

論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Chapter 1 introduced the background of this study and strategies to improve battery performance, described the challenges in previous studies, and provided an overview of the electrochemical reactions at the electrode/electrolyte interface. The cathode/electrolyte interface can be viewed as integrating the electrode surface, electrolyte decomposition interphases, and electrolyte-side interfaces. Previous studies have mainly focused on the electrode-side interface, such as the electrochemical stability of the cathode electrode surface and the ionic conductivity of the electrolyte decomposition interphases. The improvement in the intercalation rate has been widely adopted to stabilize the electrode-side interface. However, it is still difficult to establish a connection between the electrode-side interface and the intercalation rate because the electrode-side interface is still a solid-solid interface, which does not provide the solid-liquid interfacial information. This emphasizes the importance of in situ observation of structural changes at the electrode/electrolyte interface.

In Chapter 2, the thin film model electrodes were synthesized by pulsed layer deposition. The synthetic thickness and density of the thin-film electrodes were characterized using X-ray diffraction and X-ray reflectivity. Electrochemical measurements were performed to investigate the intercalation rates. Ex situ neutron reflectometry and X-ray photoemission spectroscopy were employed to detect the cathode surface after cycling. In situ neutron reflectometry (NR) was used to investigate the entire cathode/electrolyte interface because of its high sensitivity to light elements, strong penetration ability, and negligible damage. In addition, the procedure for calculating the scattering length density for various ion concentration ratios was explained.

In Chapter 3, the lithium intercalation mechanism of LiCoO₂ and Li₂ZrO₃ surface-modified LiCoO₂ cathodes was investigated by in situ neutron reflectance analysis. The LiCoO₂ film synthesized by pulsed laser deposition had a (104) orientation and an extremely flat surface with a surface roughness of approximately 1 nm, which was suitable for simplifying the observation of interface phenomena with organic electrolytes. Charge-discharge measurements revealed that the lithium intercalation reaction into LiCoO₂ was accelerated by the surface modification of Li₂ZrO₃ with a low ionic conductivity. No changes in the crystal structure were observed on the surface of either the unmodified or modified LiCoO₂ after charging and discharging. This clearly indicated that the conventional model, in which the reaction rate can be improved by preventing electrode surface degradation through modification, could not explain this phenomenon. Ex situ NR and X-ray photoelectron spectroscopy showed similar thicknesses and compositions of the electrolyte decomposition solids formed on the surface of both unmodified and modified samples, indicating that the ionic conductivity in the surface layer could be similar. In situ NR analysis clarified that an interfacial layer with a double-layer structure was formed at the cathode/1 mol dm⁻³ LiPF₆ ethylene carbonate-diethyl carbonate electrolyte interface for both unmodified and

modified LiCoO₂. For the unmodified sample, the LiCoO₂ side interface was mainly composed of the electrolyte and inorganic solids generated by electrolyte decomposition, while the electrolyte-side interface was primarily composed of the electrolyte and organic solids generated by electrolyte decomposition. Li₂ZrO₃ modification sample showed an increased proportion of solid phase within the interfacial layer. Based on these observations, a lithium intercalation model was proposed, suggesting that the interfacial layer formed on the surface of Li₂ZrO₃ modification sample accelerated the process of desolvation and surface adsorption of lithium ions in the electrolyte. Furthermore, analysis of the interface layer structure after disassembling the battery and cleaning the samples yielded different compositions and morphologies compared to in situ observations. Therefore, it was concluded that in situ observation of the electrochemical interface structure is essential for understanding the intercalation mechanism.

In Chapter 4, based on the constructed electrode model and neutron reflectometry analysis in Chapter 3, the influence of the electrolyte composition on the interfacial layer structure was investigated. The charge-discharge measurements showed that the lithium intercalation reaction at the Li₂ZrO₃ modified LiCoO₂ cathode/2 mol dm⁻³ LiPF₆ ethylene carbonate-diethyl carbonate electrolyte interface has a larger overvoltage at the end of discharge compared to the 1 mol dm⁻³ electrolyte. *In situ* NR analysis showed that the interface between Li₂ZrO₃ modified LiCoO₂ cathode/2 mol dm⁻³ electrolyte formed a dense double interfacial layer containing more inorganic phases derived from the LiPF₆ salt and a small amount of liquid electrolyte impregnation. The densified interfacial layer leads to a reduced interfacial area, reduced frequency of desolvation and surface adsorption, and increased lithium diffusion distance in low-ionic-conductivity solids, resulting in decreased intercalation reaction rates.

Chapter 5 summarized the above results and proposes factors that may affect the intercalation rate at the solid-liquid interface and future research.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note：Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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