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# 論文要約

系・コース：応用化学系・エネルギーコース
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要約

The thesis title is "Lithium insertion/desertion activity at $LiFePO_4$ cathode/solid electrolyte interfaces analyzed using model film batteries". It describes the structural and morphological characterization of $LiFePO_4$ thin film fabricated by radio frequency magnetron sputtering on the Pt/Ti/Si (PTS) substrate and the electrochemical behavior of solid-state thin-film battery using $LiFePO_4$ cathode.

In Chapter 1, development and advantage of using all-solid-state lithium-ion batteries (ASSLiBs), the necessity of establishing the (electro)chemically stable interface between electrode and electrolyte, and merits of using olivine $LiFePO_4$ in ASSLiBs, and purpose of utilizing thin film in this study are described.

In Chapter 2, the deposition conditions for olivine $LiFePO_4$ cathode and $Li_3PO_4$ electrolyte by radio frequency magnetron sputtering, $Li_3PS_4$ electrolyte by pulsed laser deposition, and thermal vapor deposition of Li metal anode are described. The structural characterization of film and electrochemical investigation methods of film battery are described.

In Chapter 3, the fabrication of $LiFePO_4$ films on PTS substrate and their structural characterization is described. Growth of polycrystalline olivine $LiFePO_4$ thin film on the PTS substrate was confirmed by the grazing incidence X-ray diffraction and Raman spectroscopy. The formation of PtSi alloy and Pt hillocks occurred during the high temperature annealing of PTS substrate. The surface morphology becomes rough due to the hillocks, however, $LiFePO_4$ film was deposited with the uniform thickness (~60 nm) which was observed from the transmission electron microscopy (TEM). The cross-sectional area SEM/EDX analysis showed $Li_3PO_4$ electrolyte was densely fabricated on the uniform thickness $LiFePO_4$ film on the PTS surface, forming well-

contacted interface. The fabricated $LiFePO_4/Li_3PO_4$ interface was considered to be appropriate to investigate electrochemical reaction at the film battery.

In Chapter 4, the $Li/Li_3PO_4/LiFePO_4$ thin film battery was fabricated to investigate the Li insertion/desertion activity at the $LiFePO_4/Li_3PO_4$ interface. The thin film battery showed the flat voltage plateau at around 3.49 and 3.38 V, indicating the reversible and stable Li-ion transportation activity through the interface at room temperature (25 °C). The film battery showed its reversible electrochemical behavior until 60 °C operation temperature without any degradation. An irreversible oxidation reaction at 100 °C was occurred at the first charge reaction of the thin film battery. The correspondence to the increase in charge-transfer resistance might be related to the interface resistance increase due to the first charge oxidation reaction. Charge-discharge cycles were proceeded without great decrease in capacity, indicating the interface was left electrochemically activated even though the interface degradation was suspected. However, the film battery showed severe degradation of capacity at 125 °C operation for numerous cycles, suggesting the side-reaction at the $LiFePO_4/Li_3PO_4$ interface. These results suggest the stable temperature range for operating the battery consists of $LiFePO_4/Li_3PO_4$ interface. The electrochemical impedance spectroscopy results showed the 25.8 kJ $mol^{-1}$ activation energy for charge-transfer process, which was lower than $LiFePO_4$/liquid organic electrolyte. The overvoltage of the lithium insertion reaction increased with the thickness of $LiFePO_4$. This indicates that the interfacial interaction is faster than the conduction in $LiFePO_4$. The $LiFePO_4$ is additionally applied with the $Li_3PS_4$ sulfide solid electrolyte which is expected to perform high energy density in the battery due to its higher ionic conductivity than that of oxide solid electrolyte. However, the consistent oxidation reaction was occurred during the charge-discharge cycles, suggesting the necessity of interface stability improvement such as buffer layer for the battery operation.

In Chapter 5, the summary, results, and important findings are described for each chapter. The $Li/Li_3PO_4/LiFePO_4$ film battery showed highly reversible and stable electrochemical performance at certain range of high temperature, suggesting the feasibility of long life and high performing ASSLiBs using $LiFePO_4$ cathode. The high thermal stability investigation of $LiFePO_4$ using thin film electrode might produce the wide selection for the ASSLiBs.