Local Structure Analysis for Metal Polysulfide Electrode Materials Using Soft X-ray XAFS Measurements

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Nowadays, lithium ion batteries are important energy storage system that are widely developed for several applications such as electric vehicles. With the requirements for improving the battery performance, research on battery component, particularly cathode active material, has been widely carried out. Sulfur-based material is one of the most promising next-generation cathode active materials that have high theoretical capacity of more than 600 mAh/g and has an advantage that sulfur is abundant as natural resources. Among them, metal polysulfide, Li_xMS_y (M = V, Ti, Fe, etc.), is one of the typical materials that shows relatively high discharge capacity (> 700 mAh/g) in the cell with liquid electrolyte [1-3]. For further improvement of the battery performance, analyses of the charge/discharge mechanism, as well as the degradation mechanism with cycling, are necessary. In the present work, we have carried out S K-edge XANES measurements for Li_xFeS_y samples to examine, at first, the local structure around S atoms.

Li_xFeS_y was prepared after the previously reported procedure [3]; Li_2S and FeS were mixed and treated by SPS (spark-plasma-sintering) process at 600°C, followed by mechanically milled for 2 h to form Li_xFeS_y ($6 \leqq x \leqq 12$, $4 \leqq y \leqq 7$). The obtained Li_xFeS_y samples were characterized by XRD measurements. Electrochemical charge/discharge tests were carried out using lithium coin-type cells. A solution of 1M $LiPF_6$/(EC+DMC) was used as the electrolyte, and the electrochemical measurements were carried out at a current density of 46.7 mA/g between 1.0 and 2.6 V. S K-edge XAFS measurements were carried out at BL-10 of SR center in Ritsumeikan University. The incident X-ray beam was monochromatized with a Ge(111) crystal ($2d$ = 6.532 Å) pair. The photon energy was calibrated with a strong resonance of K_2SO_4 (S $1s \rightarrow t_2$) appearing at 2481.7 eV. All samples were sealed in an Ar-filled transfer vessel to carry to the beam line of SR center.

The obtained Li_xFeS_y samples were black in appearance, and their XRD patterns were assigned as low-crystalline Li_2S structure (anti-fluorite). The electrochemical tests demonstrated that the Li_xFeS_y sample cells showed the initial discharge capacity of more than 700 mAh/g. Figure 1 shows the S K-edge XAFS spectra for the Li_xFeS_y samples. Spectra of some reference samples (S and Li_2S) are also shown for comparison. The spectra of the Li_xFeS_y samples showed several peaks; the ones at 2477 and 2483 eV were very similar to those of Li_2S, suggesting that the Li_xFeS_y samples have basically anti-fluorite structure. And the peak at 2470 eV, which was observed similarly in the spectrum of Li_2FeS_2 [4], could be assigned to a bound state resonance due to an electronic transition between the S 1s (in S^{2-}) and p-hybridized Fe 3d band. This is suggestive of the formation of Fe – S bond, and its peak intensity increased with the relative amount of Fe in Li_xFeS_y. Therefore, the Fe atoms were substituted for some Li atoms in the anti-fluorite structure with remaining the local structure around S atoms nearly unchanged. We are now examining the spectral changes after charge and discharge, and further analyses results will be reported elsewhere in the near future.

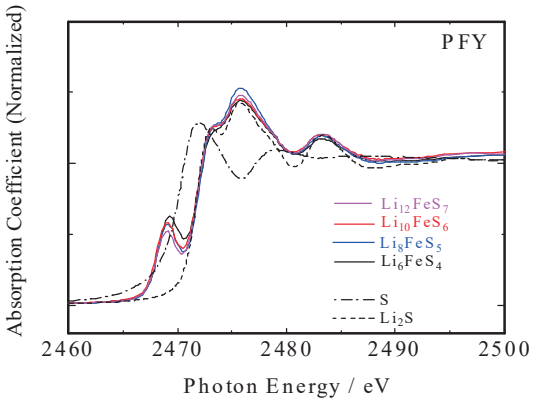

Fig. 1 S K-edge XAFS spectra for the Li_xFeS_y samples. Spectra of some reference materials (S and Li_2S) are also shown for comparison.

References

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