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Structure, electrochemical properties and thermal stability of
cathode materials for Li-ion battery

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Lithium ion batteries for vehicle have been required high energy density, high power density, long-life working, and high safety. The electrochemical properties of the batteries are closely related to those of the electrode materials, then high performance electrode materials have been required. In this thesis, two types of next generation cathode materials, $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{1-x}Co_xO_2$ (x = 0, 0.1, 0.2) were studied.

Both materials have high energy density. However, $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{1-x}Co_xO_2$ (x = 0, 0.1, 0.2) have many issues to be solved, for example, the cycling performance and the thermal stability. In the present study, the reaction mechanism was examined to improve these issues. The results in the present study are summarized as follows.

1. $LiNi_{0.5}Mn_{1.5}O_4$

Structure and electrochemical properties for $LiNi_{0.5}Mn_{1.5}O_4$ surface were investigated using epitaxial thin film, which provides an ideal two-dimension reaction field. The orientation and thickness of the $LiNi_{0.5}Mn_{1.5}O_4$ thin films were controlled by changing the substrate orientation and the pulse laser deposition time.

As the film thickness increased, the oxidation state of Mn decreased and lattice parameter increased. The thick film (ca. 30 nm) exhibited a large capacity degradation between the 1st and 2nd discharge process. This is due to the increasing the rate of Mn^{3+}, which caused Mn dissolution and instability of structure by Jahn-Teller effect.

Electronic state of Mn was controlled by surface Li_3PO_4 coating to improve cycling performance. Li_3PO_4 coating changed the lattice parameter and electronic state of Mn. The increase of the oxidation number of Mn by Li_3PO_4 coating caused the improvement of cycling performance. Controlling the electronic state of surface is important of the cycling performance.

2. $LiNi_{1-x}Co_xO_2$ (x = 0, 0.1, 0.2)

The thermal stability for $Li_{1-y}Ni_{1-x}Co_xO_2$ (x = 0, 0.1, 0.2, 1.0; y = 0.4, 0.8) was investigated. Their crystal structure changed from a layer to a spinel followed by a rocksalt accompanied by the oxygen release at high temperature. Oxygen release amount due to heating decreased as the cobalt content increased.

When the crystal structure changed and oxygen was released, the oxidation state and occupation site for transition metal also changed. The oxidation number of nickel decreased larger than that of cobalt at high temperature. Furthermore, the change of the occupation site of nickel was different from that of cobalt. Nickel ions migrated from the octahedral sites in the transition metal layer to the octahedral sites in the lithium layer through the tetrahedral sites. On the other hand, the migration of cobalt ions from the tetrahedral sites to the octahedral sites in the lithium layer, which caused structure change from the spinel to the rocksalt, was at high temperature than that of nickel ions. The stability of the high oxidation state and occupation of the tetrahedral site is important for improving the thermal stability of the delithiated cathode.

These results on the reaction mechanism might be important for the development of future materials for the next-generation batteries.