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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis describes the results of research on lithium insertion/desertion activity at $LiFePO_4$ cathode/solid electrolyte interfaces analyzed using model film batteries, and consists of five chapters. All solid-state lithium-ion batteries (ASSLiBs) are expected to exhibit superior chemical and electrochemical stability at the interface between the electrode and solid electrolyte materials. Although $LiFePO_4$ is highly (electro)chemically stable over wider temperature regions, there are few studies on the electrochemical behavior of $LiFePO_4$ in ASSLiBs because of the technical difficulty in fabricating a cathode composite. Therefore, thin-film model batteries consisting of nanosized $LiFePO_4$ cathode and microsized electrolyte films were fabricated, and their electrochemical properties were evaluated at different temperatures to investigate the electrochemical stability of $LiFePO_4$ at the interface with solid electrolytes.

In Chapter 1, the electrode and electrolyte materials for ASSLIBs, the significance of constructing interfaces with high electrochemical stability, and the importance of olivine-type $LiFePO_4$ as a cathode are overviewed, followed by a description of the purpose and significance of this study using thin-film model batteries.

In Chapter 2, the details of the physical vapor deposition methods used for synthesizing model thin-film batteries are described, along with the evaluation methods for the interface structures and electrochemical properties.

In Chapter 3, the fabrication of $LiFePO_4$ films using magnetron radio frequency sputtering on an electronically conductive Pt/Ti/Si (PTS) substrate and their structural characterization are described. Polycrystalline $LiFePO_4$ films with an olivine-type structure were grown on PTS, as confirmed by grazing incidence X-ray diffraction and Raman spectroscopy. Transmission and scanning electron microscopy images revealed the uniform and dense formation of nanosized $LiFePO_4$ films at 500 °C, although morphological changes occurred on the PTS surface owing to the formation of Pt hillocks and PtSi alloys. $Li_3PO_4/LiFePO_4$ solid-solid interfaces formed by stacking amorphous Li_3PO_4 films on the $LiFePO_4$ film showed no voids and no elemental diffusion between the materials. These results emphasize the suitability of the bilayer film for detecting the electrochemical phenomena at the $Li_3PO_4/LiFePO_4$ interface.

In Chapter 4, electrochemical properties of the interfacial regions between the $LiFePO_4$ cathode and solid electrolytes are described. Thin-film batteries were successfully fabricated by depositing a Li anode film via vacuum evaporation on $Li_3PO_4/LiFePO_4$/PTS. The $Li/Li_3PO_4/LiFePO_4$ batteries exhibited a voltage plateau originating from the lithium desertion/insertion reactions of $LiFePO_4$ at around 3.5 V in the constant-current charge-discharge curves, confirming the charge-discharge activity at the

Li_3PO_4/$LiFePO_4$ interface. Reversible lithium desertion/insertion proceeded at room temperature and 60 °C, without any side reactions at the interface. An irreversible oxidation reaction occurred during the initial charging process at 100 °C, leading to an increase in the charge-transfer resistance of the $LiFePO_4$/Li_3PO_4 interface, with no significant decrease in capacity. This suggests that lithium desertion/insertion can proceed through a resistive interphase formed by the oxidative decomposition of Li_3PO_4. In contrast, a severe decrease in capacity was observed at 125 °C. $LiFePO_4$ itself might be involved in side reactions, resulting in a phase transition to an electrochemically inactive phase. These results clarify the stable temperature range of the Li_3PO_4/$LiFePO_4$ interface. Electrochemical impedance spectroscopy conducted in the non-degradation temperature range revealed that the activation energy of the charge transfer process was 25.8 kJ mol^{-1}, which was lower than that of the $LiFePO_4$/liquid electrolyte interfaces. The overvoltage of the lithium insertion reaction increased with the thickness of the $LiFePO_4$ film. This suggests that the interfacial processes are sufficiently faster than those within $LiFePO_4$ bulk. Furthermore, the lithium desertion from the $LiFePO_4$ film proceeded at the interface with a Li_3PS_4 sulfide electrolyte with a high lithium conductivity at room temperature. However, oxidative degradation of the sulfide electrolyte occurred, leading to rapid degradation in subsequent cycles. This highlights the need to improve interface stability by extending the potential window of the electrolyte and introducing an interface layer.

In Chapter 5, the findings obtained from this thesis and their significance are summarized, along with the remaining issues and a future outlook. Li/Li_3PO_4/$LiFePO_4$ film batteries can deliver reversible charge-discharge reactions, which demonstrates the high electrochemical stability of the Li_3PO_4/$LiFePO_4$ interface. ASSLiBs with $LiFePO_4$ cathodes have the potential for use over a wide temperature range. The findings obtained with thin-film model electrodes provide valuable insights into material selection and performance enhancement in ASSLiBs.