JOURNALOF

Ceramic Processing Research

The relationship of structural and electrochemical properties of NASICON structure Li_{1.3}Al_{0.3}Ti_{1.7} (PO₄)₃ electrolytes by a sol-gel method

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Lithium ion conducting NASICON-type electrolytes of general formula $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3$ (LATP) are fabricated by a citric acid-supported sol-gel process and analyzed for thermal stability, microstructure, crystalline phases. From these structural analyses, the relationship of microstructural changes and electrochemical properties is investigated. It is demonstrated that the sol-gel method enable to obtain pure LATP crystals at a lower temperature in a shorter synthesis time compared to conventional solid state reaction or glass-ceramics processes. The dense electrolyte pellets are prepared from the LATP nanopowders by sintering at 900 °C for 3 hours, and a room temperature conductivity of 7.8×10^{-5} S/cm and activation energy of 38.2 KJ/mol was obtained.

Key words: NASICON-type electrolytes, Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP), sol-gel process.

Introduction

Solid electrolyte for all-solid-state lithium battery has been studied extensively due to its thermal stability, electrochemical safety, and high energy density compared with secondary battery systems with liquid electrolytes [1-7]. Solid electrolytes for lithium batteries are generally divided into organic and inorganic based ones. Inorganic electrolytes are classified into non-oxide or oxide in terms of material system, and amorphous or crystalline in terms of material structure [8-9].

Amorphous oxide electrolytes have been interested due to its merits over crystalline counterparts such as isotropic electrical properties and the wide choice of composition ensuring a continuous control of electrical properties [1-3]. However, solid-state batteries employing these glass electrolytes have not been realized because glass electrolytes do not completely satisfy the material requirements, especially ionic conductivity limited to $\sim 10^{-5}$ S/cm. [10] On the other hand, non-oxide (sulfide) glasses [9] show higher ionic conductivity of $10^{-3} \sim 10^{-4}$ S/cm at room temperature and a wide electrochemical window, and a high thermal stability against crystallization. These advantages over oxide glasses were explained by larger ionic radius and larger polarization of sulfide ions, which may improve the mobility of the conduction species [11]. Along with sulfide glasses, crystalline sulfide electrolytes were also studied extensively in the hope to enhance ionic conductivity. Tatsumisago et al. reported that Li₂S-P₂S₅ glass-ceramics

crystallized partially by post-annealing process show reproducibly the ion conductivities higher than 10⁻³ S/cm [4]. However, in spite of high ionic conductivity, the sulfide materials have several drawbacks such as corrosive chemical nature resulting in the difficulty in handling and managing the fabrication, low decomposition voltage, highly hygroscopic nature, and so on.

The crystalline oxide electrolytes are classified into two groups; perovskite and NASICON and well known for high bulk conductivity of 10⁻³ S/cm and excellent chemical, thermal and mechanical stability. However, the total conductivity of the sintered electrolyte drops to 10^{-5} S/cm due to high grain boundary resistance [12]. LiTi₂(PO₄)₃ based on the NASICON structures, consisting of a three-dimensional network of Ti-O octahedral bonding corner-shared with P-O tetrahedral, has been studied as a superionic conductors with low electronic conductivity [13-14]. Aono et al. [13] and Fu [15] reported Li_{1+x}Al_xTi_{2-x}(PO₄)₃ structures with the maximum conductivity of $10^{-3} \sim 10^{-4}$ S/cm by a partial interchange $Ti^{4+} \rightarrow Al^{3+} + Li^{+}$. The conductivity enhancement by Al^{3+} ion substitution was attributed to decrease in the activation energy at the grain boundary and a densification at the grain boundary by an addition of Li⁺ ion. Recently, it drew attentions as solid electrolytes for the lithium-air cells, one of the next generations of batteries with high energy density, due to chemical and mechanical stability [16-18].

LATP electrolytes are generally synthesized by a conventional melting-quenching process [15, 19] or solid-state reaction method [20-21]. However, the melting-quenching method requires heating temperature as high as 1450 °C for melting precursors, and the solid-state reaction process suffers from the formation of harmful minor phase due to the lithium loss during

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high temperature (~ 1100 °C) sintering process [20]. Therefore, there is a need for a suitable method that can provide the LATP ceramics at lower temperatures. Hydrothermal reaction method has been reported as one of the low temperature process for a synthesis of NASICON-structured powders [22-23]. However, no Al-doped LATP structures were reported due to the difficulty in the formation of multi-component systems by hydrothermal process.

The sol-gel method is known as an effective technique to synthesize multi-component oxide materials at low temperatures. In this study, nano-powders and electrolyte pellets of the NASICON type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ were prepared by citric acid-supported sol-gel process, and their ionic conductivity was investigated. The influences of parameters such as the microstructure or crystalline phases on the total conductivity of LATP electrolyte pellets were investigated.

