

Co 2p soft x-ray emission spectroscopy of LiCoO₂ using an electrochemical *in situ* cell

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LiCoO₂ is one of the typical cathode materials for Li-ion battery. The charge-discharge capacity is 150 mAh/g when 0.5Li⁺ ions are extracted/inserted from/into the LiCoO₂ host¹. In this charge process, the average valence of Co should change from Co³⁺ (for the open circuit voltage (OCV)) to Co^{3.5+} (for the charged state: Li_{0.5}CoO₂). There are many reports about this Co 3d electronic-structure change, e.g. by means of hard x-ray absorption spectroscopy at the Co K edge². In order to investigate the electronic-structure change in more detail, we developed an *operando* soft x-ray emission spectroscopy (XES) technique by improving the similar technique for fuel cell catalysts³.

LiCoO₂ powder was fabricated by a sol-gel method. The powder was mixed with acetylene black and PVDF in an NMP solution. The LiCoO₂ slurry was put on a Ti/Au-coated SiC membrane window and dried. An *in situ* cell consisting of the LiCoO₂ electrode on the SiC membrane window, a Li-metal counter electrode, and an organic electrolyte solution was developed. The *in situ* cell was assembled in a grove box filled with Ar gas. Cyclic voltammetry (CV) was employed for the charge experiment. The scan rate was set to 0.5 mV/s. XES measurements at the Co L₃ edge were performed at BL07LSU in SPring-8. An excitation energy of 780 eV corresponding to the main peak position of the Co L₃-edge absorption spectrum was used for XES. The XES measurements were carried out using an ultra-high-resolution XES spectrometer, HORNET⁴. The total energy resolution was set to $E/\Delta E = 2400$. All the XES measurements were performed at room temperature.

Figure 1 shows the Co 2p resonant XES (RXES) of LiCoO₂ for the pristine powder and the open-circuit voltage (OCV) before charge, and the charged states. The spectrum for the powder exhibits three fine *dd*-excitation peaks, charge-transfer (CT) excitation below 774 eV, and shoulder-like structures between them. The electron configuration should be Co³⁺ low-spin (LS) state (t_{2g}^6) according to the Co L₃-edge absorption spectrum. However, the XES spectrum showed the discrete *dd*-excitation peaks which have not

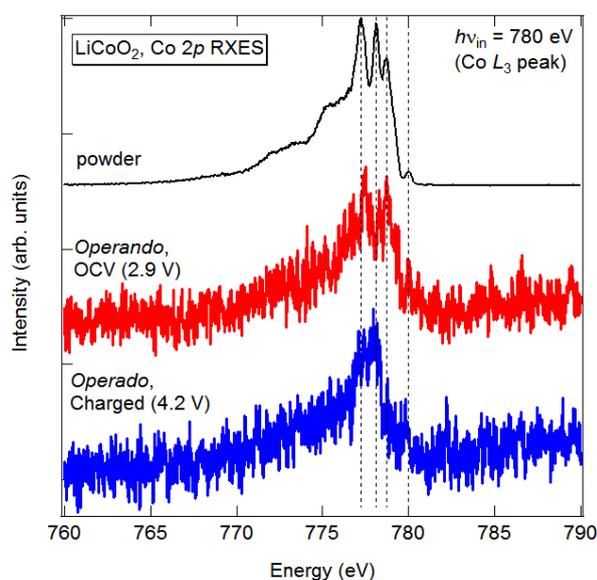


Fig. 1. *Operando* Co 2p XES for LiCoO₂.

been seen in previous low-resolution XES results for LiCoO_2 ⁵. The present result implies that the t_{2g}^6 configuration in LiCoO_2 would likely be affected by some effects such as charge transfer and/or crystal field. In future, theoretical calculations will be performed.

For the OCV state, the S/N ratio is very poor while the profile should be partially similar to that for the powder. In going to the charged state, although the low S/N ratio remains, the *dd*-excitation peaks are changed. The peak at 778.7 eV is dramatically reduced and the peak at 778.1 eV is enhanced, implying that the Co^{3+} state would be partially oxidized to Co^{4+} . A similar change has been observed for the Co 2*p* *ex situ* XES study of $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2$ ⁶.

We also investigated the reason why the S/N ratio is much degraded for the *operando* measurements. An observation by a scanning electron microscopy revealed that the LiCoO_2 slurry partially flaked off from the membrane window after the *operando* XES measurements. The partial flaking possibly caused by the incident beam should degrade the S/N ratio.

In summary, we performed *operando* Co 2*p* XES for LiCoO_2 using the electrochemical *in situ* cell. Although some changes due to the charge reaction were observed for the XES spectra, the poor S/N ratio prevents us from detailed information of the Co 3*d* state. In the near future, the thin-film structure consisting of the membrane window, Ti/Au coating layer and the LiCoO_2 slurry will be improved to avoid the flaking.

References

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