

論文 / 著書情報
Article / Book Information

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Title(English)	Synthesis of novel Li-Co-Mn-O epitaxial thin-film electrode using layer-by-layer deposition process : its structure and electrochemical properties
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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)

Electrochemical performance of lithium battery is strongly dependent on crystal structures and compositions of the electrode materials. To develop noble electrodes of new structures and compositions with enhanced electrochemical properties are very crucial. Although there have been a lot of conventional studies to develop the electrode materials, those methods provide limited phases, structures and compositions. A new synthesis technique is required to obtain noble electrodes. A new materials synthesis approach, layer-by-layer process, using pulsed laser deposition provides new structures and compositions such as super-lattice, gradation and metastable structure. In particular, the new structures show noble properties unexpected from structures synthesized by the conventional methods. The most critical point is that a variety kind of structures and compositions are designed by stacking conventional electrode materials with various deposition ways. Further, it is expected as a noble method to directly obtain a desired structure. This thesis contains a synthesis process of the new epitaxial thin film electrode material using layer-by-layer deposition and an investigation for its structural and electrochemical properties. The results in present study are summarized as follow;

In chapter 3, effects of SrTiO₃ substrate, SrRuO₃ and gold current collector on battery performances were examined to analyze specific capacities and reactions of epitaxial thin film electrodes. Epitaxial thin films, are used in the layer-by-layer deposition process, could show nano scale effects on capacities. Nano scale effects on various electrode materials have been investigated but the effects of substrates and current collectors have not been researched. A main phenomena dominating reactions of the SrTiO₃ substrate and SrRuO₃ current collector was investigated by cyclic voltammetry in a range between 1.6 and 4.5 V. Capacitive contributions of the substrate and current collector to battery capacities were also confirmed by charge-discharge measurements. Four kind of samples, SrTiO₃ substrate, SrTiO₃ substrate with gold deposition, SrRuO₃ / SrTiO₃ and LiCoO₂ / SrRuO₃ / SrTiO₃ were prepared. Cyclic voltammetry measurement revealed that the SrTiO₃ substrate has a slight electrochemical reaction under 3.0 V. When the gold current collector is deposited on the back and lateral side of the SrTiO₃ substrate, the electrochemical reactions were stimulated. However, the charge-discharge measurement demonstrated that capacitive contributions of the substrates were insignificant. A SrRuO₃ layer played a bridge role between a semiconducting substrate and electrode. In addition, the deposition of SrRuO₃ layer restrained the surface reaction of substrates. However, the SrRuO₃ it self showed reaction system dominated by electrochemical reactions at entire voltage range. Especially, a considerable capacity of 30 mAh g⁻¹ was identified under 3.0 V. The capacity contribution of SrRuO₃ should be considered when a charge-discharge measurement is performed at below 3.0 V for an electrode where the SrRuO₃ is introduced as buffer layer.

In chapter 4, a new electrode material was developed with the layer-by-layer deposition process and its structural and electrochemical properties were examined. A novel Li-Co-Mn-O epitaxial thin-film electrode (2-step film) was synthesized on the SrTiO₃ single-crystal substrate by the deposition of LiCoO₂: space group *R-3m* and LiMn₂O₄: space group *Fd-3m*. Although two materials with different structures were deposited in sequence, the synthesized film had a uniform chemical composition of Li_{0.92}Co_{0.65}Mn_{1.35}O₄ and a cubic spinel structure. The 2-step film showed larger lattice parameter than that of a 1-step film directly synthesized using a Li_{0.92}Co_{0.65}Mn_{1.35}O₄ target. HR-STEM observation indicated the 2-step film has a unique structure of considerable site disordering that Li (8a) and transition-metal (16d) sites are significantly exchanged. The unique structure could not be obtained from conventional synthesis methods. Charge-discharge measurement showed the 2-step and 1-step films electrodes have a similar reaction mechanism with comparable capacities of 310 and 294 mAh g⁻¹, respectively. In situ XANES measurement indicated both Mn and Co are involved in electrochemical reactions for the 2-step film in a range from 1.6 and 4.5 V. In particular, a Co^{2+/3+} redox couple was observed at 3.7 V during charge process and at 1.8 V during discharge process, which has not been reported ever in Li-Co-Mn-O systems. Cycle retention tests illustrated that the discharge capacity of the 2-step film was kept for 80 % after 20 cycles while the 1-step film showed 68 % of remaining discharge capacity.

Rate capability tests showed only 60 % of discharge capacity was maintained at 10 C-rate for the 1-step film while the 2-step film showed 79 % of discharge capacity was maintained at 10 C-rate. The electrochemical tests revealed the 2-step film has higher reversibility of reactions with better rate capability. These greatly enhanced electrochemical characteristics were induced by the unique structural properties of the site disordering and extended lattice parameter.

The layer-by-layer deposition process is a new synthesis concept that has never been applied for lithium battery field. This approach provided the new structure with excellent electrochemical characteristics that could not be obtained from conventional methods. The relation between the unique structural properties and the enhanced electrochemical properties are discussed. The proposed layer-by-layer deposition method can provide an expanded range of compositional and structural variations for lithium battery electrode materials.

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。

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