論文 / 著書情報
Article / Book Information

題目(和文)	LiCoO2/Li10GeP2S12 ならびにTiS2/Li10GeP2S12 複合体電極の作製と全固体電池特性
Title(English)	Fabrication and electrochemical properties of LiCoO2/Li10GeP2S12 and TiS2/Li10GeP2S12 composite electrodes for all solid-state batteries
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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電子化学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Development of all solid-state lithium batteries has been anticipated to address safety issues of conventional lithium-ion batteries when applied for large-scale devices. In this thesis, $Li_{10}GeP_2S_{12}$ (LGPS) with high lithium ion conductivity of 12 mS cm^{-1} was selected as the solid electrolyte. Two kinds of the composite cathodes were prepared by mixing the LGPS with the $LiNbO_3$-coated $LiCoO_2$ or TiS_2 cathode active materials. The mixing condition, processes for the composite cathodes and electrochemical properties were investigated to suppress the interfacial resistance between the electrode and electrolyte by increasing the contact area.

For the $LiCoO_2$/LGPS system, the composite cathode $LiNbO_3$-coated $LiCoO_2$ and LGPS were mixed with a weight ratio of 70:30 by a mill pot rotator. The fabrication conditions were mix speed, mix time and particle size of the LGPS. The $LiNbO_3$ was selected as coating material to decrease the interfacial resistance. The composite electrodes were characterized by scanning electron microscopy and X-ray diffractometry. Highly dispersed composites of $LiCoO_2$/LGPS were successfully obtained by mild grinding applying a mill pot rotation rate of 140 rpm for 30 min with 3 mmφ agate balls. the LGPS particle size of 2 μm and $LiNbO_3$ coating layer thickness of 5.8 nm. The composite cathode prepared with 5.8 nm-coated $LiCoO_2$ and 2 μm LGPS powders exhibited the first discharge capacity of 124 mAh g^{-1} when operating at a current density of 7 mA g^{-1}. However, the discharge capacity gradually decreased with the cycle number. Electrochemical impedance spectroscopy analysis clarified that the capacity fading was primarily caused by the increase in the resistance to lithium diffusion at the In-Li anode/the LGPS electrolyte interface. The LGPS electrolyte could be decomposed by the contact to the In-Li anode due to instability at low potential regions. Modification of the In-Li/LGPS interface is needed to stabilize the interface for improving the cycle stability of the batteries.

For the TiS_2/LGPS system, composite cathodes were prepared using a vortex miller at 2500 rpm for 10 min with a weight ratio between TiS_2 and LGPS of 30:70. A $TiS_2/Li_{10}GeP_2S_{12}$/In-Li cell with nano-size TiS_2 (particle size 200~500 nm) showed the first discharge capacity 239 mAh g^{-1}. However, the discharge capacity rapidly decreased even at low current density of 0.05 C. As the lithiated $LiTiS_2$ has a considerably larger lattice volume (64.1 $Å^3$) than the TiS_2 (57.1 $Å^3$), the physical contact between the TiS_2 and the LGPS could be deteriorated by the large volume change during

lithiation/delithiation processes. To clarify the influence of the volume change on the cycle stability, the charge-discharge measurements were operated with an applying pressure of 230 MPa. The first discharge capacity was 200 mAh g^{-1} at a current density of 1 C, and the discharge capacity was maintained at 168 mAh g^{-1} in the initial ten cycles. Furthermore, the capacity at 5 C was half of that at 1 C, which is much better than that of a cell under no pressure. The severe cycle retention and rate capability were greatly improved in the batteries operated with an applying pressure of 230 MPa. Eliminating the volume change of the composite electrodes is important for achieving stable battery operation and performance.

The charge-discharge reactions can proceed in all-solid state batteries with composite powder cathodes of the $LiNbO_3$-coated $LiCoO_2$/LGPS and TiS_2/LGPS. Synthesis conditions of the composite cathodes considerably affect the charge-discharge capacity, cycle retention, and rate-capability of all-solid-state batteries. For the further improvement, search for suitable coating layer material and decrease the anode/LGPS interfacial resistance are key factors for the batteries with the oxide cathodes. For the sulfide cathode, eliminating the volume change of the composite electrodes is important for achieving the stable battery operation and performance.