Experimental

The NASICON type Li_{1,3}Al_{0,3}Ti_{1,7}(PO₄)₃ nanopowders were prepared by citric acid-supported sol-gel process. Lithium nitrate (LiNO3, Junsei), aluminum nitrate nonahydrate (Al(NO₃)₃ · 9H₂O, Alfa Aesar), titanium tert-butoxide (Ti(OC₄H₉)₄, Multivalent lab.), and ammonium dihydrogen-phosphate ((NH₄)H₂PO₄, Sigma-Aldrich) were used as starting materials, and citric acid and glycol were considered as a monomer of sol-gel polymerization. The citric acid was dissolved into glycol with the mol ratio 1:4, and metal cation and phosphorous sources of the appropriate composition were mixed. The solutions were homogenized and dried in heating oven at 150 °C for 6 hours to promote esterification and polymerization between glycol and citric acid. Then the obtained brown viscous gel was calcined at $500 \sim 700$ °C for 4 hours and organic compounds was pyrolyzed to obtain amorphous nano-powders. Thermal behavior of the viscous gels was measured by TG-DTA at a heating rate of 10 °C/min over the temperature range of $25 \sim 1100$ °C in air atmosphere.

The calcined organic-free powders were pressed into pellets of 16 mm diameter and 0.8 mm thickness. Dense ceramic electrolytes were prepared by sintering the powder pellets at 700 ~ 1100 °C for 3 hours in air. Phase analysis of calcined powders and pellet electrolytes was performed by X-ray diffraction (Rigaku, Ultima IV) using Cu-K α radiation, and the microstructures were observed by scanning electron microscopy (Jeol, JCM-5700). For the electrochemical measurements, electrolyte pellets were prepared with platinum electrodes sputtered on both sides as blocking electrodes. Complex impedance analysis was carried out by a Solatron 1287 on the frequency range of 1 Hz ~ 1 MHz.

Results and Discussions

The crystallization temperatures of the dried gels

have been studied by thermal analysis. Thermogravimetric curve in Fig. 1 represents a total weight loss of about 80% in the temperature range to 700 °C. First, $\sim 5\%$ weight losses at 300 °C of product are attributed to residual solvent evaporation. A small peak at 304 °C in DSC curve shows the pyrolysis temperature of citric acid and glycol, and a weight of gel sample was gradually decreased from this temperature due to decomposition of these polymer additives to CO₂ and H₂O. On the other hand, a sharp exothermic peak at 526 °C indicates the chemical reaction of each precursor, which forms the LATP crystalline phase. No weight changes and chemical reactions were observed over 700 °C. Based on the thermal analysis, the pyrolysis process of dried gels was carried out to prepare organic-free and nano-sized Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ powders. Fig. 2 shows the X-ray diffraction patterns of the LATP nanopowders calcined at $500 \sim 700$ °C for 4 hours. The peaks in the diffraction pattern can be assigned to that of LiTi₂(PO₄)₃ (lithium titanium phosphate, JCPDS, Card 35-0754) except the tiny peak at $2\theta = 23.5^{\circ}$ for the powder calcined at low temperature. The observed X-ray diffraction patterns suggest that aluminum ion substitution was successfully carried out without the formation of secondary phases such as AlPO₄. However, the peak intensity was clearly increased over 600 °C even though the crystallization reaction starts at 526 °C as shown in DSC result (Fig. 1). This result may be



Fig. 1. TG-DSC curves of dried gel prepared by sol-gel method at heating rate of $10 \,^{\circ}$ C/min over the temperature range of $25 \sim 1100 \,^{\circ}$ Cin air atmosphere.



Fig. 2. X-ray diffraction patterns of Li1.3Al0.3Ti1.7(PO4)3 powders calcined at $500 \sim 700$ °C for 4 hours.

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Fig. 3. SEM image of inner microstructures of Li1.3Al0.3Ti1.7(PO4)3 pellets sintered at $700 \sim 1100$ °C for 3 hours in air atmosphere.



Fig. 4. X-ray diffraction of Li1. 3Al0. 3Ti1. 7(PO4)3 pellets sintered at $700 \sim 1100$ °C for 3 hours in air atmosphere.



Fig. 5. Room temperature impedance spectra of Li1. 3Al0. 3Ti1. 7(PO4)3 electrolytes sintered at various temperatures with insets showing at high frequency semicircles representing the grain resistances.

explained by LATP grain growth restrained by the remained organic components, and this explanation is supported by TG curve showing rapid weight losses up to 600 °C.

