Spectromicroscopic analysis of lithium intercalation in spinel LiMn$_2$O$_4$ for lithium-ion battery by 3D nano-ESCA

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Abstract. The process of lithium-intercalation in spinel-structured lithium manganese oxide (LiMn$_2$O$_4$) particles was probed by a highly spatially resolved X-ray photoelectron microscopy technique using our “3D nano-ESCA” (three-dimensional nanoscale electron spectroscopy for chemical analysis) equipment. We found the change of the line shape in Li 1$s$-Mn 3$p$ core-level spectra with lithiation/delithiation of the sample. Moreover, we have succeeded in detecting the photoelectron intensity mapping of chemically lithiated/delithiated Li$_{1±\delta}$Mn$_2$O$_4$ crystals. It suggests the homogeneous intercalation/deintercalation from the crystal surfaces instead of the crystal edges, and the particle size dependence of the intercalation tendency.

1. Introduction

Spinel-structured lithium manganese oxide (LiMn$_2$O$_4$)[1-3] has been extensively studied as a promising cathode material for lithium-ion batteries by virtue of its high voltage, low cost, and non-toxicity. However, high rate capability and long cycle life are needed for the application to high-power batteries for commercial use. In order to improve the specific power density, nanostructured electrodes including nanoparticles[4], nanowires[5], and nanofilms[6] have been widely investigated taking advantage of the large surface-to-volume ratio and the short lithium ion diffusion length.

Understanding the lithiation/delithiation process which is spatially inhomogeneous in a realistic battery[7] helps to realize stable cycle characteristics. However, lithium intercalation in LiMn$_2$O$_4$ nanostructures still remains unclear compared to other cathode materials such as LiCoO$_2$ and LiFePO$_4$.

Spectromicroscopic analysis with high spatial resolution is a powerful tool for elucidating the lithium intercalation mechanism in LiMn$_2$O$_4$ particles. Here we have performed nondestructive soft X-ray scanning photoelectron microscopy measurements using “3D nano-ESCA”, equipped with a

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focused X-ray probe, a piezo-driven sample stage, and an angle-resolved photoelectron spectrometer[8].

2. Experimental

LiMn$_2$O$_4$ powders were synthesized by conventional solid-state reaction using Li$_2$CO$_3$ and MnO$_2$. Stoichiometric amounts of precursors were thoroughly mixed and then pre-sintered at 850 °C for 24 h in air. Then optional 10 wt% lithium chloride (LiCl) was added into the pre-sintered powder in order to accelerate crystal growth. The self-assembled spinel LiMn$_2$O$_4$ composite was obtained by mixing them and sintering at 850 °C for 24 h in air again. The Li$_{1-\delta}$Mn$_2$O$_4$ particles are prepared by chemical oxidation reaction of LiMn$_2$O$_4$ with ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$) in pure water. They were stirred for 72 h, then filtered and dried in air. To obtain a partially lithiated sample Li$_{1+\delta}$Mn$_2$O$_4$, chemical treatment was carried out by reacting LiMn$_2$O$_4$ with lithium iodide (LiI) in acetonitrile at 60 °C for 48 h in Ar atmosphere. The product was filtered and washed, and then dried in vacuum. The Li$_{1-\delta}$Mn$_2$O$_4$ crystals were characterized by X-ray diffraction measurements[9] and scanning electron microscopy (SEM) images.

Spectromicroscopic measurements were performed by the 3D nano-ESCA system which has an X-ray focusing system with a Fresnel zone plate and a modified VG Scienta R3000 analyzer. The spatial resolution is better than 100 nm. This system has been installed at the University-of-Tokyo outstation beamline, BL07LSU at Spring-8. The following results were all taken at excitation photon energy of 1000 eV.

3. Results and Discussion

Figure 1 shows a SEM image of LiMn$_2$O$_4$ particles at a magnification of 3000×. Spinel LiMn$_2$O$_4$ octahedral crystals with different size ranging from 1 μm to 5 μm are observed.

