

Analyzing reaction mechanism of Li-ion secondary battery by element-specific *in situ* X-ray absorption spectroscopy and theoretical spectral simulations

Rechargeable Li-ion batteries (LiBs) were first commercialized as a power source for mobile electronic devices. They are now about to be applied to large-scale applications such as electric or plug-in hybrid vehicles and stationary power sources for smart energy grids. The development of better electrode materials is strongly desired to fulfill the requirements for the higher capacity and higher stability LiBs used for such large-scale applications. Primary targets in developing high-capacity positive electrode materials include multi-element or multi-component transition-metal oxides with complex structures, as represented by a Li-rich solid-solution layered system. In such complex materials, however, it is not easy to understand the roles played by each element (in each crystallographic site) in the redox reaction. Thus, it is becoming important to develop electronic structure analysis methods with elemental and crystallographic site selectivity to obtain clues to designing better materials.

To date, *in situ* X-ray absorption spectroscopy (XAS) at transition-metal *K*-edges has been most widely used to analyze the reaction mechanism during battery operations by monitoring the “valence change,” which

is determined by the absorption edge shift. However, conventional analysis of the X-ray absorption near-edge structure (XANES) simply involves comparing the absorption edge position with those of references. As long as we use such a simple method, we cannot always evaluate the true valence changes of materials. Although basically XANES reflects valence states, it is also affected by the distribution of wave functions and the electron configurations of absorbing atoms. XANES exhibits very complicated behaviors when the electronic structure and lattice structure of absorbing atoms simultaneously change. To overcome such issues, we have developed a new method taking these effects into account by first-principle XANES simulations. We demonstrated the effectiveness of this method via reinvestigation of the electrochemical process for a typical positive electrode material $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ – one basic component of a Li-rich layered solid solution.

The sample electrode was formed by mixing $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder with acetylene black and polyvinylidene fluoride (PVdf) in *n*-methyl pyrrolidone (NMP) solution. The electrolyte used was 1 M LiPF_6 in an ethylene carbonate/diethyl carbonate (EC/DEC)

