Spatial analysis of lithium intercalation in spinel LiMn₂O₄ for lithium-ion battery by 3D-nanoESCA

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Spinel-structured lithium manganese oxide $(\text{LiMn}_2\text{O}_4)[1]$ has been extensively studied as a promising cathode material for lithium-ion batteries by virtue of its high voltage, low cost, and non-toxicity. The main problem for commercial use is irreversible capacity fading during cycling. It is important to understand the lithiation/delithiation process which is spatially inhomogeneous[2]. Nanoscale spectromicroscopic analysis is beneficial to investigate inhomogeneous litium diffusion which causes local degradation of a lithium-ion battery after a number of charge cycles. In order to elucidate the lithium intercalation mechanism in spinel

LiMn₂O₄ particles, we have performed nondestructive soft X-ray scanning photoelectron microscopy measurements using "3D-nanoESCA" (three-dimensional nano-scale spatially resolved electron spectroscopy for chemical analysis) [3], which has been installed at the University-of-Tokyo Materials Science Outstation Beamline (BL07LSU) at SPring-8.

 $LiMn_2O_4$ samples were synthesized by solid-state reaction with precursors Li_2CO_3 and MnO_2 . $Li_{1\pm\delta}Mn_2O_4$ samples were obtained by lithiation/delithiation of $LiMn_2O_4$ by chemical reduction/oxidation.

Figure 1 shows the XPS spectra of Li 1s and Mn 3p core-level photoemission peaks. The Li 1s core level has a binding energy of 56.8eV. This energy shift to higher binding energy from Li metal (54.7eV) indicates that lithium exists as Li⁺ ions[4]. The peak which has larger intensity at 51.3 eV is attributed to the Mn 3p component.

Figure 2 presents a Li 1*s* and Mn 3*p* photoelectron intesity map with binding energy ranging from 45 eV to 69 eV shown in Fig. 1 for the $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ particle. The Li 1*s* peak intensity has a uniform distribution within the spatial resolution of 70 nm. Phase separation inside an individual particle, which is discussed in LiFePO₄[5], was not found, suggesting that lithium ions might be intercalated or deintercalated from the crystal surface instead of the particles edges.

The Li 1*s* and Mn 3*p* photoelectron intesity map for the $\text{Li}_{1+\delta}\text{Mn}_2\text{O}_4$ particles (Figure 3) suggests that the lithiation process has particle size dependence in the particle size of μ m order.



Fig. 1 Li 1s and Mn 3p XPS spectra of LiMn₂O₄ and Li_{1 $\pm\delta$}Mn₂O₄.



Fig. 2 Li 1s and Mn 3p core level photoelectron intensity map of a $Li_{1-\delta}Mn_2O_4$ particle.



Fig. 3 Li 1s and Mn 3p core level photoelectron intensity map of $Li_{1+\delta}Mn_2O_4$ particles.

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