Figure 2 displays the X-ray photoemission spectroscopy (XPS) spectra of Li 1s and Mn 3p core-levels for LiMn$_2$O$_4$ and chemically lithiated/delithiated Li$_{1+\delta}$Mn$_2$O$_4$ particles. In order to compensate charging effects, the C 1s peak at 284.5 eV was used as a reference for the determination of the core-level binding energies (BEs). The Li 1s core level has a BE of 55.0 eV. This energy shift to higher BE from Li metal (54.7 eV) indicates that lithium exists as Li$^+$ ions[10]. The peaks which have larger intensity at around 49.3 eV are attributed to the Mn 3p components. As Li concentration increases, the Li 1s components clearly increase. The Mn 3p peaks are deconvoluted into four peaks corresponding to the Mn$^{3+}$ and Mn$^{4+}$ contributions and their multiplets.

We have also measured valence band spectra for these samples. As shown in Figure 3, the valence band becomes sharper with increasing Li content, which is consistent with the previous report[4]. Furthermore, the Mn 3d $e_g$ shoulder peak appears in the Li$_{1+\delta}$Mn$_2$O$_4$ sample, suggesting the increase of Mn$^{3+}$ component.
Figure 2. Photoelectron spectra of Mn 3p and Li 1s and their deconvolution for LiMn$_2$O$_4$ and Li$_{1+\delta}$Mn$_2$O$_4$ samples. Red curves indicate Li 1s. Green (Mn$^{4+}$) and blue (Mn$^{3+}$) curves indicate Mn 3p components.

Figure 3. Photoelectron spectra of valence bands for LiMn$_2$O$_4$ and Li$_{1+\delta}$Mn$_2$O$_4$ samples.

For Li$_{1+\delta}$Mn$_2$O$_4$ particles, imaging analysis of XPS spectra has been performed. Figure 4 presents a Li 1s and Mn 3p photoelectron intensity map with binding energy ranging from 40 eV to 64 eV for the Li$_{1,\delta}$Mn$_2$O$_4$ particle. Pin-point measurements of XPS spectra exhibit the line shape shown in the left-hand side of Fig. 2 at any point on the Li$_{1,\delta}$Mn$_2$O$_4$ crystal in Fig. 4. This homogeneity suggests a possibility that lithium ions might be intercalated or deintercalated from the crystal surface instead of the particle edges.

On the other hand, Figure 5 shows a photoelectron intensity map covering the Li 1s and Mn 3p core-level region for the Li$_{1+\delta}$Mn$_2$O$_4$ particles. The spectrum of each point in the map is decomposed into two peaks, Li 1s components (blue contrast) and unresolved Mn 3p components consisting of Mn$^{4+}$ and Mn$^{3+}$ (grayscale). Fully charged particles (enclosed by white circles in Fig. 5) and fully discharged particles are dominant although a state-of-charge particle (enclosed by white dashed circles in Fig. 5) is also detected, which conflicts with the core-shell model[11]. Furthermore, the averaged size of lithium-rich particles seems to be smaller than that of lithium-poor particles. This difference in the particle size suggests that smaller particles are lithiated preferentially.
Figure 4. X-ray photoelectron intensity map of a chemical oxidized Li$_{1+\delta}$Mn$_2$O$_4$ particle.

Figure 5. X-ray photoelectron intensity map of a chemical reduced Li$_{1-\delta}$Mn$_2$O$_4$ particle. The grayscale corresponds to the Mn 3p core-level intensity and the blue contrast to the Li 1s core-level intensity, respectively.

In conclusion, we have investigated the lithiation/delithiation process of spinel LiMn$_2$O$_4$ crystal particles by using the 3D nano-ESCA, a spectromicroscopic technique with a high spatial resolution. We have confirmed that the line shape of Li 1s core level spectra change as the sample are lithiated/delithiated. The photoelectron intensity mapping of the Li 1s and Mn 3p core-level region for Li$_{1+\delta}$Mn$_2$O$_4$ particles suggests the homogeneous intercalation from crystal surfaces and the particle size dependence of the lithiation process.

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