題目(和文)	リチウムイオン導電体Li10+δGe1+δP2-δS12固溶体の合成：導電メカニズム及び全固体電池への応用
Title(English)	Synthesis of a solid solution for the lithium ion conductor, Li10+δGe1+δP2-δS12 : its conduction mechanism and application to all-solid-state batteries
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論文要旨

THESIS SUMMARY

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Chapter 1. Introduction

Recently, all-solid-state lithium batteries with a solid-state electrolyte have been given great attention as the next generation battery due to their high safety and high reliability compared to the lithium ion batteries with organic liquid electrolytes. Moreover, all-solid-state batteries can achieve higher energy density due to simplified construction such as bipolar stacking. However, several key issues for practical application of all-solid-state battery are remained such as low ionic conductivity of solid electrolyte and resistive interfacial layer between oxide electrodes and sulfide electrolytes.

In this thesis, a solid solution of high lithium ion conductor with a sulfide system has been synthesized to achieve the higher ionic conductivity and the cycling characteristics of the all-solid-state batteries using the solid electrolyte have been examined.

Chapter 2. Experimental

The LPGS solid solution was synthesized using a solid-state reaction and determined by X-ray and neutron diffraction method. Surface coated $LiCoO_2$ cathode for all-solid-state batteries was synthesized using a sol-gel method. Surface morphologies of modified $LiCoO_2$ were investigated by XRD, EDS/SEM, TEM, ICP-MS and XPS.

Chapter 3. Synthesis, structure, and conduction mechanism of the lithium superionic conductor $Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$

The LGPS solid solutions fabricated during this study were based on the Li_3PS_4 – Li_4GeS_4 pseudo-binary system, and compositions similar to the parent LGPS ($Li_{10}GeP_2S_{12}$) phase were synthesized according to the compositional formula $Li_{10+\delta}Ge_{1+\delta}P_{2-\delta}S_{12}$. The monophasic character of the LGPS phase was observed in those materials in which δ was at or near zero, with a continuous peak shift to lower angles with increasing values of δ, suggesting the formation of a solid solution in the LGPS phase. The structure of LGPS solid solution with a new Li4 site was confirmed by neutron diffraction Rietveld refinement. The highest ionic conductivity value of 1.42×10^{-2} S cm^{-1} at 300 K was obtained for the composition in which δ was 0.35, and this conductivity exceeds the value of 1.20×10^{-2} S cm^{-1} reported previously for such materials. The lithium conduction mechanism was investigated based on neutron diffraction analysis. Temperature dependence of site occupancies, lattice parameters, Li-Li bond distance, and thermal displacement parameters for both $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ and $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ were clarified. Based on structural analysis, one-dimensional conduction along *c*-axis around room temperature and two-dimensional conduction on *ab* plane at high temperature were indicated. Lithium ion distribution was visualized using the MEM analysis in conjunction with the neutron diffraction data obtained for $Li_{10.05}Ge_{1.05}P_{1.95}S_{12}$ ($\delta = 0.05$) ($x = 0.65$ in $Li_{4-x}Ge_{1-x}P_xS_4$) at 100 and 750 K. This indicates that the one-dimensional conduction pathway represents the primary means of lithium ion conduction at 100 K. Addition to the one-dimensional connection between the Li1, Li1, and Li3 sites, continuous lithium distribution between the Li1 and Li4 sites is also observed. These results demonstrate that the lithium ion conduction takes on a three-dimensional character, as opposed to one-dimensional, at higher temperatures.

Chapter 4. Application of $Li_{10}GeP_2S_{12}$ solid electrolyte to all solid-state batteries with surface-modified $LiCoO_2$ cathodes

In order to realize all-solid-state battery with high power density, the formation of resistive interfacial layer should be overcome. **A**morphous Li_xMO_y (M = Nb, Ta, Zr, P, Al, V) surface layers were coated at the $LiCoO_2$ surface using a sol-gel method. The surface morphology was investigated by XRD, SEM/EDS, TEM, and ICP-MS. The surface-modified $LiCoO_2$ cathodes showed the first discharge capacities from 82 to 127 mAh g^{-1} depending on the coating materials. Among the coating materials, $LiNbO_3$ and $LiTaO_3$ showed high discharge capacities of 125 and 126 mAh g^{-1}, respectively, with excellent capacity retention of 100 % up to 50th cycle.

Crystalline-based surface modification was achieved with Li_2WO_4 in all-solid-state battery system. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the chemical compositions of Li_2WO_4 on the $LiCoO_2$ surface by comparing its intensity of Co $2p_{3/2}$ and shape of W 4f peaks.

The cell delivered the discharge capacity of 98 and 55 mAh g^{-1} at the 1 C and 5 C rate, respectively. The Li_2WO_4-modified $LiCoO_2$ with the LGPS electrolyte showed the high rate capability performance. No capacity fading was observed even after high rate test. According to AC impedance measurement, it confirms that the Li_2WO_4 coating decreases the interfacial resistance.

Detailed mechanism of the Li_2WO_4 coating effect on the battery performance was investigated using two different electrochemical interfaces, LGPS/crystalline Li_2WO_4/amorphous Li_2ZrO_3/$LiCoO_2$ (LWO/LZO/LCO) and LGPS/amorphous Li_2ZrO_3/crystalline Li_2WO_4/$LiCoO_2$ (LZO/LWO/LCO). The chemical composition of each sample was investigated by peak area ratio of W 4f/Zr 3d from XPS measurement.

The LWO/LZO/LCO and LWO/LWO/LCO showed similar discharge capacities of about 120 mAh g^{-1}. In contrast, LZO/LWO/LCO and LZO/LZO/LCO showed the smaller discharge capacity of 101 mAh g^{-1} than that of the LWO/LZO/LCO and LWO/LWO/LCO. These results demonstrate that the major effect of the surface coating is to prevent the resistive layer formation at the LGPS side interface.

Chapter 5. General conclusions

A solid solution of $Li_{10}GeP_2S_{12}$ was confirmed, and highly disordered $Li_{10}GeP_2S_{12}$ structure at high temperature was identified by neutron structure analysis. The electrochemical property in all-solid-state batteries was mostly controlled by interfacial reaction between coating layer and sulfide electrolyte. Therefore, advanced all-solid-state batteries are achievable by taking ionic conductivity of solid electrolyte and compatibility between solid electrolyte and coating layer into consideration.