Electronic state analysis of Li-compounds

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Abstract

We have measured the electronic states of Li-compounds by synchrotron-radiation photoelectron spectroscopy. In order to obtain the intrinsic electronic states, we have examined an optimal photon energy, a sample mounting to reduce a charging effect, and a surface cleaning condition by Ar^+ ion sputtering. From the result, the peak positions of Li $1s$ core-levels are found to be almost the same before Ar^+ ion sputtering while some move higher binding energy side after Ar^+ ion sputtering. Therefore, Li compounds that have saved in the atmosphere are thought to be covered by the same contaminated Li. We assign the contaminated Li likely to $LiOH$, Li_2O, $LiNO_3$. Moreover, we focus on the valence band and have found the intensity modulation with photon energy across the Li absorption.

1. Introduction

Li ion batteries have been used in our life, such as cellphone, PC, home appliances, and so on. It is important to understand the electronic states of solid electrolyte interface (SEI) that was made electrode surface to improve performance of Li ion battery. The photoelectron spectroscopy (PES) measurements have revealed a variety of Li states for compositions in the SEI and there are a lot of previous works. However, the compositions in the SEI are not revealed well. The binding energy of Li 1s core-level for a Li compound differs among references. It may be because PES is surface sensitive then depends on a various conditions. In consideration of a contamination or an excitation photon energy or a charging effect, we have measured the Li 1s core-levels for some Li compounds by synchrotron-radiation (SR) PES. Furthermore, we have also measured valence band with various photon energies.

2. Experimental

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, SCIE NTA SES2002. The measurements were performed at room temperature under ultrahigh vacuum of ~1×10^{-7} Pa. We prepared 5 Li compounds; $LiCl$, Li_3PO_4, $LiOH$, Li_2O, and $LiNO_3$. Energy calibration was made by Au Fermi edge.

Firstly, we considered about an optimal photon energy. From previous work [1], the intensity of Li 1s core-level was sensitive to photon energy. We measured Li 1s core-level spectra of $LiCl$ with changing photon energies from 110 - 150 eV as shown in Fig. 1(a). We evaluated a peak top signal divided by a back ground signal (S/B ratio) as shown in Fig. 1(b). We decided the optimal photon energy from these S/B ratios as the photon energy of 140 eV. This ratio is larger than that of laboratory X-ray PES by about 8 times [Fig. 1(b)].
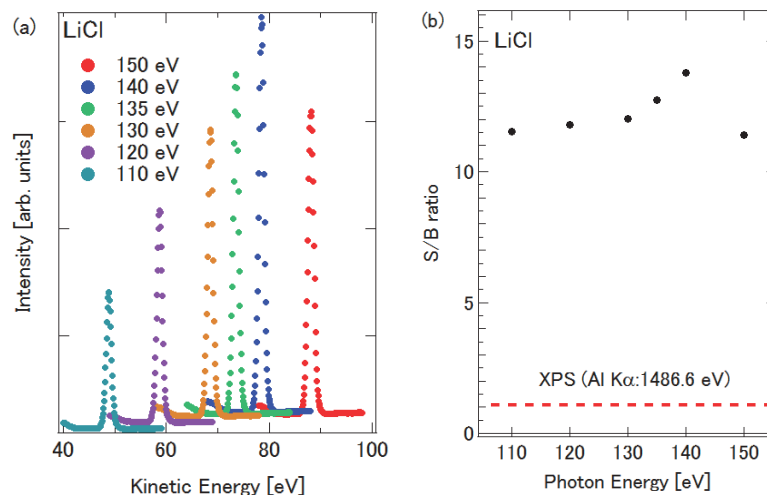
Fig. 1 Photon energy dependent Li 1s core-level spectra of $LiCl$ (a) and their S/B ratios (b).

