

Fast lithium ion conducting ceramics for all-solid-state lithium-ion battery

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Lithium ion rechargeable batteries have been used as large-scale power sources such as an electric vehicle because they have high energy densities. However, there are some safety issues with lithium ion rechargeable batteries since they employ organic liquid electrolytes. Therefore, it is important to improve their safety and reliability. All-solid-state lithium ion rechargeable battery is the one of promising next-generation battery that is very safe since they employ inorganic solid electrolyte instead of organic liquid electrolyte. However, it is difficult for all-solid-state rechargeable batteries to achieve a similar electrochemical performance to the batteries using liquid electrolytes. Two major causes, which adversely affect electrochemical performance at the electrode–electrolyte interface, are considered. One is the formation of high resistance layer formed at the interface between electrode and electrolyte. The other is the small contact area between active materials and solid electrolytes. In the case of using solid electrolytes, the interfacial area between active materials and solid electrolytes become smaller than the interfacial area between active materials and liquid electrolytes because the solid electrolytes are difficult to infiltrate like liquids. Therefore, It is important to fabricate a large contact area between active materials and solid electrolytes.

In particular, many researchers focused on $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$ (LATP) ceramic electrolyte having a NASICON type crystal structure. The LATP ceramic electrolyte exceptionally has high water-resistant, though general lithium-ion conducting electrolytes are unstable with water. It is therefore expected as a possible material for lithium-air batteries, which have an energy density theoretically far greater than that of lithium ion batteries as well as to all-solid lithium ion batteries. The maximum conductivity ($1.3 \times 10^{-3} \text{ S/cm}^{-1}$ at 298 K) was achieved. However, the total conductivity due to the high grain-boundary resistance is substantially decreased. Therefore, a negligibly small grain-boundary resistance is important if polycrystalline ceramic-type materials are used. In conventional processing of LATP-based glass-ceramic electrolyte, the raw material is melted at over 1400°C , and the powder formed by vitrification is used for the electrolyte sheet manufacturing. After making a green sheet, it is sintered at around 1000°C . Therefore, production cost is high. Additionally, it is difficult to prepare a dense, large-area thin electrolyte sheet, which are necessary for making large-scale batteries, because of hard ceramic materials and glass-ceramic easily cling to a supporting plate during a sintering operation.

In recent years, we successfully prepared a large-scale thin LATP-based ceramic electrolyte. At the same time, new preparation process significantly reduces grain-boundary resistance that has been a problem with ceramic electrolytes and achieved the overall conductivity of the polycrystalline electrolyte close to the inherent ion

conductivity within the crystals. The developed ceramic electrolyte sheet not only demonstrates a high overall conductivity ($1 \times 10^{-3} \text{ S/cm}$) at room temperature, it provides sufficient strength against bending stress; a ceramic electrolyte sheet $80 \mu\text{m}$ thick was unbroken after repeated bending (curvature radius of approximately 5cm). In this research, we demonstrate to fabricate a multi layered LATP-based ceramic electrolyte sheet with high-specific surface area that is able to make a large contact area between active materials and solid electrolytes. Additionally, we developed a protection layer on LATP sheet for direct contacting with lithium metal.

$\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$ and $\text{LiZr}_2(\text{PO}_4)_3$ were prepared by conventional solid state reaction with Li_2CO_3 , $\text{Al}(\text{OH})_3$, ZrO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$, TiO_2 , SiO_2 and CaCO_3 as the starting materials. The chemicals were mixed in a pot for 4 h using roller mill. Initially, the obtained batch was contained in an aluminum crucible and then transferred to electric furnace. The furnace was heated to 200°C at the rate of $1^\circ\text{C}/\text{min}$ and held at that temperature for 2 h. The powder for synthesis was reground and then placed in a platinum crucible and heated to 750°C at the rate of $1^\circ\text{C}/\text{min}$ followed by a soaking for 2 h. The calcined powder was milled in the planetary-type mill for 1 h. The fine powder was in consecutive order dried and mixed with 5-20wt% polyvinyl butyral (PVB) as binder, 4wt% diethyl adipate as plasticizer, 2wt% diamine RRT as dispersant and solvent (toluene + butanol). The slurry composition needs to be adjusted to get the various porosity of sheets or the dip coating solution. Several types of green sheets were prepared by a tape casting method with a thickness of $10\text{--}400 \mu\text{m}$ on a polyester film. Laminated green sheets were disposed on a setter plate (supporting plate). They were subsequently sintered in the temperature range of $850\text{--}1150^\circ\text{C}$ for 2 h.

We achieved to fabricate a LATP-based bilayer electrolyte sheet for direct contacting with lithium metal. The total ionic conductivity of the bilayer electrolyte sheet is about $7.4 \times 10^{-5} \text{ S/cm}$.

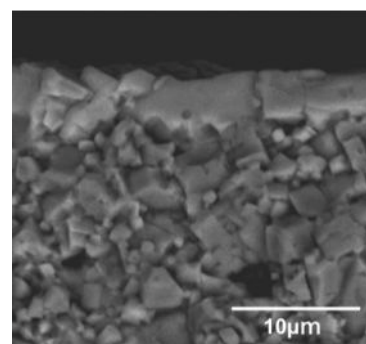


Fig. 1. Cross-sectional image of bilayer electrolyte.

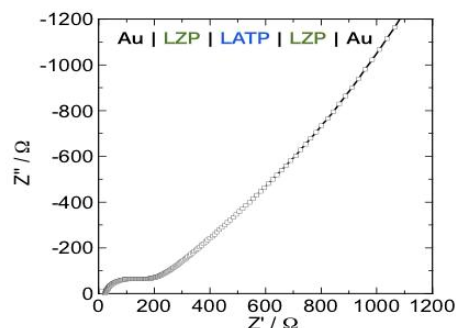


Fig. 2. AC impedance plot of bilayer electrolyte sheet.

