Electrochemical reaction of LiCoO$_2$ electrode in a Li-ion battery observed by spatially-resolved TEM-EELS

A. Shimoyamada$^1$, K. Yamamoto$^1$, R. Yoshida$^1$, Y. Iriyama$^2$, and T. Hirayama$^1$

$^1$Nanostructures Research Laboratory, Japan Fine Ceramics Center, Japan.
$^2$Department of Materials, Physics and Energy Engineering, Nagoya University

Rechargeable batteries have been considered as important energy technology. As one of the next generation Li-ion batteries, all-solid-state Li-ion batteries (LIBs) have been expected. The analysis of the electrochemical reactions in LIBs in nanometer scale is important for the research of the battery materials [1]. Degradation of electrodes caused by the Li insertion/extraction is one of the serious problems preventing the practical use of all-solid-state LIBs. In this report, we have clarified the mechanism of the degradation of LiCoO$_2$ positive electrode in the all-solid-state LIB by using TEM and spatially-resolved (SR)-TEM-EELS.

Figure 1 (a) shows the schematic illustration of the LIB model sample. A Li$^+$ conductive glass ceramic sheet of the composition Li$_{1+x+y}$Al$_x$(Ti,Ge)$_{2-y}$Si$_{3+y}$P$_{3-y}$O$_{12}$ (LATP) was used as the solid electrolyte. A crystalline LiCoO$_2$ electrode deposited on the LATP by pulsed laser deposition was used as the positive electrode. On the other hand, the “in-situ formed negative electrode” irreversibly formed by the Li insertion to the negative side LATP was used as the negative electrode [2]. The region around the LiCoO$_2$/solid-electrolyte interface was lifted out by a micro-sampling method in a FIB system and the TEM sample was prepared after the bulk LIB sample was charged/discharged 20 times in a vacuum. The TEM image in the positive electrode region (Fig. 1 (b)) shows a different contrast at around 300nm from the interface. It was revealed by the electron diffraction and HRTEM analysis that nanocrystalline compounds of LiCoO$_2$ mixed with CoO existed in the region. Figure 1 (c) shows the spectrum image of Co L-edge detected by SR-TEM-EELS, where the vertical and horizontal axes correspond to the sample position of the Fig. 1 (b) in the vertical direction and the electron energy loss, respectively. The Co L$_3$-edge spectrum image was clearly shifted to the direction of lower energy loss at the 300nm from the interface. This shows Co was changed to Co$^{2+}$. The change of the O spectrum also indicated that CoO existed in the region. We conclude from the TEM and SR-TEM-EELS result that the formation of CoO causes the degradation of the LiCoO$_2$ electrode in this battery.

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References

Fig. 1 (a) Schematic illustration of the all-solid-state Li-ion battery sample. (b) TEM image near the LiCoO$_2$/LATP interface. (c) SR-TEM-EELS image of Co L$_{2,3}$-edges. The dotted line shows the interface.