Identification of Reduction Products of Li_3PS_4 Solid Electrolyte by Soft X-ray Absorption Spectroscopy

Masakuni Takahashi[1], Toshiki Watanabe[1], Kentaro Yamamoto[1], and Yoshiharu Uchimoto[1]

1) Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan

All-solid-state batteries that use lithium metal as the anode have high energy density. However, in order to use lithium metal as the anode, a formation of Li dendrites must be suppressed. Recently, it has been found that an addition of lithium iodide (LiI) to sulfide solid electrolytes has the effect of suppressing the formation of Li dendrites.[1,2] One of the reasons for this suppression is thought to be the improvement of the stability of between the lithium anode and the solid electrolyte interface.

In this report, LiI-doped Li_3PS_4 and Li_3PS_4 solid electrolyte were synthesized and short-circuit tests were conducted. As a result, the LiI-doped Li_3PS_4 solid electrolyte did not short-circuit to a higher potential, and the effect of LiI doping was clarified. The P K-edge and S K-edge XANES spectra were measured to compare the chemical states of LiI-doped Li_3PS_4 and Li_3PS_4 before and after the short-circuit test in order to verify the effect of LiI doping on the stability.

LiI-doped Li_3PS_4 ($70Li_3PS_4$-30LiI) and Li_3PS_4 were synthesized by the following procedure. The amount of LiI added was 30 vol%. Li_2S (Sigma-Aldrich, > 99.9%), P_2S_5 (Sigma-Aldrich, 99%), and LiI (Sigma-Aldrich, > 99.99%) were mixed in appropriate molar ratios using an agate mortar. The mixed powder was ball-milled at 600 rpm for 10 hours. All the above procedures were carried out under Ar gas atmosphere. The synthesized solid electrolytes were molded into φ10 mm pellets to produce Li metal/solid electrolyte/Li metal laminated cells. Short-circuit tests of these laminated cells were conducted. P and S K-edge XANES measurements before and after short-circuit tests of LiI-doped Li_3PS_4 and Li_3PS_4 were performed at BL-10, SR Center, Ritsumeikan University. The measurements were performed by fluorescence yield method.

Fig. 1 shows the XANES spectra of (a) the P K-edge and (b) the S K-edge, where the spectra of Li_3PS_4 and $70Li_3PS_4$-30LiI are shown as the difference spectra before and after the short circuit test. The P K-edge (Fig. 1a) shows the XANES spectrum of Li_3P, the S K-edge (Fig. 1b) shows the XANES spectrum of Li_2S, and both figures show the XANES spectrum of the standard Li_3PS_4. In the difference spectrum of Li_3PS_4 before and after the short-circuit test, the peak of Li_3PS_4 decreased and the peaks of Li_3P and Li_2S were observed after the short-circuit test, indicating that Li_3PS_4 was decomposed to form Li_3P and Li_2S. On the other hand, for $70Li_3PS_4$-30LiI, almost no change in XANES spectra was observed before and after the short circuit test, indicating that it remained in the state of Li_3PS_4 after the test. Suyama et al. reported that decomposition products formed at the interface between the Li anode and the Li_3PS_4 solid electrolyte after the short-circuit test, resulting in the formation of cracks at the interface. On the other hand, for Li_3PS_4 solid electrolyte doped with LiI, it was found by SEM observation that a uniform interface was maintained even after the short circuit test.[2] These results suggest that the addition of LiI to the Li_3PS_4 solid electrolyte inhibits the decomposition of the electrolyte into Li_3P and Li_2S and retains a uniform interface, thus suppressing the growth of Li dendrites.

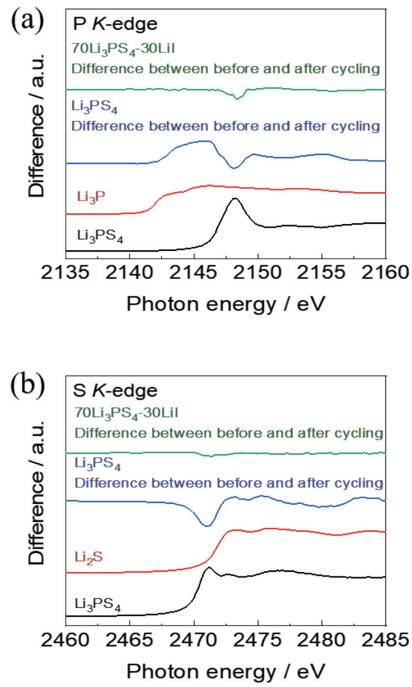

Fig. 1 (a) P K-edge XANES and (b) S K-edge XANES difference spectra of two samples.

References

[1] F. Han, J. Yue, X. Zhu, and C. Wang, *Adv. Energy Mater.*, **2018**, *8*, 2.

[2] M. Suyama, A. Kato, A. Sakuda, A. Hayashi, and M. Tatsumisago, *Electrochim. Acta*, **2018**, *286*, 158.