Electronic States Analysis of Li Metal Surfaces Scraped in Ultra-high Vacuum by X-Ray Absorption Spectroscopy

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Li metal has attracted much attention, because a Li-air battery is able to have high energy and high capacity. Previous research has revealed a chemical property of Li oxides during charge-discharge process [1]. In addition, it is reported that many kinds of lithium compounds appeared on the surface [2]. Due to the high activity of Li metal with gases, however, it is difficult to control and understand the fresh Li metal surfaces. Even in a vacuum chamber, its surface reacts with residual gases. Therefore, it is important to confirm the changes from Li metal to other Li compounds in ultra-high vacuum (UHV). Since x-ray absorption spectroscopy (XAS) is a powerful method for understanding an electronic state, we have measured the electronic state changes of Li metal surfaces in UHV.

The XAS measurement was carried out at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University. XAS spectra were obtained by a total electron yield (TEY) mode. Measurement time was about 15 min. The measurements were performed at room temperature under the UHV of $\sim 5 \times 10^{-8}$ Pa. The residual gasses were mainly H₂, H₂O, and CO, whose masses (2, 18, and 28) were detected by Q-mass analysis. Li metal plates from HONJO METAL CO. were transferred to the measurement chamber without being exposed in the air. The sample surfaces were scraped *in situ* with a diamond file to obtain clean surfaces.

Figure 1 showed a series of Li K-edge spectra after scraping in UHV. Immediately after scraping the Li metal surface, XAS spectrum (0 min) show an only prominent absorption around 55 eV, which is a characteristic structure of metallic Li. (The weak absorptions around 58 eV and 63 eV are maybe due to the measurement time.) Even after keeping in UHV (2, 4, and 6 hours), the structures around 58 eV and 63 eV increased. These features can be considered to be Li₂O [3]. Other Li compounds, such as Li2CO3 and LiOH are excluded because the photoelectron spectroscopy measurements did not detect carbon signals and the XAS spectral shapes Since the residual gases in the are different. measurement chamber contained oxygen (H₂O and CO), it was possible that a fresh Li metal easily reacted with oxygen to form Li₂O. However, a metallic Li does not disappear on the surface, since the intensity of 55 eV structure still remains in the XAS spectrum after 6 hours though the ratio of Li₂O/Li increases.

We have measured XAS spectra of Li metal after scraping and analyzed time dependence in UHV. After scraping in UHV, new structure around 55 eV appeared. On the other hand, the intensity of 58 eV and 63 eV peaks increased. These peaks were assigned to Li_2O .



Fig. 1 Li K-edge spectra after scraping in UHV.

References

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