For improvement of the properties of Li ion battery materials, a lot of modification processes such as surface modification have been examined [1]. To study the mechanism of these modification effects on the materials, it is very important to understand atomic structures and chemical states of modified materials. Analytical TEM measurement such as STEM-EELS method is a powerful tool for investigating local information about the sample [2].

In the present study, we prepared a cathode material (LiCoO$_2$) with small particle size by Pechini method in order to avoid damage from sample preparation such as ion beam milling and focused ion beam [3]. Surface modification was performed using the sol-gel method. Al oxide, Mg oxide, and Si oxide coating sample were prepared. And the samples dispersed on Cu mesh with carbon micro-grid were directly observed without thinning process. A TITAN$^2$ G2 60-300 electron microscope (FEI), equipped with EDS(Super-X : Bruker) and EELS(Quantum : Gatan) was used for analytical TEM measurement. For EELS measurements, a monochromator was used to achieve higher energy resolution. ZLP was less than 0.3 eV with 0.05 eV/ch.

The EELS measurement around the Li K-edge is carried out for surface modified cathode materials. Although the Co M-edge completely overlaps Li K-edge, it becomes possible to obtain a sharp Li K-edge peak by using a monochromator. Using this benefit, we constructed an elemental map using the Li-K edge in nm-order spatial steps, and discussed the relationship between electrochemical properties and Li concentration distribution in the particle.

A schematic image of the EELS analysis of the Li K-edge is shown in Figure 1. Using the Co-M edge intensity, we constructed a Li-K/Co-M intensity ratio map [4]. The Li distribution in the LiCoO$_2$ particle after charge discharge cycle was drastically changed by the coating species, and the homogeneity of Li ion distribution as shown in figure 2 corresponded well with the trend of capacity retention after the cycling test.

Reference

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Fig. 1: (a) Schematic image for reconstruction of the map of Li-K/Co-M edge intensity map of bare LiCoO$_2$. (b) EELS spectra around Li-K edge for both the initial LiCoO$_2$ and the charged state (4.2V ~ Li$_{0.5}$CoO$_2$) are shown at bottom left. Difference spectrum of (initial LiCoO$_2$) – (4.2 V charged LiCoO$_2$) is shown at bottom right.

Fig. 2: Li-K/Co-M intensity map for 100$^{th}$ discharged (3.0-4.5V /Li metal) (a) bare LiCoO$_2$, (b) coated LiCoO$_2$ (MgO 1 wt%). The contrast of the image is normalized as the Li-K/Co-M intensity ratio. The x in the intensity scale corresponds to the x in Li$_x$CoO$_2$.