Next, we considered about a charging effect. All samples were powder. When we measured powder samples on carbon tapes, the charging effect strongly shifted the Li $1s$ peak positions. Then, we measured samples put on Indium plates. As shown in Fig. 2(a), position-resolved PES spectra of the LiCl enables us to see the difference of Li $1s$ peak positions (two broken lines), indicating that the charging effect still shifted the Li $1s$ peak positions in some regions. It is because an Indium plate is too soft to mount powders uniformly. On the other hand, position-resolved PES spectra of the LiCl mounted on a Cu plate show a constant Li $1s$ peak position (one broken line) [Fig. 2(b)]. This result suggested that we could mount powders on Cu plates uniformly and free from the charging effect.
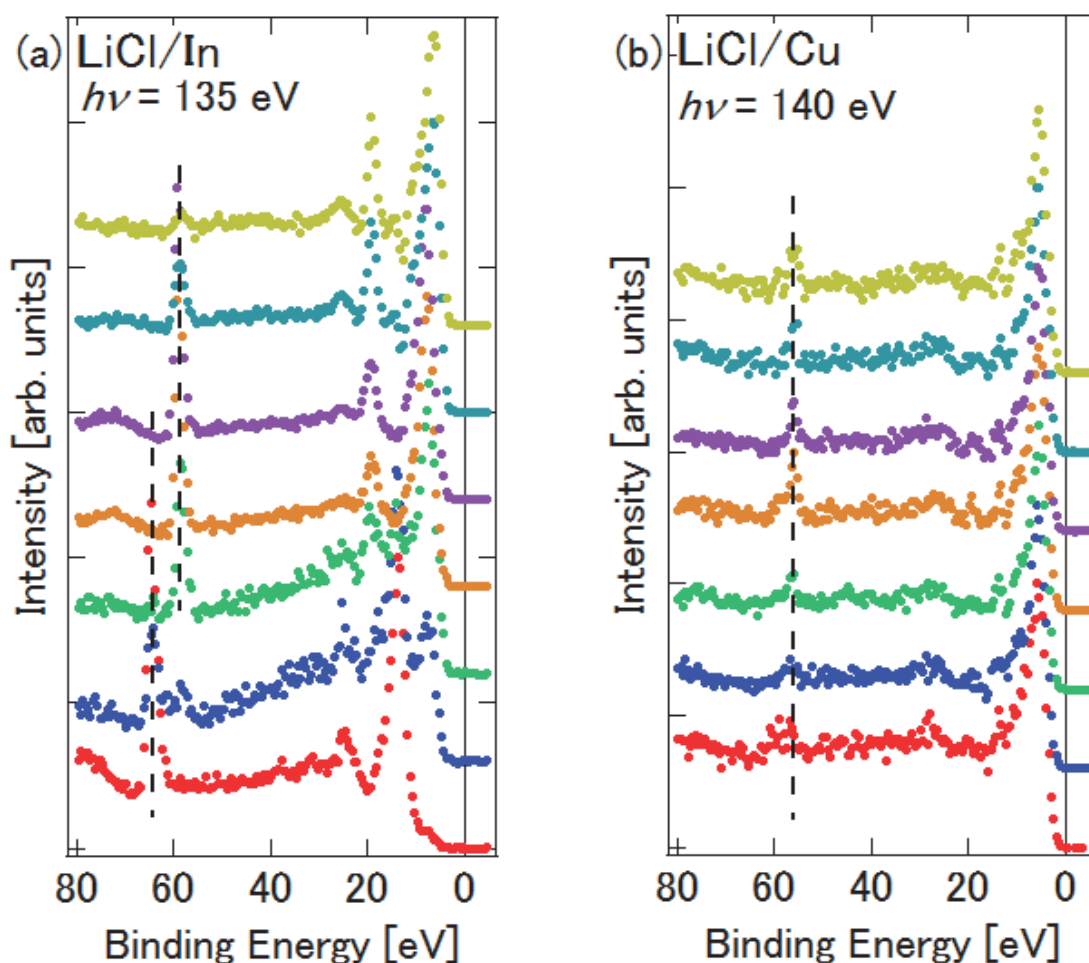
Fig. 2 Position-resolved Li $1s$ core-level spectra of LiCl. The powders were put on an Indium plate (a) or a Cu plate (b).

