

# Electronic state analysis of Li compounds by utilizing Ar<sup>+</sup> ion bombardment

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It is desired to understand the physical properties of Li compounds in order to improve the Li ion battery. A photoelectron spectroscopy (PES) is a powerful technique to elucidate these electronic states. However, PES reveals the electronic state only near the surface region, which comes from mainly contaminations, oxidations, and so on. To obtain the intrinsic electronic state, a surface cleaning procedure is done before performing a PES measurement, e.g. Ar<sup>+</sup> ion bombardment. However, Ar<sup>+</sup> ion bombardment may destruct the compound itself. In this study, we report the PES spectral changes of Li compounds after Ar<sup>+</sup> ion bombardment.

We have prepared 9 Li compounds; LiF, LiCl, CHLiO<sub>2</sub>-H<sub>2</sub>O, Li<sub>3</sub>PO<sub>4</sub>, Li<sub>2</sub>O, LiNO<sub>3</sub>, CH<sub>3</sub>COOLi, Li<sub>2</sub>CO<sub>3</sub>. The powder samples were put on Cu plates. 1 keV Ar<sup>+</sup> ion bombardment was done under the Ar pressure of  $\sim 10^{-3}$  Pa for 30-60 min.

The experiment was performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, SCIENTA SES2002. The measurements were performed at room temperature under ultrahigh vacuum of  $\sim 1 \times 10^{-7}$  Pa. Photon energy was set to 135 eV.

Figure 1 shows the Li 1s spectra of the samples. Because of the extrinsic charging effect, Li 1s peak position and shape were different among the positions in the Cu plate. Therefore, by performing the position-resolved PES measurements, we have chosen the Li 1s core-level spectra with the lowest binding energy and the sharpest ones, which are considered to represent the electronic states free from charging effect.

For LiCl, CHLiO<sub>2</sub>-H<sub>2</sub>O, Li<sub>3</sub>PO<sub>4</sub>, and LiOH, the signals of Li 1s increased compared with those of valence band including surface contamination after Ar<sup>+</sup> ion bombardment (not shown), indicating that the surface contaminations were successfully removed. Therefore, before Ar<sup>+</sup> ion bombardment the observed Li 1s core-level spectra may be assigned to contaminated Li, located nearly the same binding energy of 55.5 eV for these samples (for LiCl, lower binding energy side one) [Fig. 1(a)]. After Ar<sup>+</sup> ion bombardment Li 1s electronic states of Li compounds

were obtained, especially for LiCl the sharp signal was obtained.

On the other hand, for  $\text{Li}_2\text{O}$ ,  $\text{LiNO}_3$ , and  $\text{Li}_2\text{CO}_3$ , the shallow core-levels of C  $2s$ , N  $2s$ , and O  $2s$  around the binding energy of 20 eV disappeared after  $\text{Ar}^+$  ion bombardment (not shown), indicating the destruction of the Li compounds. Before  $\text{Ar}^+$  ion bombardment the observed Li  $1s$  core-level spectra may also be assigned to contaminated Li, located nearly the same binding energy of 55.5 eV [Fig. 1(a)]. After  $\text{Ar}^+$  ion bombardment Li  $1s$  electronic states of destructed Li compounds were obtained, which have the similar peak positions and shapes.

For LiF and  $\text{CH}_3\text{COOLi}$ , the signals of Li  $1s$  were very weak both before and after  $\text{Ar}^+$  ion bombardment. Therefore, it is not clear whether the Li  $1s$  spectra show the intrinsic electronic state or not.

In summary, we have successfully obtained Li  $1s$  electronic states for LiCl,  $\text{CHLiO}_2\text{-H}_2\text{O}$ ,  $\text{Li}_3\text{PO}_4$ , and LiOH after  $\text{Ar}^+$  ion bombardment.

