Changes in Electronic Structure of the Electrochemically Na-ion Deintercalated $Na_{2/3}Co_{2/3}Mn_{1/3}O_2$ System Investigated by Soft X-ray Absorption Spectroscopy

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The changes in electronic structure of $Na_XCo_{2/3}Mn_{1/3}O_2$ was investigated by soft X-ray spectroscopy. The experiment was done at NSRRC beamline 20A1 recorded in electron yield mode and fluorescence mode.

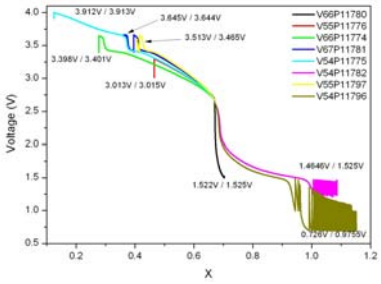

Fig. 1: The charging and discharging curve of $Na_XCo_{2/3}Mn_{1/3}O_2$ system

The Co $L_{II,III}$-edge electron yield XAS for $Na_XCo_{2/3}Mn_{1/3}O_2$ with different Na-ion content was showed in Fig. 2. There are two main peaks of L_{III} and L_{II} edges due to electronic transitions of Co $2p_{3/2}$ and $2p_{1/2}$ core electrons, split by the spin-orbit interaction of the Co 2p core level, to an unoccupied 3d level highly hybridized with oxygen 2p orbital. The intense peak at ~778.2eV representing the dipole-allowed 2p to 3d transition. The two shoulder peaks appear for Na-ion intercalated samples indicating that the local structural environment of Co was changed significantly during charging due to Co 2p-3d electrostatic interaction and the crystal field effect of octahedral symmetry.

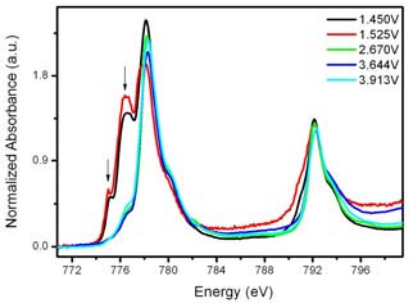

Fig. 2: Normalized Co $L_{II,III}$-edge spectra of $Na_XCo_{2/3}Mn_{1/3}O_2$ with different x content using electron yield method.

The Mn $L_{II,III}$-edge electron yield XAS for $Na_XCo_{2/3}Mn_{1/3}O_2$ with different Na-ion content was showed in Fig. 3. Fron the corresponding 1st derivative spectra, the appearance of shouder peak can be seen clearly. This appearance of shoulder peak indicating the electronic structure and geometry around Mn ion was altered significantly during charging, the same observation as in the Co $L_{II,III}$-edge spectra.

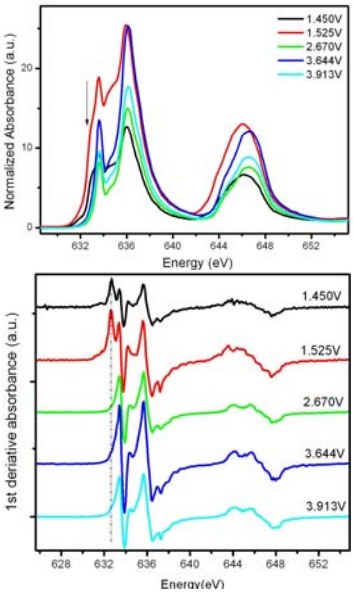

Fig. 3: Normalized Mn $L_{II,III}$-edge spectra of $Na_XCo_{2/3}Mn_{1/3}O_2$ and its corresponding 1st derivative spectra with different x content using electron yield method.

The oxygen K-edge spectra for $Na_XCo_{2/3}Mn_{1/3}O_2$ with different Na-ion content collected by EY and FY mode was shown in Fig. 4. The peak features of O K-edge XAS spectra change dramatically during charging and discharging due to the strong hybridization of metal 3d and oxygen 2p orbitals. For spectra recorded at EY and FY mode shows the same trend, indicating that the electrochemically Na-ion intercalation was taked place at bulk and surface.

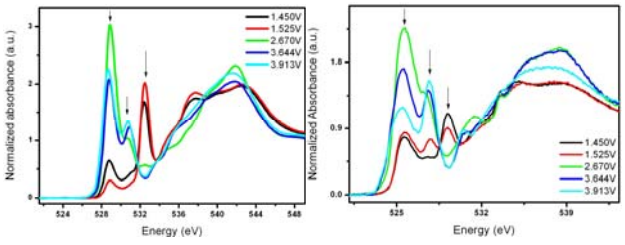

Fig. 4: Normalized O K-edge spectra of $Na_XCo_{2/3}Mn_{1/3}O_2$ with different x content using electron yield(left)and fluorescence(right) method.