PREPARATION OF Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3 SOLID ELECTROLYTE BY SOL-GEL METHOD

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Abstract: Li_{1+x}Al_xGe_{2-x}(PO_4)_3 (LAGP) solid electrolyte is one of the promising solid electrolytes for lithium ion batteries. The LAGP electrolyte was prepared by a sol-gel method. A gelation powder was calcined at 500 °C to obtain precursor powder for LAGP. The obtained powder was pelletized and calcined at 800, 850, and 900 °C. The pellets possessed NASICON structure, indicating that the LAGP was successfully prepared. The pellet calcined at 850 °C showed the highest lithium ion conductivity, 1.4×10^{-4} S cm^{-1}, which is acceptable for all-solid-state lithium battery. Although some modification is still needed to improve the lithium ion conductivity of LAGP prepared by the sol-gel method, this finding provides us a new route for LAGP preparation.

INTRODUCTION

All-solid-state batteries are expected as next generation Li ion battery because of their safety, reliability, durability and incombustibility1. In order to realize the all-solid-state battery, ceramics Li ion conductor with high Li ion conductivity, wide electrochemical decomposition window, and good stability against chemical reaction with both cathode and anode materials has been required2-4.

Li_{1+x}Al_xGe_{2-x}(PO_4)_3 (LAGP) solid electrolyte is a member of Li ion conductive ceramics with NASION (Na super ion conductor) type structure. The total ionic conductivities of LAGP are 4.22 × 10^{-3} S cm^{-1}5, that is comparative to Li_{1+x}Al_xTi_{2-x}(PO_4)_3 (LATP)6,7 and Li_{0.35}La_{0.55}TiO_3 (LLT)8,9 which are anticipated to be applied to the all-solid-state battery. The electrochemical windows of LATP and LLT are limited by facile reduction of Ti^{4+} at 2.4 V vs. Li/Li^{+}10, 11. The LAGP has an advantage for electrochemical window because Ge^{4+} is insensitive to reduction12 in contrast with Ti^{4+}.

The LAGP preparation has been performed by melt-quenching13-15 or solid-solution method16. These methods need high temperature (> 1000 °C). From view of energy saving, low temperature synthesis of the LAGP is required. The sol-gel method allows us to prepare inorganic materials at low temperature17. We have succeeded on preparation of the LATP solid electrolyte by the sol-gel process18.

The aim of this study is exploration of possibility of sol-gel method to prepare LAGP solid electrolyte.

MATERIALS AND METHODS

A precursor sol of LAGP was prepared by mixing Ge(OC_2H_5)_4, Al(OC_4H_9)_3, n-C_4H_9OH, CH_3COOLi, NH_4H_2PO_4 and H_2O in a molar ratio of 1.5:0.5:50:1.5:3:800, respectively. The precursor sol was converted to a gel at 100 °C overnight. The gel was ground in a mortar and then calcined at 500 °C for 4h to obtain amorphous LAGP powder. The powder was pressed into a pellet at a pressure of 250 kg cm^{-2} (24.5 MPa) followed by calcination at 800, 850, and 900 °C for 6h to obtain sintered pellet. Crystal structure of the pellet was identified by XRD (RINT-2000, Rigaku). Li ion conductivity of the obtained LAGP pellet was performed by AC impedance method. Prior to measure, Au was sputtered on both sides of the pellet to ensure electric contact. Data was collected at ±50 mV voltage signal in a frequency range of 5 Hz ~ 13 MHz using as-prepared cell at OCV (open circuit potential) at 30 ~ 60 °C.

