Synthesis of NASICON type Li$_{1.4}$Al$_{0.4}$Ge$_{0.2}$Ti$_{1.4}$(PO$_4$)$_3$ solid electrolyte by rheological phase method

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ABSTRACT

NASICON-type Li$_{1.4}$Al$_{0.4}$Ge$_{0.2}$Ti$_{1.4}$(PO$_4$)$_3$ solid electrolyte (AG-SE) was synthesized using a rheological phase method precursor. The AG-SE powders prepared by this method had a low crystalline temperature of 595.5°C and much fewer impurity phases than that prepared by the conventional solid-state method. An AG-SE pellet sintered at 900°C for 14 h had a high relative density of 95.3%, with total and grain boundary room temperature conductivities of 1.21 and 4.35 mS cm$^{-1}$ individually. The total activation energy for the AG-SE was as low as 0.29 eV. The 3-point bending strength was determined to be 102 N/mm$^2$, which was higher than that of AG-SE prepared by solid-state and liquid-phase method precursors.

1. Introduction

Various structured solid electrolytes for selective Li-ion conducting and passing, for instance rhombohedra Li$_{1.4+y}$Al$_y$Ti$_2$$_x$(PO$_4$)$_2$ (LATP) known as NASICON-type [1], perovskite Li$_{0.35}$La$_{0.65}$TiO$_3$ (LLTO) [2], garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) [3], thio-LISICON-type Li$_{10}$GeP$_2$S$_{12}$ [4], glass-ceramic 7Li$_2$S$30P$_7$S$_5$ [5] and anti-perovskite-type Li$_2$OCl [6], have been reported in the last three decades. Among them, the electrical conductivity of LATP with $x = 0.3$ was reported to be 0.7 mS cm$^{-1}$ at room temperature [1]. This value was further improved up to more than 10$^{-3}$ S cm$^{-1}$ by co-doping germanium and aluminum [7]. The NASICON-type solid electrolytes have several advantages over other potential candidates, such as stability in ambient air and in an aqueous solution with a lithium salt [8], and ease of preparation of a thin film with a high bending strength over 200 N mm$^{-2}$ by a conventional tape casting method [9]. The stability in aqueous solution makes this available for application as the separator in aqueous lithium-air batteries [10].

The Li-ion conductivity of typical solid electrolyte is dependent on the synthesis method and route of the precursor, which leads to various particle sizes and morphology of the product, and the sintering method of the powder to a pellet. The room temperature bulk conductivity of LATP was reported to be 1–3 mS cm$^{-1}$ and no significant improvement in the conductivity has been reported ever since [11,12]. Meanwhile, the grain boundary conductivity is extremely dependent on the LATP powder preparation method and the sintering conditions [13,14]. Xiao et al. recently reported a review of the method for the preparation of LATP [15]. The fabrication processes could be divided into main three categories: melt-quenching [16,17], solid-state [18,19], and liquid-phase methods [20–22]. The melt-quenching method involves the melting of the starting materials, subsequent pressing, and sintering. The melting temperature is as high as 1400°C. Therefore it is always a challenge to control the composition of the reaction products because lithium evaporates at the high reaction temperature. The liquid-phase methods, which include the sol-gel and precipitation methods, are appropriate to prepare nanosize particles. However, these methods can be affected by many factors, such as the solubility of the starting materials and products, the pH and chemical equilibrium. In comparison, the solid-state method can use relatively inexpensive starting materials (mainly metal oxides) and production can be easily scaled up; however, the annealing temperature to obtain acceptable lithium-ion conductivity is greater compared to those by liquid-phase routes and excessive energy consumption by ball milling.

