Type of presentation: Poster

IT-5-P-2927 Evaluation of valence state in manganese oxide by transition edge x-ray sensor.

Tanaka K.[1,5], Ohgaki M.[2,5], Miyayama M.[3,5], Matsumura S.[4]

[1]Hitachi High-Tech Science Corporation, Shizuoka, Japan, [2]Hitachi High-Tech Science Corporation, Tokyo, Japan, [3]The University of Tokyo, Tokyo, Japan, [4]Kyushu-University, Fukuoka, Japan, [5]Japan Science and Technology Agency, CREST, Tokyo, Japan

Email of the presenting author: tanaka-keiichi@hhs.hitachi-hitec.com

Electrochemical capacitors are promising candidates for future energy storage devices because of their high power density, long cycle life, and relatively high energy density. There has been considerable interest in MnO2 as a cathode material for such capacitors because of its low toxicity, environmental safety, cost effectiveness, and large capacitance. In particular, two-electron redox reactions involving Mn2+ and Mn4+ are expected to yield a high energy density. Valence states in transition metals are often studied by determining the branching ratio of the L3 and L2 absorption edges using transmission electron microscopy together with electron energy loss spectroscopy (TEM-EELS). In the case of Mn, EELS can distinguish the L3 (640 eV) and L2 (651 eV) absorption edges, and an adequate signal can be obtained.
In the present study, an attempt was made to evaluate the valence state for manganese oxide particles using scanning electron microscope with a transition edge sensor (SEM-TES). A TES is a kind of energy dispersive X-ray spectrometer, but it has a very high energy resolution (typically 10 to 15 eV) and can separate extremely close X-ray peaks. The valence state was determined based on the branching ratio for the Lb and La X-ray emission lines. It was found to be possible to determine the valence state even in stacked structures with layer thicknesses of about 100 nm. Positive electrode powder samples with a composition Hx(Ni1/3Co1/3Mn1/3)O2 were evaluated using both SEM-TES and TEM-EELS. Three types of samples were examined: charged (as-prepared), discharged and recharged. Using SEM-TES, the branching ratios for the three samples were determined to be 0.76, 0.699 and 0.73, respectively. Using TEM-EELS, the values obtained were 2.3, 5.2 and 2.6, respectively. The discharge sample changed valence state from as-prepared one and discharged one. Thus, the SEM-TES shows the capability of identifying a different valance state in the case of the discharged sample.

Acknowledgement: This work was supported in part by the CREST program, JST, MEXT, Japan. The SEM-TES measurements were performed as part as a research program (A-12-KU-0018) of the Nanotechnology Platform Project conducted by MEXT.