

Electronic state analysis of Li metal under electron irradiation

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Li metal has been used in Li-ion battery, and its surface reacts during charge/discharge process. Extensive measurements have revealed a chemical property about Li metal to improve the performance. In addition, Li compounds are reported to be modified by an electron or soft x-ray irradiations [1, 2]. Then, it is possible to change Li metal to other Li compounds by utilizing electron beam. In order to understand a fundamental property of Li metal, we have tried to measure the electronic state of Li metal by photoelectron spectroscopy (PES).

The measurement was carried out at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University. The PES measurements were performed at room temperature under the ultrahigh vacuum of $\sim 10^{-8}$ Pa. The energy resolution was set to be ~ 200 meV. We have used photon energy of 45 eV, 140 eV, and Al K α . The sample is Lithium metal plate from HONJO METAL CO. This sample was not exposed in air and the surface was shaved by plastic cutter under Ar atmosphere. To understand a fundamental mechanism, we have performed Ar⁺ sputtering and electron irradiation on Li metal. The Ar⁺ sputtering was conducted with 2 keV for 2 hours. The electron irradiation was conducted with 1500 eV for 2 hours, whose diameter was ~ 1 mm.

Figure 1 shows the PES results of Li metal with the various treatments. The Li 1s peak positions change with the treatments [Fig. 1(a)]: 58.2 eV for no surface treatment, 56.7 eV after the Ar⁺ sputtering, and 55 eV after the electron irradiation. Especially, the intense background intensity at the higher binding-energy side due to the plasmon-loss appeared after the electron irradiation. Moreover, the Li 1s peak position is located at the lowest binding energy among other Li compounds. The valence band spectra also change with the treatments [Fig. 1(b)]. The most significant change is the appearance of the Fermi edge after the electron irradiation. This Fermi edge is related to the lowest binding-energy peak of Li 1s. Although the Li surface after the electron irradiation has a metallic property, this Fermi edge could not be due to a Li metal. This is because the contamination peaks of C 1s and O 1s remain even after the electron irradiation [Fig. 1(c), (d)]. Since the compound produced by the discharge process in Li-O system, i.e., Li₃O₄ has metallic property [3], this compound could be produced by

the electron irradiation with the residual gas. After the Ar⁺ sputtering, on the other hands, the contamination peak of C 1s is removed while that of O 1s remains [Fig. 1(c), (d)]. This suggests that Li₂CO₃-like compounds on the Li metal surface change to Li₂O by Ar⁺ sputtering [4]. Therefore, in this study, Ar⁺ sputtering is not effective to obtain a pure Li metal surface.

Utilizing various energies of photon including X-ray, we have analyzed the inner and shallow core-levels and the valence band of Li metal with the various treatments. Although it is difficult to obtain a pure Li metal surface, the electronic structure of Li metal surface is found to be changed and show a metallic property even with oxygen/carbon.

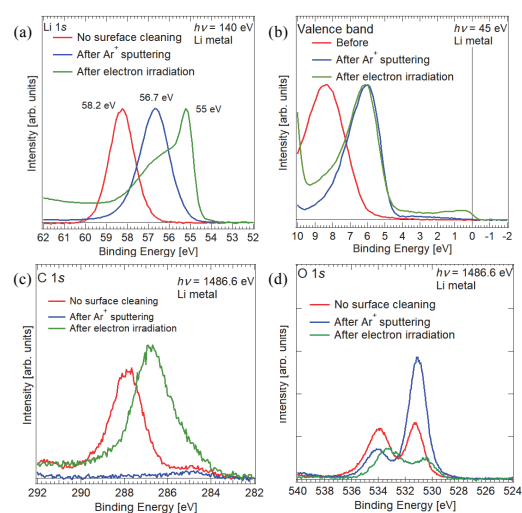


Fig. 1 (a) Li 1s core-level spectra and (b) valence band spectra (c) C 1s core-level spectra (d) O 1s core-level spectra of Li before and after the Ar⁺ sputtering or the electron irradiation.

References

- [1] Jun Kikkawa, Taishi Shiotsuki, Yusuke Shimo, Shogo Koshiya, Takuro Nagai, Takehiro Nito, and Koji Kimoto, *Jpn. J. Appl. Phys.* **2018**, 57, 035802.
- [2] Ruimin Qiao, Yi-De Chuang, Shishen Yan, and Wanli Yang, *PLOS ONE*, 2012, 7, e49182.
- [3] Guochun Yang, Yanchao Wang, and Yanming Ma, *J. Phys. Chem. Lett.*, 2014, 5, 2516.
- [4] Kristina Edström, Marie Herstedt, and Danil P. Abraham, *J. Power Sources*, **2006**, 153, 380.