Sun et al. [22] combined the advantages of solid-state and liquid-phase methods to propose a simple synthetic route of the precursor with homogeneous solid and traceable amount of liquid, which is referred to as the rheological phase reaction method [22,23]. Taking advantage of the close contact between a solid and liquid, this method can overcome the energy consumption and inhomogeneous problems inherent with the melt-quenching and solid-state methods. And the complexity of reactant selectivity in the liquid-phase chemistry can be avoided. Therefore, this
The thermal behavior of the powder prepared by the rheological phase method was examined using a thermogravimetric (TG) analyzer (Rigaku Thermo Plus-TG 8120) with a ramp rate of 2°C/min and a platinum sample pan. X-ray diffraction (XRD) measurements of precursor powders and sintered pellets were conducted using a diffractometer (Bruker D8 Advance) in the 2θ range from 10° to 90° with Cu Kα radiation. The obtained patterns were deconvoluted by the Rietveld refinement software TOPAS 4.2. The precursor particle and pellet surface morphologies were characterized by Hitachi S4800 field emission scanning electron microscopy (SEM) and elemental distribution by affiliated EDS (energy dispersive spectrometry). The AG-SE powders were homogenized in distilled water using sonication and the particle size distribution was then measured using a particle distribution analyzer (Microtrac S3500). And also the primary particle size was directly determined from SEM images using a professional software Image-pro plus 6.0 (Barco). Electrical conductivity measurements were performed for the sintered AG-SE pellets (ca. 0.7 mm diameter and ca. 0.55 mm thick) with gold sputtered electrode (ca. 1 mm thick) using an impedance phase analyzer (Solartron 1260) in the frequency range from 0.1 Hz to 1 MHz with a bias voltage of 10 mV at various temperatures. The bulk and grain boundary conductivities were estimated from complex impedance plots using Zview software. The three point bending strength of bar-shaped samples (ca. 10.0 × 0.5 × 0.5 mm) was measured using a tensile tester (Shimadzu EZ-50). Fourier transform infrared spectroscopy (FT-IR) measurements were conducted using a spectrometer (Nicolet ISSOR) with a diamond detector (Thermo Fisher). Water penetration test was done by using an H-type cell with a sandwiched structure of distilled water, AG-SE, and saturated aqueous LiCl solution [9]. The chloride concentration on the distilled water side was measured using a chloride meter CL-5Z (Kasahara, Japan).

3. Results and discussions

Figure 1(a) presents a schematic flow of the rheological phase synthesis. The solubility of the starting materials was not important for the solid-liquid rheological body; therefore, less expensive GeO₂ was used as a starting material. In addition, a simple agate mortar was used to mix the components instead of high-energy ball-milling, as used for the solid-state reaction because of improved contact of the starting materials compared to the solid-state method. Figure 1(b) shows an FT-IR spectrum of the precursor heated in an autoclave at 150°C. The broad peaks between 3550–3200 cm⁻¹ are attributed to water present in the precursor and the peak at 1710 cm⁻¹ for COOH stretching can be assigned to citric acid, while the strong peak at around 960 cm⁻¹ suggests the vibration mode of PO₄. Figure 1(c) shows an XRD pattern of the as-prepared precursor. The low intensity
dispersed peak at $2\theta$ of ca. 27° indicates an amorphous phase. Figure 1(d) shows SEM-EDS images of the precursor. The elemental dispersion maps indicate that all elements are homogeneously distributed with no severe agglomeration in the observed range. This directly shows the feasibility of the rheological phase method for the preparation of a uniform precursor of AG-SE.

Figure 2(a) shows the TG analysis profile of the AG-SE precursor prepared by the rheological phase method in the scale from ambient temperature to 800°C. A weight loss of 60% was found up to 500°C, which can be put down to the evaporation of water and decomposition of the starting materials. No obvious weight loss was observed above 500°C. An exothermic peak at 596°C could be ascribed to the formation of the NASICON crystalline phase. We note this crystalline transition temperature was significantly lower than that obtained by the solid-state reaction method, which was reported to be around 700°C [28]. This result could be explained by the advantage of the rheological phase method in terms of facilitating reaction in the precursor. Figure 2(b) shows XRD patterns of the rheological phase precursor heated at temperatures from 500°C to 1000°C for 7 h. The sample heated at 500°C showed no crystalline phase and those sintered at 600 and 700°C showed the NASICON-type phase with an impurity phase at around 23.6°. The impurity phase vanished for the sample sintered at above 800°C. Figure 3 compares the XRD patterns of AG-SE powders prepared at 800°C for 7 h by the solid-state reaction and rheological phase methods. Both XRD patterns could be indexed as orthorhombic structures, and more impurities such as aluminum phosphate, germanium oxide, titanium dioxide, and tetra-lithium diphosphate were observed in the AG-SE powder prepared by the solid-state method, as shown in Figure 3(b).

