

## Direct Observation of d-band Structure Change during Metal-Insulator Transition of $\text{LiCoO}_2$

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Metal-insulator transition (MIT) phenomenon in  $\text{LiCoO}_2$  occurs with decreasing Li content in charging process, because the completely filled  $t_{2g}$  band with d-electrons in low spin state has holes in this process gradually, that is, p-doped semiconductor and the electronic conductivity is drastically increased. These increased holes in  $t_{2g}$  band can change the valence band structure which is composed of d ( $t_{2g}$ ) character of Co and p character of oxygen (mainly, d of Co). In this study, we have tried to directly observe the change of valence band structure in  $\text{Li}_x\text{CoO}_2$  ( $0 < x < 1$ ) by using synchrotron radiation to show the mechanism of MIT phenomenon. Unfortunately, it was not so successful, because the cross section of Co to high energy X-ray was too small to obtain reasonable data to understand its d-band structure. However, with core level data obtained it was possible to show the trend of electronic structure change as a function of  $x$  in  $\text{Li}_x\text{CoO}_2$ , by combining the other tools for electronic structure analysis, such as EELS and XANES.

### Background

Metal-insulator transition (MIT) occurs with decreasing Li content in charging process of  $\text{LiCoO}_2$  which has been considered as a positive electrode materials for Li-ion batteries. The origin of this MIT phenomenon is the structure change of the  $t_{2g}$  level as a function of  $x$ . The d-orbital of the Co ion having an octahedron structure surrounded by 6 oxygen ligands is separated into two orbitals,  $t_{2g}$  and  $e_g$  in crystal field. Since the distance of the 1st nearest neighbor of Co is less than  $R_c$ , it can make a band and the electrons could be delocalized in entire Co plane. However, according to the Hubbard model [1] considering electron-electron repulsion as well as the hopping integral, this material is Mott insulator. In the fully lithiated state ( $x=1$ ), the  $t_{2g}$  level is

completely occupied with d electrons in the low spin state, such that the material becomes a band insulator. However, for partially delithiated state ( $x < 1$ ), it becomes metallic as a p-doped semiconductor with the decrease of  $x$ , because the valence state of the Co ion is gradually changed from  $3+$  to  $4+$ , resulting in the increase of carrier concentration and the change of d-band structure. (Fig. 1) In this study, we have tried to directly observe the change of d-band structure in MIT process by using HXPES technique with very

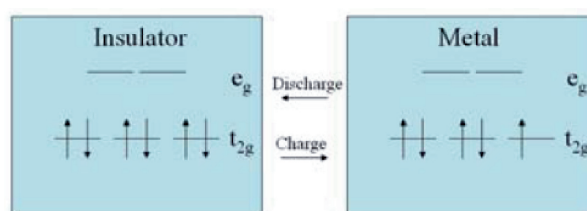


Fig. 1. Mechanism of MIT phenomenon

strong X-ray in undulator beamline (47XU).

## Experimental

All the data have been obtained from the powder samples adhered onto conducting tape. The samples were totally 6 kinds of samples as a function  $x$  in  $\text{Li}_x\text{CoO}_2$  ( $x=1, 0.97, 0.94, 0.85, 0.75, 0.7$ ). The photon energy of 8 KeV was employed for all the experiments.

## Results and discussion

Up to now, some indirect evidences of this transition have been reported with several experimental and theoretical tools, such as Li MAS NMR, EELS, EIS and DFT calculation [1-3]. However, since there has been no report on the direct observation of d-band structure change with photoelectron spectroscopy, we have challenged to observe it with HXPES technique. Unfortunately, it was not so successful in actual experiment. As shown in Fig. 2, there is a large noise level to signal, because the photon energy of 8 KeV has too small cross section for photoelectron emission for Co to obtain a significant signal. Originally, we have employed this technique with an intention to avoid the effect of sole surface passivation layer which is generated in

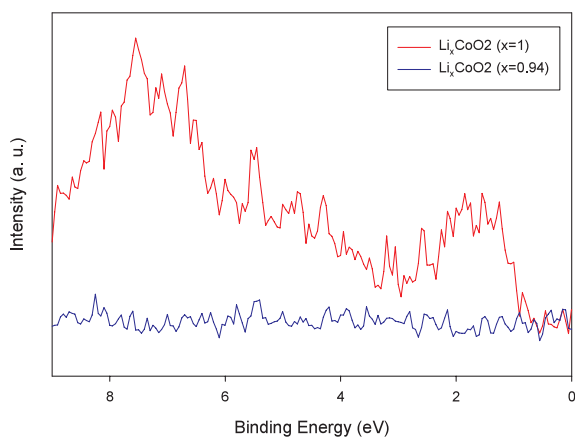


Fig. 2. Valence band structure of  $\text{Li}_x\text{CoO}_2$  as a function of  $x$

charge/discharge process and has perfectly different electronic structure from bulk, because the available UPS technique can reflect just very thin surface layer. However, the photon energy used was too strong for d-band of Co, so we have finally failed to obtain exact valence band spectra for  $\text{LiCoO}_2$  (especially, charged samples) in this study. Also, one more reason for this failure is the insufficient sample amount for experiment, because the charged samples ( $x<1$ ) should be prepared by collecting the charged  $\text{LiCoO}_2$  powders from the electrode having limited area in the coin cell. From this failure, we can just suggest that if one would like to try to measure the photoelectron emission spectra on the electronic structure having a lower photoelectron emission cross section, such as valence band and higher core level of light transition metal with HXPES technique, they should prepare sufficient amount of samples and give an enough time to measurement. However, we could obtain some core level spectra on Co 2p or O 1s of the samples, although the quality of these data are not so good but just detectable. These data provide a consistency with the results obtained with the previously mentioned techniques; the valence state of the Co ion is gradually changed from 3+ to 4+ and there is a considerable amount of charge compensation to Co by oxygen with the decrease of  $x$  by charging process.

## References

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