

Phase evolution of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ high-voltage cathode under high-rate charge-discharge reaction

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Lithium ion battery is one of the candidate to meet the demand of power sources with high energy density and high out-put density. The utilization of high-working potential cathode, one of which is $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel compound, is effective to attain the battery performance. It is difficult to prepare the stoichiometric $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel compounds. We studied the low-temperature magnetic properties of $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ [1], and successfully prepared the stoichiometric spinel compounds with high purity [2].

From the low-temperature magnetic measurement, the obtained $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel compound was high purity as well as high crystallinity: the magnetization at 5 K almost coincided to the theoretical value based on the ferrimagnetic alignment. They showed only twin redox signals around 4.7 V, and the low-rate capacity was high enough (about 140 mAh/g). Additionally, they exhibited good cycling performance and relatively high capacity at high current density. It was considered that the cycle stability is attributed to the high crystalline particles with average particle size of approximately 1 μm . The solid/electrolyte contact area was remarkable small, and the side reaction was effectively eliminated. One of the experimental evidence was obtained from heat evolution measurement of the operating coil cell. These imply that the cathode particle with both high-purity and high crystallinity play a significant role in the battery application.

Futhermore, the phase evolution of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode was studied with use of home-made cell having specifically designed X-ray window. From the operand X-ray diffraction study, it was found that the electrochemical reactions were composed of three cubic spinel phases, the lattice parameters of which were 0.8165, 0.8087 and 0.8000 nm. The Li^+ extraction/insertion at low current reversibly progressed with two consecutive two-phase reactions, and only the phase fraction changed linearly with the SOC degree. But as the current density was raised, three phase coexistence appeared and the crystallinity of the intermediate phase decreased. In addition, the phase evolution was not reversible at high current density. In other word, the deviation from the quasi-equilibrium state was much more significant in the lithiation process. The phase evolution under various current density will be discussed in the conference.

References:

[1] T. Nakamura, M. Tabuchi and Y. Yamada, *J. Appl. Phys.*, Vol. 98 (2005) 093905.

[2] R. Hanafusa, K. Kotani, K. Ishidzu, Y. Oka and T. Nakamura, *Solid State Ionics*, Vol. 288 (2016), 180-183.