The particle size and size distribution of the starting powder are important factors in obtaining a dense pellet [29]. Figure 4(a,b) presents the primary particle size distribution of the powders prepared at 800°C by...
solid-state and rheological phase methods. It was calculated directly from the SEM images of Figure 4(d). The distribution histogram clearly indicated that the particles prepared by rheological phase method were more uniform and smaller than those prepared by solid-state method. The particle size distribution was also measured in water by a distribution analyzer in Figure 4(c). Both samples showed two peaks, where the left peak could be attributed to the primary and right one to the secondary particles. The average particle diameter by mass $D_{50}$ of the powder prepared by the rheological phase and solid-state methods were 5.1 and 19.2 $\mu$m, respectively. Figure 4(d) shows SEM images of both powders at different magnifications. These figures agree well with the difference in the particle size calculated above. The particles prepared by the rheological phase method are more uniform in the observed region with isolated cubic shaped particles of less than 1 $\mu$m.

The powders heated at 800°C were ball-milled to separate the loosely contacted particles and then sieved through 20 $\mu$m mesh to achieve powder for the fabrication of dense AG-SE pellets. The powders were pressed isostatically into a pellet at 160 MPa and then sintered on an Au sheet at various temperatures with sintering periods of 7 to 21 h. Figure 5 shows the impedance spectra of the samples sintered from 850°C to 950°C. The impedance spectra have a semicircle with non-ideal blocking behavior of Au at low frequency. According to the report by Bruce and West [30], the observed semicircle is the contribution of the grain boundary impedance, while the semicircle for
bulk AG-SE was out of the frequency range at the measurement temperature of 25°C. The diameter of the semicircle and the starting point of the semicircle on Z’ axis correspond to the bulk (R₁) and grain boundary (R₂) resistances, respectively. An equivalent circuit to estimate the electrical conductivity is shown in the inset of Figure 5(a). Table 1 summarizes the electrical conductivity data along with the relative density of different AG-SE pellets in a variation of sintering conditions. The highest total conductivity (bulk plus grain boundary) surpassing 1.20 mS cm⁻¹ at 25°C was obtained for AG-SE sintered at 900°C for 14 and 21 h, where the bulk and grain boundary conductivities were recorded around 1.65 and 4.40 mS cm⁻¹, respectively. This conductivity is approximately 50% higher than previous AG-SE fabricated through a solid-state method [28] and comparable to those in the route of sol-gel processing [31]. We note that the AG-SE prepared at 900°C and 14 h, which exhibited the highest grain boundary conductivity, also had the highest relative density of 95.3%.

Figure 6 presents the temperature dependence of the total conductivities of AG-SE in the relation of both sintering temperatures and time. The lowest activation energy for total conductivity of 0.29 eV was recorded for AG-SE that was sintered at 900°C for 14 h, which is comparable to that reported previously for AG-SE prepared by the sol-gel method [31]. And it is worth mentioning that the typical activation energies for bulk and grain boundary conductivities of AG-SE sintered at 850–900°C were around 0.2 and 0.55 eV, respectively.

Figure 7 shows XRD patterns with Rietveld refinement results and cross-sectional SEM images for AG-SE annealed at various temperatures. Both lattice parameters and the impurity phase content estimated by Rietveld refinement for AG-SE at these conditions are shown in Table 2. The content of the LiTIOPO₄ impurity phase was decreased with an increase of the sintering period, while that of the GeO₂ impurity phase increased. AIPO₄ was observed in the sample sintered at 850°C, which could decrease the grain boundary conductivity. The increase of the GeO₂ content could be effective to increase grain boundary conductivity observed in the LATP-GeO₂ system [18]. Furthermore, the grain boundary conductivity decrease for AG-SE sintered at 950°C could be attributed to microstructure change and formation of microcracks by abnormal grain growth as shown in Figure 7 (h). Spencer et al. studied the critical grain size for microcracks in Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃ system [32] and found that the large abnormal grain would be easy to trigger microcracks. More recently, we studied the ionic conductivity and mechanical strength of Li₁+xAlₓGe₀.₂Ti₁.₈-x(PO₄)₃ as a function of x and the abnormal grain growth was found in Li₁.₄Al₀.₄Ge₀.₂Ti₁.₄(PO₄)₃ sintered at 950°C [33]. In addition, the decrease in the amount of LiTIOPO₄ could be effective to increase the grain boundary conductivity.

