Development of all-solid-state secondary lithium battery using garnet-type single crystal electrolyte

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Recently, all-solid-state lithium batteries are being researched and developed in many areas as one of next generation energy devices. The high voltage positive electrodes and metallic lithium can be used in all-solid-state lithium batteries, therefore it is thought that high energy density batteries can be manufactured. [1-3] Furthermore, since organic liquid electrolyte is not used, it is possible to solve the many problems of conventional lithium batteries such as ignition, and use under high temperature. In order to realize the all-solid-state lithium battery, it is important to develop lithium ion solid electrolyte. Research and development of lithium ion solid electrolyte is actively carried out, and the type of solid electrolyte is roughly divided into sulfide-type and oxide-type. The oxide-type solid electrolyte is relatively stable in the atmosphere and maintains high safety, but because of its low lithium ion conductivity and not plasticity, it is difficult to make interfaces between solids. We have been conducting research and development focusing on the high safety of oxide-type solid electrolyte. In order to improve the lithium ion conductivity, we tried to grow single crystal without grain boundary. Single crystals of $Li_{7-x}La_3Zr_{2-x}Nb_xO_{12}$ (X=0.2, 0.35, 0.45, 0.5, 0.6, 0.8) samples were synthesized by floating zone method. The typical single-crystal rod size of $Li_{6.5}La_3Zr_{1.5}Nb_{0.5}O_{12}$ (LLZNb05) were about 6mm in diameter and 60mm length. A single-crystal was collected diffraction data for the structure analysis by single-crystal X-ray and single-crystal neutron diffraction methods. $Li_{6.5}La_3Zr_{1.5}Nb_{0.5}O_{12}$ crystallizes in the cubic system, space group *Ia*-3*d*, and the lattice parameters of a =12.9130(8) Å. The crystal structure of LLZNb05 was refined to the conventional values of R = 4.25% and wR = 5.82% for single-crystal X-ray diffraction data, and R = 7.09% and wR = 7.94% for single-crystal neutron diffraction data. Li ions in the crystal structure occupied two kinds of sites, and each sites were distorted tetrahedron 96*h* site and distorted octahedron 96*h* site. The total Li-ion conductivity in LLZNb05 was estimated to be 1.39×10^{-3} S cm^{-1} at 298 K from the results of AC impedance measurement using a thin-plate specimen having a diameter of 6 mm and a thickness of 0.8 mm obtained by cutting a single-crystal rod. Electrochemical charge and discharge tests of the all-solid-state secondary lithium battery were performed using a two-electrode flat cell. The solid electrolyte was a single-crystal plate with a diameter of 6 mm and a thickness of 0.7 mm, which were obtained by cutting a single-crystal rod. The positive electrode was formed on the solid electrolyte by the aero-sol deposition method.

References:

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