

# Electrochemical reaction of LiCoO<sub>2</sub> electrode in a Li-ion battery observed by spatially-resolved TEM-EELS

A. Shimoyamada<sup>1</sup>, K. Yamamoto<sup>1</sup>, R. Yoshida<sup>1</sup>, Y. Iriyama<sup>2</sup>, and T. Hirayama<sup>1</sup>

<sup>1</sup>Nanostructures Research Laboratory, Japan Fine Ceramics Center, Japan.

<sup>2</sup>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<sub>2</sub> 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<sup>+</sup> conductive glass ceramic sheet of the composition Li<sub>1+x+3y</sub>Al<sub>x</sub>(Ti,Ge)<sub>2-x</sub>Si<sub>3y</sub>P<sub>3-y</sub>O<sub>12</sub> (LATP) was used as the solid electrolyte. A crystalline LiCoO<sub>2</sub> 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<sub>2</sub>/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<sub>2</sub> 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<sub>3</sub>-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<sup>2+</sup>. 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<sub>2</sub> electrode in this battery.

This work was supported by the RISING project of the New Energy and Industrial

Technology Development Organization (NEDO) in Japan.

## References

- [1] K. Yamamoto et al., *Angew. Chem. Int. Ed.* **49** (2010) 4414-4417.
- [2] Y. Iriyama et al., *Electrochem. Commun.* **8** (2006) 1287-1291.

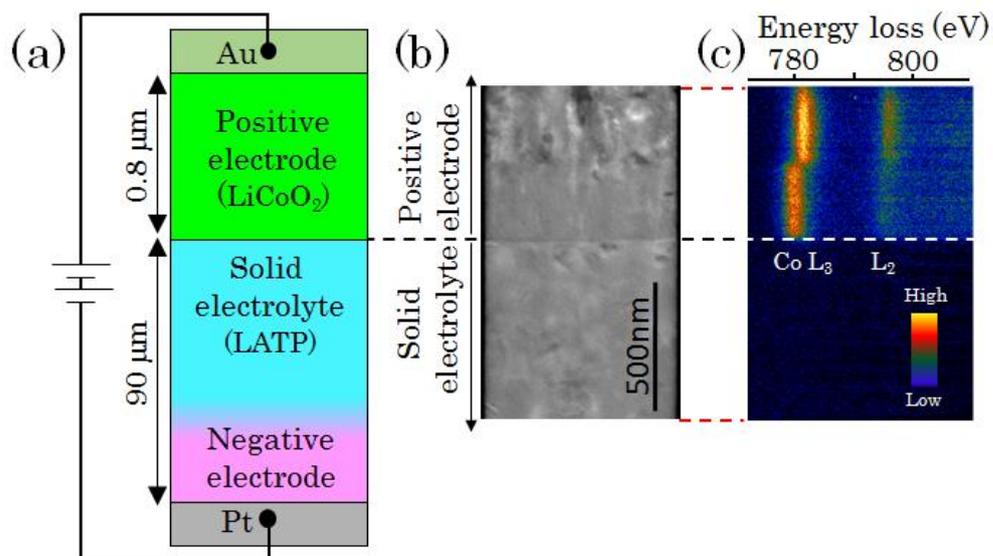


Fig. 1 (a) Schematic illustration of the all-solid-state Li-ion battery sample. (b) TEM image near the LiCoO<sub>2</sub>/LATP interface. (c) SR-TEM-EELS image of Co L<sub>2,3</sub>-edges. The dotted line shows the interface.