Excellent mechanical properties are an important requirement for the solid electrolyte separator in lithium-air batteries for electric vehicle (EV) applications because if the separator is destroyed, the lithium

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**Table 1.** Bulk, grain boundary, and total conductivities, and relative density of AG-SE pellets measured at 25°C.

| Sample temperature (°C) | Period (h) | Bulk conductivity (mS cm⁻¹) | Grain boundary conductivity (mS cm⁻¹) | Total conductivity (mS cm⁻¹) | Relative density (%) |
|-------------------------|-----------|-----------------------------|--------------------------------------|-----------------------------|---------------------|
| 850                     | 7         | 0.96                        | 0.48                                 | 0.32                        | 80.0                |
| 900                     | 7         | 1.61                        | 1.65                                 | 1.82                        | 92.6                |
| 900                     | 14        | 1.67                        | 4.35                                 | 6.02                        | 95.3                |
| 900                     | 21        | 1.67                        | 4.39                                 | 6.06                        | 95.0                |
| 950                     | 7         | 1.69                        | 0.45                                 | 2.14                        | 90.6                |
anode and water react vigorously, which results in hydrogen evolution. The 3-point bending strengths of sintered pellets prepared by various reaction conditions are shown in Figure 9. The highest bending strength of 102 N mm$^{-2}$ was referred to AG-SE pellets starting from rheological phase precursor with sintering temperature of 900°C and 14 h, which is superior to a previous AG-SE from a so-gel precursor at similar sintering conditions (57 N mm$^{-2}$)\[31\]. It is also noteworthy that the value is still lower than a commercialized and patented Ohara Li$_{1+x+y}$Al$_x$(Ti, Ge)$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$ glass-ceramic (140 N mm$^{-2}$) by melt-quenching technique [34]. Nevertheless, the Ohara glass-ceramic performance was limited around 0.1 mS cm$^{-1}$ at 298 K, of which was only about one-twelfth of the sample prepared in this paper. The reason for the enhancement of bending strength could be assigned to the secondary phases inside AG-SE dense pellet. Kyono et al. studied the mechanical strength of AG-SE doped with metal oxide [31] and observed a significant increase of mechanical strength by doping with TiO$_2$, although the electrical conductivity was slightly lower than 1 mS cm$^{-1}$. Similar enhancement of the mechanical properties of solid
lithium-conducting solid electrolytes was achieved with MgO-doped Li$_7$La$_3$Zr$_2$O$_{12}$ [35]. Therefore, the GeO$_2$ precipitated at the grain boundaries of AG-SE may also play a similar role in the improvement of the mechanical strength of AG-SE in this case. Water impermeability through AG-SE is an important requirement for the separator in aqueous lithium-air batteries. The water penetration test using H-type cell confirmed no water penetration through the AG-SE sintered at 900°C for 14 h with a high relative density of 95.3%, while the AG-SE sintered at 850°C for 7 h was observed the water penetration as presented in Figure 9.

4. Conclusion
A novel route of fabricating NASICON-type AG-SE Li-ion conducting powders was managed by the rheological phase method. The rheological phase AG-SE powder had a reduced particle size and particle size distribution. And an AG-SE pellet prepared from the rheological phase powder annealed at 900°C and 14 h had a high relative density of 95.3%, high total and grain boundary conductivities of 1.21 and 4.39 mS cm$^{-1}$ at 25°C discretely. Moreover, an increase in solid electrolyte mechanical bending strength of 102 N/mm$^2$ was recorded. The rheological phase method thus has potential application for the preparation of fine metal-ion conducting solid electrolyte powder because it is a simple preparation method with less energy and solvent consumption compared to conventional solid-state and liquid-phase methods.

Disclosure statement
The authors declare that they have no conflict of interest.

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