

# Visualization of Electrochemical Reactions in an All-Solid-State Li-Ion Battery by Spatially-Resolved TEM-EELS

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All-solid-state lithium-ion batteries (LIBs) with solid electrolytes have high potential to overcome some present problems of LIB with liquid electrolytes: safety, reliability, lifetime, cost, and energy density. However, the large interfacial resistance of Li-ion transfer at the electrode/solid-electrolyte interfaces prevents their practical use. One effective solution is an *in situ* formation of electrode active materials from the parent solid electrolytes. Because the electrodes grow from the solid electrolytes with excess Li insertion reaction, both materials become connected to each other at an atomic scale. Such electrodes were discovered in Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-based glass-ceramic solid electrolytes [1] (LATP, manufactured by OHARA Inc., Japan). However, the structural growth mechanism and the electronic structure changes due to the Li insertion are still unclear. Here, we used spatially resolved electron energy loss spectroscopy in TEM mode (SR-TEM-EELS) [2] to directly visualize the nano-scale Li-concentration profiles and the influence on other important elements (Ti and O).

Figure 1(a) illustrates the all-solid-state LIB sample. A Si- and Ge-doped LATP sheet (LASGTP, 90- $\mu$ m thick) was used as the solid electrolyte. The 800-nm thick film of the LiCoO<sub>2</sub> positive electrode was deposited on one side of the sheet by PLD. On the negative side, the Pt current-collector was directly deposited on the other side of the LASGTP. Cyclic voltammetry (CV) was carried out for 50 cycles in a vacuum with a sweep rate of 40 mV min<sup>-1</sup> (Fig. 1(b)), and the negative electrode was formed *in situ* near the LASGTP/Pt interface by decomposition with the Li insertion. After the CV, the region of negative side was lifted out and the TEM sample was prepared by FIB.

Figure 2(a) shows the TEM image around the negative side. A slightly uniform contrast layer (about 400 nm) was observed near the Pt. Electron diffraction showed this region was amorphous structure. The SR-TEM-EELS images around the Li-K-edge, Ti-L-edge, and O-K-edge were recorded by the CCD camera as shown in Figs. 2(b) - 2(d). The Li signals obviously increase in the 400-nm-width region. This is clear evidence that the negative electrode was formed in this region. In the spectrum image of Ti-L-edge (Fig. 2(c)), we can observe clear chemical shifts of the L<sub>2</sub> and L<sub>3</sub> edge lines, which shows that the Ti electronic state changed from Ti<sup>4+</sup> to Ti<sup>3+</sup> due to the Li insertion. The

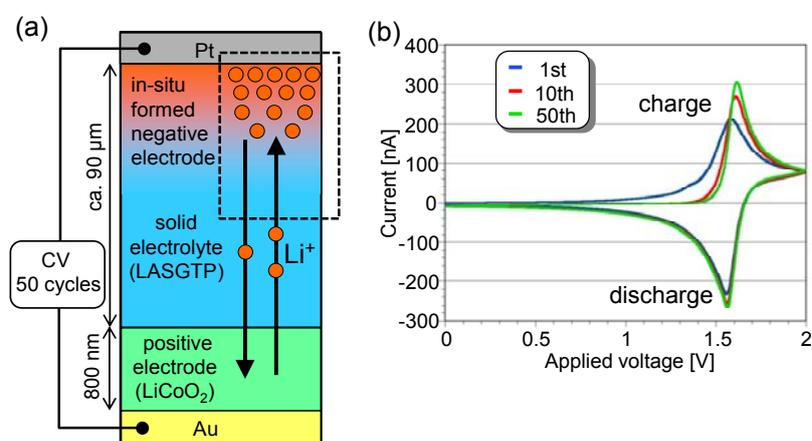
spectrum image of O-K-edge in Fig. 2(d) also shows the spectrum shifts. This indicates that the O contributed to the electron charge compensation due to the Li insertion as well as Ti.

In conclusions, we succeeded in simultaneous observation of the crystal and electronic changes of the *in-situ*-formed negative electrode due to the Li insertion. This technique can potentially be applied not only to LIBs but also to fuel cell batteries, electric double-layer capacitors, and other electrochemical devices.

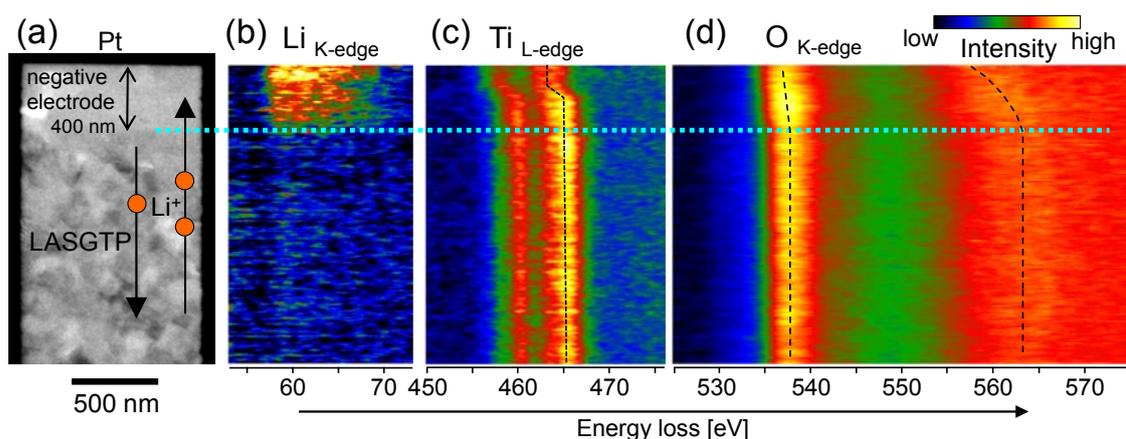
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#### References

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**FIG. 1 All-solid-state LIB sample and its cyclic voltammogram.** (a) Illustration of the prepared LIB sample. (b) Cyclic voltammogram measured in a vacuum with a sweep rate of  $40 \text{ mV min}^{-1}$ .



**FIG. 2 TEM image and the SR-TEM-EELS images.** (a) TEM image around the negative side. SR-TEM-EELS images, (b) Li-K-edge, (c) Ti-L-edge, and (d) O-K-edge in the region of (a).