, the ionic conductivity of the sample was dramatically increased to $3.3 \times 10^{-4}\text{ S cm}^{-1}$ and the activation energy was about 31 kJ mol^{-1} . It should be noted that crystalline Li_3PS_4 has been previously reported to have very poor ionic conductivity of about $2\text{--}4 \times 10^{-6}\text{ S cm}^{-1}$ [8, 10, 12]. The high ionic conductivity and low activation energy of the prepared crystal Li_3PS_4 are also in comparable to those of the $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass prepared by the conventional planetary ball-milling method as reported elsewhere [13]. Liu et. al reported that the ionic conductivity of $\beta\text{-Li}_3\text{PS}_4$ was about $1.6 \times 10^{-4}\text{ S cm}^{-1}$ with the pellet for impedance measurement prepared by cold-pressing at room temperature [7]. In this study, the sample was prepared by a different procedure as described above, in which the interfacial resistivity among the solid electrolyte particles might be improved and slightly higher conductivity and lower activation energy were obtained. The ionic conductivity of about $1.7 \times 10^{-4}\text{ S cm}^{-1}$ was obtained when the pellet was prepared by cold-pressing the sample dry at 160°C at room temperature. From all the structure characterization and conductivity measurement results, it may be concluded that the prepared sample was $\beta\text{-Li}_3\text{PS}_4$ as reported elsewhere [7].

Fig.5 shows the change in current with time after applying constant DC voltage, 1 V, to the sample. When lithium sheets were used as non-blocking electrodes for lithium ion ($\text{Li}|\text{Li}_3\text{PS}_4|\text{Li}$), a constant current was observed. The value is in good agreement with the calculated current value, I , from the total conductivity measured by AC impedance spectroscopy:

$$I = V_{\text{DC}} \cdot \sigma \cdot A / L$$

where V_{DC} is the constant applied DC voltage, σ is the total conductivity obtained by AC impedance measurement, A is the electrode area and L is the pellet thickness. The observed current value ($9.5 \times 10^{-4}\text{ A}$) is slightly smaller than the calculated one ($1.0 \times 10^{-3}\text{ A}$). The high resistant at $\text{Li} - \text{Li}_3\text{PS}_4$ pellet interface may be the main reason for this observation since Li sheets were just physically attached to the sample surface. In the case of blocking electrodes ($\text{SUS}|\text{Li}_3\text{PS}_4|\text{SUS}$), a large current decrease due to polarization was initially observed and then the current became nearly constant. The constant current in this case was at least 3 orders of magnitude lower than the one in case of non-blocking electrodes. These results meant that the prepared sample was

single ion conducting material. It could be also estimated that the lithium-ion transport number is higher than 0.999.

Fig.6 shows the cyclic voltammogram of the Li|Li₃PS₄|SUS cell, in which Li and SUS served as reference and counter electrodes. The potential was scanned from -0.5 to 5.0 V vs. Li/Li⁺ at a scan rate of 5 mVs⁻¹. The cathodic current corresponding to lithium reduction just only started at about 0 V, indicating that the prepared solid electrolyte was stable against lithium metal. Except for the cathodic anodic peaks, none of the other peak was observed in the scanned range. Thus the prepared Li₃PS₄ was compatible with the Lithium metal up to 5 V.

4. Conclusion:

Crystalline Li₃PS₄ with anomalous high ionic conductivity of about $3.3 \times 10^{-4} \text{ S cm}^{-1}$ was successfully prepared using ethyl acetate as the synthetic medium. This result is expected to encourage more studies of solid electrolyte preparation via soft chemical methods which have high potential for industrial application.

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Fig. 1: TG-DTA curves of the sample obtained by evacuating the residue collected from the synthetic mixture at room temperature and TG-DTA curves of the sample evacuated at 90 $^{\circ}\text{C}$ for 2h (small inset).

Fig. 2: XRD patterns of (a) Li_2S ; (b) P_2S_5 ; (c) $\text{Li}_3\text{PS}_4 - 2\text{EA}$; (d) Li_3PS_4 dried at 110°C and (e) Li_3PS_4 dried at 160°C

Fig. 3: Raman spectra of (a) Li_2S ; (b) P_2S_5 ; (c) $\text{Li}_3\text{PS}_4 - 2\text{EA}$; (d) Li_3PS_4 dried at 110°C and (e) Li_3PS_4 dried at 160°C

Fig. 4: Temperature dependence of the ionic conductivities of the prepared Li₃PS₄ (filled circle) and 75Li₂S·25P₂S₅ glass (filled triangle) obtained from ref [13]

Fig.5: Change in current, relative to time, after applying a dc constant voltage of 1 V to the pellet obtained by cold-pressing the sample dried at 160 °C at 360 MPa

Fig.6: cyclic voltammogram of the Li|Li₃PS₄|SUS cell, in which Li and SUS served as reference and counter electrodes. The potential was scanned from -0.5 to 5.0 V vs. Li/Li⁺ at a scan rate of 5 mVs⁻¹.