

## Electrochemical reactions in an all-solid-state Li-ion battery observed by *ex situ* and *in situ* spatially-resolved TEM EELS

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All-solid-state lithium-ion batteries (LIBs) with incombustible solid electrolytes have advantages of safety, reliability, lifetime, cost, and energy density. However, a serious problem is the large interfacial resistance of Li-ion transfer at the electrode/solid-electrolyte interfaces. One effective solution is an *in situ* formation of electrode active materials from parent solid electrolytes. Because the electrodes grow from the solid electrolytes with Li insertion reaction, both materials become connected to each other at an atomic scale, leading to a low interfacial resistance. 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 solid electrolytes (LATP) [1]. However, the electrochemical reactions, such as the structural growth mechanism and electronic structure changes, are still unclear. Here, we used *ex situ* and *in situ* spatially resolved TEM EELS (SR-TEM-EELS) to directly observe the nano-scale Li profiles and the influence on other elements, Ti and O [2].

Figure 1(a) shows a schematic illustration of the prepared LIB sample. A Si- and Ge-doped LATP sheet (LASGTP, 90- $\mu$ m thick) was used as the solid electrolyte. The 800-nm thick LiCoO<sub>2</sub> positive electrode was deposited on one side of the sheet by PLD. On the other side, the Pt current-collector was directly deposited. For the *ex situ* SR-TEM-EELS experiment, cyclic voltammetry (CV) was performed 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 irreversibly formed near the LASGTP/Pt interface by decomposition with the Li insertion. After the CV, the TEM sample of the negative side region 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 GIF CCD camera (Figs. 2(b) - 2(d)). The Li signals increase in the 400-nm-width region. It means that the amorphous 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 reaction. The spectrum image of O-K-edge in Fig. 2(d) also shows the spectrum shifts, indicating that the O also contributed to the electron charge compensation due to the Li insertion. We will also report the *in situ* observation results showing the changes of the Li concentration profiles during charge and discharge processes.

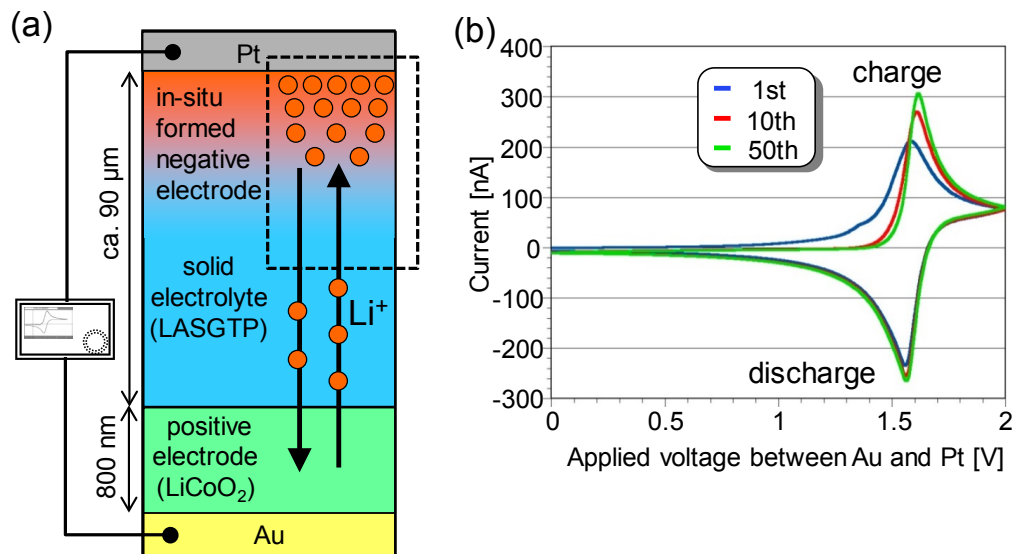
In summary, we successfully observed the electrochemical reactions using *ex situ* and *in situ* SR-TEM-EELS, and revealed how the negative electrodes were formed by Li insertion reaction and what influenced on the other important elements.

#### References:

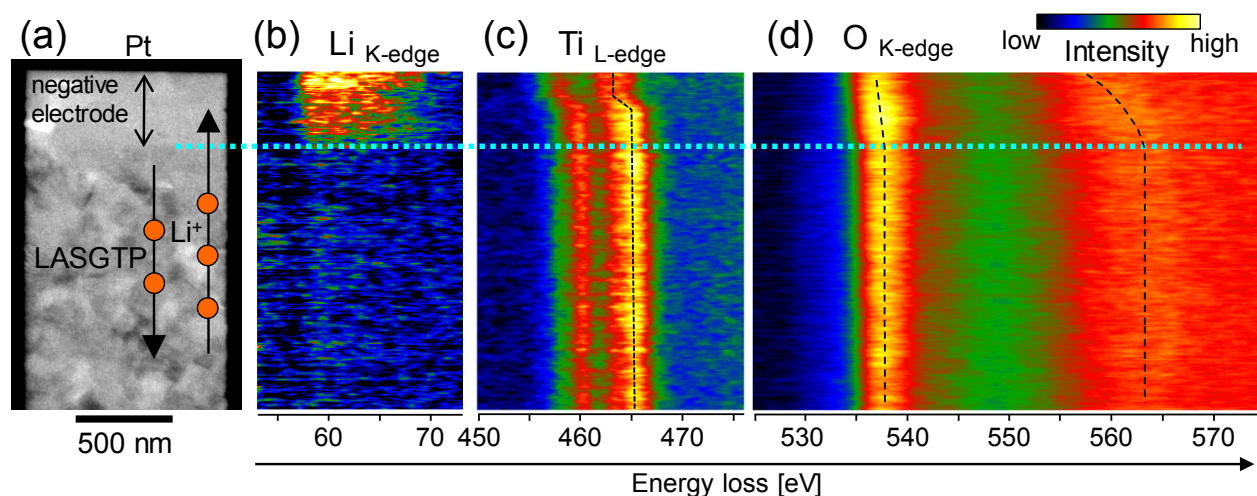
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**FIG. 1 All-solid-state LIB sample and cyclic voltammogram (CV).** (a) Illustration of the LIB sample. (b) Cyclic voltammogram measured in a vacuum with a sweep rate of  $40 \text{ mV min}^{-1}$ . As the negative electrodes grow with cycling, the charge current peak becomes higher and sharper in the CV.



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