LITHIUM RICH LAYERED CATHODE MATERIALS - HIGH PRESSURE AND EPITAXIAL FILM SYNTHESES

Yoshifumi Mizuno, Sou Taminato, Kota Suzuki, Masaaki Hirayama, Ryoji Kanno
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midoriku-ku, Yokohama, 226-8502

kanno@echem.titech.ac.jp

Structures, electrochemical properties and reaction mechanism of lithium rich layered cathode materials were studied for the samples synthesized by high pressure and epitaxial thin film synthesis methods.

Lithium-rich layered rock-salt type oxides, $Li_{1.2+x}M_{0.8-y}O_2$ (M = Mn/Co/Ni), were synthesized using a high-pressure method and the relationship of the phases appeared in the ternary system, Li_2MO_3–$LiMO_2$–Li_2MO_2, was clarified. The phases were synthesized by changing Li/M/O ratios, Mn/Co/Ni ratios, and reaction conditions, and their structures were characterized by synchrotron X-ray and neutron diffraction analyses. The amount of excess lithium in the transition metal layer increased with increasing lithium content. Furthermore, additional Li was detected at the tetrahedral site in the transition metal layer in the structure. X-ray absorption near-edge structure spectra confirmed that the oxidation state of the transition metals increased with the increase in the amount of excess lithium. The effects of the excess lithium and the Mn/Co/Ni ratio to the electrochemical properties were investigated.

The reaction mechanism of the lithium excess phases was studied using epitaxial-films fabricated by pulsed laser deposition method. The initial lithium intercalation-deintercalation reaction was investigated using surface X-ray diffraction and hard X-ray photoelectron spectroscopy. The charge and discharge capacities drastically increased with decreasing film thickness for the Li_2MnO_3 system. The 12.6 nm thick film showed a high capacity of 300 mAh g^{-1} during over 50 cycles, indicating that the surface region is actively reconstructed to generate a high-capacity phase. Surface structural changes at the initial cycling have a pronounced effect on the power characteristics and the capacity of lithium-rich layered rocksalt type cathodes. Based on the materials synthesized by high pressure and thin film methods, the reaction mechanisms of the lithium excess cathode materials will be discussed.