

# Charge Mechanism Analysis of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ using the Soft X-Ray Absorption Fine Structure (XAFS) Spectroscopy

Masato Mogi, Kei Kubobuchi, Masashi Matsumoto, Toshihiro Asada,  
Chikai Sato, Teruhisa Baba, Yohei Takahashi, and Hideto Imai

*NISSAN ARC Ltd., 1 Natsushima, Yokosuka, Kanagawa-ken 237-0061, Japan*

## 1. Introduction

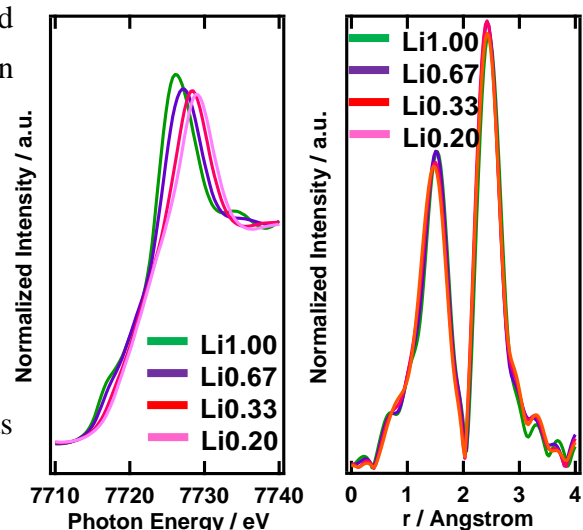
Understanding of role of transition metals that are involved in the cathode materials of Li-ion batteries is a key to design better Li-ion batteries, because 3d electrons of transition metals primary contribute to the redox reaction of the battery, and thus structural changes around each transition metal strongly affects stability of the cathode.

X-ray absorption fine structure (XAFS) spectroscopy at transition metal K-edge of cathodes is often used to analyze the redox-reaction (valence state of the transition metal components) of the cathode. In some cases, however, the interpretation of the XANES spectra (the chemical shift) is not straightforward, and we cannot discuss the valence states. [1] On the other hand, L-edge absorption spectra are more suitable to monitor the redox-reaction, because that arose transitions from 1s core levels to 3d bands that directly correlate with the charge compensation and oxidation during battery reactions.

Here, we report the results of L-edge absorption spectroscopy for  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM), especially focusing of the role of cobalt. Although NMC was developed as a better cathode than  $\text{LiCoO}_2$ , the role of Co is unclear: the valence change is not unclear from K-edge XANES spectra and local structure of Co seems to be unchanged during the charge-discharge processes. (Figs. 1(a) and 1(b)) Our present result on L-edge absorption spectroscopy clearly suggests the valence change of Co at high voltage regions.

## 2. Experiment

The Co L-edge XANES measurements were carried out at BL10 beamline at Ritsumeikan SR Center. The electrode was disassembled in a globe box filled with inert atmosphere and transferred to the chamber without exposing to the air.



**Fig. 1** (a) Co K-edge XANES spectra. (b) The  $k^3$ -weighted Fourier transform magnitudes

### 3. Results and Discussion

Figure 2 shows Co L-edge spectra obtained using a TEY mode. We can see that spectra remained almost unchanged during Li1.00 and Li0.67, but slightly sifted to lower energy at Li concentration of 0.2. This result indicates that valence of Co slightly changes at high-potential regions (Low Li concentration regions). Similar results were reported for LiCoO<sub>2</sub>, in which rehybridization of Co-O molecular orbital and change in the effective nuclear charge of Co is considered to be occurred at high potential regions. [1]

We further confirmed such behavior by first-principles electronic structure calculations of Li-de intercalated NMCs. Then valence changes were calculated using WIEN2K Atom in Molecules (AIM) program. The calculations were carried out after geometry optimization using VASP code.

As shown in Table 1, the valence of Mn was not change. The valence of Ni changed about 0.2, while the valence of Co changes slightly at low Li concentration. This implies the oxidation of Co was occurred only at high potential regions [2].

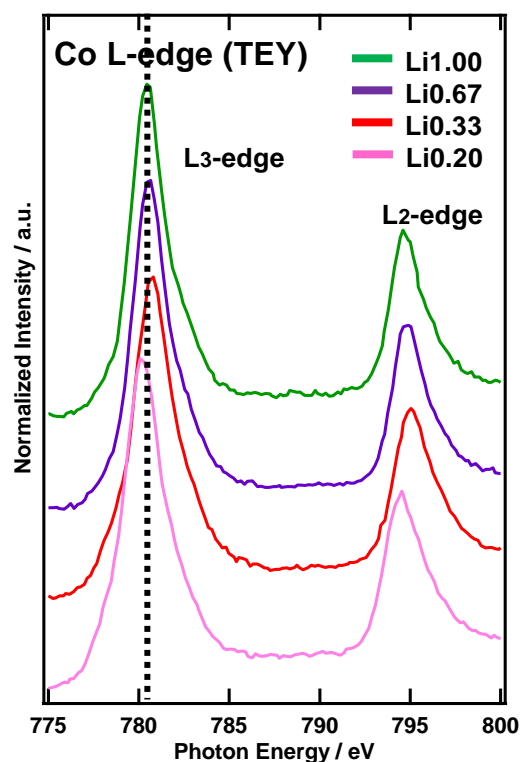


Fig. 2 The experimental Co L-edge XANES spectra.

**Table 1** Integrating valence electron density

T. M.	$x = 1.00$	$x = 0.67$	$x = 0.33$
Ni	1.54	1.65(+0.11)	1.75(+0.21)
Co	1.68	1.73(+0.05)	1.17(+0.08)
Mn	2.25	2.25	2.25

### References

[1] H. Imai, K. Kubobuchi, M. Mogi, M. Matsumoto, M. Nishijima, T. Yamamoto, T. Matsumoto, and Y. Nitta, "Combined in situ x-ray absorption spectroscopy and first-principle calculation studies on local structural and electronic structural alternations of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>". 222th Electrochemical Society Meeting, Honolulu, Hawaii October 7-12, 2012.

[2] Won-Sub Yoon and Kwang-Bum Kim, J. Phys. Chem. B 2002, 106, 2526-2532