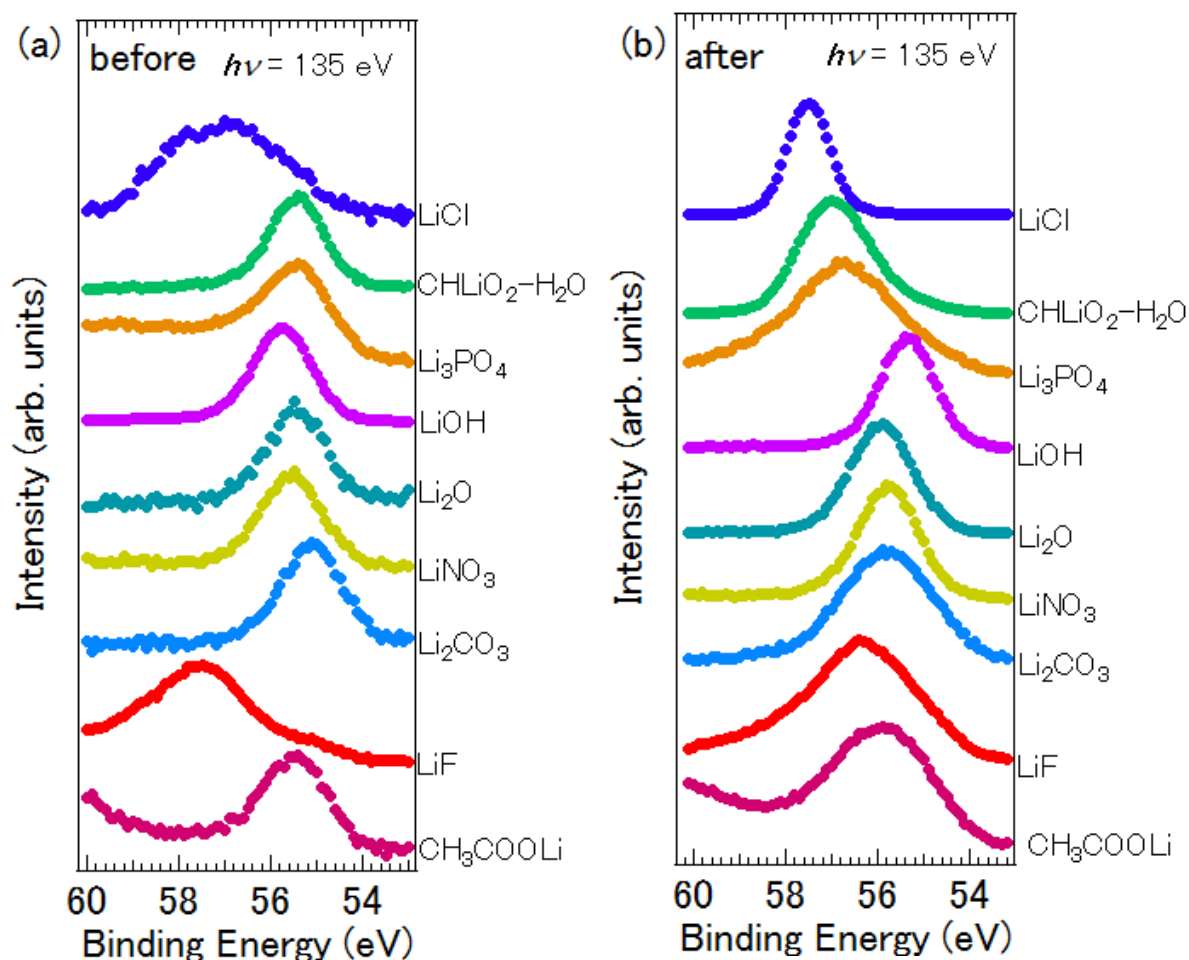


Fig. 1 Li  $1s$  PES spectra of Li compounds. (a) Before  $\text{Ar}^+$  ion bombardment. (b) After  $\text{Ar}^+$  ion bombardment.