Finally, we considered about a cleaning of surface. We cleaned surfaces of samples to obtain intrinsic electronic states without contaminations because these samples were saved in the air. Ar^+ ion sputtering to clean the surface was done under the condition of 1.0 kV with 10 mA for 30 min at $P_{Ar} = 1.0 \times 10^{-3}$ Pa. However, some samples were broken or modified by Ar^+ ion sputtering. So, these changeable samples were cleaned under condition of 0.5 kV

until sample was changed. As shown in Fig. 3, Ar^+ ion sputtering time dependent PES spectra suggests the modification of LiCl. The shallow core-levels of O 2*s* or C 2*s*, the sign of contaminations in atmosphere, appears before and after 5 min Ar^+ ion sputtering. After 10 min Ar^+ ion sputtering, the shallow core-levels of O 2*s* or C 2*s* disappears and only the shallow core-level of Cl 3*s* is clearly seen. After 15 min Ar^+ ion sputtering, however, the shallow core-level of Cl 3*s* disappears. So, these spectra suggest that sample was changed. Therefore, we selected the spectrum of after 10 min as cleaned one. For others samples, we also decided the appropriate Ar^+ ion sputtering time (30 min for Li_3PO_4 and LiOH, 5 min for LiO_2, 15 min for $LiNO_3$).

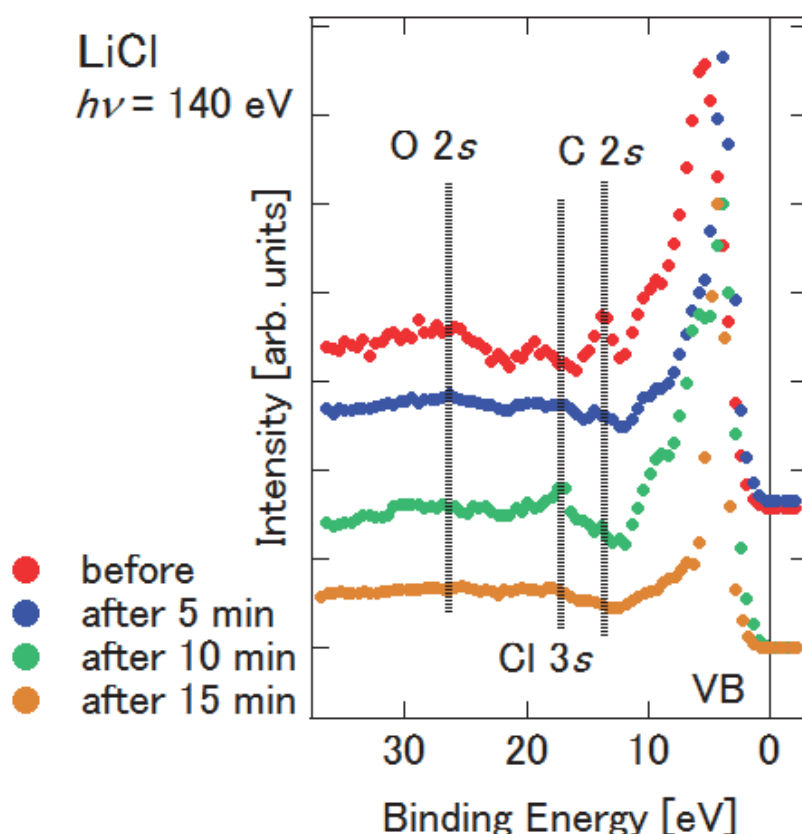**Fig. 3** Ar^+ ion sputtering time dependent PES spectra of LiCl.

