

Changes in electronic structure upon Li-ion extraction of LiCoPO₄ using X-ray absorption spectroscopy

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LiMPO₄ (M=Mn, Fe, Co, Ni) with olivine-related structure are one of the most promising materials as positive electrodes for lithium-ion battery. These materials have relatively larger theoretical capacity and higher voltage than practically used LiCoO₂, LiNiO₂, and LiMn₂O₄.

These phosphate materials contain tetrahedral PO₄ units with strong covalent bonding. As a result, the valence electrons of transition metals tend to localize. Such a unique electronic structure would be related to the observed high voltage properties and low electronic conductivities. To elucidate the electronic structure of phosphate materials, the electronic structure of the Li_{1-x}CoPO₄ which shows the highest voltage ~4.8V among the olivine system¹⁻² has been investigated using X-ray absorption spectroscopy (XAS).

The olivine-type LiCoPO₄ was synthesized by solid-state reaction. The mixture of stoichiometric Li₂CO₃, CoC₂O₄·2H₂O and NH₄H₂PO₄ was heated at 350°C in air. Then the sample was palletized and heated again at 600°C for 12h. XRD patterns of synthesized powder showed single phase LiCoPO₄ olivine. Lithium extraction reaction was performed using a three-electrode electrochemical cell. XAS measurement was carried out using synchrotron X-ray radiation at Photon Factory (KEK), Japan. Co K-edge XAS was measured by transmission method at the beam line BL-7C. O K-edge and P K-edge XAS were measured at the beam line BL-11A, BL-11B, respectively by total electron yield method. Electrode samples were treated in Ar or N₂ gas atmosphere through all the experiment.

The Co K-edge XAS for Li_{1-x}CoPO₄ is exhibited in the Fig. 1. During the charge reaction, the threshold energy gradually shifted to the higher energy side. Therefore the results indicate that Co ion oxidized for the charge compensation in the entire region of the charge reaction (from $x = 0.0$ to 1.0).

Fig. 2 shows O K-edge XAS for Li_{1-x}CoPO₄. In the energy region between 530 and 535 eV, absorption peak A is observed. This peak is known as the transition of O 1s electron to the hybridized state of O 2p and transition metal d orbital. At the lower x region ($0.0 \leq x \leq 0.5$), the energy of the peak A shifted to lower energy side. Moreover, the intensity of the peak increased with composition x , indicating the increase of hole state at oxygen site. Such a behavior would imply that Co-O hybridized state contributes to charge compensation accompanying lithium extraction. On the other hand, at the higher x region ($x > \sim 0.5$), only a little change was observed.

P K-edge XAS was also measured for Li_{1-x}CoPO₄. The shape of main absorption peak is almost constant in the whole charge process. Nevertheless, slight energy shift was observed. This indicates that phosphorus

also changes to the higher oxidization state.

From above spectral data, there is a tendency about the changes in electronic structure of LiCoPO₄ during lithium extraction. When lithium content is high, charge compensation is performed by the change of Co-O hybridized state. As lithium content decreases, only Co compensates charge balance during lithium extraction.

References

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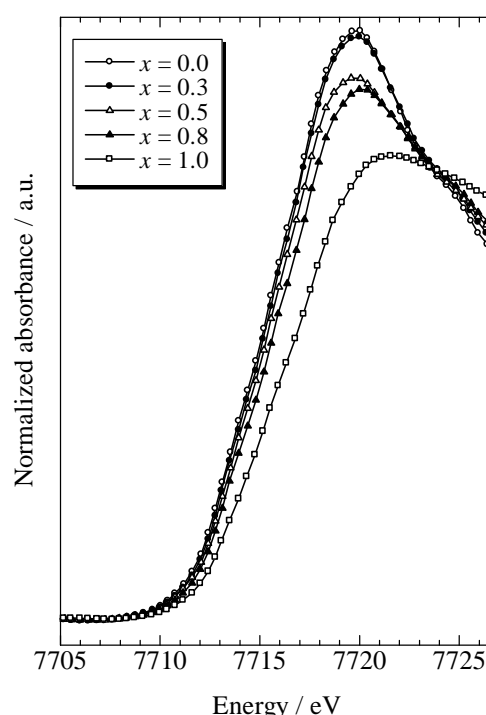


Fig. 1 Co K-edge XAS for Li_{1-x}CoPO₄.

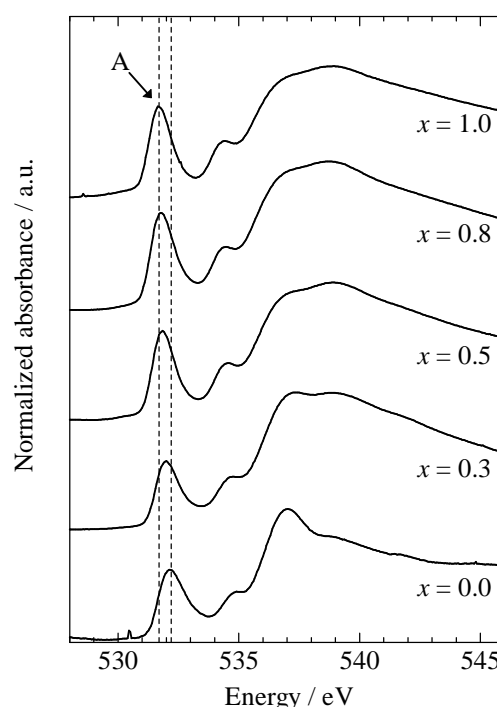


Fig. 2 O K-edge XAS for Li_{1-x}CoPO₄.