

Lithium K-edge X-ray Absorption Measurement of Cathode Materials

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Lithium ion insertion / extraction reaction accompanying oxidation and reduction of 3d transition metal is utilized as cathode material of lithium ion battery. The theoretical charge-discharge capacity of cathode materials is determined by the number of mobile lithium ions and the oxidation number that transition metal can take. In recent years, lithium-rich cathode materials that utilize oxidation-reduction of anions with high capacity and high potential are one of interesting topics[1-4]. However, there is a problem such as irreversible behavior accompanied by oxygen evolution at the initial charge, and it has not been put to practical use. Electronic structure change of the transition metal and anion is one of the factors determining the insertion / extraction amount of lithium ions. In order to increase the capacity of the active material, the electronic structure of the active material should be deeply understood for the material design. Numerous electronic structural analyzes of transition metals and oxygen have been made so far, however, few analysis of the electronic state of lithium carrier ions has been made. This is assumed that the carrier ion does not change, there are not many methods for observing the lithium of the light element, and the surface film deposited after charging and discharging makes analysis of the active material bulk structure difficult. In this study, the electronic structure change of lithium was analyzed by soft X-ray absorption spectroscopy which can directly observe the electronic state of lithium. To prevent the surface film formation, lithium was chemically extracted from LiCoO₂, LiMn₂O₄, Li-rich NCM as representative cathode materials.

LiCoO₂, LiMn₂O₄ and Li_{1.2}(Ni_{0.13}Co_{0.13}Mn_{0.53})O₂ powders and the oxidizing agent Br or NO₂BF₄ were stirred in acetonitrile for 48 hours. The molar ratios of the oxidizing agents used were cathode materials: Br = 1: 9 and cathode materials: NO₂BF₄ = 1: 1. After filtration, washing with acetonitrile and drying in vacuum gave a powder sample. Li K-edge X-ray absorption spectra were measured at the beam line BL2 at SR Center of Ritsumeikan University. The spectra were corrected by the total electron yield method.

In general, the detection depth of Li K-edge X-ray absorption spectroscopy is very small due to low X-ray energy, and after the charge-discharge reaction, the film component containing Li formed on the active material surface occupies most of the spectral component. Therefore, powder samples by chemical desorption were measured. In the case of Li_xMn₂O₄ from which lithium was extracted, no film component such as LiF or Li₂CO₃ was detected, whereas the behavior of peak intensity changing with the initial LiMn₂O₄ was observed. Therefore, the electronic structure of lithium was changed by the charge-discharge reaction.

References:

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