Spatial analysis of lithium intercalation in spinel LiMn$_2$O$_4$ for lithium-ion battery by 3D-nanoESCA

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Spinel-structured lithium manganese oxide (LiMn$_2$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 lithium 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 LiMn$_2$O$_4$ 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$_2$O$_4$ samples were synthesized by solid-state reaction with precursors Li$_2$CO$_3$ and MnO$_2$. Li$_{1+\delta}$Mn$_2$O$_4$ samples were obtained by lithiation/delithiation of LiMn$_2$O$_4$ by chemical reduction/oxidation.

Figure 1 shows the XPS spectra of Li 1$s$ and Mn 3$p$ core-level photoemission peaks. The Li 1$s$ 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 3$p$ component.

Figure 2 presents a Li 1$s$ and Mn 3$p$ photoelectron intensity map with binding energy ranging from 45 eV to 69 eV shown in Fig. 1 for the Li$_{1+\delta}$Mn$_2$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 LiFePO$_4$[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 intensity map for the Li$_{1+\delta}$Mn$_2$O$_4$ particles (Figure 3) suggests that the lithiation process has particle size dependence in the particle size of $\mu$m order.
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References


Fig. 3 Li 1s and Mn 3p core level photoelectron intensity map of Li1+δMn2O4 particles.