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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電気化学　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 ）

All solid-state lithium batteries using an inorganic solid lithium conductor as an electrolyte represent one of the ideal rechargeable battery systems. The solid electrolyte is a key material because the performance of all solid-state batteries is dependent on the properties of the solid electrolyte. Recently, a new sulfide solid electrolyte, $Li_{10}GeP_2S_{12}$, exhibiting a high lithium ion conductivity of 12 mS cm^{-1} at room temperature has been reported. In addition, it is essential to apply higher potential cathode materials and anode with lower potential in the battery; increase of the cell voltage contributes higher energy density of the battery. Therefore, the $LiNi_{0.5}Mn_{1.5}O_4$ spinel with high reaction voltage of 4.7 V (vs. Li/Li^+) can be considered as the optimal cathode material for the battery with high energy density. Applying the new cathode requires the interfacial reaction analysis, because the solid/solid interface between the electrode and solid electrolyte also affects to the battery performance. In this study, electrochemical stability of the electrode/electrolyte interface was investigated based on X-ray diffraction (XRD) measurement and electrochemical impedance spectroscopy. The formation of a solid electrolyte interphase (SEI) layer, which is an important factor for delivering reversible charge-discharge cycles in high-voltage type all solid-state batteries, is discussed.

The $LiNi_{0.5}Mn_{1.5}O_4$ powder was coated with $LiNbO_3$ layer by sol-gel method to reduce interfacial resistance; three different coating thicknesses were examined, 6.5, 9.7 and 14.3 nm. Cathode composites were prepared by mixing the $LiNbO_3$-coated $Ni_{0.5}Mn_{1.5}O_4$, $Li_{10}GeP_2S_{12}$ and acetylene black (AB) as an electronic conductor. The all solid-state batteries were assembled with the cathode composite, $Li_{10}GeP_2S_{12}$ as the solid electrolyte, and Li-In alloy or Li metal as the anode. The coating-thickness effect was examined using Li-In anode. The discharge capacities of the cell were 38, 53, and 26 mAh g^{-1} for the coating-thickness of 6.5, 9.7, and 14.3 nm, respectively. The $LiNbO_3$ coating delivered reversible lithium (de)intercalation reaction of the $LiNi_{0.5}Mn_{1.5}O_4$. However the observed largest discharge capacity for the 9.7 nm-thick coated $LiNi_{0.5}Mn_{1.5}O_4$ was much smaller than that of the $LiNi_{0.5}Mn_{1.5}O_4$ using a liquid-type cell. Since the low electronic conductivity of $LiNi_{0.5}Mn_{1.5}O_4$ (10^{-6} S cm^{-1} at room temperature) could increase the resistance of the charge transfer reaction, oxygen-deficient $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ with higher electronic conductivity (8.9×10^{-4} S cm^{-1}) was prepared via a high-temperature annealing in air. The 9.7

nm-$LiNbO_3$-coated $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ showed better electrochemical properties; a discharge capacity of 80 mAh g^{-1} at the first cycle with a cell voltage of 4.1 V was confirmed. This result indicates that high electronic conductivity of the $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ contributed to decreasing the charge transfer resistance at the electrode/electrolyte interface. In order to increase the cell voltage, Li metal with lowest redox potential was applied as the anode. The initial charge and discharge capacities for the cell using the lithium anode were 94 and 78 mAh g^{-1}, respectively. Further the higher average cell voltage around 4.3 V was confirmed during cycling. However, the decrease in the capacity is observed, indicating the deterioration of materials or increasing the resistance of the cell.

To elucidate the capacity fading mechanism, the interfacial reactions between the each electrode and the solid electrolyte in 9.7 nm-$LiNbO_3$-coated $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ / $Li_{10}GeP_2S_{12}$ / Li cell have been investigated by an analysis of *ex situ* XRD and AC impedance. The SEI layer, which suppresses further decomposition of the $Li_{10}GeP_2S_{12}$, was observed on the anode side. In contrast, it was revealed that the interfaces among components in the cathode composite could attribute to the deterioration of the cell performance; the $Li_{10}GeP_2S_{12}$ decomposed at the interface of the AB/$Li_{10}GeP_2S_{12}$ at the high voltage region. The product layer formed by the interfacial reaction could hinder electron and/or lithium ion conductions in the cathode composites. The decomposition might be related to the electrochemical instability of the $Li_{10}GeP_2S_{12}$ at high voltage.

High voltage-type all solid-state lithium batteries using the $LiNi_{0.5}Mn_{1.5}O_4$ spinel and $Li_{10}GeP_2S_{12}$ solid electrolyte were examined in this study. Although the battery prepared in this study still shows severe capacity fading, the usage of the 5 V-class cathode materials could contribute to the development of next-generation batteries with high energy density. The SEI layers formed by the interfacial side reactions prevent the migration of Li ions and/or electrons especially in the cathode composite. These results represent that understanding and controlling the interfacial side reactions at high voltage could be a key factor for practical use of the high voltage cathode. Therefore, it is necessary to develop novel solid electrolytes or coating technique for solid electrolyte, which has higher electrochemical stability in contact with the electrodes and electric conductor as well as high ionic conductivity. This study is indicating an important perspective for developing of novel solid electrolyte materials used in high voltage-type all solid-state batteries.

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