Analytical transmission electron microscopy study for $LiCoO_2$ prepared by Pechini method

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Various techniques are widely studied to improve electrochemical performance of cathode materials in Li ion batteries [1, 2]. In order to study a mechanism of degradation effects on Li ion battery materials, it is very important to understand atomic structures and chemical states of the materials. Analytical transmission electron microscopy is one of the powerful tools in view of spatial resolution. Especially, a direct analysis of Li ion using electron energy-loss spectroscopy (EELS) can be one of the crucial methods to understand a degradation mechanism for Li ion battery materials [3]. Usually, a particle size of commercially available powders of cathode materials is in μm order and it is difficult to observe them in transmission electron microscopy without sample preparation process such as polishing or grinding which may damage surface region of the oxide materials. In our present study, we prepared smaller particles via Pechini process [4, 5] in order to avoid these damages.

Analytical transmission electron microscopy measurements were carried out for $LiCoO_2$ prepared by Pechini method. TITAN^3 G2 60-300 electron microscope (FEI), equipped with energy dispersive X-ray spectroscopy (EDS : Super-X, Bruker), and EELS (Gatan GIF Quantum) operated at 200 or 300 kV accelerating voltage was used. The electrochemical cell was assembled using Li metal as negative electrode.

Atomic resolution EDS measurement of $LiCoO_2$ was carried out. However, due to a small amount of signal, it was hard to discuss on a significant difference of a spectrum for each pixel (Fig. 1 upper). We applied noise filter using Principle Component Analysis (PCA). The noise decreased spectrum is obtained in Fig. 1. (Lower). Using the denoised spectra, we reconstructed an intensity map for Co, O and Cu (Cu-mesh: a system background signal) (Fig. 2). Each signal at the Co atomic columns are relatively strong compared with the region between atomic columns. Intensity distribution of Cu (background) was quite small compared with Co signals. Thus, enough signals to distinguish the Co atomic columns are considered to be obtained. As for the signals of O, a certain lattice structure was hard to be obtained.

From EELS measurements using a monochromator, we successfully obtained a series of spectra at Li-K edge region as a spectrum image. Normalizing Li-K edge signals using Co-M edge signals, we constructed Li distribution maps [5]. Fig. 3 shows a Li distribution map using Li/Co intensity ratio of a charged (cell voltage : 4.2 V) and a cycled particle (Cell Voltage : 3.0 – 4.2 V). There are inhomogeneous Li distributions in the $LiCoO_2$ particle especially around near surface region.

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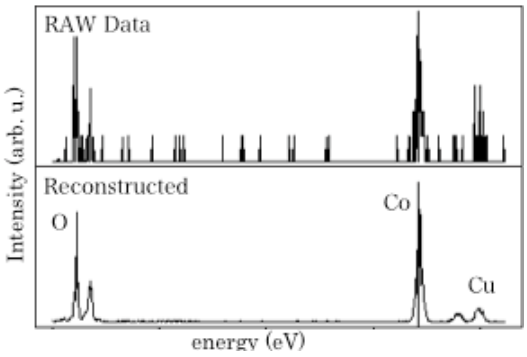

FIG. 1. EDS spectrum at a pixel of $LiCoO_2$ (Upper row : Raw spectrum, Lower row: reconstructed).

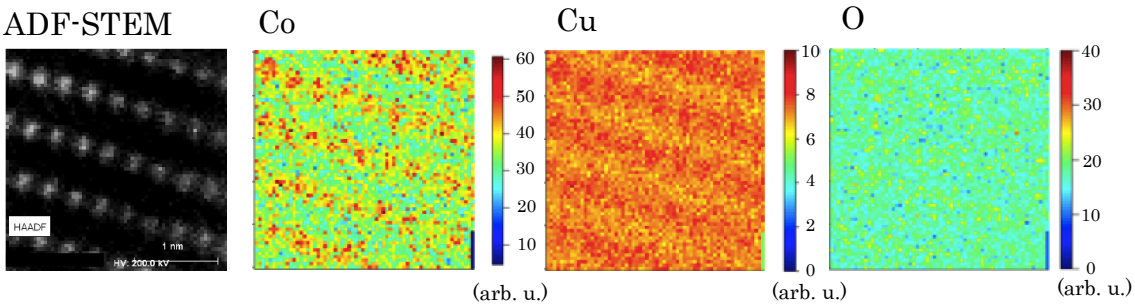

FIG. 2. ADF-STEM image and reconstructed ROI map of Co, Cu, and O of $LiCoO_2$.<100>

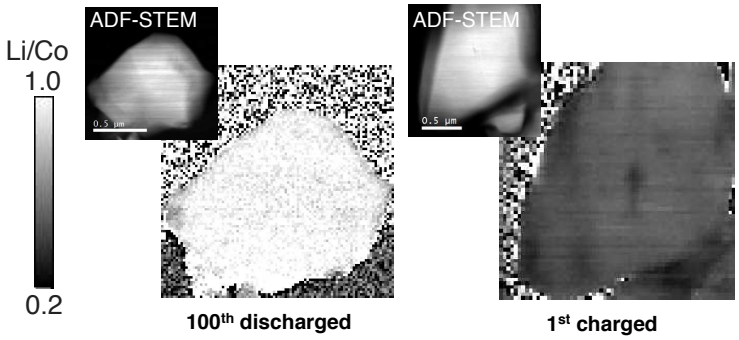

FIG. 3. Li/Co intensity map for 100th discharged and 1st charged state. ADF-STEM images are also shown at top left corner of Li/Co intensity map. A scale bar in the ADF-STEM images corresponds to 500 nm.