Electronic state analysis of $(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ nanosheets with exfoliation-induced structural distortion by soft X-ray absorption fine structure

Shinya Suzuki and Masaru Miyayama
School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Li–Ni–Co–Mn oxide represents a promising alternative to commercial $LiCoO_2$ and $LiNi_xCo_{1-x}O_2$ cathode materials, owing to its large electrical capacity and low cost. Despite the possible application of Ni–Co–Mn oxide nanosheets as electrode materials for thin-film energy storage devices, very few studies have been conducted on the preparation of Ni–Co–Mn oxide nanosheets(1), and so far the detailed properties are not clear. In this study, we have studied the electronic state of Ni, Co, Mn in Ni–Co–Mn oxide nanosheets by X-ray absorption spectroscopy (XAS) measurements. Ni–Co–Mn oxide nanosheets were prepared by the exfoliation of $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$ as follows. Layer-structured $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$ compound was oxidized in an aqueous solution of $Na_2S_2O_8$ at a temperature of 70 °C for 24 h to promote the ion-exchange reaction. The proton-exchanged form of $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$ was prepared by mixing the oxidized product with 1 M HNO_3 for 3 d at room temperature. Ni–Co–Mn oxide nanosheets were prepared by exfoliating the proton-exchanged $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$ via its reaction with a tetrabutylammonium hydroxide aqueous solution for 3 d at room temperature. $L_{2,3}$-edge studies were conducted using the total electron yield mode of the BL-11 beamline located at the SR Center of the Ritsumeikan University.

Figure 1 shows X-ray absorption near-edge structure (XANES) spectra of (a) as-received $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, (b) oxidized $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, (c) proton-exchanged $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, and (d) Ni–Co–Mn oxide nanosheets measured at Mn $L_{2,3}$-edge, Co $L_{2,3}$-edge and Ni $L_{2,3}$-edge. Table 1 lists the valence states of Ni, Co, and Mn ions determined via XAS measurements. All the constituent transition metals were reduced during both the proton exchange and exfoliation into nanosheets. The chemical composition of the agglomerated nanosheets using KOH as agglomeration agent was $K_{0.03}H_{1.23}Ni_{0.31}Co_{0.33}Mn_{0.34}O_2 \cdot 1.0H_2O$, which indicates that the fraction of ion-exchangeable protons was very small. From above results we have concluded that the prepared nanosheets should be understood as not oxide but oxyhydroxide nanosheets with the formula $Ni_{0.31}Co_{0.33}Mn_{0.34}O_{0.74}(OH)_{1.26} \cdot nH_2O$.

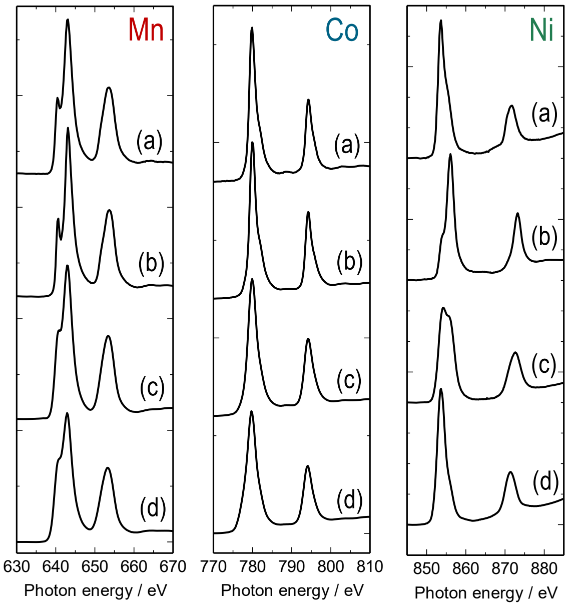

Fig. 1 X-ray absorption near-edge structure spectra of (a) as-received $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, (b) oxidized $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, (c) proton-exchanged $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, and (d) restacked nanosheets measured in the total electron yield mode at Mn $L_{2,3}$-edge, Co $L_{2,3}$-edge and Ni $L_{2,3}$-edge.

Table 1 Valence states of the Mn, Co, and Ni ions in the initial $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, oxidized $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, proton-exchanged $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$, and restacked nanosheets determined by XAS.

	Valence states		
	Mn	Co	Ni
As-received $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$	4.0	3.0	2.0
Oxidized $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$	4.0	3.0	3.9
Proton-exchanged $Li(Ni_{0.33}Co_{0.33}Mn_{0.34})O_2$	3.8	2.8	2.9
Ni–Co–Mn nanosheets	3.6	2.7	2.0

Reference

(1) E. J. Oh, T. W. Kim, K. M. Lee, M. S. Song, A. Y. Jee, S. T. Lim, H. W. Ha, M. Lee, J. H. Choy, S. J. Hwang, *ACS Nano*, **2010**, *4*, 4437.