## 3. **Results and Discussions**

Figure 4 summarizes valence band and Li 1*s* core-level spectra of the samples before and after Ar^+ ion sputtering. Note that the strong valence band signal mainly comes from Cu plates (Cu 3*d*). For LiCl, before Ar^+ ion sputtering, contamination signal of O 2*s* appears [Fig. 4(a)]. After Ar^+ ion sputtering, the intensity of O 2*s* was reduced and that of Cl 3*s* was increased [Fig. 4(b)]. In addition, Li 1*s* peak position was shifted to higher binding energy side [Fig. 4(c)(d)]. For Li_3PO_4, before Ar^+ ion sputtering, two components appears in the Li 1*s* core-level spectrum [Fig. 4(c)]. After Ar^+ ion sputtering, only one component is recognized

in the Li $1s$ core-level spectrum [Fig. 4(d)] and the shallow core-level of P $3s$ appears [Fig. 4(b)]. In addition, Li $1s$ peak position was also shifted to higher binding energy side [Fig. 4(c)(d)]. For LiOH, Li_2O, and $LiNO_3$, before Ar^+ ion sputtering, contamination signal of O $2s$ appears [Fig. 4(a)]. After Ar^+ ion sputtering, the shallow core-levels of O $2s$ or N $2s$ appears [Fig. 4(b)]. These Li $1s$ peak positions were not shifted.

 As shown in Fig. 4(c), before Ar^+ ion sputtering, the Li $1s$ peak positions are almost the same, whose binding energy is about 55.8 eV. It suggests that the same Li compounds cover on the surfaces. As shown in Fig. 4(d), after Ar^+ ion sputtering, some Li $1s$ peak positions are shifted. From these results, the intrinsic electronic states were obtained. These binding energies after Ar^+ ion sputtering were as follows; 56.3 eV for LiCl, 56.1 eV for Li_3PO_4, 55.8 eV for LiOH, 55.7 eV for Li_2O, and 55.8 eV for $LiNO_3$. By comparing the binding energies, the contaminated Li is thought to be LiOH, or Li_2O, or $LiNO_3$.
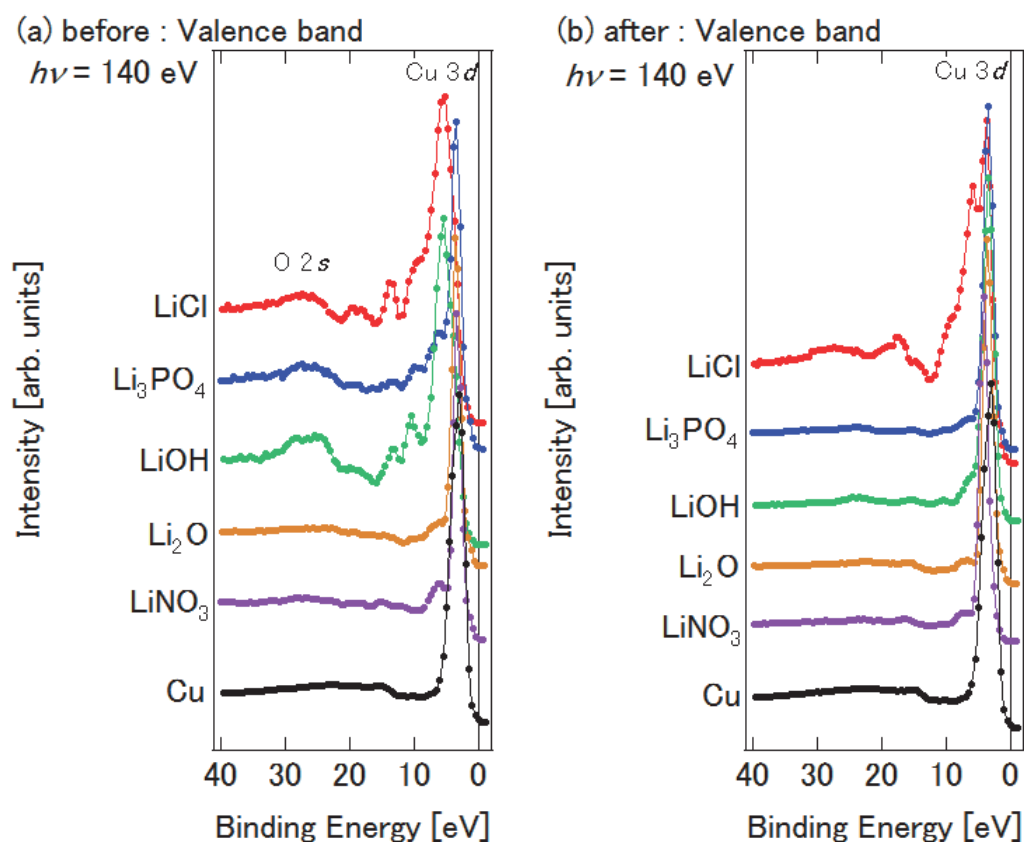

