論文 / 著書情報
Article / Book Information

題目(和文)	リチウムイオン電池用コバルトフリーニッケル系層状正極活物質の特性改善に関する研究
Title(English)	
著者(和文)	金田治輝
Author(English)	Haruki Kaneda
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12573号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:平山 雅章,荒井 創,稲木 信介,川路 均,今岡 享稔,鈴木 耕太
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12573号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学系 エネルギー	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 工学 ）
学生氏名： Student's Name	金田 治輝		審査員主査： Chief Examiner	平山 雅章	

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

This thesis describes the results of research on improving the properties of cobalt (Co)-free nickel (Ni)-based layered positive electrode materials for lithium-ion batteries (LIBs). Currently available Ni-based layered positive electrode materials for LIBs contain a certain amount of Co, but from the viewpoint of material cost reduction and resource procurement, Co-less or Co-free electrode materials with their Co content as low as possible are desired. Therefore, with the aim of developing high-performance and low-cost Ni-based layered positive electrode materials, the effect of Co on the electrochemical properties of Ni-rich layered electrode materials with Ni content of more than 80 at% was investigated and novel Co-free materials were synthesized and characterized.

Chapter 1 describes an overview of Ni-based layered positive electrode materials, characterization methods, background of Co-free materials in Ni-rich layered positive electrode materials and their issues in previous studies, as well as the purpose and significance of this study.

Chapter 2 describes the details of the synthesis and characterization methods of the Co-free Ni-rich layered materials in this study.

Chapter 3 describes the effect of Co substitution on the electrochemical properties of the Ni-rich layered materials. Co-substituted lithium nickel oxide (NC: $LiNi_xCo_{1-x}O_2$), in which a part of Ni is substituted by Co, was synthesized and its charge-discharge behavior under various electrochemical evaluation conditions was analyzed. Co substitution suppresses cation mixing and activates the reaction at the end of discharge, resulting in improved rate characteristics. In order to examine whether the improved rate capability comes from the intrinsic effect of Co substitution or comes from cation mixing restriction, $LiNiO_2$ (lithium nickel oxide: LNO) and $LiNi_{0.95}Co_{0.05}O_2$ (NC95), with and without cation mixing, were synthesized and evaluated. It was found that the reaction at the end of the discharge almost disappeared when LNO has some cation mixing whereas NC95 shows activity at the end of discharge even if it contains the cation mixing. The results of solid-state nuclear magnetic resonance showed that, regardless of the degree of cation mixing, LNO underwent significant local structural changes before and after charge-discharge reaction whereas NC95 did not show such changes. This suggests that Co-substitution has an intrinsic effect on suppressing the irreversible structural change, reducing the residual Ni^{4+} to Ni^{3+} and facilitating the reaction at the end of discharge.

Chapter 4 describes the results of synthesis and characterization of a Co-free composition system, lithium nickel aluminate (NA: $Li(Ni_xAl_{1-x})O_2$). NA-based positive electrode materials were prepared by a

novel synthesis process using AlOOH-coated precursor, and was clarified to have excellent durability (capacity retention after 500 cycles: 75%) under high load charge-discharge conditions at 45ºC and 2 C. It was confirmed that the NA-based materials exhibited higher durability than cobalt-containing $LiNi_{0.95}Co_{0.05}O_2$ and $LiNi_{0.95}Co_{0.03}Al_{0.02}O_2$ with the same Ni content. Postmortem analysis of the electrodes after cycle test such as cross-sectional SEM observation and electrochemical impedance measurements showed that the NA-based materials had less particle cracking and less charge transfer resistance increase compared to other samples. The results of these analyses revealed that the excellent durability of the NA-based materials is owing to the suppression of the H2-H3 structural phase transition by the solid-solution Al in the crystal and the suppression of hydrogen fluoride chemical attack by the nanoscale Al-rich layer on the surface. The NC-based materials were found to be effective in suppressing particle cracking, but the charge transfer resistance (R_{ct}) of NC-based materials after cycle test was significantly higher than that of the NA-based materials, indicating that Co is less effective in suppressing degradation on the surface of electrode materials.

Chapter 5 describes the results of characterization of the ultimate Co-free Ni-based layered material, LNO, as grain-boundary-free or single-crystal-like (SC) particles. By optimizing the synthetic conditions, SC-LNO was successfully obtained for the first time. SC-LNO exhibited excellent durability compared to polycrystalline LNO (PC-LNO) (capacity retention after 500 cycles at 45ºC and 2 C: PC-LNO: 36.1%, SC-LNO: 63.5%). SC-LNO after the cycle test showed no particle cracking while PC-LNO had many cracks. The results of electrochemical impedance measurements after cycle test showed that the R_{ct} of SC-LNO was significantly lower than that of PC-LNO, indicating that the surface of SC-LNO is less degraded than that of PC-LNO. TEM observation of the positive electrode after the cycle test revealed that the surface of PC-LNO was changed to electrochemically inactive rock-salt (NiO-like) structure, whereas the surface of SC-LNO had a spinel structure in addition to rock-salt structure, indicating that the Li diffusion path was maintained. Furthermore, formation of a thick but low-impedance film was observed on the surface of SC-LNO after the cycle test, suggesting unique characteristics of the SC particles.

Chapter 6 summarizes this thesis, describing the role of Co in Ni-rich layered positive electrode materials and the properties of the NA-based electrode materials and SC-LNO, which are novel high-performance Co-free electrode materials. The design guidelines for cobalt-free nickel-based layered positive electrode materials are also summarized, together with remaining issues and a future outlook.