Local Structure Analysis for Fe-Containing Polysulfide Electrode Material by XAFS Measurements

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Recently, lithium ion batteries are important energy storage system that are widely developed for several applications such as portable phones, electric vehicles, and so on. With the requirements for improving the energy density of batteries, research on battery component, particularly cathode active material, has been widely performed. Sulfur-based material is one of the promising next-generation cathode active materials that have high theoretical capacity of more than 600 mAh/g and has advantages of low cost and abundance as natural resources. Among them, metal polysulfide, Li_xMS_y (M = V, Ti, Fe, etc.), is one of the candidate materials that shows relatively high discharge capacity (> 500 mAh/g) [1-3]. For improving the battery performance, analyses of the charge/discharge mechanism as well as the degradation processes are necessary. In the present work, we have carried out S K-edge XANES measurements for Li_xFeS_y samples, particularly $Li_{10}FeS_6$ composition, to examine the local structure around S atoms.

Li_xFeS_y samples were 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. The obtained Li_xFeS_y samples were characterized by XRD measurements. 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 → t_2) appearing at 2481.7 eV. All sample 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 (space group Fm-3m). The S K-edge XAFS spectra for the Li_xFeS_y samples showed mainly three peaks; those at 2477 and 2483 eV were very similar to those of Li_2S, and that at 2470 eV was observed similarly for Li_2FeS_2 [4], being assignable to a bound state resonance due to an electronic transition between the S 1s (in S^{2-}) and p-hybridized Fe 3d band. The latter peak at 2470 eV increased in its intensity with the Fe content in Li_xFeS_y. These results suggest that the present Li_xFeS_y samples have basically anti-fluorite structure with Fe – S bond; plausibly 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 also estimated the radial structure function of the $Li_{10}FeS_6$ sample, and the results are shown in Fig. 1. Based on the atomic distances for the reference samples, the curve-fitting of the spectrum was caried out and the estimated values for the second- and third-nearest were 2.17-2.34 and 2.52-2.71 Å, respectively, which were in good agreement with the values (2.33, 2.63 Å) calculated from the above structural model. Further analyses after electrochemical charge and discharge will be carried out and reported elsewhere in the near future.

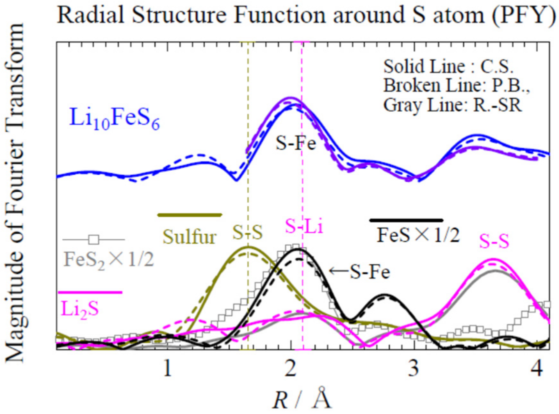

Fig. 1 Radial structure functions around S atoms (PFY) for $Li_{10}FeS_6$ sample. Results of the curve fitting are shown as dark violet line. Spectra for some reference samples (S, Li_2S, FeS_2, FeS) are also shown for comparison.

References

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