Roles of individual transition metal elements on a redox reaction of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as revealed by resonant photoelectron spectroscopy

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Understanding of roles of individual elements in positive electrode materials is pivotal to design better active materials of advanced Li-ion batteries. A layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ positive electrode material is an example in which cooperative behaviors of transition metal elements and/or oxygen significantly improve the capacity and cyclability.[1-3] In this material, Ni is considered as redox species, and the Mn doping improves the cycle performance by relaxing local lattice distortion caused by Jahn-Teller effect of Ni^{3+} tions without changing Mn valence throughout charge/discharge processes. The roles of Co and oxygen, on the other hand, remain elusive, although both components could contribute at high potential regions.

To directly clarify whether or not Co and oxygen contribute to the redox reaction, we performed 2p to 3d resonant photoelectron spectroscopy. Since resonant photoelectron spectroscopy can electively probe contribution of wanted element by enhancing spectral intensity in valence band spectra, we can directly observe contribution of 3d electrons belongs to target element discriminating contribution form unwanted elements.

$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples with x-values of 1, 2/3, 1/3, and 0.2 were prepared by using coin-type cell with a Li metal negative electrode. The cell was disassembled in a dry grove-box and the cathodes were transferred to UHV measurement chamber without exposing to the ari. The resonant photoelectron spectroscopy measurements at 2p to 3d transition for Ni, Mn, Co and O were performed at BL2 at SAGA light source. The first-principles theoretical electronic band structure calculations were carried out by using WIEN2k code.[4]

Figure 1(a) shows the results of the Co 2p to 3d resonant photoelectron spectroscopy for $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples with x-values of 1, 2/3, 1/3, and 0.2. In this measurements contribution from Co 3d electron is enhanced. We can clearly see that the contribution form Co is dominant for x=1/3 and 0.2 samples.

Figure 2 show the partial density of state of Co 3d band in $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ near the Fermi level. At x=1/3 the contribution of Co 3d shifts to a high energy side. These results are direct evidence that Co 3d electrons could be contribute to the redox reaction above x=1/3.

Results of resonant photoelectron spectroscopy measurement of Ni, Mn and O will be presented at the Meeting.

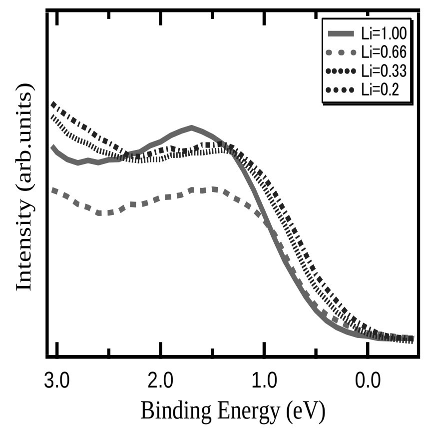

Fig. 1: (a) Co 2p→3d resonant photoelectron spectra for $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with x=1, 0.66, 0.33 and 0.2.

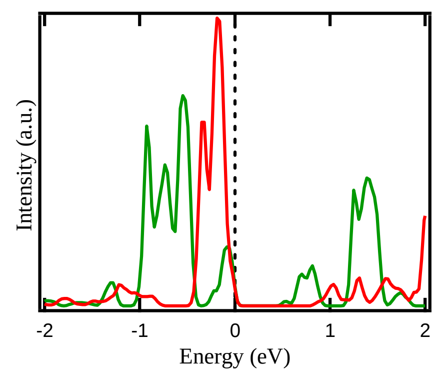

Fig. 2: 3d PDOS of Co in for $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. (geen) x=1, (red) x=1/3.

Acknowledgement: Synchrotron radiation XAS measurements were performed with an approval of SAGA Light Source (Proposal No. 1208097R) .

References:

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