Solid-State Battery assembled by LISICON-Li_3BO_3 Amorphous Electrolyte

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Oxides are generally non-flammable, durable and non-toxic materials; high safety and reliability in a battery system is assured by the use of oxide as an electrolyte instead of the highly-reactive non-aqueous liquid. To develop an oxide-based solid-state lithium-ion battery (SS-LIB) for large-scale applications such as electric vehicles, the thicknesses of stacked electrode and electrolyte layers need to be curtailed to several ten to hundred μm order. Although the powder technology is an easy formula for obtaining such thick electrode layers, some sort of powder interfacial design is required for the fast ionic transfer in oxide-based SS-LIB. LISICON-related electrolytes as $Li_{3.75}Ge_{0.75}P_{0.25}O_4$ *etc.* possess high bulk conductivities of over 10^{-5} S cm^{-1}, which are ones of suitable candidates for assembling SS-LIB.[1] However, their high-sintering temperatures produce the ionic insulating interfacial phase between electrode powder and solid electrolyte powder under the battery preparation, which prevents to show the electrochemical activity of SS-LIB. Recently, it has been reported that the amorphization of oxide electrolyte is one of the useful methods for realizing suitable electrode/electrolyte interface as sulfur electrolyte.[2]

In present study, the amorphous electrolyte prepared from the mixture of LISICON-type $Li_{3.75}Ge_{0.75}P_{0.25}O_4$ electrolyte and Li_3BO_3 by ball-milling treatment. The ionic conductivity of $0.5Li_{3.75}Ge_{0.75}P_{0.25}O_4$-$0.5Li_3BO_3$ amorphous electrolyte was 1.5 x 10^{-6} Scm^{-1} at 25ºC even after uniaxial pressing at room temperature. Spark-plasma sintering (SPS) is a unique technique by applying microscopic electrical discharge between ceramic (or metal) powders under a pressure. Transparent of the $0.5Li_{3.75}Ge_{0.75}P_{0.25}O_4$-$0.5Li_3BO_3$ pellet could be confirmed after the SPS treatment at low temperature of 400 ºC under a pressure of 600MPa, and the ionic conductivity was improved to 4.0 x 10^{-6} Scm^{-1}. A well-defined interface between $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode and the amorphous electrolyte without any impurity could be prepared since the processing temperature was low enough to prevent any side reactions during the densification. The SPS process was crucial to enhance not only the densification of the amorphous electrolyte powder but also the contact at electrode / amorphous electrolyte hetero interface. Such well-defined interface enabled to exhibit the reversible capacity (150 mAh g^{-1}, operating temperature: 60 °C, cut-off voltage range: 2.0-4.2 V vs. Li/Li^+) for 50 μm of thick composite electrode layer in SS-LIB ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$0.5Li_{3.75}Ge_{0.75}P_{0.25}O_4$-$0.5Li_3BO_3$ composite / $0.5Li_{3.75}Ge_{0.75}P_{0.25}O_4$-$0.5Li_3BO_3$/ PEO-based polymer / Li metal).

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References:

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