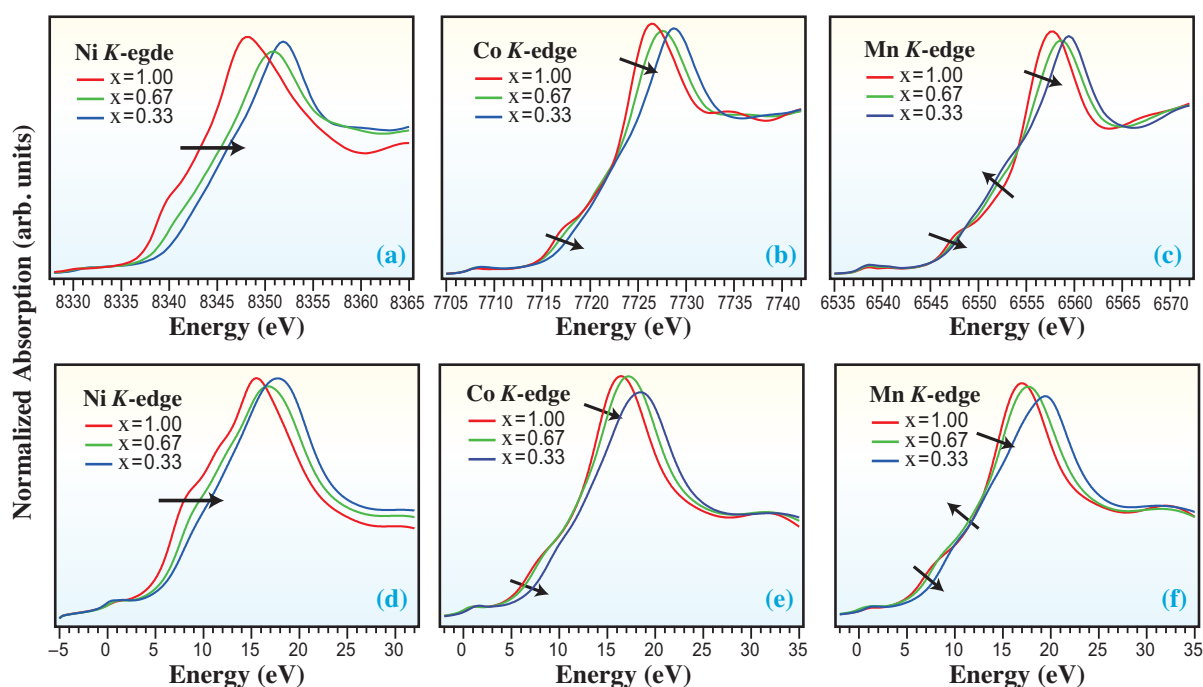


Fig. 1. Experimental *K*-edge XANES spectra of (a) Ni, (b) Co, and (c) Mn. Calculated *K*-edge XANES spectra of (d) Ni, (e) Co, and (f) Mn.

solution. Then, a laminate-type cell was assembled. *In situ* XAS measurements at the transition-metal *K*-edge were performed at beamline **BL16B2**. The XAS data were collected at the Ni, Co, and Mn *K*-edges. Simulations of *K*-edge XANES spectra were carried out by using the full-potential augmented plane wave plus local orbitals (APW+lo) package and WIEN2k [1] within the generalized gradient approximation (GGA) for the exchange-correlation functional.

Figures 1(a) to 1(c) show the results of *in situ* XAS measurements of the transition-metal *K*-edges (Ni, Co, and Mn) in the charge processes. An obvious shift in the entire XANES region was observed for the Ni *K*-edge XANES spectra, indicative of a valence change of Ni due to a redox reaction. On the other hand, it was more difficult to interpret the behaviors of the Co and Mn XANES spectra. Although the shape of the XANES spectra changed and the peak position shifted to a higher energy in the charging process, the absorption edges remained at the same position. One part of the shoulder shifted to the low-energy side and the other part shifted to the high-energy side, as shown by the arrows. In such cases, the theoretical XANES

simulation demonstrates its capability.

Figures 1(d) to 1(f) show the calculated XANES spectra for the Ni, Co, and Mn *K*-edges, respectively. Fundamental features observed in experiments were well reproduced by the simulation. The entire calculated Ni-*K* XANES spectra shifted to a higher energy, which was consistent with the experimental results. Regarding the Co *K*-edge XANES, the peak shifted to a higher energy in both the experimental data and the simulated spectra, while the absorption edge remained at the same position. The complex behaviors observed in the experimental spectra (arrows) were also mostly reproduced. These results indicate that the electronic structure and local structures of absorbing atoms determined by first-principles calculation are sufficiently good to describe X-ray absorption phenomena. The degrees of the valence change for each element in battery operation are summarized in Fig. 2.

As shown above, we successfully demonstrated that the combination of XAS methods and theoretical calculations is an effective way to analyze in details the redox behaviors of positive electrode materials.

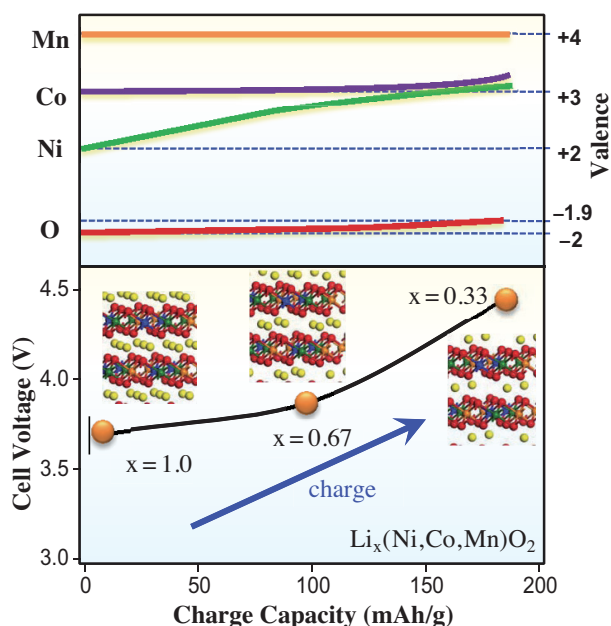


Fig. 2. Summary of valence changes of Ni, Co, Mn, and O in $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ in the charging process.

Hideto Imai*, Masato Mogi and Kei Kubobuchi

Device-functional Analysis Department
NISSAN ARC Ltd.

*E-mail: imai@nissan-arc.co.jp

Reference

[1] P. Blaha *et al.*: WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Universität Wien, Austria (2001).