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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 エネルギー	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	(Science)
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This doctoral thesis is titled "In-situ scanning electron microscope observation of microstructural changes in all-solid-state lithium batteries" and is comprised of the 6 chapters listed below.

Chapter 1, "General Introduction," describes the background of this research and the importance of all-solid-state batteries and reviews the chemical and physical microstructural degradation mechanisms of solid-solid interfaces in the cell. The importance of in-situ observation of microstructural changes in the reaction field of all-solid-state batteries and the problems of previous research are described, as are the purpose and significance of this research.

Chapter 2, "Experimental," describes the synthesis of the sulfide solid electrolyte ($Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$, LGPS) used in this study. The particle size control method by dry (hand milling, HM) and wet milling (WM), structure analysis, and methods for evaluating electrochemical properties are described. For the in-situ observation, fabrication of cross-sectioned all-solid-state batteries and observation techniques using an in-situ scanning electron microscope (SEM) are described.

Chapter 3, "Particle size control of sulfide electrolyte using dry and wet milling processes," describes the effective pulverization method of LGPS electrolyte particles. It was found that the average particle size (d_{50}) of the uncontrolled LGPS could be reduced from 2 μm to about 0.5 μm by the WM process. LGPS changes particle size distribution with the number and diameter of zirconia balls, rotation speed, and time. The WM LGPS had high crystallinity and high ionic conductivity in the bulk region, which are similar to the HM LGPS. This makes it possible to control the microstructure of the electrode composite layer and the solid electrolyte layer by the particle size of solid electrolytes.

Chapter 4, "In-situ scanning electron microscopy observation of $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ and $LiNbO_3$-coated $LiCoO_2$ cathode electrode microstructure," describes the processing of an all-solid-state cell for in-situ cross-sectional SEM observation. In-situ cells are composed of a cathode composite layer (consisting of HM LGPS and $LiCoO_2$), an LGPS solid electrolyte layer, and a Li-In alloy metal anode layer. The in-situ cell using WM LGPS for the electrolyte layer showed better processability than HM LGPS with a large and non-uniform particle size distribution, and it was found that cracks were less likely to occur during section slicing. In addition, cross-section polishing conditions were explored, and processing with less damage to sulfide electrolytes was succeeded. In situ observation of the fine structure of the positive electrode composite layer made of $LiCoO_2$ and HM LGPS during charging and discharging was successful, and crack formation during the first charge was confirmed. It is expected that the main reason for the low initial charge and discharge efficiency in all-solid-state batteries is due to the electrochemically active $LiCoO_2$ particles blocking the ion conduction pathway through crack formation.

Chapter 5, "Changes in mechanical properties according to the particle size of solid electrolyte and effect on all-solid-state battery performance," the differences in all-solid-state battery performance due to the particle size of solid electrolyte are investigated by in-situ SEM observation. In the $LiCoO_2$-LGPS positive electrode composite, it was confirmed that the initial charge/discharge efficiency was improved by using micronized WM LGPS. In addition, it was found that even when a loading level of 400 μm, which is much thicker than conventional electrodes, was applied, it still showed reversible charge and discharge. From in-situ SEM observation of this phenomenon, it was observed that cracks generated during initial charging were detected again during the next discharging process, and the microstructure change was reversible. In addition, in the Li-In alloy metal/LGPS interface, it was confirmed that the HM LGPS layer is prone to crack formation due to volume expansion and contraction during Li-In alloying and de-alloying, whereas crack formation is suppressed in the WM LGPS layer. Therefore, it was confirmed that reversible charging and discharging up to a higher current density is possible when the WM LGPS is applied. From the indentation test and the Hall-Petch equation, it is explained that the WM LGPS electrolyte has excellent plastic deformability and is hard to crack, which contributes to the improvement of the reversibility of the microstructure change in the cathode composite and the anode/electrolyte interface.

Chapter 6, "General conclusions," summarizes the above results and describes the prospects for future development of all-solid-state battery materials. In-situ observation of microstructural changes during charging and discharging of all-solid-state batteries revealed that the irreversibility of microstructural changes is a factor in the decrease in active material utilization and reaction rate during cycling. As a result, the enhancement of plastic deformability is important for reversible microstructural changes. In summary, this thesis proposes a method for observing microstructural changes in bulk-type all-solid-state batteries with in-situ SEM. Furthermore, by demonstrating the possibility of controlling microstructural changes with the particle size of the electrolyte, it provides a useful perspective from the viewpoint of material development.