Fig. 4 Valence band spectra of the samples before (a) and after (b) Ar^+ ion sputtering. Li $1s$ core-level spectra of the samples before (c) and after (d) Ar^+ ion sputtering.
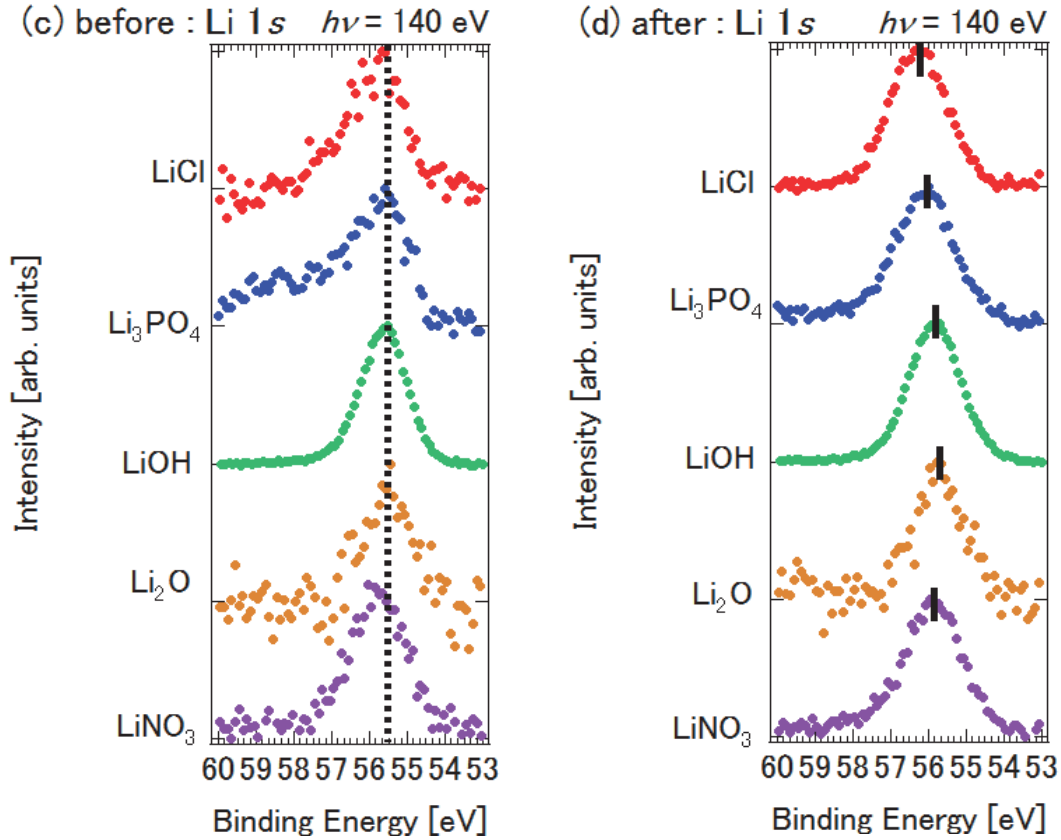
Fig. 4 (Contnued) Valence band spectra of the samples before (a) and after (b) Ar^+ ion sputtering. Li $1s$ core-level spectra of the samples before (c) and after (d) Ar^+ ion sputtering.