Since LATP powders sintered at 650 C showed the sufficient crystallinity in XRD analysis, to prepare dense LATP electrolyte pellets for electrochemical performance analysis, the organic-free nano-powders calcined at 600 °C were used since the powder sintered at higher than 600 °C exhibited superfluous grain growth. SEM images in Fig. 3 show the microstructure of pellets sintered at various temperatures. In general, increasing sintering temperature from 700 °C to 1100 °C

resulted in increase in both density and grain size. The microstructure image of 700 °C shows that spherical grain morphology was maintained without densifications or grain growths during sintering process. However, at 900 °C, the electrolyte became highly denser and the contact between grains is so tight that the grain boundary cannot be clearly distinguished. The crystallized grains are uniform with average size under 2 µm. The pellets sintered above 1000 °C showed a dense packing of a large number of cube-shaped crystals, and the size of these cube-shaped crystals reaches about 10 µm at 1100 °C. Fig. 4 shows the XRD patterns obtained from the electrolytes sintered at $700 \sim 1100$ °C for 3 hours from electrolyte pellets of LATP nano-powders pyrolyzed at 600 °C. Although the peaks corresponding to $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3$ structure were appeared at all sintering temperatures, pure LATP (JCPDS, Card 35-0754) phase was obtained only between $700 \sim 900$ °C. It is noteworthy that secondary phase AlPO₄ ($2\theta = 22^{\circ}$) were observed at 1000 °C and the crystallinity was increased to 1100 °C. This minor phase was formed due to the lithium ion loss during the sintering process at high temperature [24]. It is explained that the Li ion elimination leads to the stoichiometric imbalance, which makes Al4+ ion in octahedral site re-structuralized to Al^{3+} ion in stable AlPO₄ crystal structure.

Fig. 5 shows a typical Nyquist plots of Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ electrolytes sintered at $700 \sim 1000$ °C. Three distinct regions were observed. A straight line at low frequency represents a platinum electrode and electrolyte interface phenomenon. Two semicircles are associated with the bulk grain and the grain boundary resistance [15, 20]. The high frequency semicircle, bulk grain resistance, was about two orders smaller than the middle frequency semicircle, grain boundary resistance. From the grain resistances of electrolytes sintered at 700 °C (left) and $800 \sim 1000$ °C (right) shown in the insets, the resistance of 700 °C was much higher than that of $800 \sim 1000$ °C although the good crystallinity of all specimens demonstrated in Fig 4. It can be demonstrated that the ac impedance results is dependent on not only the crystallinity of each LATP grains but the grain necking and densification in electrolyte microstructures by the grain growth. On the other hand, the grain boundary resistances, the larger semicircles in front of the spike at low frequency, were decreased by the densification with increasing heating temperature. However, the grain boundary resistance of pellet sintered at 1000 °C was higher than that at 900 °C due to the secondary phase such as AIPO4 shown in Fig. 4 even though the denser microstructure and the higher crystallinity.

Fig. 6 shows the temperature dependence of grain, grain boundary and total conductivities of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ pellets sintered at 900 °C for 3 hours. The plots was found to be linear and fitted the Arrhenius equation, $\sigma T = A$ exp(-E_a/RT), where σ is the conductivity, A is the preexponential factor, E_a is the activation energy, and R is the gas constant. The grain and total conductivity at room



Fig. 6. Arrhenius plots of grain, grain boundary and total conductivities of Li1.3Al0.3Ti1.7(PO4)3 pellets sintered at 900 °C for 3 hours.

temperature were 9.4×10^{-4} S/cm and 7.8×10^{-5} S/cm, which are the lower values for an inorganic Li-ion conductor than the highest values previously reported [20, 25]. This difference is believed to be attributed to the difference in the densities and grain boundary structures of the pellets sintered by normal thermal sintering and spark plasma sintering. It has been reported that, in the spark plasma sintering process, the densification was remarkably improved for LATP pellets, and the maximum density of about 97% was obtained in the specimen at 1100 °C [20]. Aono et al. [13] also reported on the correlation between the porosity of electrolytes and their conductivity. The activation energies were 12.8 KJ/mol for grain and 38.2 KJ/mol for total, and were consistent with previous results [20, 24]. Generally, Al substitution in $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3$ structure reduced the barrier height of Li-ion migration at the grain boundary and resulted in lower activation energy [24]. Similar to this observation, the grain boundary resistivity and activation energy measured in this work were higher than those of the bulk, and total resistivity and total activation energy are mainly determined by these values. It can be suggested that a control the lithium ion loss, the secondary phase, and an increase grain density are needed to enhance the conductivity of LATP electrolytes.

Conclusions

The Li-ion conductor $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3$ without secondary phases was successfully prepared by a low temperature process; citric acid-supported sol-gel process. To prepare dense LATP electrolyte pellets for electrochemical performance analysis, the organic-free nanopowders were obtained by calcined the dried gels including metal cation and phosphorous sources. And then, the pure and dense electrolyte pellets could be obtained from LATP pellet sintered at 900 °C. The total conductivity and the activation energy at room temperature were 7.8×10^{-5} S/cm and 38.2 KJ/mol. The resistance and activation energy of the grain boundary was higher than the bulk resistance and mainly contributed to the total resistance. It can be expected that the conductivity of the crystalline electrolytes can be improved by controlling not only the crystallinity of each grains but the grain necking and densification in electrolyte microstructures by the grain growth.

Acknowledgment

This research was supported by the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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