RESULTS AND DISCUSSION

XRD patterns of the powder and pellet calcined at 800, 850, and 900 °C are depicted in fig. 1. After calcination of gelation powder at 500 °C (fig. 1(d)), no clear diffraction peak was observed, implying that amorphous powder was obtained. In the pellet calcined at 800 °C, all diffraction peaks are attributed to LAGP with NASICON type structure. In 850 and 900 °C calcination, the diffraction peaks became sharper and no impurity phase was observed. It is thought that LAGP with NASICON type structure could be prepared after calcination at more than 800 °C. Densities of the pellet calcined at 800, 850, and 900 °C were 3.0, 3.2, and 3.1 g cm^{-3}, respectively.
For application of LAGP solid electrolyte to the all-solid-state battery, lithium ion conductivity of the LAGP pellets calcined at various temperatures were evaluated by the AC impedance method. Figure 2 shows complex impedance plots of the LAGP pellet calcined at 800, 850, and 900 °C measured at 30 °C using Au blocking electrode. In all plots, a semicircle and Warburg-type impedance were observed at high frequency and low frequency regions, respectively. This tail at low frequencies corresponds to a usual behavior of ionically conductive ceramics. A similar behavior has been observed another ionically conductive ceramics. Estimated lithium ion conductivity of the LAGP pellets calcined at 800, 850, and 900 °C were 6.1×10⁻⁵, 1.4×10⁻⁴, and 7.0×10⁻⁵ S cm⁻¹, respectively. The LAGP pellet calcined at 850 °C possessed the highest lithium ion conductivity among the pellets, however, it was lower than reported value.

The Arrhenius plot of the LAGP pellet calcined at various temperatures is depicted in Fig. 3. The slopes of plots at 800 and 900 °C were almost identical. The pellet calcined at 850 °C showed a little gradual slope compared with others, indicated that activation energy is smaller. Estimated activation energy of the LAGP pellet calcined at 800, 850, and 900 °C was 0.40, 0.34, and 0.40 eV, respectively. The activation energy of LAGP pellet calcined at 850 °C is consistent with reported value.

LAGP with NASICON type structure was successfully prepared by the sol-gel method. The lithium ion conductivity of the LAGP pellet calcined at 850 °C was higher than that at 800 °C. This is attributed to high crystallinity of LAGP as indicated in XRD pattern. The pellet calcined at 900 °C showed lower ion conductivity than that at 850 °C. This would be due to formation of small amounts of impurity phase which could not be detected by XRD. We have found impurity phase in sol-gel prepared LATP electrolyte calcined at high temperature. The impurity phase may act as a resistance layer. In our results, the LAGP pellet calcined at 850 °C possessed the highest lithium ion conductivity, 1.4×10⁻⁴ S cm⁻¹. This value was comparable with Li₇La₃Zr₂O₁₂ ceramics electrolyte, which is acceptable for all-solid-state lithium battery. However, it was lower than reported value. It is thought that this low conductivity is due to high grain-boundary resistance because of not enough sintering of the pellet. It is expected that the grain-boundary resistance could decrease if smaller precursor powder crashed by ball-milling and so on would be used.

In conclusion, it was found that LAGP could be prepared by the sol-gel method. Although optimization of the sol-gel process is needed, this finding gives us a new picture for the LAGP preparation.

SUMMARY

LiₓAlₓGe₂₋ₓ(PO₄)₃ (LAGP) solid electrolyte with NASICON structure was successfully prepared by the sol-gel method. The lithium ion conductivity of the LAGP pellet calcined at 850 °C was higher than that at 800 °C. This is attributed to high crystallinity of LAGP as indicated in XRD pattern. The pellet calcined at 900 °C showed lower ion conductivity than that at 850 °C. This would be due to formation of small amounts of impurity phase which could not be detected by XRD. We have found impurity phase in sol-gel prepared LATP electrolyte calcined at high temperature. The impurity phase may act as a resistance layer. In our results, the LAGP pellet calcined at 850 °C possessed the highest lithium ion conductivity, 1.4×10⁻⁴ S cm⁻¹, which is acceptable for all-solid-state lithium battery. It is thought that this low conductivity is due to high grain-boundary resistance because of not enough sintering of the pellet. It is expected that the grain-boundary resistance could decrease if smaller precursor power crashed by ball-milling and so on would be used.

In conclusion, it was found that LAGP could be prepared by the sol-gel method. Although optimization of the sol-gel process is needed, this finding gives us a new picture for the LAGP preparation.
battery. However, the value was lower than reported one. In this study, it is revealed that the sol-gel method is useful method for LAGP preparation, although some modification of the process is required.

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