Next, we focus on valence band. Because valence band is related to physical properties, we thought that valence band might have important information. Because we are interested in Li electronic states, we examined Li K-edge absorption of LiCl as shown in Fig. 5(a). Most strong absorption appears around ~60.5 eV. Therefore, we measured valence band spectra by using each photon energy (I: 59 eV, II: 59.5 eV, III: 60 eV, IV: 60.5 eV, V: 61 eV). The result is shown in Fig. 5(b). Focusing on the structures around the binding energies of 8 eV and 17 eV, the intensities increase when photon energy is set to 60 eV and 60.5 eV and decrease when photon energy is set to 61 eV. From reference [2], this intensity behavior is leaded by two Auger electron processes. One process is K(exciton)-V process and the other process is K(exciton)-VV process. K(exciton)-V process leads increasing intensity of valence band and K(exciton)-VV process leads increasing intensity of Auger electron. The structure at the binding energy of 17 eV is related to Li Auger electron. Although the structure at the binding energy of 8 eV is not clear at present, it is thought to be related to Li electronic states.
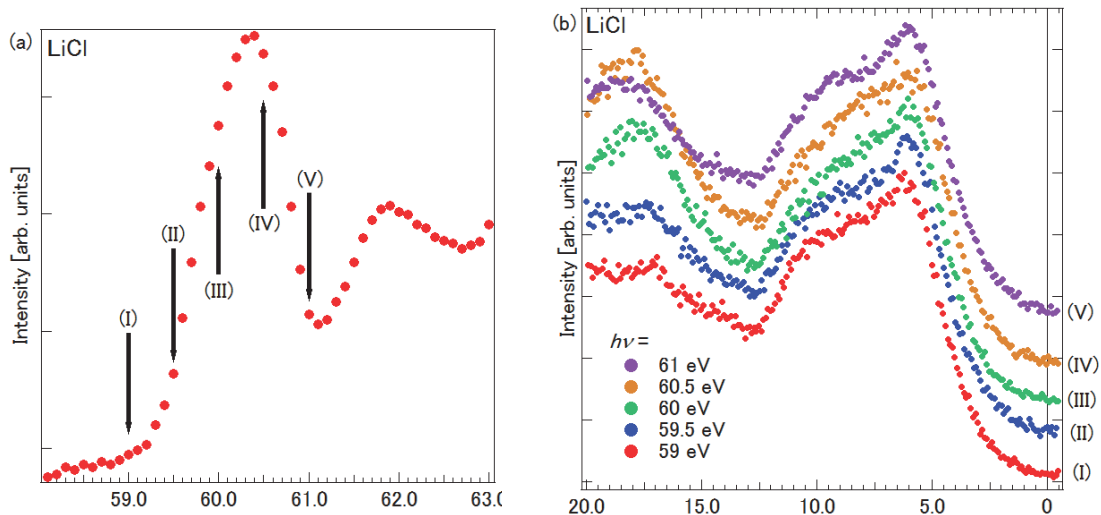
Fig. 5 Absorption spectra (a) and photon energy dependent valence band PES spectra (b) of LiCl.

4. Conclusions

We have obtained Li $1s$ electronic state for LiCl, Li_3PO_4, LiOH, Li_2O, $LiNO_3$. We have observed contaminated Li covering Li compounds saved in the air, maybe assigned to LiOH, Li_2O, or $LiNO_3$. Furthermore, we have focused on valence band and found the photon energy dependence.

References

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[2] Kouichi Ichikawa, Masao Kamada, Osamu Aita, and Kenjiro Tsutsumi, Phys. Rev. B **32**, 8293 (1985).