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# Article / Book Information

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Outline of thesis

Title

Materials developments of $Li_{10}GeP_2S_{12}$-type superionic conductors in the $Li_2X$–$P_2X_5$–$MX_2$ pseudoternary system

—Application as solid electrolytes for all-solid-state lithium batteries—

The all-solid-state lithium battery is considered as a next-generation energy storage device with a number of desirable features, including fewer safety concerns in comparison with energy devices powered by liquid electrolyte, as well as potentially high-energy and high-power densities. However, the lack of materials showing fast lithium conductivity, which can be employed as solid electrolyte in the battery, prevents all-solid-state batteries from practical applications. This study developed the material diversity of sulfide superionic conductors with $Li_{10}GeP_2S_{12}$-type structure showing high lithium conductivities over 1 mS $cm^{-1}$, which were comparable to that of liquid electrolyte. The phase diagram construction, synthesis of solid-solutions, and structure analysis using diffraction techniques were conducted for the materials discovery in the pseudoternary $Li_2X$–$P_2X_5$–$MX_2$ system ($M$ = $P^{4+}$, $Si^{4+}$, $Sn^{4+}$, $Ge^{4+}$; $X$ = S, O). Fabricated prototype batteries using novel materials exhibited excellent specific power especially at 100 °C.

This doctoral thesis consists of eight chapters. In the Chapter 1, the importance of this thesis work is presented from the scientific and industrial viewpoints. In addition, the background information on lithium ion batteries and lithium solid electrolytes is also given. The Chapter 2 overviews experimental techniques used through this research. Six results chapters (Chapter 3–8) include a short introduction, experimental procedures, results and discussion, and conclusion section.

In the Chapter 3, the pseudo-binary system $Li_4GeS_4$–$Li_3PS_4$ was studied through the use of X-ray diffraction and differential thermal analysis (DTA). The phase diagram of this binary system was determined and the structure–composition relationships between the LGPS-phase and other compounds existing in this system were clarified.

In the Chapter 4, the LGPS-related phases, $Li_{10+\delta}M_{1+\delta}P_{2-\delta}S_{12}$ where $M$ = Si and Sn, were synthesized by a conventional solid-state reaction in a sealed and evacuated silica tube. The ranges of the solid solutions were determined, and the conductivity and electrochemical stabilities were clarified. The relationships between ionic conduction, metal ions, lithium content, lattice volume, and local environment of lithium along the conduction pathway were studied on the basis of the crystal structures and conductivities of these solid solutions. The conduction mechanism is discussed for the $Li_{10+\delta}M_{1+\delta}P_{2-\delta}S_{12}$ ($M$ = Si, Ge, Sn) systems with the LGPS-type structure in order to develop further materials design of these solid lithium ion conductors.

The Chapter 5 is a study on crystal structures of the superionic conductors $Li_{9.81}Sn_{0.81}P_{2.19}S_{12}$ and $Li_{10.35}Si_{1.35}P_{1.65}S_{12}$, both having a $Li_{10}GeP_2S_{12}$ (LGPS)-type structure. Crystal structures of these phases were determined by neutron diffraction analysis over the temperature range 12–800 K. The maximum entropy method (MEM) was also employed to clarify the lithium distribution in these materials. The Sn system showed one-dimensional diffusion in the *c* direction over a wide temperature range, even though the Ge-based system typically exhibits three-dimensional conduction at higher temperatures. The ionic conduction mechanisms of analogous Si, Ge and Sn phases with LGPS-type structures are discussed on the basis of the observed structural parameter changes.

The Chapters 6 and 7 are about LGPS-type lithium ion conductors having high electrochemically stability. In the Chapter 6, oxygen atoms were doped into the LGPS-type structure. A novel member of LGPS family was discovered in the $Li_2S$–$P_2S_5$–$SiO_2$ pseudoternary system; the $Li_{9.42}Si_{1.02}P_{2.1}S_{9.96}O_{2.04}$ phase was synthesized. The properties and characteristics of this material, such as its crystal structure, conductivity, and performance as a solid electrolyte in all-solid-state cell were investigated. In the Chapter 7, a $Li_{9.6}P_3S_{12}$ phase with LGPS-type structure was synthesized and found to have high ionic conductivity and high electrochemical stability.

Finally, the charge–discharge performance of all-solid-state cells using developed solid electrolytes in this research are demonstrated in the Chapter 8. This chapter includes the fabrication of a new all-solid-state battery that has an extremely high specific energy and power especially at 100 °C and that is superior to conventional electrochemical devices powered by liquid electrolytes. These characteristics were confirmed by Ragone plots showing the relationship between the specific power and energy of the devices. Future research directions are also provided in this chapter.